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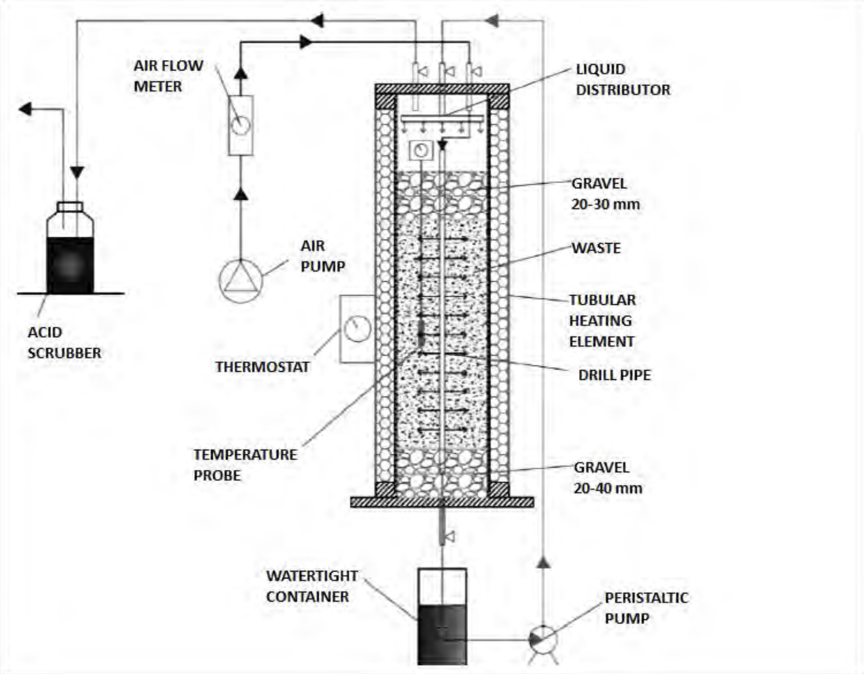
ICEA Department
MSc Environmental Engineering



Master Thesis
Cristina Tepordei
1104854

S.AN.A. HYBRID LANDFILL: NITROGEN EMISSIONS IN LAB-SCALE SIMULATION REACTORS DURING THE FINAL AEROBIC STEP

Supervisor:
Prof. Eng. Raffaello Cossu

Co-supervisor:
Eng. Luca Morello

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“Sometimes we need to feel the lack of air
to remember that we are still alive”.

SUMMARY

I) OVERVIEW OF THE STATE OF THE ART AND THEORETICAL ASPECTS

1. INTRODUCTION

1.1 State of the art

Worldwide, landfill is the predominant waste management technology. A clear evidence of a shift from landfilling to incineration and recycling was observed in the last decade in Europe but landfill continues to be the main final disposal: 34% of the municipal solid waste produced in the EU-28 Member States in 2012 was landfilled, 24% was incinerated, 27% recycled and 15% composted or anaerobically digested (ISPRA, 2014: elaboration based on Eurostat data). Landfills can be designed in many different ways, depending on the waste to be landfilled and the time period accepted before the control procedures can stop and the landfill is integrated into the surrounding environment (Christensen, 2011). Over the years the development of society and industry, coupled with growing awareness of environmental issues, has led to the application of increasingly sophisticated technological methods for handling waste (Cossu, 2009a). The focus of 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 biodegradable material.

In the last decades, the sanitary landfill method was the widely accepted and used due to its obvious advantages over open dumps and dry tombs. However, the perfect solution does not exist. Comparative studies and new researches are still continuing for a better landfill eco-design and management.

In the modern integrated waste management strategies, landfill should be applied as a last resort in view of the following disadvantages: waste of resources (land, materials); leachate emissions, potentially resulting in groundwater contamination; emission of greenhouse gases (GHGs) as methane and carbon dioxide, volatile organic compounds (VOCs) and odours, with the potential risk of fires and explosions. In this way, landfill becomes a fundamental tool (final geological sink) for controlling environmental mobility of elements and closing the material cycle (Cossu, 2009b).

As a general rule, the landfilled material is made up of different fractions: gasifiable, leachable, stable and mineralisable. Once the organic has been degraded and the leachable washed out, stable and mineralized matter represents a potential geological sink. Therefore, modern landfill design should adopt the best strategies suited to dealing with the mobile fraction, posing a potential threat to the environment in the short and long term (Cossu, 2009a).

In general, landfills should be projected, built and managed by respecting the environmental sustainability, that consists in reaching a quality of the final disposal in equilibrium with the environment in one generation period of time or in any way no longer than 30 years from the date of closure of the landfill (Council Directive 1999/31/EC). However, many researches showed that physical barriers are not able to be efficient in all this time. When the liner are broken until the estimated 30 years period of time, high concentration of pollutants may be spread into the environment and caused damages (Cossu et al., 2005).

According to the world waste hierarchy, in the modern society, the priorities of solid waste management are, in this order: waste prevention, minimization, recovery of material, recovery of energy and finally, waste disposal. As a consequence of the increasing of the world population and of the global economic development, the passage from a linear traditional to a circular approach is needed. The aim of landfill becomes closing the loop of materials ensuring their immobilization and the sustainability of the site, instead of simple storage of waste. In this way, landfill plays a fundamental role for the global carbon balance since it can become an important sink for this element. For such reason, the treatment of waste is fundamental to stabilize the mobile fraction as much as possible, not only before disposal but also within the landfill itself.

It is generally acknowledged that the major long term environmental impacts of landfilling of waste are associated with the generation and subsequent migration of leachate. Therefore, the development of leachate quality with time plays an important role landfill sustainability and in which way it may be achieved. Most definitions of sustainable landfilling include the achievement of final storage quality (FSQ) of the landfilled waste, i.e. a situation where active environmental protection measures at the landfill are no longer necessary and the leachate is acceptable in the surrounding environment respect to the low limits (Hjelmar and Hansen, 2005). Technical possible solutions to stabilize the waste as faster as possible are:

- minimize the waste by pre-treatments (e.g. mechanical, mechanical-biological, thermal treatments etc.);
- in-situ treatments (e.g. forced aeration, flushing, gas and leachate extraction etc.);
- after-care (e.g. top cover, landfill mining etc.).

These targets could be achieved through the mass balance of the landfill, the multibarrier concept and the choice of the best solutions according to the characteristics of the waste and of the environment surrounding the site. The goal is to avoid the accumulation of the elements (i.e. C, N, etc.) and their uncontrolled mobilization in the environment by creating a geological like deposit in which they are mineralized to rock or transformed into a stable form.

1.2 Aim of the thesis

A landfill is always necessary for the final disposal of waste. A well planned operating and aftercare phase may improve local environment and landscape, contributing to economic and health regeneration of the area. The aerobic phase of the S.An.A. Landfill method is the most important key to reach the stabilization of waste in one generation as required by the European Landfill Directive, bringing to fruition the removal of nitrogen that was the main challenge in anaerobic phase.

The main objective of this experimental activity was to assess, monitor and describe the final aerobic phase of the S.An.A. Landfill, developed by the University of Padova. In particular, nitrogen emissions were the main focus of this study and so, a careful monitoring, calculations and valuation of them were done and discussed. An overview of the main data obtained from the first and the second phase of the S.An.A. method (semi-aerobic and anaerobic) was also reported.

This project is based on the idea that hybrid bioreactor is the best solution for the sustainability, since it combines both the advantages of the aerobic and the anaerobic phases. In particular, S.An.A. Landfill is characterized by the alternation of three distinct management phases:

1) Semi-aerobic phase, aimed at reducing the duration of the acetogenic phase;
2) Anaerobic phase, with the goal to maximize the production of methane;
3) Aerobic phase, in which the processes of stabilization will be accelerated in order to achieve the final storage quality (FSQ) in equilibrium with the surrounding environment (Cossu et al., 2011).

The thesis is subdivided into three sections: an overview of the state of the art and theoretical aspects in the first part; a scientific paper in the second part and finally, other important information in the annexes that constitute the last part.

The first part was structured in three chapters, after a brief introduction in which the state of the art and the aim of the thesis were discussed:

- “Regulations”, which contains both the community and the Italian regulations on waste. The aim was to show a clear overview of the waste directions framework;
- “Concept of landfill”, in which are discussed: the biochemical processes in general, the concept of mass balance, the existing types of landfills, the concept of “Sanitary Landfill” and “Sustainable Landfill”, the different kinds of “Bioreactor Landfill” as aerobic, anaerobic and hybrid;
- “S.An.A. lab-scale bioreactor”, which reports an overview of the research and the results and conclusions obtained after the first and the second phase.

Starting from the data collected in the anaerobic phase, a planning of the final aerobic phase was developed and discussed in the scientific paper, which constitutes the second part. This thesis reports all the data collected, calculations and all the necessary considerations made, with a focus on nitrogen emissions, in order to understand the obtained results.

The main goals of the third phase of S.An.A. method are:

- break down the persistent carbon compounds through an aeration system and periodic analysis of all the significant parameters (TOC, COD, BOD_5, etc.);
- ammonia nitrification through aeration and nitrogen emissions monitoring in the liquid phase;
- stripping of ammonia with an acid scrubber and monitoring of the gas emissions;
- nitrogen mass balance starting from the calculated emissions;
- quantification of the long-term emissions of chlorites, sulphates and heavy metals;
- comparison of all the final emissions.

In the last part, further useful information were managed and reported in tables and graphs form.

2. REGULATIONS

2.1 EU community guidelines

The overall regulation of waste within the European Union (EU) is laid down in a so called horizontal directive "Waste Directive, 98/2008" supplemented with a lot of vertical directives on specific waste streams and/or operations and a few regulations.

The waste directive lays down all definitions (art. 183) on waste, byproducts, end of waste criteria, waste hierarchy (art. 179), operations and, as a very important part, recovery (art. 181) versus disposal (art. 182) in order to reinforce the measures that have to be adopted to prevent the waste production, considering the entire life cycle of products and materials, minimizing environmental impacts due to production and management of waste. The waste management hierarchy advised by this Directive is often graphically represented by an inverted triangle and is based on, from the most to the least preferred, Prevention, Reduction/ Re-use, Recycling, Recovery and Disposal.

- "Prevention" is related to measures taken before a substance, material or product has become waste, that reduce: the quantity of waste, including through the re-use of products or the extension of the life span of products; the adverse impacts of the generated waste on the environment and human health; the content of harmful substances in materials and products.

- **"**Re-use" means any operation by which products or components that are not waste are used again for the same purpose for which they were conceived. Preparing for re-use means checking, cleaning or repairing recovery operations, by which products or components of products that have become waste are prepared so that they can be re-used without any other pre-processing.

- "Recycling" means any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials.

- "Recovery" means any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfill a particular function, or waste being prepared to fulfill that function, in the plant or in the wider economy.

- "Disposal" means any operation which is not recovery even where the operation has as a secondary consequence the reclamation of substances or energy. Annex I of the Directive sets out a non-exhaustive list of disposal operations.

This Directive has also established some rules to monitor hazardous and non-hazardous waste traceability (S.I.S.T.R.I. for Italy) based on the computerization of data relative to the production, transport, disposal and recovery of waste.

Equally important is the Directive 1999/31/EC which prevents or reduces the adverse effects of waste on the environment. It defines the different categories of waste and classifies landfills into three categories: Landfills for hazardous waste, Landfills for nonhazardous waste, and Landfills for inert (EC, 1999).
The directive sets up which kinds of waste can be accepted in a specific landfill and a system of operating permits for landfill sites. Reduction targets for the landfilling of biodegradable waste were fixed: 75% by 2006, 50% by 2009 and 35% by 2016, based on the data of 1995.

The official title of the Waste Directive and the most important vertical directives and regulations are given in the list below, divided into framework regulations and regulations on waste management operations and on specific waste streams (Christensen, 2011):

Framework legislation on waste:

- Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives Text with EEA relevance.
- 2000/532/EC: Commission Decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.
- Regulation (EC) No 1013/2006 of the European Parliament and of the Council of 14 June 2006 on shipments of waste.

Legislation on waste management operations:

- Regulation (EC) No 2150/2002 of the European Parliament and of the Council of 25 November 2002 on waste statistics.
- Directive 2000/76/EC of the European parliament and of the council of 4 December 2000 on the incineration of waste.
- Directive 2000/59/EC of the European Parliament and of the Council of 27 November 2000 on port reception facilities for ship-generated waste and cargo residues – Commission declaration.
- Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.
- Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control (IPPC).

Legislation on specific waste streams:

- Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture.

- Directive 2006/66/EC of the European Parliament and of the Council of 6 September 2006 on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC.
- Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment.
- Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE).
- Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end of life vehicles.
- Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC – Statement by the European Parliament, the Council and the Commission.
- European Parliament and Council Directive 94/62/EC of 20 December 1994 on packaging and packaging waste.

A technical guidance for the waste production, management and regulation “Guidance on the classification and assessment of waste” was published in May 2015. The guidance explains how to assess if the waste displays a hazardous property and how to classify it. In the Chapter 2 there is the explanation of the procedure to assess and classify a waste “Waste classification and assessment”, while Chapter 3 provides examples of the assessment of asbestos, oil and coal tar containing wastes and soil “Further guidance on assessment”. The guidance contains also four appendixes (EEA, 2015):

- Appendix A: “How to use the list of waste” – contains a copy of the List of Waste (includes the code, its description, entry type and where there is a worked example available); explains how to use the list, including some examples; provides information on the different types of entry and how each is assessed. This will help you identify the most appropriate code(s). Some codes are linked so it’s common to identify more than one code at this stage.

- Appendix B: “Hazardous substances” – explains how to identify if a substance is a hazardous substance and the hazard statement codes assigned to it.

-Appendix C: “Hazardous property assessment” – explains how to identify if a waste displays one or more hazardous properties or is hazardous because it contains persistent organic pollutants.

- Appendix D: “Waste sampling” – provides guidance on how to plan the sampling of a waste to produce an accurate classification.

2.2 Italian regulations on waste

The EU Directives have been adopted in Italy with several legislative decrees:

- Decree 27/2010 that defines all the criteria for waste admission in landfill based on the Legislative Decree 36/2003.
- Decree 152/2006, called “Testo Unico Ambientale”, enacted consequently to the act 15 December 2004, n.308, and reorganizes the whole national legislation concerning environmental preservation and pollution. The Italian legislation is mainly focused on the part IV of the “Testo Unico Ambientale” which sets rules for the waste management and the remediation of contaminated sites.
- Decree 133/2005 dealing with incineration.
- Decree 36/2003 that implements the European Directive 99/31/CE about landfills. In particular, in the article 7(5) there are the definitions of all the criteria for waste admission in landfill.

Coherent with the principles of the Landfill Directive, decree 36/2003 provides prescriptions for all the different stages of the life cycle of a landfill site, such as location, construction, management, monitoring, closure and post-closure, with the aim of avoiding and minimizing any possible adverse environmental impact of the landfill. Moreover, this decree reclassified landfill sites in: I) landfill for inert waste; II) landfill for non hazardous waste; and III) landfill for hazardous waste. Decree 36/2003 was the main drive for the promotion of sustainability concept and set a biodegradable municipal waste (BMW) landfill target to be achieved within 2008 (<173 kgBMW/cap), 2011 (<115 kgBMW/cap), and 2018 (<81 kgBMW/cap). These targets were a good strategy for the waste reduction in Italy. In the year following the introduction of decree 36/2003, every region had to develop and approve a specific programme to reduce the transfer of biodegradable waste to landfill. The management of leachate in landfill is also described in the decree 36/2003 and its transport in the fourth part of the d. Lgs. 152/2006. Concerning biological and anaerobic treatments in Italy, regulations are present in the “D.G.R.V. n. 568/05”, that defines technical requirements for the treatment of organic fractions using composting, biostabilization and anaerobic degradation. The waste admission in landfill is established by the D.M. 27/2010 respecting the waste hierarchy and the specific national and regional limitations.

A guideline for the waste management and landfill building was proposed by the Lombardia Region Regional Committee “Waste Management Regional Program (P.R.G.R.)” with Decree 2014/06/20 n.1990.

The PRGR also includes the Regional Hardening Plan (P.R.B.) and the Strategic Environmental Evaluation (V.A.S.). In its terms, the PRGR is divided into 4 sections: municipal waste, special waste, landfilled organic waste reduction program, and packaging management program. It establishes the minimum technical requirements, applications and interpretation of the legislative decree 36/2003 to which the design, approval, implementation, management, operation and after-care of landfills must be adapted.

3. MUNICIPAL SOLID WASTE LANDFILLS

3.1 Biochemical processes

Degradation processes occurring inside a landfill body are performed by microorganisms under specific environmental conditions. Putrescible organic compounds can be used as carbon source by heterotrophic microorganisms (bacteria, fungi), and as energetic source by heterotrophs and chemoautotrophs (nitrifies and methanogen bacteria).

All the reactions occurring inside the landfill (aerobic respiration, denitrification, sulphate reduction, etc.) can take place simultaneously or in different moment of the landfill life. For simplicity, biochemical processes can be subdivided into aerobic and anaerobic due to the presence or absence of oxygen.

Generally, municipal solid waste (MSW) deposited in a landfill tends to undergo five sequential and distinct phases of decomposition (Fig. 1), starting with a brief aerobic phase (hydrolysis), through two anaerobic phases (acidification and acetogenesis) followed by a methane generation phase (methanogenesis) and finally maturation (Pichtel, 2005).

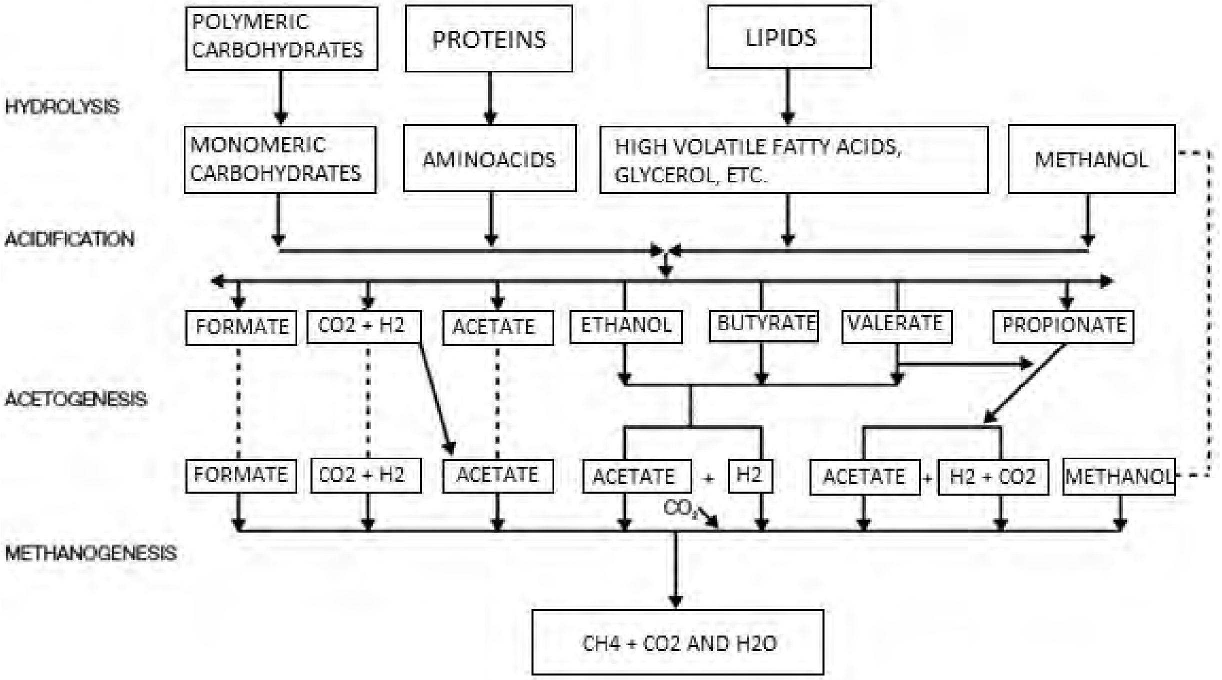

Fig. 1: Biodegradation processes

The first phase of a biodegradation process is called "Hydrolysis". Literally means reaction with water and so it is an aerobic phase. The presence of oxygen guarantees high biochemical reaction kinetics, fast bacteria growth and the possibility to hydrolyse complex organic particular matter into dissolved compounds with a lower molecular weight, plus the nitrification of ammonia-nitrogen. The presence of air means no methane generation. The off gases quality is mainly composed by carbon dioxide, oxygen, free nitrogen, steam and some trace compounds. The general reaction of a chemical compound by incorporation of water is the following:

$$X\text{-}Y + H_2O \rightarrow H\text{-}X + Y\text{-}OH$$

$$\text{e.g.: } (C_6H_{10}O_5)_Z + (z-1)H_2O \rightarrow {}_ZC_6H_{12}O_6$$

During the aerobic phase, polymeric carbohydrates are degraded into monomeric carbohydrates (that are soluble sugars) and then to carbon dioxide (CO_2) and water (H_2O); proteins are degraded via peptides to aminoacids, and then to CO_2, H_2O, nitrate (NO_3^-) and sulfate (SO_4^{2-}), typical products of catabolism; fats are hydrolyzed into volatile fatty acids (VFAs) and glycerol. Then, through the production of VFAs and alkali, they are further converted into more simple catabolites. The hydrolysis is the slowest phase of all the process and governs all the following reactions.

The dissolved compounds produced in the first phase are taken up by the fermentative microbes in the "Acidogenesis" (Acidogenic phase). Acidogenic fermentation is carried out by a diverse group of bacteria, that are very heterogeneous group facultative anaerobic as well as anaerobic micro-organisms. The products of this phase are simple organic compounds like volatile fatty acids, alcohols and mineral compounds like CO_2, H_2, NH_3, H_2S, CH_3COOH, and acids as propionic acid, butyric acid and other organic acids. The main reactions occurred in this step are:

$$C_6H_{12}O_6 + H_2O \rightarrow 2CH_3COOH + H_2 + 2CO_2$$

$$C_6H_{12}O_6 \rightarrow C_3H_7COOH + 2H_2 + 2CO_2$$

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$$

The reactions are generally simultaneous but the change in some parameter equilibrium can favour some of them.

The third step is called "Acetogenesis". The products of acidogenesis are converted into the final precursors for methane generation: acetic acid (CH_3COOH), hydrogen (H_2) and carbon dioxide (CO_2). It is commonly an exothermic process but, if H_2 concentration rises up, it becomes endothermic, the metabolism of other organic acids (accept acetic acid) is not possible anymore and other organic acids accumulate. Otherwise, a low concentration of H_2 promotes the methane generation in the methanogenesis phase. The pH decreases due to the growth of acetogenic microorganisms and consequently, due to the acidic conditions, metal species are more soluble and mobilized from the waste into the leachate. Consequently, also organic acids, chlorides ions, ammonia ions and phosphates ions will be higher forming complexes with metal ions (De Abreu et al., 2005). Also the formation of hydrogen sulphide (H_2S) is possible in this stage, due to the presence of sulphate compounds that are reduced to H_2S by the sulphate reducing microorganisms (Christensen et al., 1989; Christensen et al., 1996).

The main reactions are reported below:

$$CH_3\ CH_2COOH + 2H_2O \rightarrow CH_3COOH + 3H_2 + CO_2$$

$$CH_3\ C_2H_4COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2$$

$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2H_2$$

$$C_6H_5OH + H_2 \rightarrow CH_4 + H_2O$$

During the “Methanogenesis”, methane (CH_4) is produced by methanogenic bacteria, which can use both CH_3COOH and H_2 as substrate. Methanogenic bacteria are very specialized, the most sensible to pH, nutrient and temperature and can use only a specific substrate. The initial part of this phase is “unstable” because the gas composition is variable and fermentative microbes coexist with methanogens creating a passage condition. After that, the process becomes stable and the concentration of methane and carbon dioxide in gas reach the standard of 50-60% CH_4, and 40-50% CO_2 (Senior, 1990). Methanogenic phase starts and goes on generally 10-20 years after closure (Ritzkowski et al., 2006).

The main reactions are reported below:

$$CH_3COOH \rightarrow CH_4 + CO_2$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$HCOOH + 3H_2 \rightarrow CH_4 + 2H_2O$$

$$CH_3OH + H_2 \rightarrow CH_4 + 2H_2O$$

A final “Oxidation phase” (maturation) follows when the biodegradable organic substances are completely degraded and the concentration of methane and fatty acids are practically zero. Only the more refractory organic carbon (humic acids, fulvic acids, etc.) remains into the landfill body and gives a residual COD of about hundred mg/L (U.S.EPA, 1998). At the end of the process, a reduction of volume and mass of organic waste is achieved; the gas is recovered and the stabilization and hygienization of organic waste is possible. A so called “complete stabilization” is when the waste material no longer breaks down into by-products that are released into the environment (Walsh and O’Leary, 2002). Table 1 provides data on key leachate parameters and the ranges in concentration associated with each phase of biodegradation.

Table 1: Leachate concentration ranges as a function of stabilization (Pohland and Harper, 1986; Reinhart and Townsend, 1997)

Parameter	Phase II Transition	Phase III Acid Formation	Phase IV Methane Formation	Phase V Final Maturation
BOD_5 (mg/L)	100 -10,000	1,000 – 57,000	600 – 3,400	4 - 120
COD (mg/L)	480 – 18,000	1,500 – 71,000	580 – 9,760	31 - 900
TVA (mg/L) as Acetic Acid	100- 3,000	3,000 – 18,800	250 – 4,000	0
BOD_5/COD	0.23 – 0.87	0.4 – 0.8	0.17 – 0.64	0.02 – 0.13
Ammonia (mg/L)	120 - 125	2 – 1,030	6 - 430	6 - 430
pH	6.7	4.7 – 7.7	6.3 – 8.8	7.1 – 8.8
Conducitivity (µmhos/cm)	2,450-3,310	1,600-17,100	2,900-7,700	1,400-4,500

BOD_5 = Biochemical Oxygen Demand (in 5 days); COD = Chemical Oxygen Demand; TVA = Total Volatile Acids; mg/L = milligrams per litre; µmhos/cm = micromhos per centimetre (a measure of electrical conductivity); Phase I is the phase where waste is initially placed in the landfill.

A comparison of aerobic and anaerobic processes according to the balances for mass and energy is reported below (Gallert et al., 1998):

Aerobic:

$$\text{1 Mol Glucose} + \text{3 Mol } O_2 \rightarrow \text{3 Mol } CO_2 + \text{3 Mol } H_2O + \text{0.5 Mol Glucose as Biomass}$$

$$\text{180 g Glucose} + \text{96 g } O_2 \rightarrow \text{186 g respiration products } (CO_2, H_2O) + \text{90 g Biomass}$$

$$\text{2,870 kJ / mol} \rightarrow \text{890 kJ as Heat} + \text{1,980 kJ in Biomass}$$

Anaerobic:

$$\text{1 Mol Glucose} \rightarrow \text{2.85 Mol } CH_4 + \text{2.85 Mol } CO_3 + \text{0.05 Mol Glucose as Biomass}$$

$$\text{180 g Glucose} \rightarrow \text{171 g } (CH_4 + CO_2) + \text{9 g Biomass}$$

$$\text{2,870 kJ / mol} \rightarrow \text{2,360 kJ in Biogas} + \text{312 kJ as Heat} + \text{198 kJ in Biomass}$$

3.2 Mass balance

Mass balance is a useful tool to study the emissions from a landfill for a long period of time and for approaching the concept of sustainable landfill. The main goals of this approach are to study and understand the distribution in time of a compound, among the principal emission forms (leachate, biogas, residual waste). It allows analysing the mobility and the chemical and biological reactions of the given compound, also in relation with other important parameters.

With the mass balance, it is possible to determine the effects of different alternatives for waste and landfill management, on the reductions of the emissions. 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 modelling approach to the mass balance tries to simplify the system with a Continuous Stirred Tank Reactor (CSTR). The basic assumption is 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. With this assumption, liquid, solid and gaseous materials interact in the given CSTR making rise to liquid (leachate), gas emissions (biogas) and the remaining solid phase that represent a source of the potential emissions (landfilled waste) (Cossu et al., 2004). Considering the landfill as a CSTR, the parameter model of mass balance can be summarized with the following basic equation**:**

ACCUMULATION = INPUT – OUTPUT + GENERATION - CONSUMPTION

Considering the mass conservation concept, this formula means that the remaining solid material in the landfill body, after a certain time after the filling (ACCUMULATION) is equal to the incoming waste (INPUT), minus the output waste (OUTPUT), in terms of wanted or unwanted emissions of leachate and biogas, plus the production (GENERATION) and minus the consumption (CONSUMPTION) of materials due to the biological reactions. A simple scheme of the landfill reactor is shown in Fig. 2.

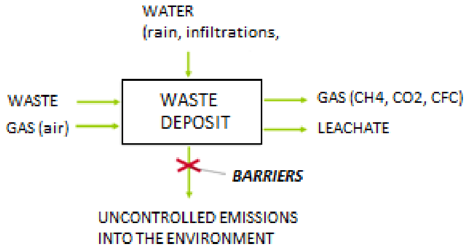

Fig. 2: Landfill reactor scheme

A landfill should be considered as a physical-chemical reactor where the input are represented by the waste landfilled, atmospheric air, rain and any kind of water infiltration; the output consists of leachate and biogas, generally depending on the kinetics of the biological reactions inside the landfill and uncontrolled emissions into the environment that should be stopped with proper barriers (Fig. 3).

The total balance for the system is shown in the figure below:

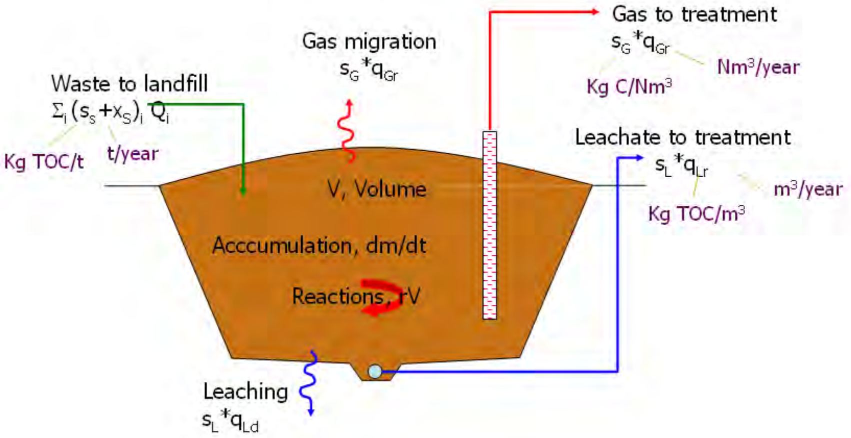

Fig. 3: Mass balance terms in a landfill body

Accumulation = Inlet– Outlet – Degradation

$$dm/dt = \Sigma_i(S_s + X_s)_iQ_i - s_Lq_L - s_Gq_G - rV - S_sQ_s$$

$$0 = \Sigma_iX_{si}Q_i + \Sigma_iS_{si}Q_i - (s_Lq_{Lc} + s_Lq_{Ld}) - (s_Gq_{Gc} + s_Gq_{Gd}) - rV - S_sQ_s$$

$$s_Lq_{Ld} + s_Gq_G + S_sQ_s = Kx + \Sigma_iS_{si}Q_i - s_Lq_{Lc} - s_Gq_{Gc} - rV$$

Assuming that in a sustainable landfill the uncontrolled emissions have to be minimized, this can be achieved by means of:

- reduce the amount of diffused leachate and biogas (e.g. with a good lining);
- reduce and contain the accumulation inside the landfill body;
- reduce the mobile fraction entering (e.g. by reuse, recycle, avoidance, minimization etc);
- increase the collected amount of leachate and gas (e.g. by leachate recirculation, allowing water input in landfill, promoting gasification, good collection pipes);
- increase the reaction rate of degradable compounds (e.g. by adding water and oxygen in order to increase kinetics).

The mass balance is a tool that could be used for all kind of pollutants. In a landfill, generally, the main significant compounds that need to be monitored by means of mass balance are carbon (C) and nitrogen (N). The main goal in a long-term period is to achieve a stable form of mass balance, forming the basis for the geologic deposit.

3.3 Types of landfills

Landfilling is the oldest and the simplest form of waste disposal. Until the late 1800s, dumping waste remained the primary disposal option in Europe and the United States. Garbage was generally placed in leaking barrels on the street edge and picked through by salvagers and otherwise left for animals. Towards the end of the 19th Century, many cities realized that throwing waste into the streets was causing health and political problems. Garbage collection and disposal systems using horse-drawn carts were realized in order to bring the waste in open dumps, incinerators or at sea.

In 1935, the precursor to the modern landfill was started in California where waste was thrown into a hole in the ground that was periodically covered with dirt. The American Society of Civil Engineers in 1959 published the first guidelines for a “sanitary landfill” that suggested compacting waste and covering it with a layer of soil each day to reduce odours and control rodents. In reality, this method was introduced for the first time in England in 1912, where it was called “controlled tipping”. The first legislation addressing solid waste management was the Solid Waste Disposal Act (SWDA) of 1965 in America.

Starting from that period, many state laws banned the open burning of waste at dumps and began replacing them with sanitary landfills. In few decades, landfills changed from little more than holes in the ground to highly engineered state-of-the-art containment systems requiring large capital expenditures. Typically, older landfills were designed by excavating a hole or trench, filling the excavation with waste, and covering it with soil. In most instances, there was no barrier or containment layer that prevented leachate from moving out of the landfill and contaminating groundwater (NSWMA, 2008).

A lot of troubles happened due to this traditional waste disposal approach: air pollution and health hazard, explosion risks, vegetation depletion, odours, presence of animals/birds/insects, noise, etc. Therefore, was necessary to be developed a new concept of landfill. The main goal of a modern landfill is to protect human health and the environment and so it should be specifically designed to do this.

In general, landfill is an engineered and licensed facility where waste is deposited for permanent storage. There are different types of landfills. Depending on design and management strategy, landfills are generally classified as (Hoornweg and Bhada-Tata, 2012):

- Open dumps: absence of any kind of operation and engineering measures;
- Semi-controlled and Controlled dumps: few or some engineering controls, no engineering measures in water monitoring, unrestricted contaminant release by leachate, no landfill gas management;
- Contained/Controlled/Engineered landfills: registration and placement of waste, use of daily cover material, surface and ground water monitoring, infrastructure and liner in place, containment and

some level of leachate treatment, reduced leachate volume through waste cover, passive ventilation or flaring for landfill gas management;

- Sanitary landfills: registration and placement of waste, use of daily cover material, measures for final top cover and closure, proper siting, infrastructure, liner and leachate treatment in place and post-closure plan, containment and leachate treatment (often biological and physico-chemical treatments), flaring with or without energy recovery from landfill gas.

Despite the progress of civilization, it is possible to find all the aforementioned forms of waste storage, including open dumps, depending on the level of economic development of the country.

According to the construction method we can classify landfills into:

- under-ground landfill;
- above-ground landfill;
- landfill in steep areas, in trenches or valleys.

According to the type of waste, as suggested by the European Directive 1999/31/EC, there are:

- landfill for hazardous waste (class I);
- landfill for non-hazardous or low level hazardous waste (class II);
- landfill for inert waste (class III).

3.4 Sanitary landfill

For years, the so called “contained landfill” was considered the best landfill design. From the general definition, it is a landfill designed in such a way to reduce infiltrations and block the leaching by a proper lining system that physically separates the waste from the environment. However, it was shown that the physical barriers are not efficient for 30 years and, since the degradation processes are not able to stabilize the waste in this period of time, uncontrolled emissions of contaminants are possible. A new design concept was necessary for the modern approach of landfill. Sanitary landfill is today the most common way to eliminate municipal solid waste due to its economic advantages and public acceptance.

Sanitary landfills are sites where waste is isolated from the environment until it is rendered innocuous through the biological, chemical and physical processes of nature, so it is safe. Through sanitary landfilling, disposal is accomplished in such a way that contact between waste and environment is significantly reduced, and waste is concentrated in a well-defined area. The result is a good control of landfill gas and leachate, and limited access of vectors (e.g. rodents, flies, etc.) to the wastes.

The basic concept of sanitary landfill was considered the best way of landfilling for about one hundred years. The method is based on the idea to deposit waste in thin layers and promptly compacted by heavy machinery. The layers are placed and compacted on top of each other to form a refuse cell that will be covered with a layer of compacted soil to prevent odours and windblown debris. When the landfill is completed, it is capped with a layer of clay or a synthetic liner in order to prevent water from entering. Finally, a control and prevention systems of negative impacts on the public health and on the environment should always be present.

In high-income countries, the level of isolation achieved may be high. However, meeting all specific aspects may be technologically and economically impractical in many developing countries (UNEP, 2004). Four basic conditions should be met before a site can be regarded as a sanitary landfill (McElhatton et al., 2012):

1. Full or partial hydro-geological isolation: if a site cannot be located on land which naturally contains leachate security, additional lining materials should be brought to the site to reduce leakage from the base of the site (leachate) and help reduce contamination of groundwater and surrounding soil. Leachate collection and treatment must be stressed as a basic requirement.
2. Formal engineering preparations: designs should be developed from local geological and hydro-geological investigations. A waste disposal plan and a final restoration plan should also be developed.
3. Permanent control: trained staff should be based at the landfill to supervise site preparation and construction, the depositing of waste and the regular operation and maintenance.
4. Planned waste emplacement and covering: waste should be spread in layers and compacted. A small working area which is covered daily helps make the waste less accessible to pests and vermin.

The ways of doing this should always be adapted to local conditions. For example, the implementation of sanitary landfilling are severely constrained in economically developing countries by the lack of reliable information specific to these countries, as well as by a shortage of capital and properly trained human resources. Therefore, the short-term goal should be to meet the more important aspects to the extent possible under the existing set of technical and financial circumstances. The long-term goal should be to eventually meet the specific aspects of the design and operating conditions. Only when a fill meets all the specific conditions, the benefits associated with a sanitary landfill could be realised (UNEP, 2004).

The basic design and operating aspects of a sanitary landfill in terms of routes of impact outside the fill and of meeting the three basic conditions are illustrated in Fig. 4.

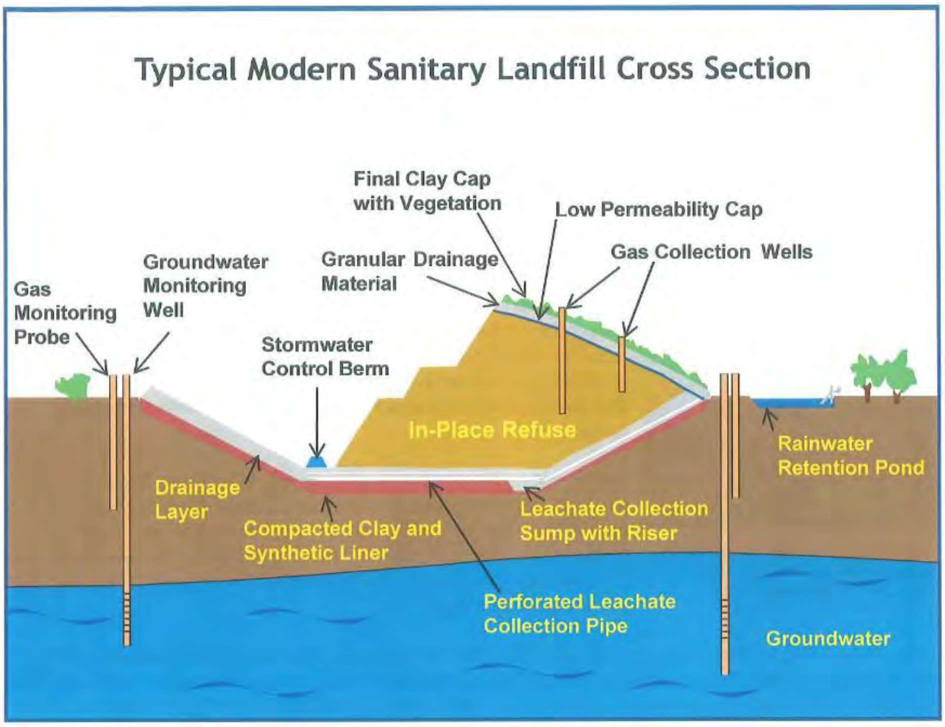

Fig. 4: Schematic diagram of basic aspects of a sanitary landfill (NSWMA, 2008)

3.5 Sustainable landfill

The term “sanitary” was and still is an apt prefix to “landfill” to describe the quantum leap away from open dumping. However, the release from a sanitary landfill consists mainly of leachate which could be strongly polluted and so has become the subject of recent interests. Leachate may contain large amounts of biodegradable and non-biodegradable organic matter, ammonia-nitrogen, heavy metals, chlorinated organics, inorganic salts, etc. (Renou et al., 2008).

Modern sanitary landfills are considered sustainable because they conform in most respects to the common definition of sustainability (Ross et al., 2011):

“Sustainable developments are those that meet society’s present needs without compromising the ability of future generations to meet their needs” (definition of the UN Brundtland Committee).

It follows from this definition that every generation should solve its own problems. Very often a maximum period of 30 years is assumed. However, there is no internationally accepted definition of sustainable landfill. A selection of definitions 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 management and gas management) and monitoring systems are no longer required.
- DHI (Hjelmar et al., 2005): *Waste at 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, the main important point of them is to reach a state where the undisturbed contents no longer pose a threat to human health and the environment in a limited period of time. At that moment, often called “completion”, aftercare can be ended.

It should be noted that it is not landfill in itself that is undesired, but its environmental impact. Pollutants are transported through the environment when there are differences in their concentration. If there is no significant difference, there is no transport. Therefore, as soon as the internal environment of a landfill is stabilized and comparable to the conditions in the surrounding soil there are no natural gradients. When waste is landfilled in a sustainable way, pollutants are broken down into harmless substances and/or flushed out (and therefore rendered harmless) or immobilized in the landfill and so remain there forever.

The main goal of the “sustainable landfill” will be tackle the environmental impacts. Recently enormous progress has been made in understanding and predicting landfill processes (Scharff, 2006).

Finally, sanitary landfills can be readily modified to be operated as bioreactor landfills, with the objective of accelerating the decomposition of deposited organic wastes.

3.6 Bioreactor landfill

Bioreactor landfill is a new and promising trend in solid waste management based on the idea of increasing degradation process and achieving a greater stabilization than that in conventional landfills (Long et al., 2009). One significant benefit of this approach is the “creation” of additional air space into which new deliveries of waste materials can be deposited (Ross et al., 2011). In this way the microbial processes are enhanced and the stabilization is achieved in a shorter time.

System design of bioreactor landfills provides the flexibility in the location and duration of liquid and air injection, allowing for adjustment of pH, oxidation-reduction potential (ORP), and moisture content to create an environment conducive to microbial degradation and biological nitrogen removal. System design is rigid with respect to parameters such as waste composition and age (i.e. organic carbon content); waste components cannot be controlled and vary from landfill to landfill, while waste age varies from location to location within a landfill. Thus, in a landfill, the active control of in-situ reactions and nitrogen removal/ transformation is generally restricted by the location and volume of injected liquid and air (Berge et al., 2006).

The advantages of bioreactor landfills could be summarized as:

- Increasing the feasibility for cost-effective landfill gas recovery, which in turn reduces fugitive emissions; more landfill gas-to-energy potential (Fig. 5).
- Decomposition and biological stabilization in years vs. decades in conventional landfills (dry tombs);
- Lower waste toxicity and mobility due to both aerobic and anaerobic conditions;
- Reduced (or eliminate) leachate treatments/ disposal costs;
- A 15 to 30% gain in landfill space due to an increase in density of waste mass;
- Reduced post-closure care.

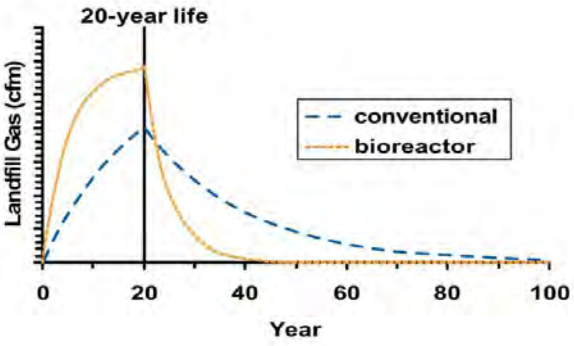

Fig. 5: Modeled behavior of Conventional and Bioreactor Landfills (recreated from graphic in Waste Management presentation to NDEQ, 2003; S.W.M.P., 2004)

Bioreactor landfills are engineered systems that incur higher initial capital costs and require additional monitoring and control during their operating life, but are expected to involve less monitoring over the duration of the post-closure period than conventional “dry tomb” landfills.

Issues that need to be addressed during both design and operation of a bioreactor landfill include: increased gas emissions, increased odours, physical instability of waste mass due to increased moisture and density, instability of liner systems, surface seeps, landfill fires, etc. (Pichtel, 2005)

There are different types of bioreactor landfill configurations. The main commons are (EPA, 2015):

1. Aerobic: means that air is allowed and/or injected inside the landfill in order to accelerate the waste stabilization. Generally, this type of bioreactor is characterized by the leachate removal, storage and re-circulation into the landfill body in a controlled manner.
2. Anaerobic: consists on biodegradation of waste in the absence of oxygen producing landfill gas (LFG). A central point of this kind of bioreactor is the re-circulation of leachate and other sources in order to obtain the optimal level of moisture.
3. Hybrid: is based on the alteration of aerobic and anaerobic treatment phases in order to enhance better the degradation without lost the potential producible biogas.

Other possible configurations are:

- Facultative bioreactor landfill: operates anaerobically and has recirculation of “nitrated” leachate, coming from ammonia degradation processes. Nitrated leachate results when leachate is collected, aerated, and treated (nitrification) in a surface contact biological reactor to reduce ammonia concentration for better leachate quality. The facultative bioreactor has characteristics similar to both anaerobic and aerobic bioreactors, however, additional site space and equipment for the leachate treatment system may be required (S.W.M.P., 2004).
- Biological permeable cover: consists of permeable material (tire chips, geonet, glass cullet, gravel, etc.) underlying a layer of compost or soil capable of supporting vegetation. The cover allows infiltration of rainwater to keep MSW wet for continued biodegradation, while bacteria in the cover biologically digest the methane produced by the landfill (S.W.M.P., 2004).
- Flushing: based on the concept to actively encourage degradation in a landfill to breakdown and release the organic pollution load and the waste is then flushed to wash out any soluble degradation products (Beaven and Know, 1999; Fellner et al., 2011).

Each of these systems operates with different schemes to obtain optimal results and has gotten a patented process (Berge et al., 2005; Long et al., 2009).

3.6.1 Aerobic bioreactor landfill

The aerobic bioreactor process is analogous to a composting operation in which input materials are rapidly biodegraded using air, moisture, and increased temperatures brought about by biological processes. Aerobic bioreactors operate by the controlled injection of moisture and air into the waste mass through a network of pipes (Pichtel, 2005). Adding air to landfills has been shown to enhance degradation processes in landfills, as aerobic processes tend to degrade organic compounds typically found in municipal solid waste (MSW) in shorter time periods than anaerobic degradation processes.

Decomposition of organic matter under aerobic conditions results in the production of simple mineral compounds i.e. carbon dioxide and water, but also humic-like substances (Ritzkowski et al., 2006). However, due to the heterogeneity of waste structure, the oxygen does not reach in the same amount all the places in landfill, therefore its concentration is determined by the waste moisture and porosity. Reported advantages of operating the landfill aerobically rather than anaerobically include:

- Increased rate of landfill settlement;
- Decreased metal mobility;
- More rapid waste and leachate stabilization;
- Reduced ex-situ leachate treatment required;
- Lower leachate management and methane control costs;
- Reduction of environmental liabilities;
- Potential for landfill mining.

Many of the nitrogen transformation and removal processes are favoured by aerobic processes, including nitrification, ammonia air stripping or volatilization. This is due to the fact that in aerobic bioreactor landfills the pH levels and the temperatures are higher. The additional gas flow associated with air injection may also induce greater masses of ammonia-nitrogen removal. Further, the fairly neutral pH level decreases metal mobility, while the elevated temperatures increase evaporation, which results in a significant loss of leachate. As a consequence, there is less leachate to manage.

Odours often associated with anaerobic systems, such as hydrogen sulphide and volatile acids, are reduced in aerobic bioreactor landfills. Aerobic processes do have some odour associated with them; however, it is an earthy smell (Berge et al., 2006).

3.6.2 Anaerobic bioreactor landfill

Anaerobic bioreactor landfills are those in which moisture addition is practiced. Sources of liquid addition may include groundwater, storm-water, infiltrating rainfall, or leachate. Moisture content adjustment results in enhanced methane production, faster than a conventional landfill or aerobic bioreactor (S.W.M.P., 2004). The total gas produced increases with the recycling of organics in the leachate, however, the vast majority of the gas is generally produced relatively early after landfill closure (within 20 years) and limited methane production will continue over long periods (Berge et al., 2006).

Compared to other types of bioreactor landfills, anaerobic systems tend to have lower temperatures and slower degradation rates. Waste biodegradation occurs at a slower rate than the aerobic or hybrid bioreactor and one of the main disadvantages is the accumulation of ammonia-nitrogen due to the absence of oxygen. An advantage of operating the bioreactor anaerobically when compared to other bioreactor landfill types is that air is not added; therefore the operational costs are less than what would be incurred aerobically and methane can be captured and reused (Berge et al., 2006).

In general, anaerobic bioreactor method has the most similarities to conventional landfilling, except with higher quantities of liquids addition and increased landfill gas production (S.W.M.P., 2004).

3.6.3 Hybrid bioreactor landfill

Bioreactor and bio-stabilization technologies accelerate decomposition and stabilization of landfilled waste and have the potential to reduce long-term risks, in comparison to conventional “dry tomb” MSW landfills (S.W.M.P., 2004). The concept of hybrid bioreactor landfills is based on the idea of combination of both aerobic and anaerobic conditions, taking the advantages of both of them and, on the other hand, filling the gaps of both the treatments. For example, in anaerobic conditions the main advantage is the methane production but we will manage the accumulation of ammonia; on the contrary, in aerobic conditions we don’t have energy recover but the degradation kinetics of organic substances is much higher that is an advantage for the stabilization.

Fewer studies were performed to evaluate the effect of cyclic air injection on the performance of hybrid bioreactor landfill. Some results showed that cyclic air injection system biologically stabilized the leachate in a shorter time than purely aerobic system (Pichler and Kogner-Knabner, 2000; Berge, 2001; Reinhart et al., 2002; Long et al., 2009).

There are a lot of proposed definitions of “hybrid reactors landfill”. The ones proposed by the Solid Waste Association of North America (SWANA) is the following:

> *“Any landfill cell where liquid or air is injected in a controlled fashion into the waste mass in order to accelerate or enhance biostabilization of the waste" (EPA, 2015).*

The main important point of all the definitions is the moisture addition and/or air injection that are used as enhancements to create a solid waste environment capable of actively degrading the biodegradable organic fraction of the waste (Berge et al., 2006).

While landfills simply recirculate leachate for liquids management, bioreactors often need other liquids such as storm-water, wastewater and wastewater treatment plant sludge to supplement leachate. One of the main advantages of bioreactor landfills is that the increasing waste degradation rate allows the expansion of the bioreactor landfill life respect to the conventional landfills (EPA, 2015). Liquid addition to landfills has many advantages associated with it, while the recirculation involves the collection and redistribution of leachate through the landfill. Moisture addition and movement are important factors affecting waste biodegradation resulting in an increase in the moisture content of the waste and distribution of nutrients throughout the landfill, respectively. Optimal levels of moisture content have been found to be between 40 and 70%, on a wet weight basis. If there is an insufficient leachate available, it is necessary to supplement with other liquids such as groundwater, stormwater, wastewater, or surface water.

Due to the waste heterogeneities and differences in compaction within landfills, achieving uniform liquid distribution is often difficult. 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 (that may be due to waste heterogeneity or differences in compaction ratios) (Berge et al, 2006).

Although the lot of advantages, one of the remaining challenges is the ammonia-nitrogen concentration found in the leachate. The reason of this is that recirculating leachate increases the rate of ammonification and results in accumulation of higher levels of ammonia-nitrogen concentration, even after the organic fraction of the waste is stabilized (Berge et al, 2006). Studies on hybrid reactors showed that the combination of facultative anaerobic and aerobic conditions was indeed effective in eliminating ammonia both from the leachate and the refuse thoroughly (Long et al., 2008).

The ammonia-nitrogen in leachate is derived from the nitrogen content of the waste, generally from the proteins contained in yard wastes, food wastes and bio-solids. As the proteins are hydrolyzed and fermented by microorganisms, ammonia-nitrogen is produced. This process is termed “ammonification”.

Ammonification is a two-step process consisting of the enzymatic hydrolysis of proteins by aerobic and anaerobic microorganisms releasing aminoacids and the subsequent deamination or fermentation (depending on aerobic vs. anaerobic conditions) of the acids to carbon dioxide, ammonia-nitrogen, and volatile fatty acids. Once ammonification occurs, the ammonia-nitrogen is dissolved in the leachate. Removal of ammonia-nitrogen from leachate to low levels is necessary because of its aquatic toxicity and oxygen demand in receiving waters (Berge et al., 2005).

Nitrification/denitrification processes are an advantageous removal mechanism because complete destruction of nitrogen can be achieved. Therefore it is often used and practiced, primarily outside of the landfill. However, additional costs are associated with ex-situ treatment of ammonia, as separate treatment units on site must be maintained or the leachate must be pumped to a publicly owned wastewater treatment facility. Therefore, the development of an in-situ nitrogen removal technique would be an attractive alternative (Berge et al., 2006).

Leachate composition is quite variable, depending highly on waste composition, moisture content of the waste, and age of the landfill (Table 2).

Table 2: Ammonia-nitrogen concentrations in both conventional bioreactor landfills with respect to degree of landfill biological stabilization (Reinhart and Townsend, 1998)

	Concentration (mg/L as N)	
Stabilization phase	Conventional landfills	Bioreactor landfills
Transition	120-125	76-125
Acid formation	2-1,030	0-1,800
Methane fermentation	6-430	32-1,850
Final maturation	6-430	420-580

The figure below illustrates the potential nitrogen transformation and/or removal pathways that may occur in bioreactor landfills.

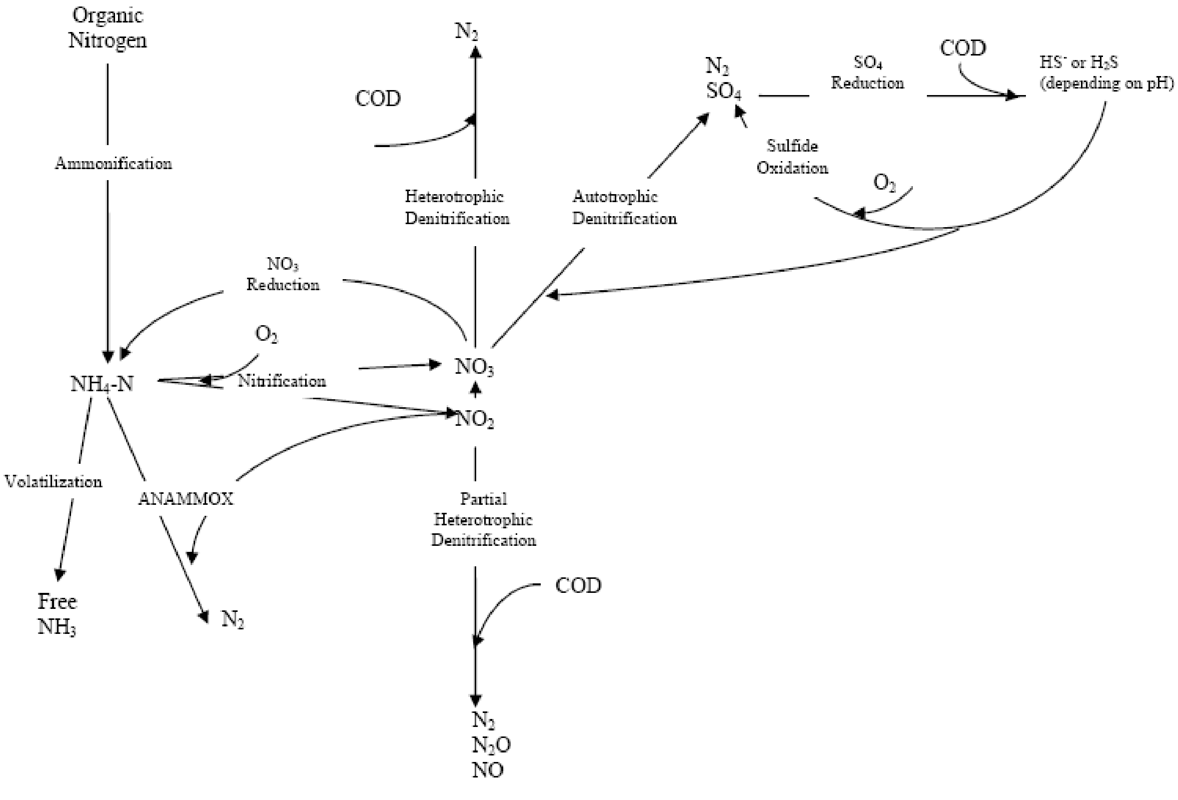

Fig. 6: The potential pathways of nitrogen transformation and/or removal in bioreactor landfills (Berge et al., 2005)

As concern gas composition in the particular case of a bioreactor landfill, gas production and composition in time and stabilization characteristics within a bioreactor landfill unit are reported in Fig. 7.

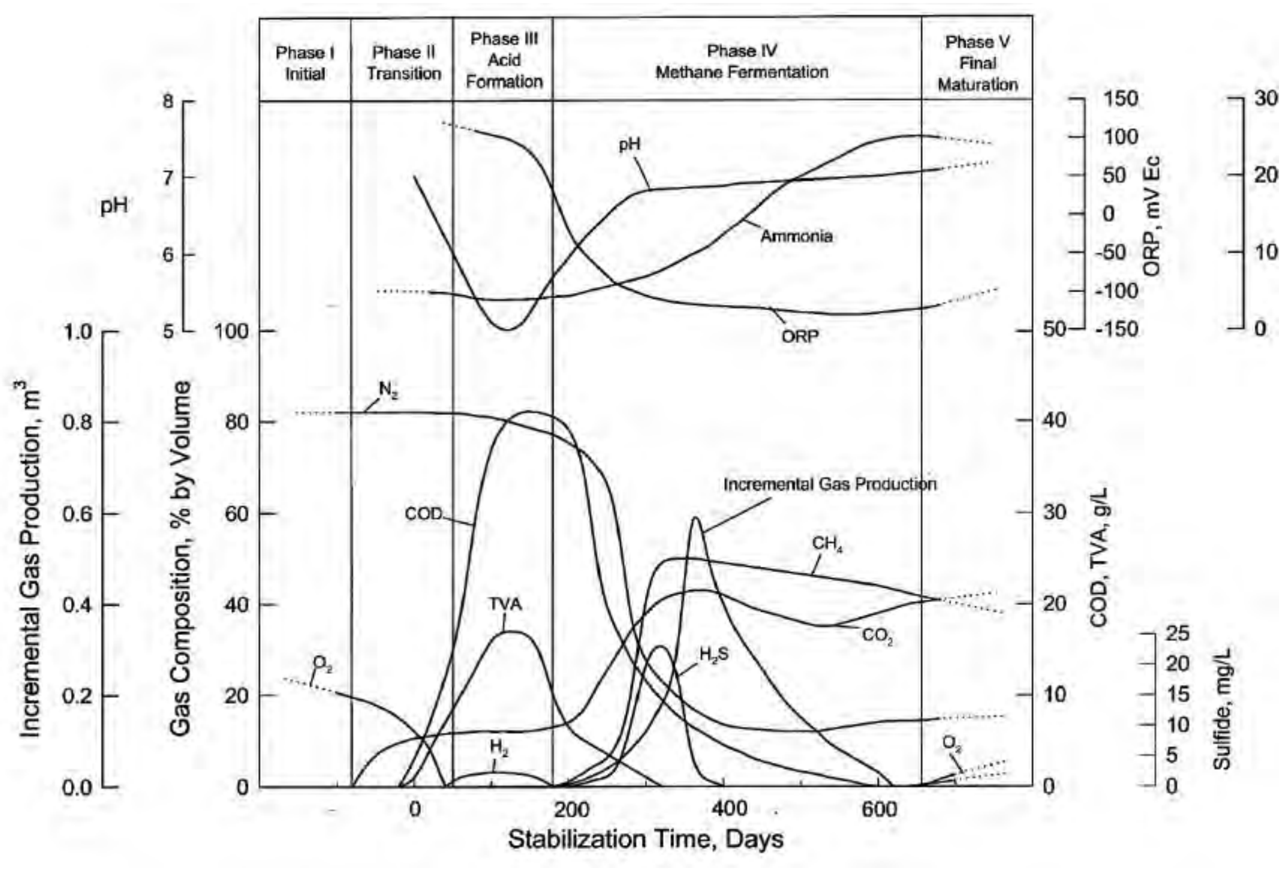

Fig. 7: Time depending concentrations of the main landfill gas compounds (below side); Stabilization characteristics within a bioreactor landfill unit (above side), (Reinhart and Townsend, 1997)

4. S.An.A. LAB-SCALE BIOREACTOR

4.1 Goal of the research

S.An.A. (**S**emi-aerobic, **An**aerobic, **A**erobic) Landfill model is a test carried out by the Environmental Sanitary Engineering Laboratory (LISA) of the University of Padova (IT), starting from an idea of Spinoff S.r.l., a company promoted and participated by the University of Padova (Repetti et al., 2013).

It started as a development of a previous lab-scale test carried out by Cossu et al., (2003) based on the combination of mechanical-biological pre-treatment, landfill aeration by the semi-aerobic method and flushing (PAF model). The main goal was to investigate the different technologies in order to decrease the long-term impacts. The basic idea was to flush the waste through the entry of water into the landfill through permeable top cover and recirculation of leachate (Cossu et al., 2003).

S.An.A. Landfill model was based on six hybrid bioreactor simulators: four managed as hybrid, having a first semi-aerobic phase, a second anaerobic and a third aerobic; while the remaining two were used as anaerobic control bioreactors. The initial waste characteristics, amount, density and the hydraulic characteristics in terms of daily leachate recirculation and moisture content of all the columns were the same. The main goal of the research was to join the advantages of both aerobic and anaerobic processes in order to increase the decomposition kinetics of organic matter without compromising the biogas production, and reduce the post-operational phase.

Obviously the sustainability is a central point of the research. This kind of innovative landfill started from the positive aspects of the “modern” landfills but goes further, trying to respond to the long-term environmental issues reaching the equilibrium between landfill and nature in a shorter time.

According to the European regulation, the time fixed for reaching the sustainability is one generation time corresponding to 30 years. It is generally acknowledged that in traditional landfills, the final storage quality (FSQ) is not achieved after 30 years and so, the landfill sites become contaminated sites. Reaching the FSQ point in time, in fact, marks the end of the aftercare period within the landfill. However, common landfill design and operation are often likely to increase rather than decrease the time needed to reach FSQ i.e. by preventing or reducing access of water, which is necessary for the processes (Hjelmar and Hansen, 2005).

Several researches on hybrid landfill bioreactors have been done in the last years. Starting from the data given by the literature, S.An.A. model study has the aim to conjugate the already proved advantages of leachate recirculation and aeration, with a greater methane production. The most innovative aspect was the first semi-aerobic phase before the anaerobic step and the moment of starting the anaerobic phase, not decided a priori but when the chosen chemical parameters reached the optimal conditions for methanogenic bacteria.

The aims of the whole experimental activity were mainly,:

- demonstrate the benefits of the semi-aerobic phase as a pre-treatment of waste before the anaerobic phase in terms of both biological degradation and methane production;
- calculate the necessary time of aeration based on reaching the optimum values of a certain parameters and not decided a priori;
- assess the benefits of different types of aeration (intermittent and continuous) and predict a range of air flux that maximise the methane production;
- find the optimal combination of processes and method of operation for reaching the final storage quality (FSQ) in the shorter time;
- monitor nitrogen removal and deal with the persistence of ammonia in the last aerobic step;
- complete the stabilization of the residual contaminants through aeration and flushing.

4.2 Waste samples characterization

The sample of waste used for the experiment was constituted by 200 kg of residual municipal solid waste (MSW) provided by a public waste management company from Livorno Province, Tuscany (Italy). The sample was sieved with a 80 mm mesh and only the undersieve fraction (107.6 kg), that corresponds to 53% of the initial waste, was then loaded into the bioreactors. The waste characterization showed high amount of putrescible waste while inert was present in minor quantities (Fig. 8).

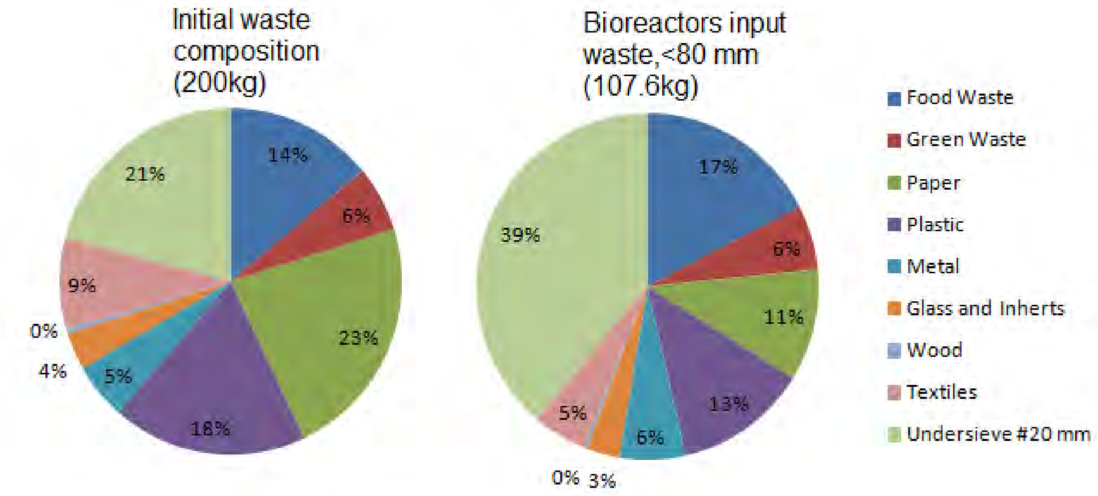

Fig. 8: Sample waste composition for S.An.A. Landfill test

The characteristics of waste samples in terms of mass, total and volatile solids (TS, VS), moisture, total organic carbon (TOC) and Total Kjehldahl Nitrogen (TKN) are reported in Table 3. Only one of the anaerobic columns has different values (ANa).

Table 3: Waste characteristics in each column

	All no ANa	ANa
Mass (kg)	18.4	15.6
TS (%)	55.5	55.5
VS (%TS)	58.9	58.9
Moisture (%)	44.5	44.5
TOC (g/kgTS)	367.7	367.7
TKN (g/kgTS)	9,701.0	9,701.0

4.3 Bioreactors description

The six bioreactors used for the experiment (Fig. 9) were filled with the undersieve waste fraction (<80mm) and closed on the bottom and on the top. The density of the waste inside was kept equal to 0.5 t/m3 in each column in order to guarantee the correct distribution of air and water. A 10 cm layer of gravel, greater than 2 cm in size, was placed on the bottom and on the top of the waste, in order to facilitate the distribution and the homogenization of recirculated leachate. The recirculation of leachate was possible using a peristaltic pump placed on the top of the reactor. A plastic bag container (5 L) was used for leachate collection and extraction on the bottom of each column.

A slotted PVC pipe was placed at the centre of the waste layer in order to guarantee the distribution of air and leachate into the column. The gas generated was collected in bags (20 L) and measured every day in volume composition (%O_2, %CH_4, %CO_2). The temperature was also assessed and monitored with a temperature probe installed inside the reactor.

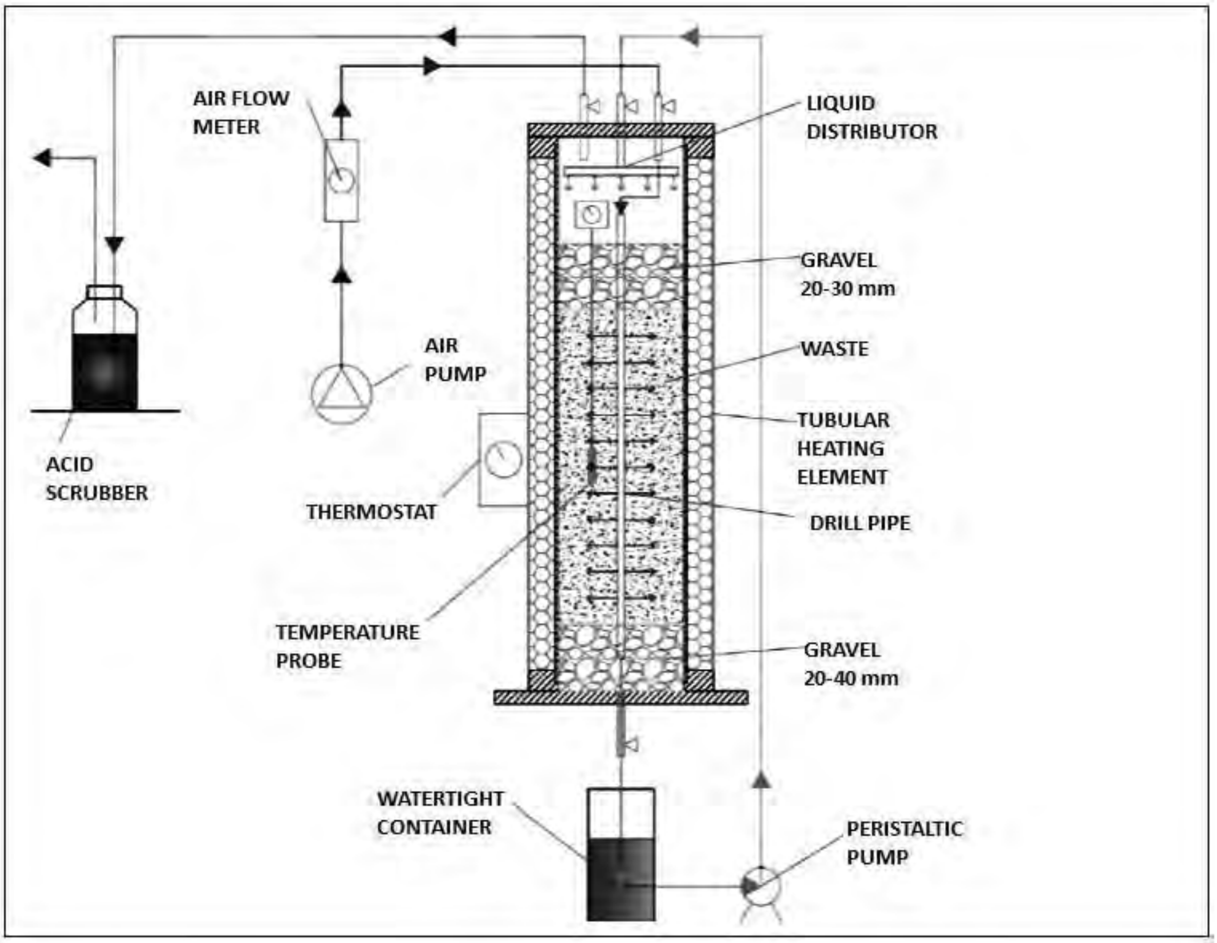

Fig. 9: Sketch of S.An.A. landfill bioreactor

Technical data of a typical S.An.A. landfill bioreactor used for the test are the following:

Table 4: Technical data of S.An.A. landfill bioreactor

Diameter	24 cm
Internal height	106 cm
Material	Polynmethyl methacrylate (Plexiglas ®)
Reactor's closure	Bolted flanges with double rubber seals
Valves in the upper part of the column	3 inox valves: for the input flux of air; gas collection and extraction; input of water or leachate recirculation
Valves in the bottom part of the column	1 inox valve for the leachate flowing by gravity
Leachate recirculation pump	Peristaltic pump Heidolph PD 5001
Leachate collection container	5 liters plastic leachate collection container
Temperature probe	Thermo Systems TS100
Air input pump	Prodac Air Professional pump 360
Airflow regulation	Sho-Rate GT1335 flow meter (Brooks instrument)
Gas collection	20 liters Tedlar® sampling bag

Starting from 3/07/2014 the four hybrid columns were aerated with the semi-aerobic method for 36 days, then the managed was different for each column according to the trend of parameters until 24/10/2014, the day from which all the columns were maintained in anaerobic conditions. The last aerobic phase started on July 13, 2015 in all the hybrid columns, while the anaerobic two columns were used as controlled bioreactors and so always kept in anaerobic conditions (Fig. 10).

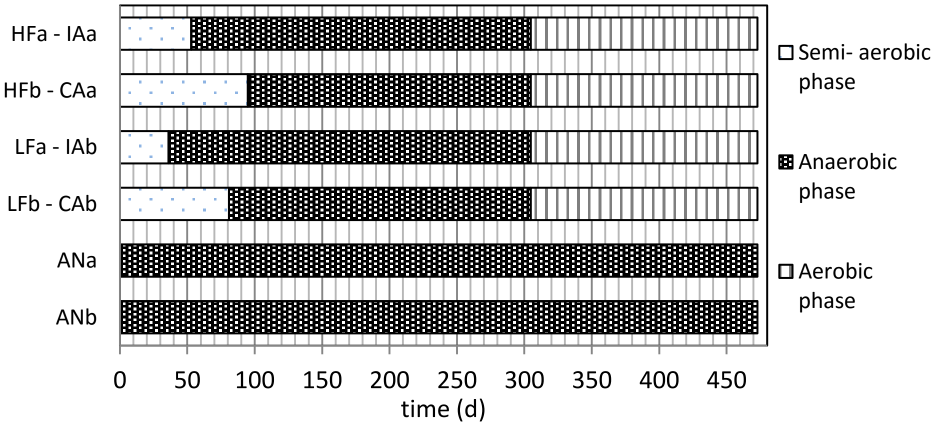

Fig. 10: Operative conditions in time

HF: High Flux; LF: Low Flux; AN: Anaerobic; IA: Intermittent Aeration, CA: Continuous Aeration, a, b double series of columns. The daily aeration was the same for all pre-aerated columns (50 L/d at 20°C and 1 atm).

4.4 First semi-aerobic phase

The first semi-aerobic phase has been thought as a pre-treatment of waste before the anaerobic phase. The greater part of decomposition that occurred directly after the waste was buried is aerobic and continued to be aerobic until all of the oxygen in the interstitial air has been consumed. The duration of the aerobic phase depended on different factors as waste compaction, moisture content, etc.

Fewer laboratory tests on waste and leachate based on this treatment sequence were made before. In fact, the first semi-aerobic phase was one of the news of the S.An.A. method as hybrid reactors.

The aeration consisted in natural air flow with the aim to achieve the values of pH, volatile fatty acids (VFAs), alkalinity and temperature that will be the optimum values for the following anaerobic phase. The main goal is to degrade quickly the readily biodegradable fraction of waste, reduce the duration of the acetogenic phase and accelerate the methanogenesis. In a real landfill, the natural convection of air is guaranteed by the differences of temperature between the landfill waste body (around 50-70°C due to the biological degradation) and the atmospheric air. A particular type of semi-aerobic landfills is the Fukuoka landfill method: the air enters through the slotted leachate collection pipes placed on the bottom and through the vertical gas venting pipes disposed in all the landfill body. Leachate is collected as quickly as possible in order to keep low the hydraulic gradient inside. The benefits obtained are both in terms of COD and BOD_5 reduction in leachate and methane (CH_4) and H_2S reduction in gas (Shimaoka et al., 2000).

For the aeration, in the S.An.A. landfill model, air was injected into the waste in order to simulate the natural convection caused by the temperature gradient between the external environment and the landfill body. Also the recirculation of leachate was done in order to ensure better nutrient distribution and proper moisture content. The aeration was different for the hybrid columns:

- an intermittent aeration was performed for twelve hours a day (12h/24h) in the first two columns (IAa and IAb);
- a continuous aeration (24h/24h) for the remaining columns (CAa and CAb);
- for the anaerobic reactors, no flux of air was supplied.

At the beginning of the test, the airflow was set up at a low regime and then was incremented gradually until oxygen was detectable in the off gasses (O_2> 1-2%).

The experiment started with the same quantity of waste in all the columns (18.4 kg). Some distilled water (6 L in columns I, II, VI and 5 L in columns III, IV, V) was added in each column in order to keep the moisture inside around 55-60% and allow the production of leachate. The recirculation of leachate was done daily for all the quantity extracted, except when the samples for chemical analyses were taken.

The analyses on leachate were done according to the IRSA-CNR 29/2003 methods. The results were always compared with the values given by the literature.

4.5 Second anaerobic phase

The end of the first semi-aerobic phase was not decided a priori but when the specific chemical parameters (temperature, pH, alkalinity, VFAs and N-NH_4^+) reached the optimal conditions for the methanogenic bacteria. This passage was a crucial point of this research test. Criteria of the selected parameters are reported in Table 5.

Table 5: Optimum range and criteria of the main parameters for the methanogenic bacteria

Parameter	Values Range	References
Temperature (°C)	30-40	Christensen et al.,1996; Mata-Alvarez, 2003;
	35-40	Yuen et al.,1995;
	35	Cossu et al., 2005;
	34-41	Yuen, 2001; De Abreu et al., 2005;
	max 55	Khanal, 2008;
	Criteria: 30-40	
Moisture (%)	60-80	Farquhar and Rovers, 1973;
	Criteria: 55-60	
pH	7-7.2	Pfeffer, 1974;
	6-8	Zehnder et al., 1982; Yuen, 2001;
	approx 7	Christense and Kjeldsen, 1989;
	6.7-7.4	Lay et al., 1998;
	6.4-7.2	Chugh et al., 1998;
	7-7.2	Gerardi, 2003;
	6.5-8.2	Sekman et al., 2011;
	6.65-7.41	Sandip et al., 2012;
	Criteria: 6.5-7.5	
Alkalinity ($mgCaCO_3/L$)	1,000-5,000	Agdag et al., 2005;
	2,000-3,500	Ozturk, 1999; Sekman et al., 2011;
	Criteria: 1,000-5,000	
VFAs ($mgCH_3COOH/L$)	< 6,000	Wang et al., 1999; Christensen and Kjeldsen, 1989;
	1,500-2,000	Labatut and Gooch, 2012;
	Criteria: <6,000	

When the optimum values were achieved for each selected parameter, the transition to the second phase was possible. This is because the methanogenic bacteria are more sensible than others: operate in a narrow pH-range and are very susceptible to pH variation. The pH, in turn, could be controlled by the alkalinity that has a buffer capacity and prevents rapid change in pH values. Temperature and moisture are both important to enhance the gas production.

The main goal of this phase was to maximise the production of methane. Due to the previous semi-aerobic phase, the methanogenic phase was reached faster compared to the traditional anaerobic methods. Moreover, the methane production was higher and the methanogenic phase reached faster in the intermittent columns respect to the continuous ones. Volatile Fatty Acids (VFAs) were important to be monitored because can cause stress to microbial fermentation if present in high concentration. The data of methane production obtained in the different columns are reported in Table 6.

Table 6: Methane production at the end of the anaerobic phase

	Experimental Data			
	Total volume of injected air (NL/kgVS)	Pre-aeration time (d)	Maximum daily methane production (NL/kgVS/d)	Cumulative methane production (NL/kgVS)
IAa	357.4	54	2.9	75.1
IAb	210.4	35	2.8	101.7
CAa	674.5	95	2.3	53.7
CAb	566.2	81	2.5	80.2
ANa	0.0	0	1.6	55.2
ANb	0.0	0	1.2	32.0

IA: intermittent Aeration, CA: Continuous Aeration, AN: Anaerobic conditions; a, b double series of columns.

The best result seems to be given by the column “IAb” – that corresponds to the intermittent aerobic reactor characterized by a lower volume of air injected respect to” IAa”. The pre-aeration time took 35 days and reached a peak of daily methane production equal to 2.8 NL/kgVS/d for a cumulative methane production of 101.7 NL/kgVS/d.

In conclusion, the intermittent aeration was more efficient than continuous aeration, but there was a limit of the air flux. If the injected air was too high, the efficiency of methane production decreased. A mathematical evaluation considering the Gompertz Model showed that the optimal range for the intermittent aeration was between 200-400 NL/kgVS.

4.6 Summary of the results of the first and second phases

The results obtained showed that a moderate or an intermittent pre-aeration has positive effects both on methane potential and on the degradation rate of organic substances. The pre-aerated reactors produced a higher biogas volume and reached the methanogenic phase in a quicker time, earlier and with a higher methane production velocity in intermittent aerated bioreactors. In Table 7, data on solids composition are reported for each column.

Table 7: Solid composition in time in S.An.A. Landfill lab-scale reactor

Solid phase:	Start 03/07/2014	End second phase 04/05/2015					
	Initial waste	HFa - IAa	HFb - CAa	LFa - IAb	LFb - CAb	ANa	ANb
Weight (kg tal quale)	18.4	14.9	15.5	15.3	14.9	14.7	16.9
TS (%)	55.5	39.4	47.9	35.7	44.1	61.4	41.3
Weight (kg TS)	10.2	5.2	6.1	5.6	6.5	5.5	6.8
Waste height (m)	0.8	0.6	0.6	0.6	0.6	0.6	0.7
Waste density (kg/L)	0.5	0.6	0.5	0.5	0.6	0.5	0.6
VS (%TS)	58.9	40.6	32.4	39.5	31.0	25.8	44.2
RI_4 (mgO_2/gTS)	76.9	7.2	6.5	8.3	2.8	8.1	13.9
TKN (mgN/kgTS)	9,701	7,596	8,013	7,317	8,498	7,683	7,586
TKN (gN)	99	45	60	40	56	69	53
TOC (gC/kgTS)	368	180	208	231	303	282	274
TOC (gC)	3,755	1,060	1,550	1,265	1,987	2,537	1,915

HF: High Flux, LF: Low Flux, AN: Anaerobic; IA: Intermittent Aeration, CA: Continuous Aeration, a, b double series of columns

Landfill leachate is one of the most pollution problems caused by municipal solid waste (MSW). Its quality depends on many factors as landfill age, precipitation, seasonal weather variation, type and composition of waste, quality of life, social behaviour etc. In particular, the composition of landfill leachate varies greatly depending on the age of the landfill, for e.g. in young landfills there are large amounts of biodegradable organic matter and so a rapid anaerobic fermentation takes place, resulting in volatile fatty acids (VFAs) and high humidity. As a landfill matures, the VFAs are converted into biogas, the organic fraction becomes non-biodegradable and so the presence of humic substances is predominant (Renou et al., 2008). The characteristics of the landfill leachate are generally represented by the basic parameters: pH, TOC, COD, BOD_5, BOD_5/COD, Alkalinity, VFAs, Total Kjeldahl Nitrogen (TKN), ammonium nitrogen ($N\text{-}NH_4^+$), organic nitrogen and heavy metals. In particular, the relation between the organic matter composition and the age of the landfill may provide useful criteria to choose the proper treatment and assess the waste stabilization process. According to the landfill age, three types of leachate landfill could be defined: recent/young, intermediate and old (Table 8). Generally a landfill contains areas of waste of varying ages and states of decomposition at the same time.

Table 8: Landfill leachate vs. age, Landfill classification (modified by Chian and DeWalle., 1976; Renou et al., 2008)

	Recent/young	Intermediate	Old
Age (years)	<5	5-10	>10
pH value	<6.5	6.5-7.5	>7.0
COD (mg/L)	>10,000	4,000-10,000	<4,000
BOD_5/COD	<0.3	0.1-0.3	<0.1
TOC	>3,000	200-3,000	<200
Ammonia nitrogen	>100	40-100	20-40
Nitrate	>25	10-25	2-10
Organic compounds	80% VFAs	5-30% VFAs + humic and fulvic acids	humic and fulvic acids
Heavy metals	low-medium	medium	low
Biodegradability	important	medium	low

Table 9: Leachate composition in time in S.An.A. Landfill lab-scale reactor

	Start 03/07/2014	End second phase 04/05/2015					
	Initial waste	HFa - IAa	HFb - CAa	LFa - IAb	LFb - CAb	ANa	ANb
pH	6.2	8.5	8.3	8.4	8.3	8.1	8.3
TOC (mgC/L)	3,640	1,810	1,150	1,370	1,315	845	1,040
COD (mg/L)	14,682	4,939	2,939	4,791	4,836	2,889	4,834
BOD_5 (mg/L)	7,504	365	308	309	337	393	477
Alkalinity (mg$CaCO_3$/L)	273	985	783	1,038	842	587	1,056
VFAs (mgCH_3COOH/L)	728	154	120	143	141	107	121
TKN (mgN/L)	756	490	237	406	411	131	261
N-NH_4^+ (mg/L)	78	431	141	265	236	66	98
N-Norg (mg/L)	679	59	95	141	175	65	163
Cl^- (mg/L)	619	343	233	243	362	376	324
SO_4^{2-} (mg/L)	<500	<500	<500	<500	<500	<500	<500

HF: High Flux, LF: Low Flux, AN: Anaerobic; IA: Intermittent Aeration, CA: Continuous Aeration, a, b double series of columns

4.6.1 pH trend

The pH in a landfill varies according to the age of landfill. Generally stabilized leachate has higher pH (>7.5) than young leachate (<6.5) (Adhikari et al., 2013).

pH represents the main inhibition factor for methanogenic bacteria that works efficiently only in a small range of about 6-8, depending on the author (Table 5). For this experimental study, the criteria chosen as optimum value for the pH was 6.5-7.5. The values of pH have risen up to about 6.5 in the first week from the beginning of the experiment in all the columns. After two weeks the values dropped to about 5.7 indicating the accumulation of organic acids. It was observed that in the intermittent columns (IAa and IAb), the pH values started to increase faster than in continuous ones (CAa and CAb), starting at day 50 and day 110 respectively, up to maximum 7.8. The increasing in pH value suggested that a steady state has been reached between acidic producing processes and acid consuming processes. The anaerobic columns, on the contrary, remained in acidic or slight acidic conditions for all the period of time. This fact reflected the accumulation of fermented acids and so the acidogenesis phase (Sang et al., 2009).

As a consequence, pH value depended by the aeration: with the intermittent aeration, the increasing of pH is faster and so the acidic phase was shorter, means that the methanogenic phase was anticipated. At the passage to the second anaerobic step, all the columns were in acidic conditions. However, "CAb" bioreactor was not able to start the methanogenic phase at a pH equal to 6.1 and a rising in value up to 6.5 was necessary. The lowest pH was registered in the third column (IAb) with 6.25 pH value (Fig. 11).

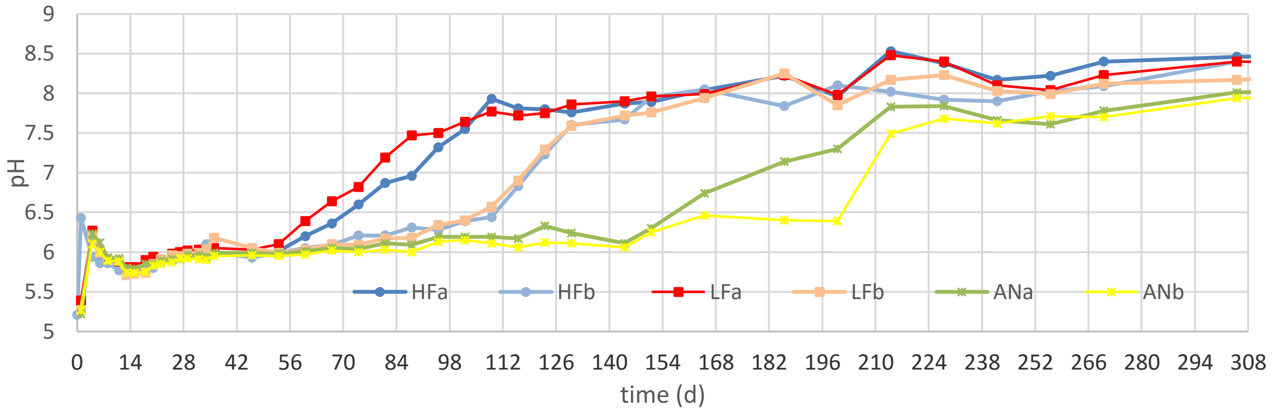

Fig. 11: pH value trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

A close attention was paid on the concentration of volatile fatty acids (VFAs) that constitute the feed for methanogenic bacteria: when VFAs increased, pH value decreased (Fig. 12). However, if the concentration is too high, for e.g. above 6,000 mg/L, pH decreases too much causing the inhibition of methanogenic activity. The "excess of loading" is generally kept under control by monitoring the German FOS/TAC parameter.

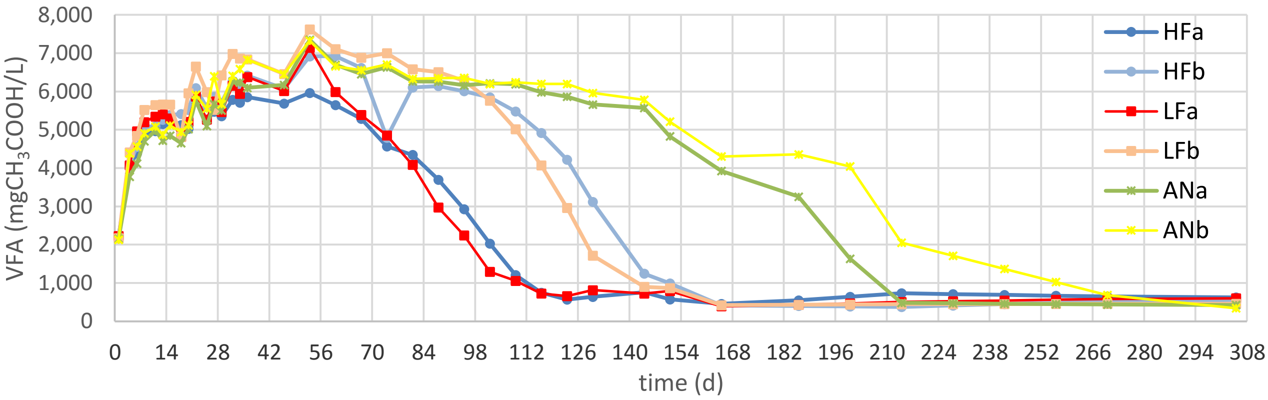

Fig. 12: VFAs ($mgCH_3COOH/L$) trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

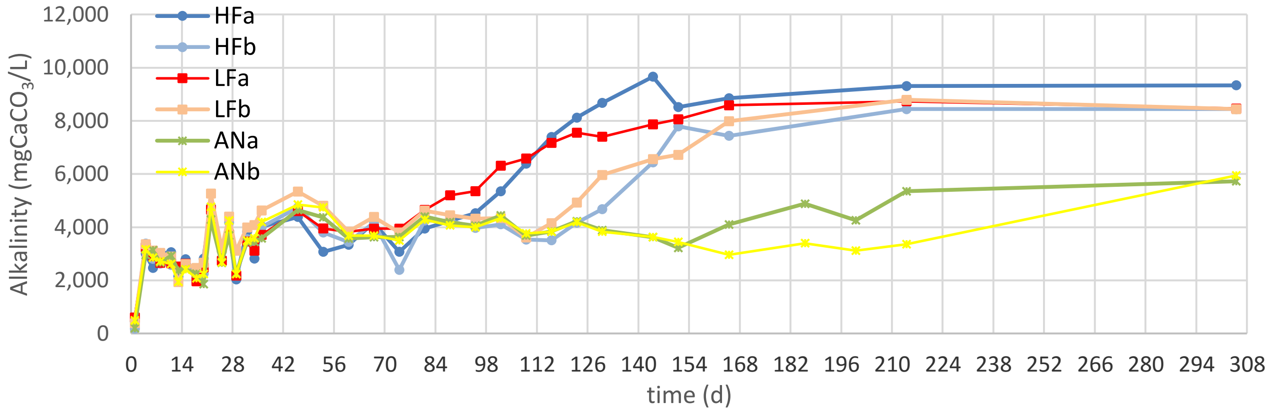

Fig. 13: Alkalinity ($mgCaCO_3/L$) trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

4.6.2 FOS/TAC

The ratio between the volatile fatty acids (VFAs), in terms of acetic acid, and the alkalinity, in terms of calcium carbonate, is an important parameter to control the stability of the anaerobic process. It gives an indication of the equilibrium between acids and buffer capacity of the system.

The alkalinity started to increase after a constant period of two months in all the hybrid columns, very quick in the intermittent air flux columns and slower in the continuous air flux ones.

The concentration of volatile fatty acids (VFAs) showed a similar trend with COD in all the reactors. In the first 50 days, a high accumulation of organic acids due to the hydrolysis process was present, so also the VFAs concentration was high. The values of VFAs started to decrease with the second anaerobic phase with the biogas production. The methanogenic bacteria, in fact, use VFAs as substrate to produce biogas and new cells. The ratio between FOS and TAC remained greater than one up to day 80 in first (IAa) and third columns (IAb) and up to day 120 for the second (CAa) and the forth ones (CAb). Then the value dropped to 0.8, a good value for the methane production (Farquhar et al., 1973). On the contrary, in the control anaerobic columns, the ratio was greater than 1.5 for a long time due to the well-developed acidic conditions. It started to decrease after about 150 days and the decreasing becomes very quick as the methane production was established (Fig. 14).

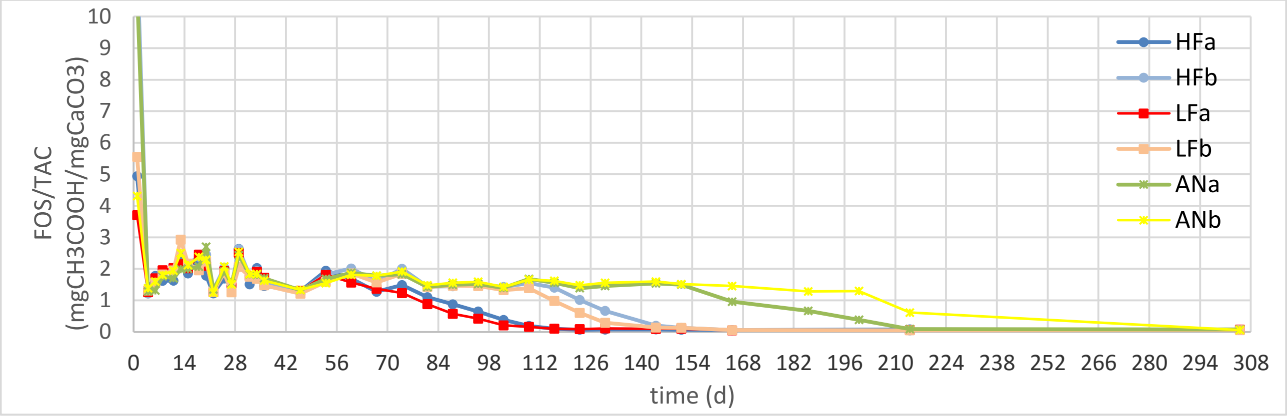

Fig. 14: FOS/TAC ratio trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

4.6.3 Dissolved organic matter

The degradation process starts with the hydrolysis, the process in which the complex organic molecules are breaking down in smaller simple compounds increasing in this way the easily degradable organic matter. The COD (chemical oxygen demand) measures the requirement of oxygen for complete chemical degradation of both biodegradable and non-biodegradable organic compounds. The highest COD value was registered in the column "CAa" equal to 104,000 mgO_2/L at the day 25. It was observed that in the intermittent columns, COD values dropped quickly than in the continuous ones, starting from the day 74 and 120 respectively (Fig. 15).

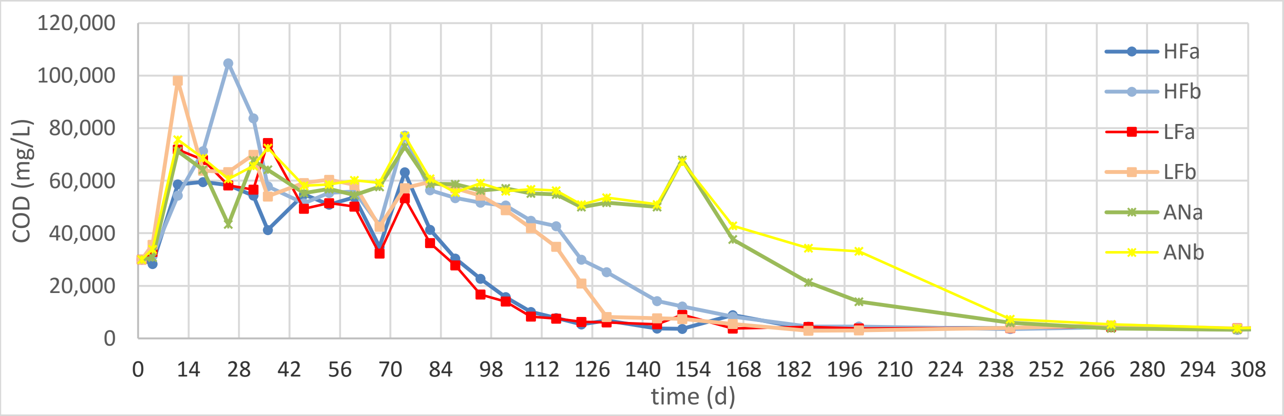

Fig. 15: COD (mgO_2/L) trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

Similar trend was observed on TOC values. The highest value was observed in the first column (IAa) equal to 16,650 mgC/L, means that the intermittent aeration accelerate the time needed for the stabilization. The trend of TOC showed an initial increasing and then a fast drop in all the columns. The rapid reduction of the TOC was seen in the hybrid reactors, while the anaerobic ones were characterized by a slower decreasing.

The decreasing in time of the TOC values indicated the decreasing of the availability of organic carbon for effect of degradation and leaching processes (Fig. 16).

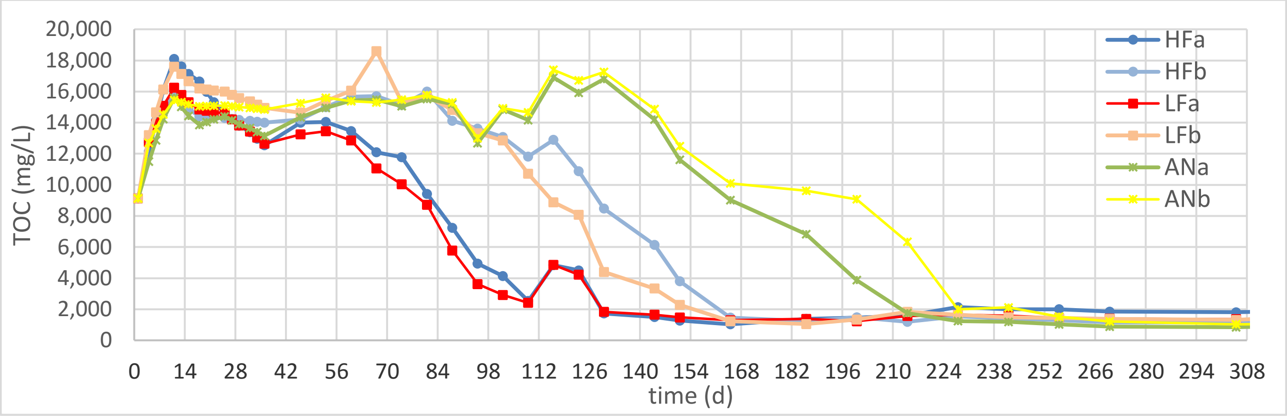

Fig. 16: TOC (mgC/L) trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

It was observed that in the anaerobic reactors both TOC and COD concentrations remain almost constant in time due to the slight acidic pH. In fact, the low level of pH tends to favor the accumulation of organic acids from the hydrolysis process of complex organics.

The ratio BOD_5/COD is also an important parameter of leachate indicating the amount of biodegradable substances. At general level, a low level of BOD_5/COD suggests a leachate with low concentrations of volatile fatty acids (VFAs) and relatively higher amounts of humic and fulvic-like compounds. This means that lower the ratio is, older is the landfill.

The initial values of BOD_5 and COD in S.An.A. Bioreactor Landfill were, respectively, 27,431 and 30,000 mg/L, calculating a ratio BOD_5/COD of 0.91 that corresponds to a highly biodegradable matter. The decreasing in the biodegradability was faster in the intermittent aeration columns. The ratio of BOD_5/COD remained high in the continuous aeration columns, while in the anaerobic ones, decreased in the first period but then remained constant under 0.1 (Fig. 17).

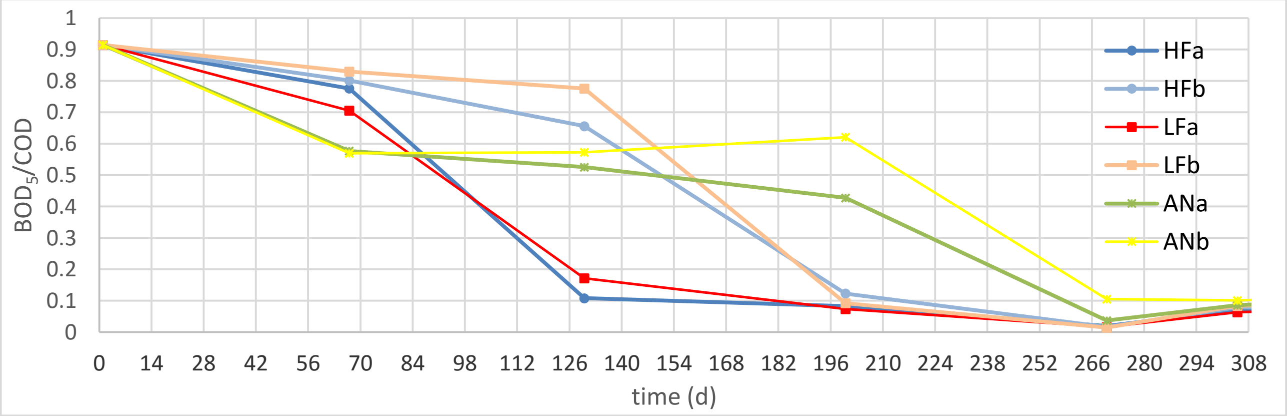

Fig. 17: BOD_5/COD ratio trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

The carbon mass balance was performed on TOC in terms of gC/kgTS:

$$TOC_{ACC} = TOC_{IN} - TOC_{L} - TOC_{G}$$

considering the initial carbon content of waste “TOC_{IN}”, the carbon removed by leachate extraction TOC_L” and the carbon removed by the biogas “TOC_G” (methane and carbon dioxide).

It was observed that the carbon removed in the intermittent air flow column was greater than in the continuous ones. The major degradation of carbon was observed in gas form and in particular carbon dioxide was the main product obtained.

4.6.4 Nitrogen compounds

Nitrogen could be present in a wide variety of chemical forms including organic nitrogen, ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), nitrous oxide (N_2O), nitric oxide (NO) or inorganic nitrogen gas (N_2). The useful parameters for this experiment study were organic nitrogen, ammonium and Total Kjeldahl Nitrogen (TKN) that is the sum of organic nitrogen, ammonia and ammonium.

In the anaerobic control bioreactors a constant nitrogen compounds were generally present due to the absence of nitrification and volatilization processes. On the contrary, in the presence of oxygen, the conversion of ammonia into nitrites and nitrates occurred during the nitrification process.

The accumulation of ammonia nitrogen was registered in all the columns with values below 1,500 mgN/L only in the reactor “ANb”. This result was expected due to the daily recirculation of leachate that normally always increase ammonia concentration and intensify the toxicity of the leachate. Another reason of the accumulation of nitrogen in the S.An.A. landfill experiment was the absence of nitrification and denitrification processes probably due to the insufficient oxygen supply. In fact, neither nitrate nor nitrite were detected and this fact contributed to ammonium accumulation. A similar trend could be observed both for $N\text{-}NH_4^+$ and TKN (Fig. 18, Fig. 19). Only after about 300 days the organic nitrogen, calculated as a difference between TKN and $N\text{-}NH_4^+$, was lower than 200 mgN/L in all the bioreactors.

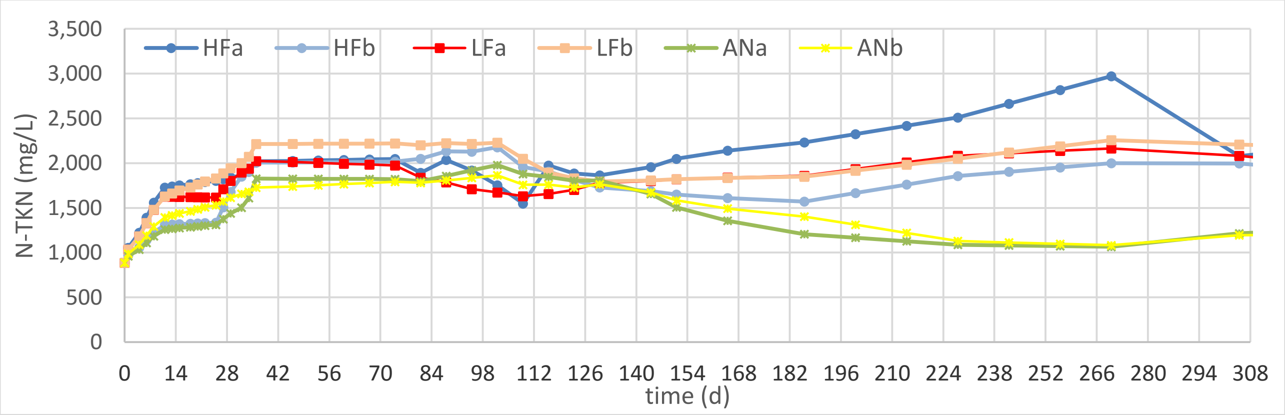

Fig. 18: TKN (mgN/L) trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

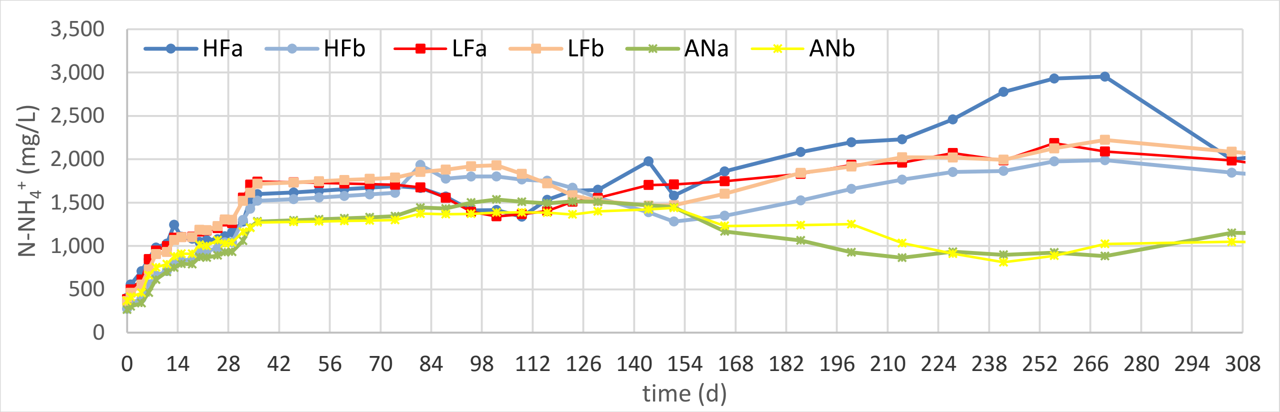

Fig. 19: N-NH_4^+ (mgN/L) trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

The nitrogen mass balance was performed on TKN in terms of mgN/kgTS:

$$TKN_{ACC} = TKN_{IN} - TKN_{L}$$

where TKN_{IN} is the initial nitrogen mass in the waste, TKN_{L} is the nitrogen mass removed with the extraction of leachate, while TKN_{ACC} is the nitrogen accumulated or better the nitrogen mass remained into the waste. Large amount of nitrogen remained into the solid waste and only 10% was removed. It was not possible to take into account the nitrogen mass escape via biogas (ammonia gas or nitrogen gas), and so the removed nitrogen was considered in terms of leachate only. For this reason, the final nitrogen remained should be a little bit lower than the calculated, considering in this way the uncounted gas losses.

The reasons for which nitrogen remained mainly into the solid waste mass are the washout of the daily recirculation, the pH value <8 that do not allow ammonia volatilization, the absence of oxygen that inhibit the nitrification and denitrification processes.

4.6.5 Leachable compounds

Chloride is one of the major inorganic anions present in wastewater and leachate generally removed via washout. Chloride is considered as a “conservative” and inert parameter, therefore, it can be used as a “tracer” parameter (De Abreu et al., 2005). The chloride monitoring is important for the assessment of the leachate dilution and washout effects. It was observed that the concentration of chloride increased with the increasing of pH, due to the increasing of its dissolution. In the first month of the research, the pH values were acidic in all the reactors and also the chloride concentration was low. Since the day 70 from the initial of the experiment, an oscillating trend in the intermittent columns was observed (Fig. 20).

The concentration of sulphate decreased in all the reactors due to the presence of the sulphur-reducing bacteria. These type of bacteria are strict anaerobic and convert hydrogen (H_2), acetic acid (CH_3COOH) and volatile fatty acids (VFAs). The presence of sulphur-reducing bacteria also in the aerated columns is possible due to the presence of anaerobic zones inside the waste body. Since the increasing in sulphate decreases methanogenesis, the downward trend (Fig. 21) was a positive result. In particular, the performance was better in the columns with intermittent aeration.

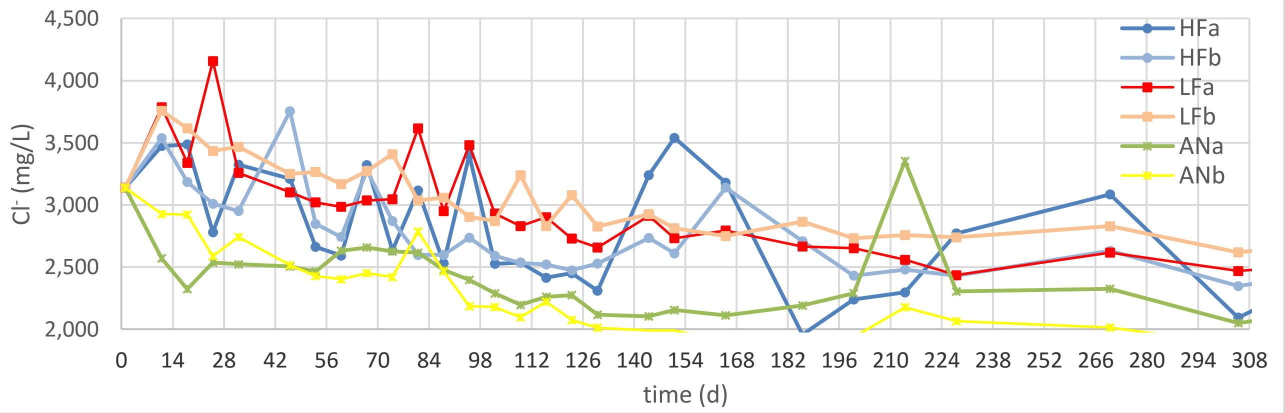

Fig. 20: Chlorine (mg/L) trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

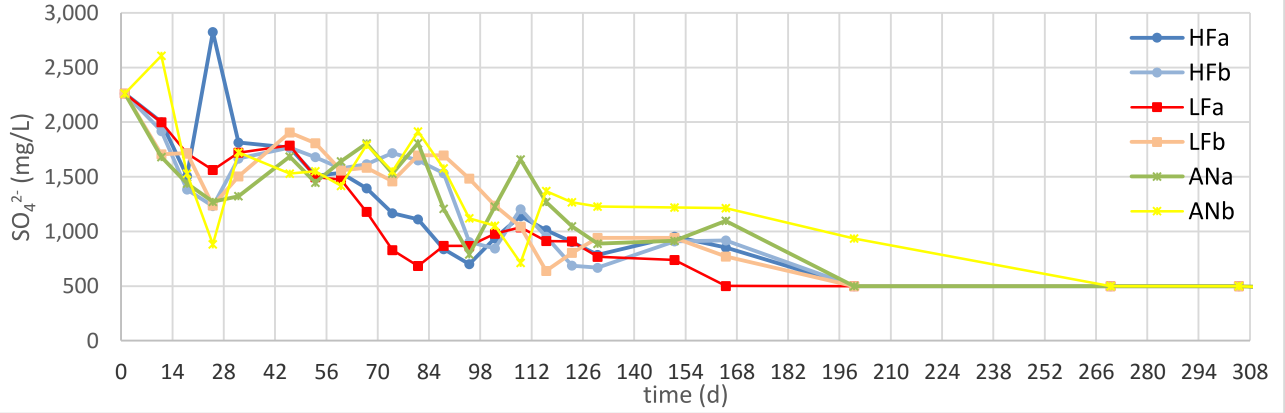

Fig. 21: Sulphate (mg/L) trend, from the beginning of the experiment, S.An.A. lab-scale landfill reactor

4.6.6 Methane production

After a few days of acclimatization, in the anaerobic phase the production of methane started. The methanogenic conditions were confirmed by the change in gas composition to about 55-60%CH_4 and 30-35%CO_2. The volume of methane per kilogram of organic matter is an indicator of the waste stabilization. It was observed that the anaerobic bioreactors never reached a stable methane production mainly due to the constant acidic conditions that tend to mummify the waste.

Since the pH reached the value of 6.5, the injection of air was stopped and all the system was switched to anaerobic conditions. The two intermittent air flow hybrid reactors were converted to anaerobic conditions earlier (on day 56 and 36) than the continuous air flow ones (on day 95 and 81). The production of methane was higher in the intermittent than continuous aerated and anaerobic bioreactors with a cumulative methane produced equal to about, respectively, 75-100 NL/kgVS, 53-80 NL/kgVS and <55 NL/kgVS (Table 10, Fig. 22). Also in other studies, performed in the last years, the maximum methane concentration was higher in the intermittently aerated reactors respect to the continuously aerated ones. The reason for which the waste stabilization and the methane production is enhanced with the intermittent aeration could be the alternation of aerobic and anaerobic microbial community formed in a non-continuous aeration condition that stimulate better the degradation process (Sang et al., 2009).

Table 10: Methane production in the different bioreactors, at the end of the anaerobic phase

	Experimental data				
Bioreactors	Total volume of air Injected (NL/kgVS)	Pre-aeration time (d)	Methane production period (d)	Maximum daily methane production (NL/d/kgVS)	Total volume of methane produced (NL/kgVS)
IAa	357.4	54	149	2.9	75.1
IAb	210.4	35	163	2.8	101.7
CAa	674.5	95	106	2.3	53.7
CAb	566.2	81	133	2.5	80.2
ANa	0.0	0	130	1.6	55.2
ANb	0.0	0	130	1.2	32.0

The results obtained showed that the pre-aeration process is always good to increase the methane production, but a right quantity of injected air flux per kg of total solids should be calculated. In fact, if it is too high, the organic substances may be degraded too much and so may not be available anymore for methane production, reducing in this way the quantity of methane produced. For example, the first column

"IAa" was aerated two weeks more than the other intermittent air flow column "IAb" and this fact affected negatively the production of methane (Table 10, Fig. 22). The point is that both the continuous and the intermittent air flux bioreactors had the same daily inlet flux of oxygen but for a different period of time. The intermittent aeration, characterized by an aeration for 12 hours per day, accelerated the stabilization process due to the more dynamic conditions created, respect to the traditional anaerobic conditions.

As concern the two anaerobic control bioreactors, insignificant amount of methane with a percentage range between 8% and 10% was produced inside. The lower value of methane emissions from the anaerobic reactors is probably due to the acidogenesis phase before the methanogenesis (Sang et al., 2009). Another important point for the methane production was leachate recirculation: during the first two weeks, there was no leachate recirculation and the methane concentration obtained was about 30%; starting with the recirculation process, the percentage increased over 60% in a short time (5 days) and remained more or less stable.

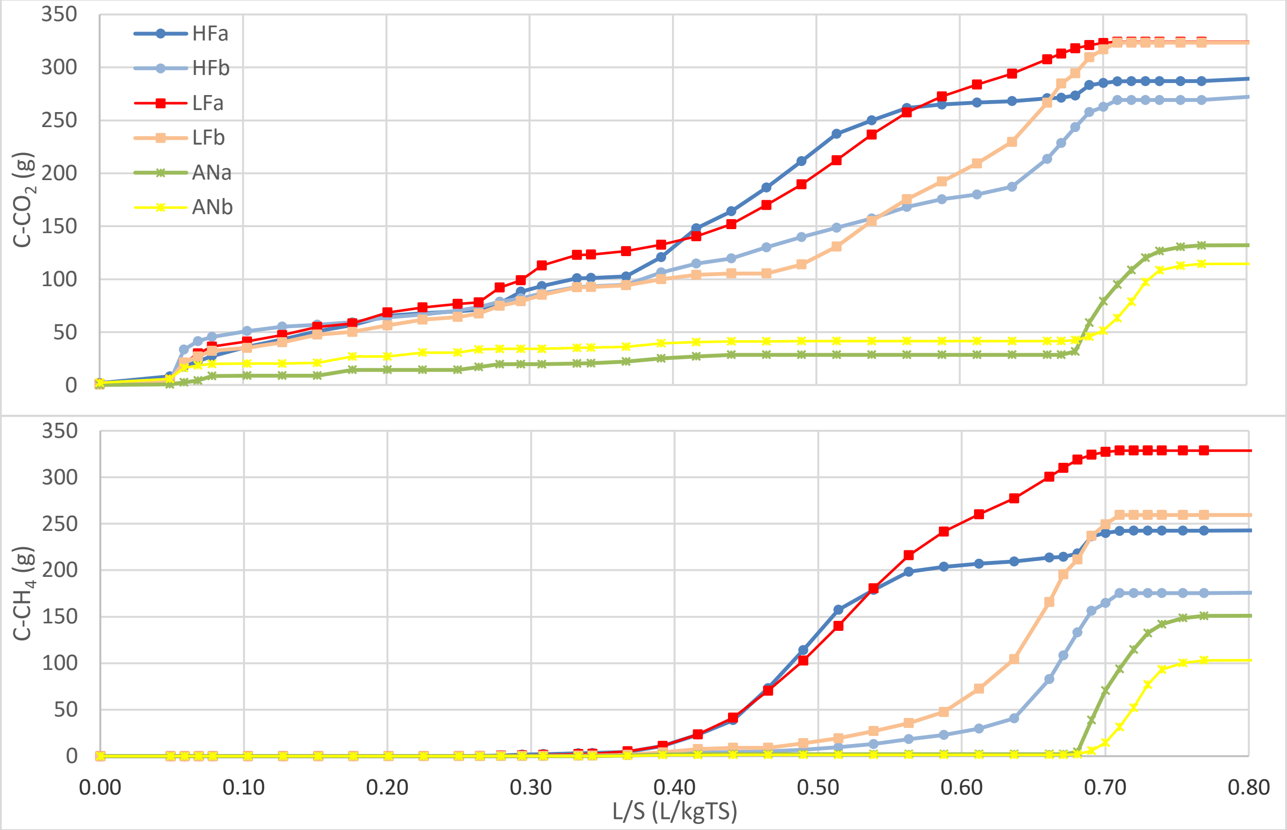

Fig. 22: Cumulative emissions of C-CO_2 (g) and C-CH_4 (g), from the beginning of the experiment, S.An.A. lab-scale landfill reactor

A useful mathematical tool for linking air injection and methane production is the modified Gompertz Equation. The model parameters (BGP, Rm, λ) were calibrated by minimizing the mean square deviation of the values measured and calculated. The main goal was to compare the model parameters with the total air supplied in order to establish the best conditions of pre-aeration. The maximal biogas yield potential

(BGP) represents the total methane production potential per kg of VS. “Rm” is a parameter that models the kinetic of the methane generation reactions. The bacteria growth lag time (λ) indicates the period required for the acclimation of the methanogenic bacteria and it corresponds to the time required for starting the methane production (Fig. 23). The optimum range of air supply was mathematically calculated in this experiment, corresponding to 200-400 NL/kgVS.

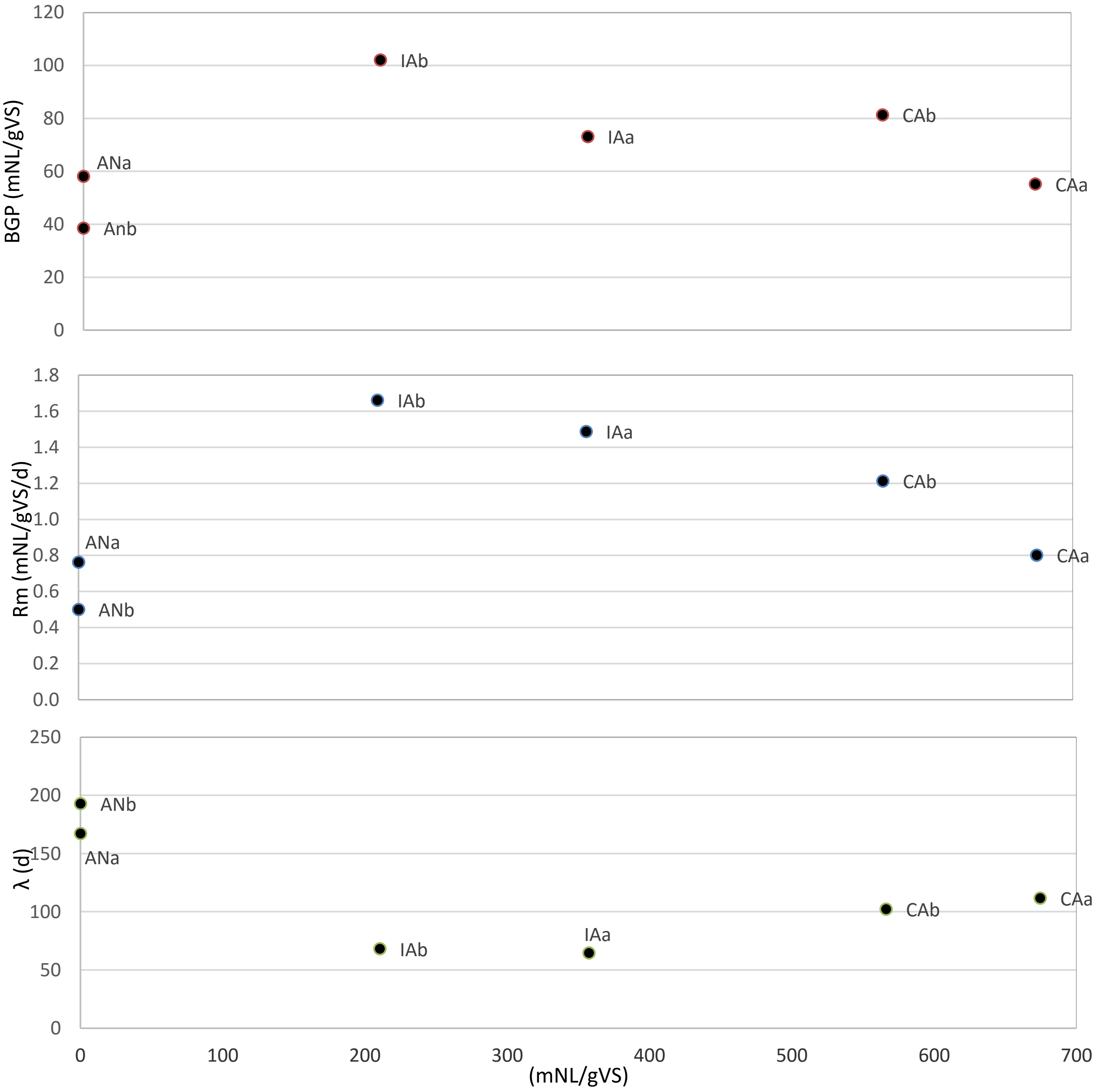

Fig. 23: Results of Gompertz Equation

4.7 Discussion of the first and second phases

The initial sample of waste was the same in terms of both quality and quantity in all the columns. The analyses were carried out both on solids and on leachate samples.

Leachate samples were analyzed in terms of pH, VFAs, alkalinity, carbon indexes (COD, TOC, BOD_5), nitrogen indexes (TKN, $N\text{-}NH_4^+$, NO_3), SO_4^{2-}, S^{2-}, Cl^- and heavy metals as Cd, Cr, Cu, Fe, Mg, Ni, Zn. Biogas collected in bags was measured in terms of oxygen, methane and carbon dioxide. Solid waste was studied for the determination of TS, VS, TKN, $N\text{-}NH_4^+$, TOC, IR_4, IR_7 and heavy metals as Cd, Cr, Cu, Fe, Mg, Ni, Zn.

Hybrid bioreactors were better than anaerobic ones, in the first two phases, because:

- the pollution concentration was higher in the traditional anaerobic columns in terms of TOC, COD and ammonia;
- the production of biogas was delayed in the anaerobic reactors due to the VFAs accumulation that tend to decrease the pH value;
- the methanogenic phase was reached earlier due to the pre aeration phase;
- the total gas production and the methane generation was higher than in anaerobic conditions;
- the carbon removal achieved acceptable values in a shorter time due to the gasification enhanced by the semi aerobic conditions;

Intermittent aeration was better than continuous, in the first two phases, for different reasons:

- the acidic formation phase was reduced and so the time needed to start the anaerobic phase was shorter and so the production of methane was earlier;
- the achievement of stable methane conditions was faster;
- the maximal daily biogas yield was higher;

As a consequence, the semi aerobic phase was always better than a traditional landfill. The production of methane was higher in intermittent aeration but a careful consideration must be taken in order to stabilize the right flux of oxygen and avoid over aeration. If the inlet air flux increases too much, the methane generation decreases due to the lower carbon availability for the following anaerobic phase. On the other hand, the air flux should not be too low because it is essential for the VFAs reduction.

4.8 Third aerobic phase

The study of the third phase of the experiment started on July, 2015. The last phase has the aim to accelerate the process of stabilization and leaching of the remaining potentially contaminating substances (refractory compounds), in order to achieve faster the final storage quality (FSQ). In particular, the main goal was to deal with the persistence of ammonia by monitoring the effectiveness of nitrogen removal. This research study wanted to demonstrate that with adequate treatment technologies, such as aeration and flushing, the low limits could be easy reached.

The two anaerobic reactors remained in anaerobic conditions and were used as control reactors. The four hybrid reactors, managed with intermittent and continuous aeration flux in the first semi-aerobic phase, are now all managed as continuous but with different discharge of air: reactor n. 1 and n. 2 with high flux aeration equal to 200 NL/d (HFa, HFb) and reactor n. 3 and n. 4 with low flux aeration equal to 40 NL/d. Since the weight (kg tal quale) was different in each column, it was decided to homogenize this value and so, the same total solids (5.2 kgTS) was considered and the excess of waste not more considered in this experiment study. The humidity maintained in all the reactors is of 55-60% and the leachate extracted weekly for sampling was fixed to 0.3 L that will be restored for the same quantity with fresh water. The recirculation of leachate was daily while the sampling weekly (Table 11).

Table 11: Management scheme of the aerobic phase

Reactor name in phase I, II	IAa	CAa	IAb	CAb	ANa	ANb
Reactor name in phase III	HFa	HFb	LFa	LFb	ANa	ANb
Weight (kg tal quale)	14.9	13.3	14.2	11.8	13.8	12.9
Weight (kg TS)	5.2	5.2	5.2	5.2	5.2	5.2
Waste height (m)	0.50	0.45	0.45	0.45	0.50	0.50
Waste density (kg/L)	0.66	0.65	0.70	0.58	0.61	0.57
Humidity (%)	55-60	55-60	55-60	55-60	55-60	55-60
Water in = Leachate out (L/w)	0,3	0,3	0,3	0,3	0,3	0,3
Test length (m)	6	6	6	6	6	6
L/S reachable (L/kgTS)	2.25	2.25	2.25	2.25	2.25	2.25
Leachate recirculation	daily	daily	daily	daily	daily	daily
Temperature (°C)	40	40	40	40	40	40
Aeration concept	forced	semi-aerobic	forced	semi-aerobic	anaerobic	anaerobic
Aeration modality	cont	cont	cont	cont	cont	cont
Aeration (NL/d)	200	200	40	40	0	0

The aerobic step of the experiment was a key point to monitor the different nitrogen forms repartition (ammonia, nitrates, organic nitrogen and ammonia gas) and ensure the reaching of the law limits in the shorter time. The guideline for the waste management and landfill building proposed by the Lombardia Region suggests a maximum value of ammonia-N and nitric-N respectively equal to 50 and 20 mg/L. The law limits of the main important parameters given by Lombardia guidelines are reported in

Table 12: Law limits given by Lombardia guidelines in leachate, biogas and solids

Leachate:

Parameter	Law limit (mg/L)
COD	1,500
BOD_5/COD	0.1
N ammonia	50
Cd	0.02
Cr	2
Cu	1
Fe	2
Ni	2
Pb	0.2
Zn	3
$SO4^{2-}$	1,000
N nitric	20

Biogas:

Parameter	Law limit ($NLCH_4/m^2/h$)	($NLCH_4$/ h)
Emissions	0.5	0.022608

Solids:

Parameter	Law limit
RI_4 (mgO_2gST)	2
RID (mgO_2/kgSV/h)	100
GB_{21} (NL/kgST)	5

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II) SCIENTIFIC PAPER: S.AN.A. HYBRID LANDFILL: NITROGEN EMISSIONS IN LAB-SCALE SIMULATION BIOREACTORS DURING THE FINAL AEROBIC STEP

S.AN.A. HYBRID LANDFILL: NITROGEN EMISSIONS IN LAB-SCALE SIMULATION BIOREACTORS DURING THE FINAL AEROBIC STEP

COSSU RAFFAELLO, MORELLO LUCA, TEPORDEI CRISTINA

Abstract

The aim of this experimental activity was monitoring the biochemical processes in S.An.A. Hybrid Bioreactor Landfill and evaluate the nitrogen removal during the last aerobic phase. The whole test was planned in three phases: semi-aerobic, anaerobic, aerobic, and the results obtained from the first two phases confirmed the advantages of waste pre-treatment before the anaerobic phase in terms of organic material degradation and methane production. Although the leachate recirculation could accelerate the waste stabilization in bioreactor landfills, the removal of ammonia from the leachate remained a challenge due to the absence of oxygen and nitrification in anaerobic conditions. It has been suggested that ammonia is one of the most significant long-term pollutant in landfills and is likely a parameter that will determine when landfill post-closure monitoring may end. Therefore, the aim of the aerobic step is to deal with the persistence of ammonia by monitoring the effectiveness of nitrogen removal and to complete the stabilization of the residual contaminants through aeration and flushing.

1. Introduction

The aim of the modern landfill management is to meet the sustainability concept, consisting in reduce environmental impacts over one generation (30 years), in order to no longer significantly affects the quality of the surrounding environmental compartments: air, water and soil (Cossu et al., 2007). The different methods of pre-treatments (ex-situ and in-situ) should therefore be developed and designed according to an integrated view. Nowadays, a relatively new concept of Municipal Solid Waste (MSW) treatment is known as bioreactor landfill technology: a sanitary landfill that use microbiological processes purposefully to transform and stabilize the biodegradable organic waste fraction in a shorter period of time (Pacey et al., 1999; DeAbreu et al., 2005). During the recent years, bioreactor landfill technology demonstrated the biodegradation and stabilization of MSW through water addition, leachate recirculation and/or air injection (Erses et al., 2008; Shao et al., 2008; He et al., 2011; Sekman et al., 2011; Sandip et al., 2012; Sun et al., 2013; Xu et al., 2014). An optimum moisture content is necessary to guarantee the metabolic processes, microorganisms growth and nutrient transport (Norbu et al., 2005), while the injection of air enhances and accelerate the degradation kinetic (Cossu et al., 2003; Ritzkowsky, 2013). The general advantages of bioreactor landfills with leachate recirculation are: I) distribution of nutrients and enzymes throughout the waste mass, II) pH buffering, III) dilution of inhibitory compounds, IV) recycling and distribution of methanogens, V) improvement of landfill gas production rate, VI) liquid storage and reduction in time and cost of post-closure monitoring (Reinhart and Townsend, 1998; De Abreu et al., 2005). Regarding the limitations of leachate recirculation, the primary criticism is an increase in the hydraulic loading and the leachate pollutants (Lee and Lee, 1994; De Abreu et al., 2005).

Bioreactor landfills could be managed as aerobic, anaerobic or hybrid (EPA, 2015). There are different proposed definitions of “hybrid bioreactors landfill”, but all are based on the idea of combination of aerobic and anaerobic conditions, taking the advantages of both of them (Long et al., 2009). In the aerobic phase, high degradation kinetics of organic substances is possible, enhancing in this way the waste biostabilisation (Nikolaou et al., 2010). Otherwise, in the absence of oxygen (anaerobic conditions), the degradation rate is slower but methane production is favoured (Sandip et al., 2012). Several bioreactor hybrid landfills performed by researchers during the last years, generally based on two sequencing stages of facultative anaerobic and aerobic conditions (Berge et al., 2006; Erses et al., 2008; Long et al., 2008; Yan et al., 2009; Sandip et al., 2012; Xu et al., 2014), demonstrated the reaching of the final storage quality (FSQ) in one generation time (30 years) as request by the current regulations in Europe. In particular, laboratory-scale tests (Onay and Pohland, 1998) showed that in-situ nitrification-denitrification process appeared more promising than the conventionally adopted ex-situ processes owing to its lower operational cost and lower space requirements (He et al., 2006; Shao et al., 2008).

S.An.A. (**S**emi-aerobic, **An**aerobic, **A**erobic) is a three phases hybrid landfill bioreactor with the purpose to join the advantages of an alternation of processes, in order to increase the decomposition kinetics of organic matter without compromising the biogas production and, at the same time, reduce the post-operational phase (Repetti et al., 2013). The performed experimental activity is based on six lab-scale bioreactors: four of them was managed as hybrid, having a first semi-aerobic phase, followed by a second anaerobic and a third aerobic phase. The remaining two were used as anaerobic control bioreactors. The first semi-aerobic phase of S.An.A. Landfill was one of the novelty of these lab-scale hybrid reactors. Each reactor was loaded with the same waste in terms of composition, amount, density and hydraulic properties. Two of the hybrid reactors were continuously aerated (24h/24h) and the other two reactors were intermittently aerated, with a cyclic 12-h aeration and 12-h non-aeration. An equal daily air flow rate (50 L/d at 20 °C, corresponding to 5 NL/d/kgTS in our specific case) was adopted for all the pre-aerated reactors (4.2 L/d in the intermittently and 2.1 L/d in the continuously aerated bioreactors) and was chosen considering previous lab-scale experiments carried out on landfill bioreactors in semi-aerobic conditions with average values between 4-10 NL/kgTS/d (Cossu et al., 2005; Sun et al., 2013). The main goal of the first semi-aerobic phase was to pre-treat the waste before the anaerobic phase in order to enhance the biodegradation process. Another novelty of this lab-scale study was the transition from semi-aerobic to anaerobic phase. It was not a previously fixed condition but it was time-depending, evaluating the desired optimum range of values (temperature: 30-40°C; moisture: 55-60%; pH: 6.5-7.5; alkalinity: 1,000-5,000 $mgCaCO_3/L$; VFAs:< 6,000 $mgCH_3COOH/L$). In this way, each hybrid bioreactor started the anaerobic phase at different moments (55, 95, 35, 81 days respectively the 1st, 2nd, 3rd and 4th hybrid bioreactor). It was shown that organic matter contents were markedly lower in the hybrid bioreactors than in the control anaerobic ones, in which remained almost constant due to the acidic pH values. In particular, the waste degradation was higher with intermittent aeration and recirculated leachate due to the mixture of aerobic and anaerobic metabolism in the reactors. Another positive effect of the intermittent aeration was the faster increase of the pH value, and the consequently shorter acidic phase and an anticipated methanogenesis respect to the continuous aeration system. This fact was also confirmed by the FOS/TAC ratio, a German control parameter for anaerobic digestion processes (Voss et al., 2009), which dropped below 1 $mgCH_3COOH/mgCaCO_3$ in a shorter time in the intermittent bioreactors. Consequently, also the methane production was higher in the intermittent columns in terms of both maximum daily biogas yield and cumulative methane production. However, a correlation with the air injection rate was observed. The production of methane was stimulated by the dynamic conditions of the intermittently aerated bioreactors, but an optimum range of air flux should be provided. The injected air per volatile solids (VS) unit was compared with the parameters of the Gomperetz Model, calibrated with the experimental data, and the range of air injection that maximize methane production was identified (200-400 NL/kgVS) in this experimental study.

As concern nitrogen values, the accumulation of ammonia was observed in all the columns since it is almost inert under anaerobic conditions (Pohland, 1995; He et al., 2006). In fact, neither nitrates nor nitrites were detected in the first two phases of the experiment. The reasons of the ammonia accumulation were principally the daily recirculation of leachate, which normally increase ammonia concentration and intensify the toxicity of leachate, and the insufficient oxygen supply. Only about 10% of nitrogen was removed in the first step of the lab-scale simulation landfill reactors, while the rest part remained into the solid waste. During the last years some concepts of nitrogen management have been proposed and verified in lab-scale research. Berge et al. (2006) confirmed that ammonia was greatly degraded when recycled leachate passed through landfilled layers with continuous ventilation, with nitrate quantity in the effluent less than the corresponding reduced ammonia, suggesting the simultaneous presence of nitrification and denitrification processes. In-situ aeration has become increasingly popular in the last decade worldwide and several lab- and full-scale applications (Cossu et al., 2001; Hayer et al., 2005; Ritzkowski et al., 2006; Prantl et al., 2006; Raga and Cossu, 2013) confirmed the acceleration of the biological stabilisation of waste, shortest landfill post-closure care, reduction of both current emissions and residual emission potential, pre-treatment of waste before landfill mining (Raga and Cossu, 2013).

The aim of the final aerobic step of the S.An.A. Hybrid Landfill was: I) performing the remaining potentially contaminating substances; II) simulating 20 years of operation time in six months; III) improving leachate quality; IV) accelerating landfill settlements; V) creating a bio-stabilized landfill in view of faster achieving of the FSQ.

It has been suggested by researches that ammonia nitrogen is a significant long-term pollution problem in landfills and it is likely that its presence will influence when post-closure monitoring may end (Kjeldsen et al., 2002; Prince et al., 2003; Berge et al., 2006). Studies on hybrid bioreactors showed that the combination of facultative anaerobic and aerobic conditions was indeed effective in eliminating ammonia both from the leachate and the refuse thoroughly (Long et al., 2008; Shao et al., 2008; Xu et al., 2014). The aerobic step of the experiment is a key point to monitor the different nitrogen forms partitioning (ammonia, nitrates, organic nitrogen and ammonia gas) and ensure the reaching of the law limits in a shorter time. The guideline for the waste management and landfill building proposed by the Lombardia Region (Dgr Regione Lombardia n.2461/14) suggests a maximum value of ammonia-N and nitric-N respectively equal to 50 and 20 mg/L.

2. Materials and methods

2.1 Lab-scale equipment

Six Plexiglass® (polymethyl methacrylate) cylindrical bioreactors of 24 cm diameter and 106 cm height were constructed to simulate the concepts of hybrid and anaerobic landfill bioreactor. A 10 cm layer of gravel, greater than 2 cm in size, was placed on the bottom and on the top of the waste in order to facilitate the distribution and the homogenization of recirculated leachate.

The reactors' configuration included three independent inox valves in the upper part, for the input of air flux into the reactor, gas sampling and extraction, as well as input of water and leachate recirculation; an another one in the lower part of the columns was used for leachate flowing by gravity and extraction. A bolted flange with double rubber seals was used for the reactor's closure. The leachate was collected in 5 litres plastic containers and then recirculated from the top of the reactor using a Peristaltic pump Heidolph PD 5001. A vertical slotted PVC pipe was installed at the centre of the columns in order to channel better the air into the waste body and so guarantee an uniform distribution. Temperature was monitored by means of Thermo Systems TS100 probes installed inside the reactor and was maintained constant (40 °C) for all the duration of the experiment by means of thermo-regulated insulation system, enveloping all the reactor body. The air input was performed by a Prodac Air Professional Pump 360, while the airflow was controlled by a Sho-Rate GT1335 flowmeter (Brooks Instruments). The produced gas was collected in 20 litres Tedlar® sampling bag and then measured both quantitatively and in composition. Technical data and sketch of the bioreactors used for the test are shown in Fig. 1.

Diameter	24 cm
Internal height	106 cm
Material	Polymethyl methacrylate
Reactor's closure	Bolted flanges with drubber seals
Leachate recirculation	Peristaltic pump Heidolph PD 5001
Leachate collection	5 L plastic container
Temperature probe	Thermo Systems TS100
Air input pump	Prodac Air Professional pump 360
Airflow regulation	Sho-Rate GT1335 flowmeter
Gas collection	20 L Tedlar® sampling bag

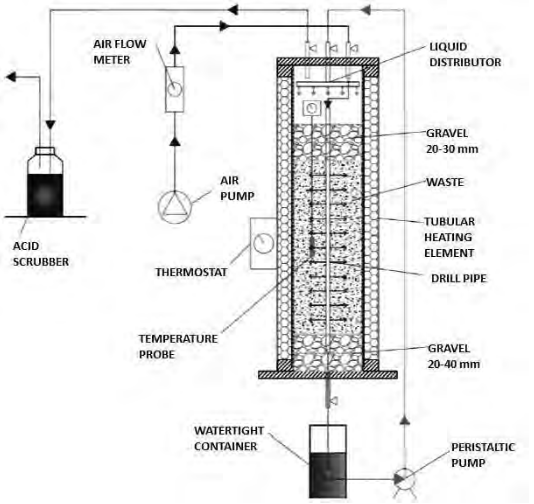

Fig. 1: Technical data and sketch of S.An.A. Landfill bioreactor

2.2 Waste samples

Samples used for the experiment were constituted by the 80 mm undersieve fraction of an amount of 200 kg of residual municipal solid waste provided by a public waste management company from Livorno Province, Tuscany (Italy). The undersieve waste fraction corresponded to 53% of the initial waste, for an amount of 107.6 kg and was mainly characterized by food waste, paper, plastic and fine fraction (Table 1). Waste was mixed before filling the reactors, in such a way that the same material was used. Each bioreactor was loaded with 18.4 kg of waste, except the anaerobic reactor "ANa" loaded with 15.6 kg. The initial waste characteristics were identical in all the columns: 55.5% of total solids (TS), 58.9% of volatile solids (VS) respect to the TS, 44.5% of moisture, 367.7 g/kgTS of Total Organic Carbon (TOC) and 9,701 g/kgTS of Total Kjeldahl Nitrogen (TKN).

At the end of the second phase of the experiment, the weight samples (kg tal quale) was different in each column. In order to homogenize this value, it was decided to keep fixed the total solids (5.2 kgTS) as a starting point for the aerobic phase. The waste density was about 0.6 kg/L and the humidity was around 55-60% in all the bioreactors (Table 2).

Table 1: Municipal solid waste and 80 mm undersieved composition

Trade class	Food waste	Green waste	Paper	Plastic	Metal	Glass & inert	Wood & textiles	Undersieve <20 mm
Raw waste (%)	14.0	6.1	22.9	18.4	5.2	3.5	8.9	20.9
Undersieved <80 mm (%)	17.4	6.0	10.5	12.6	6.2	3.2	5.4	38.8

Table 2: Waste characteristics in the aerobic phase

Reactor name	HFa	HFb	LFa	LFb	ANa	ANb
Weight (kg tal quale)	14.9	13.3	14.2	11.8	13.8	12.9
Weight (kg TS)	5.2	5.2	5.2	5.2	5.2	5.2
TS (%)	39.4	35.7	47.9	44.1	61.4	41.3
VS (%TS)	40.6	39.5	32.4	31.0	25.8	44.2
Waste height (m)	0.50	0.45	0.45	0.45	0.50	0.50
Waste density (kg/L)	0.66	0.65	0.70	0.58	0.61	0.57
Moisture (%)	55-60	55-60	55-60	55-60	55-60	55-60

2.3 Methodology

Before starting the aerobic phase, the reactors were emptied and the samples mixed and analyzed, both in solid phase and as eluate. Then the reactors were refilled with the same waste and distilled water was introduced and recirculated until waste field capacity was reached. The two anaerobic reactors (ANa, ANb) were used as control reactors. The four hybrid reactors (HFa, HFb, LFa, LFb), managed with intermittent and continuous aeration flow in the first semi-aerobic phase, are now all managed in continuous but with different air flow rate: reactors “HFa” and “HFb” with high flow aeration, equal to 200 NL/d, and reactors “LFa” and “LFb” with low flow aeration, equal to 40 NL/d (Table 3). The daily air flows were chosen taking in account several lab-scale bioreactors in forced aerated conditions: they range from 0.2-0.6 NL/d/kgTS (Ritzkowski et al., 2006) to 536 NL/d/kgTS (Cossu et al., 2003). At the start up of the test, the air flow was set up at a low regime and was incremented until oxygen was detectable >14% in the high flux reactors (Ritzkowski and Stegmann, 2013) and >1-2% in the low flux reactors. Temperature was maintained constant around 40°C. The recirculation of leachate was done daily while the leachate samples were taken weekly for a quantity of 0.3 L and the same quantity of distilled water was replaced inside the reactors in order to guarantee the necessary moisture content (Table 3). The extraction of leachate was set up simulating the typical precipitations in Northern Italy (suggested by ARPAV), considering a landfill top-cover permeable for about 30%, in order to simulate 20 years in six months. Leachate recirculation is a key step to create a landfill bioreactor because guarantees the increasing of moisture content in the waste sample (Townsend et al., 1996; Reinhart et al., 2002; Xu et al., 2014).

Table 3: Management scheme of the aerobic phase

Reactor name	HFa	HFb	LFa	LFb	ANa	ANb
Water in = Leachate out (L/w)	0.3	0.3	0.3	0.3	0.3	0.3
Test length (months)	6	6	6	6	6	6
L/S reachable (L/kgTS)	2.25	2.25	2.25	2.25	2.25	2.25
Leachate recirculation	daily	daily	daily	daily	daily	daily
Temperature (°C)	40	40	40	40	40	40
Aeration concept	forced	semi-aerobic	forced	semi-aerobic	anaerobic	anaerobic
Aeration modality	cont	cont	cont	cont	cont	cont
Aeration rate (NL/d)	200	200	40	40	0	0
Air flow rate (NL/d/kgTS)	38.5	38.5	7.7	7.7	0	0

2.4 Analytical methods

International standard methods were used for the analysis of solid samples, leachate and biogas.

The analysis on solids were carried out by extracting the waste from bioreactors and mixing it in a tank in order to increase the homogeneity. Then, a waste sample of 500 g was taken from each column and milled until 4 mm before the determination of TS, VS, TKN, N-NH_4^+, TOC, RI_4. Total organic carbon (TOC mgC/kgTS) on solid samples was measured with TOC-VCSN Shimadzu Analyzer. Respiration Index (RI_4 mgO_2/gTS) was determined by means of Sapromat apparatus (H+P Labortechnik, Germany). A leaching test was carried out according to the standard UNI EN 12457-2 on the initial waste sample (L/S was brought to 10 L/kgTS, mixing for 24 hours and filtrated at 0.45 µm). The obtained eluate was analyzed in order to evaluate the potential emissions of the same contaminants considered in leachate (pH, VFAs, alkalinity, COD, TOC, BOD_5, TKN, N-NH_4^+, SO_4^{2-}, Cl^-). All tests on solid samples were performed in duplicate.

Leachate was collected for sampling on a weekly basis, and then analyzed for pH, COD, BOD_5, TOC, TKN, N-NH_4^+, NO_x, Cl^- and SO_4^{2-}.

The biogas produced was collected in the sampling bags and analyzed daily in the case of hybrid reactors and weekly in the case of anaerobic ones. Its composition in terms of oxygen (%O_2), methane (%CH_4) and carbon dioxide (%CO_2) was obtained by means of a portable analyzer (Eco-Control LFG20). The Tedlar bag was connected to the syringe and the measured gas quality was adjusted on atmospheric values.

In the hybrid bioreactors, the gas stream was bubbled through a boric acid scrubber (Fig. 1) with the aim to trap the ammonia present in the gas into the acid solution. Periodically the solution was titred with H_2SO_4 (0.1N) in order to quantify the NH_3(g) exiting the system in the gas phase. Two indicators (Methylene Blue, Methyl Red) were used to verify if the pH value of scrubbers rose up 4, by changing the colours from purple to green, meaning that NH_3(g) was emitted.

2.5 Nitrogen mass balance

The reference parameter for the nitrogen mass balance was Total Nitrogen (TN), calculated as the sum of TKN and NO_x. In general, nitrogen enters the system in the form of organic nitrogen or ammonia. The influent TKN gives a measure of the amount of these compounds present, while if the system is also nitrifying, the majority of the influent TKN is converted to nitrate (Barker and Dold, 1995). Denitrification occurs only in unaerated zones, consisting in nitrate conversion to nitrogen gas or intermediates ($NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2$). Due to the contemporary progress of different processes during these kinds of tests, determine the fate of different forms of nitrogen is a complex issue (Raga and Cossu, 2012).

For the mass balance calculations, the data on leachate samples were expressed as mass “Mi” (g/kgTS) by multiplying the concentration “C” (g/L) of the parameter “i” in leachate with the liquid solid ratio L/S (L/kgTS):

$$Mi = Ci \times L/S$$

It should be possible to account the following fractions: nitrogen species in solid phase at the beginning and the end of the period of time: TKN(s); nitrogen species in liquid phase: TKN(l), NO_x(l); and nitrogen in gas phase: NH_3(g), N_2(g) (Table 4). The total nitrogen at the end of the aerobic phase is calculated as the sum of total nitrogen in solid phase, in the leachate present at that moment, in the leachate extracted during sampling and the nitrogen supposed to have been transformed and/or to have left the reactors with the gas phase.

Table 4: Nitrogen species considered for the mass balance

Nitrogen (N) fractions	Calculations
Initial content in solid phase:	$\mathrm{TKN(s)_{initial\ content}} = \left(\frac{\mathrm{kg}}{\mathrm{kgTS}}\right) \mathrm{x} \left(\frac{\mathrm{gN}}{\mathrm{kg}}\right)_{\mathrm{initial\ content}}$
Final content in solid phase:	$\mathrm{TKN(s)_{final\ content}} = \left(\frac{\mathrm{kg}}{\mathrm{kgTS}}\right) \mathrm{x} \left(\frac{\mathrm{gN}}{\mathrm{kg}}\right)_{\mathrm{final\ content}}$
N species in liquid phase:	$\mathrm{TN(l)} = \mathrm{N_{NH_4^+}}_{(l)} + \mathrm{N_{Norg}}_{(l)} + \mathrm{N_{NOx\,(l)}} = \left(\frac{\mathrm{gNH_4^+}}{\mathrm{kgTS}}\right)_{(l)} + \left(\frac{\mathrm{gN_{org}}}{\mathrm{kgTS}}\right)_{(l)} + \left(\frac{\mathrm{gNO_x}}{\mathrm{kgTS}}\right)_{(l)}$
N species in gas phase:	$\mathrm{TN_{(g)}} = \mathrm{N_{NH_3\,(g)\,stripp}} + \mathrm{N_{N_2\,(g)}} = \left(\frac{\mathrm{gNH_3stripp}}{\mathrm{kgTS}}\right)_{(g)} + \left(\frac{\mathrm{gN_2}}{\mathrm{kgTS}}\right)_{(g)}$

The difference between the initial content of nitrogen in solid phase and the final content, evaluated in solid, liquid and gas phases represents the missing nitrogen:

$$N_{missing} = \mathrm{TKN(s)}_{\mathrm{initial\ content}} - \mathrm{TKN(s)}_{\mathrm{final\ content}} - \mathrm{TN(l)} - \mathrm{TN(g)}$$

$$\mathrm{N}_{\mathrm{missing}} = \mathrm{TKN(s)}_{\mathrm{initial\ content}} - \mathrm{TKN(s)}_{\mathrm{final\ content}} - \mathrm{N}_{\mathrm{NH_4}^{+}\mathrm{(l)}} - \mathrm{N}_{\mathrm{NO_x}^{-}\mathrm{(l)}} - \mathrm{N}_{\mathrm{NH_3\ (g)\ stripp}} - \mathrm{N}_{\mathrm{N_2\ (g)}}$$

The final values calculated for the anaerobic step represent the initial values for the aerobic phase. Tests on solid established that TKN was 8.48 gN/kgTS, 8.63 gN/kgTS, 8.38 gN/kgTS, 9.00 gN/kgTS, 8.01 gN/kgTS, 8.08 gN/kgTS, respectively in the six bioreactors, each containing 5.2 kgTS. The leachate was extracted weekly, its volume was measured and the TKN and NO_x analysed, while the gas analysis was performed in acid boric scrubbers. The aim was to calculate the removed nitrogen mass (mgN/kgTS) in the aerated period of time and to compare it with the starting mass.

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3. Results and discussion

3.1 Solid waste

The data obtained from the analysis carried out on waste (solid and eluate), calculated at the beginning of the aerobic phase, are reported in Table 5. The main important observations, respect to the initial data of the whole experimental activity, were:

- a strongly decreasing of the respirometric index (RI_4), up to 96% in "LFb", that indicated a low oxygen consumption and a slow biological activity;
- a decreasing of: TOC (gC/kgTS) up to 51% in "HFa"; BOD_5 (mgO_2/L) up to 96%; and COD (mgO_2/L) values up to 80% in "HFb", that confirmed the degradation of the biodegradable waste;
- a still high values of TKN both in solids (mgN/kgTS) and eluate (mgN/L) due to the absence of nitrification process in the anaerobic phase and an increasing of ammonia ($N\text{-}NH_4^+$) up to 5.5 times more than the initial content. Approximately 50% of total nitrogen content was present as ammonia nitrogen at the beginning of the aerobic step;
- high values of Cl^- (2.3-3.8 gCl^-/kgTS) due to the increasing of the pH value and of the solubility.

For the mass balance of the aerobic phase and the comparison between the initial and final solid content values, the characterization of waste should be done also at the end of the experimental activity.

Table 5: Waste samples analysis, on solids and eluate, at the beginning of the aerobic phase

	HFa	HFb	LFa	LFb	ANa	ANb
Weight (kgTS)	5.2	5.2	5.2	5.2	5.2	5.2
RI_4 (mgO_2/gTS)	7.2	6.5	8.3	2.8	8.1	13.9
TKN (mgN/kgTS)	7,596	8,013	7,317	8,498	7,683	7,586
TOC (gC/kgTS)	180	208	231	303	282	274
Cl^- (mg Cl^-/kgTS)	3,432	2,333	2,433	3,624	3,758	3,241
pH	8.5	8.1	8.4	8.2	8.0	7.9
TOC (mgC/L)	1,810	1,150	1,370	1,315	845	1,040
COD (mgO_2/L)	4,939	2,939	4,791	4,836	2,889	4,834
BOD_5 (mgO_2/L)	365	308	309	337	393	477
$N\text{-}NH_4^+$ (mgN/L)	1,999	1,984	1,844	2,086	1,151	1,048
TKN (mgN/L)	2,077	2,082	1,997	2,208	1,215	1,195
Cl^- ($mgCl^-$/L)	343	233	243	362	376	324
SO_4^{2-} ($mgSO_4^{2-}$/L)	<500	<500	<500	<500	<500	<500

3.2 Leachate

The main impact produced by landfills is represented by the release of leachate emissions (Cossu and Lai, 2012). Landfill leachate is a complex "cocktail" mainly constituted by nutrients, especially nitrogen, volatile organic compounds, heavy metals, and toxic organic compounds. There are many factors affecting the quality and the quantity of leachate, i.e. age, precipitation, seasonal weather variation, waste type and composition (Bialowiec, 2011). S.An.A. Landfill leachate characteristics were similar in all the bioreactors at the beginning of the aerobic phase: negligible volatile fatty acids (VFAs) values (<600 mgCH$_3$COOH/L); FOS/TAC ratio almost zero; pH values around 8; TOC ranged between 1,100 and 2,100 mg/L; COD between 5,500 and 7,800 mg/L; BOD$_5$ between 360 and 810 mg/L; TKN values around 1,200-2,400 mg/L with high values of ammonia nitrogen (N-NH$_4^+$) ranged between 1,000 and 2,300 mg/L, while the organic nitrogen was below 290 mg/L in all the reactors; chloride was about 2,500 mg/L, while sulphate was always below 500 mg/L. The results obtained were typical of a "Methanogenic anaerobic phase" of a bioreactor landfill (Table 6). Once the aerobic phase has evolved, the leachate produced in S.An.A. bioreactors becomes an old-like leachate landfill (Post-methanogenic phase, Table 6), means rich in refractory organic compounds such as humic substances: humic acid, fulvic acid and humin (MacCarthy, 2001) that cannot be removed by biological treatment methods; and highly contaminated with ammonia resulting from hydrolysis and fermentation of nitrogen (Renou et al., 2008). Flushing bioreactor landfills have been introduced as a method for the rapid removal of the non biodegradable waste content from landfills because they could have long-term environmental impacts potentially lasting for centuries (Cossu et al., 2003).

Table 6: Comparison of MSW landfill leachate as a function of the degree of stabilization for conventional landfills (A), bioreactor landfills (B) (Reinhart and Townsend, 1998) and S.An.A. Hybrid Bioreactor Landfill (C) at a time corresponding to 1.5 L/kgTS

Parameter	Transition from aerobic phase		Acid anaerobic phase		Methanogenic anaerobic phase		Post-methanogenic phase		
	A	B	A	B	A	B	A	B	C
pH	6.7	5.4-8.1	4.7-7.7	5.7-7.4	6.3-8.8	5.9-8.6	7.1-8.8	7.4-8.3	7.5-8.1
BOD$_5$ (mgO$_2$/L)	100-10,000	0-6,893	1,000-57,000	0-28,000	600-3,400	100-10,000	4-120	<100	0-20
COD (mgO$_2$/L)	480-18,000	20-20,000	1,500-71,000	11,600-34,550	580-9,760	1,800-17,000	31-900	770-1,000	8000-3,500
BOD$_5$/COD	0.23-0.87	0.1-0.98	0.4-0.8	0.45-0.95	0.17-0.64	0.05-0.8	0.02-0.13	0.05-0.08	<0.02
N-NH$_4^+$ (mgN/L)	120-125	76-125	2-1,030	0-1,800	6-430	32-1,850	6-430	420-580	8-380

In order to compare results of different scales, all data in the following are reported as L/S ratio, indicating the amount of water passing through the waste.

3.2.1 pH values

The aeration causes a significant increase in the pH value of the leachate, and keeps its value above 7. Several laboratory tests conducted in aerobic simulated landfill bioreactors (with leachate recirculation) evidenced the increasing of the pH values above the neutral value in only few days (Erses et al., 2008), reaching a range between 7.5 and 8 until the end of the experiment; while in anaerobic reactors an initial decreasing of pH up to 6 within 3 weeks and then a gradually increase reaching the value of 7.5, was observed (Sang et al., 2008).

In S.An.A. Landfill, as the anaerobic process concluded, the pH started to increase with values stably around 7.5 for all the aerobic period of time (Fig. 2). This fact confirmed the occurring of the stabilization process: generally stabilized leachate has higher pH (>7.5) respect to young leachate (<6.5) (Adhikari et al., 2013). The stabilization process was also confirmed by the decreasing of the VFAs ($mgCH_3COOH/L$) content, the increasing of the alkalinity ($mgCaCO_3/L$), the decreasing of the BOD_5/COD ratio and of the TOC (mgC/L).

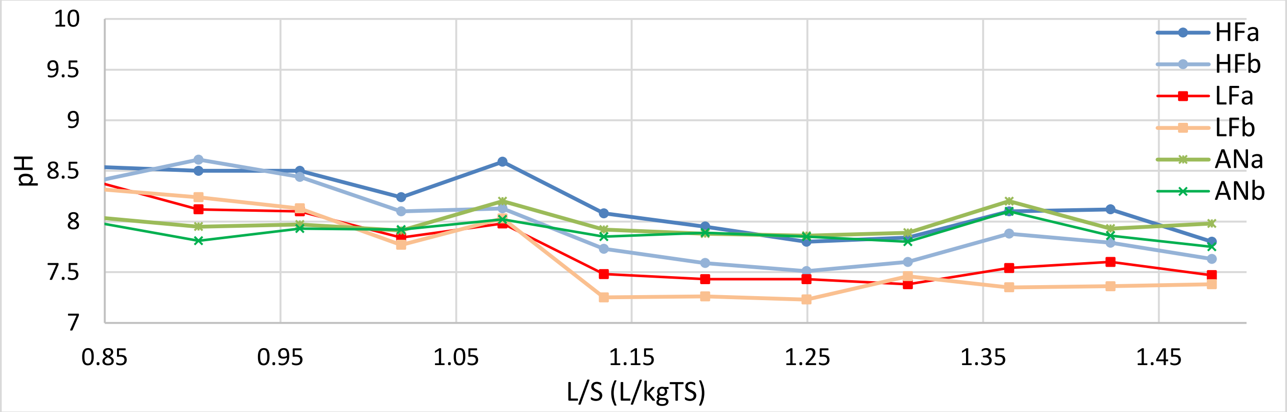

Fig. 2: pH value trend. Aerobic phase

3.2.2 Leachable compounds

Chloride is an inert compound used as a tracer for groundwater contamination from landfill leachate. Its concentration was monitored in order to assess the leachate dilution and the washout effect: if the pH value increases, the dissolution of chloride increases (Bilgili et al., 2006). In fact, in situ aeration cannot be considered as a tool for the abatement of long term emission potential as chloride and sulphate (Raga and Cossu, 2012). The results showed a slight decreasing trend due to the washout effect in all the reactors during the aerobic phase.

The initial content of chloride content in solids was about 2.3-3.7 $gCl^-/kgTS$; while in leachate ranged between 2.0-3.1 gCl^-/L (Fig. 3 (a)). After a liquid-solid ratio (L/S) equal to 1.5 L/kgTS, the concentration of chloride in leachate decreased of about 10-35% in concentration and 30-50% in mass. From a mass balance point of view, the final content of chloride in solids is needed. Anyway, according to Raga and Cossu (2012), the sum of the mass of chloride in the solid fraction at the end of the experiment and the mass extracted with leachate always exceeds the initial values measured in the solid fraction.

Sulphate concentrations started to increase in the aerated phase up to about 1,000 mg/L. Its production was expected due to the sulphate reduction processes occurred in the anoxic spots of the reactors. According to Berge et al. (2006), the increasing of sulphate could be related with a decrease in nitrate concentration, suggesting a fraction of nitrate removal attributed to autotrophic denitrification. Autotrophic denitrification follows reaction (I) and is favoured by a low biodegradable environment in the presence of inorganic sulphur compounds, such as H_2S (Koenig and Lui, 1996).

$$^{1}/_{5}\,NO_3^- + {}^{1}/_{8}\,HS^- + {}^{3}/_{4}\,OH^- \rightarrow {}^{1}/_{10}\,N_2 + {}^{1}/_{8}\,SO_4^{2-} + {}^{1}/_{10}\,H_2O \qquad (I)$$

However, as oxygen is diffused in the anoxic parts of the reactor, the reduction processes decrease and the sulphate concentration remains below the limit suggested by Lombardia Guidelines equal to 1,000 mg/L (Fig. 3 (b)) for all the bioreactors.

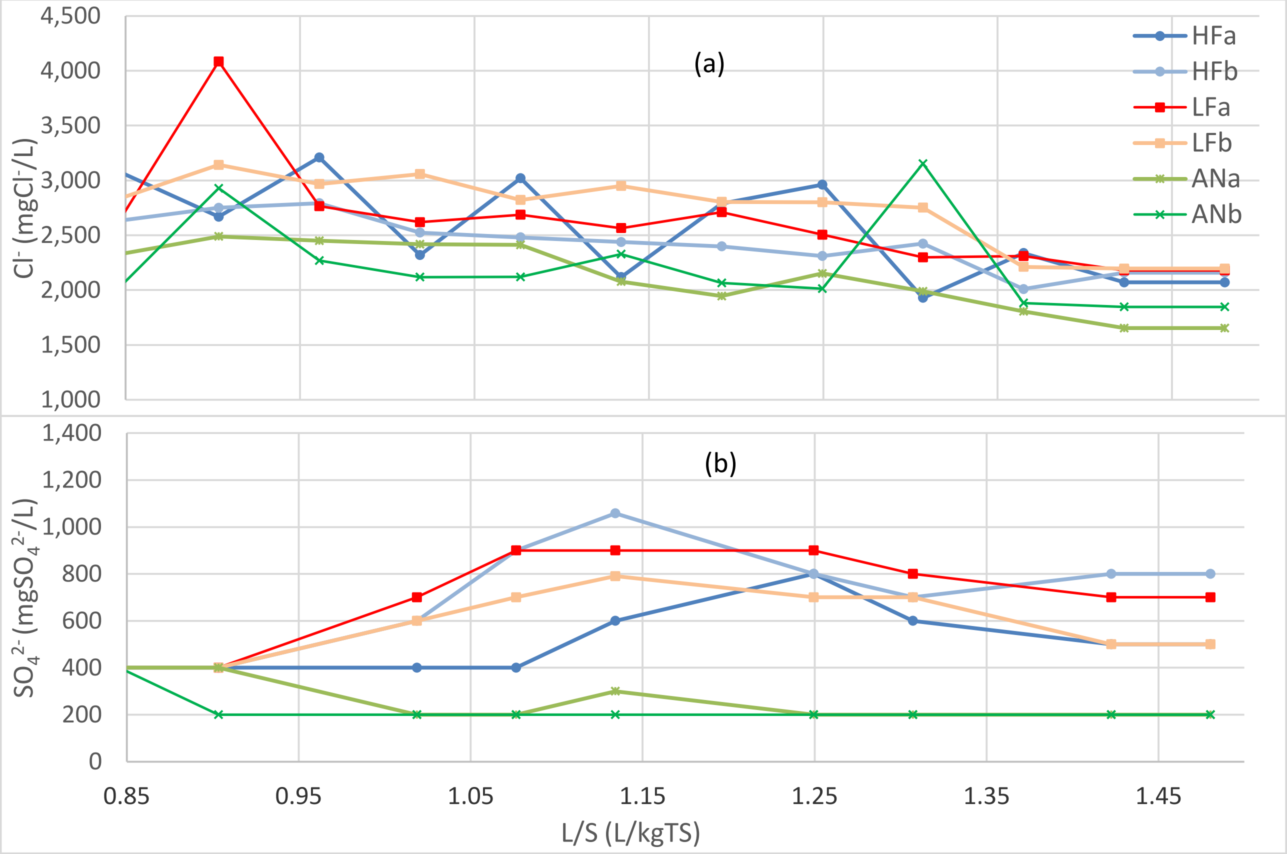

Fig. 3: Leachable compounds trend: (a) Chloride, (b) Sulphate. Aerobic phase

3.2.3 Dissolved organic matter

The majority of leachable organic carbon in landfilled solid waste is biodegradable and can be removed by biological processes, which can be accelerated by operating a landfill as a bioreactor (Kjeldsen et al., 2002). Oxygen demand measurements, biochemical (BOD) and chemical (COD), are two widely used parameters for indirect quantification of the organic matter. BOD indicates the content of oxygen needed to decompose organic compounds in leachate by bacteria, usually in 5 days analysis time (BOD_5); COD defines the amount of oxygen which would be needed when all organic compounds would be oxidised completely. Total organic carbon (TOC) assesses the quantity of CO_2 formed during the combustion of the organic matter. The evolution of organic carbon in discharged leachate is an important parameter to predict waste stabilization. The results of several laboratory and field studies showed that the aeration of waste causes an accelerated reduction of the organic matter contained in the leachate compared to the anaerobic reactors. Consequently, a reduction of the mass of organic substances also occurs (Pawlowska, 2014). According to Prantl (2006), the stabilization rate is confirmed by the reduction of TOC to about 10-25% and a respirometric index (RI_4) lower than 0.5 mgO_2/gTS. BOD_5/COD ratio is an important parameter that indicates the amount of biodegradable compounds still present in a liquid (Cossu et al., 2012), indicating a low biodegradability with values between 0.02 and 0.13 (Sekman et al., 2011) and high biodegradability if it ranges between 0.4 and 0.8 (Kjeldsenet et al., 2002).

In S.An.A. hybrid bioreactor landfill, the combination of semi-aerobic and anaerobic phases resulted effective in removing the organic matter; then, aerobic phase further positively affected waste and leachate quality in the reactors, promoting the transformation of the fraction more hardly biodegradable in humic substances. After a L/S ratio equal to 1.5, TOC values were ranged between 280-1,500 mg/L decreasing around 76-90% in mass respect to the initial values of the aerobic phase (Fig. 4 (a)); COD was between 800-3,500 mg/L, with a decrease of about 65-93% in all the bioreactors (Fig. 4 (b)); BOD_5 was lower than 20 mg/L, decreasing more than 95% respect to the initial values in all the hybrid bioreactors. As a consequence, the BOD_5/COD ratio was always lower than 0.02, confirming the low biodegradability of the waste.

In the anaerobic bioreactors TOC value was about 1,100 mg/L, COD about 2,700 mg/L and BOD_5 80 mg/L. BOD_5/COD ratio was 0.03 indicating, as in the case of hybrid bioreactors, a low biodegradability of waste but having higher organic matter content.

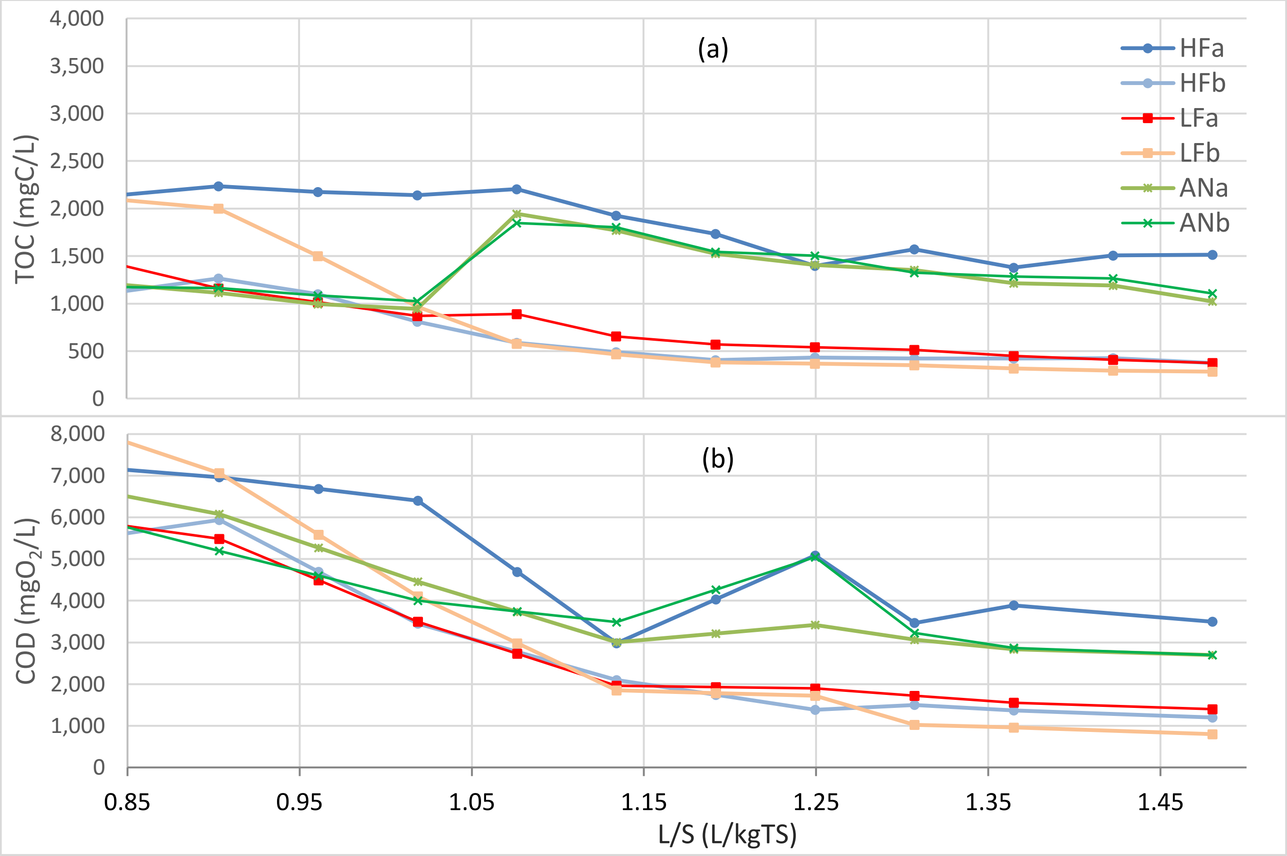

Fig. 4: Carbon indexes trend in leachate: (a) TOC, (b) COD. Aerobic phase

3.2.4 Nitrogen compounds

Ammonia accumulation occurs even when the organic fractions of waste have been stabilized in anaerobic conditions, since ammonia is difficult to be removed when O_2 is inhibited, or be converted to N_2 by the Anammox process due to the deficient nitrite (Burton and Watson-Craik, 1998). Moreover, the recirculation of leachate tends to increase the ammonification process, resulting in higher values than in conventional sanitary landfills. Air flow supply can provide a favourable environment for simultaneous nitrification and denitrification, allowing a rapid reduction of ammonium in well-decomposed landfill layers (Berge et al., 2007; Shao et al., 2008). Several lab-scale aerobic tests showed that ammonia removal can be attributed in part to nitrification consisting in an increase in nitrite/nitrate concentrations. However, this latter was always observed lower than the stoichiometrically predicted values, suggesting the occurrence of denitrification (Berge et al., 2006).

The results obtained in the aerobic process of S.An.A. Landfill showed a significant reduction of TKN (Fig. 5 (a)) and N-NH_4^+ (Fig. 5 (b)) in the hybrid bioreactors respect to the traditional anaerobic ones in which ammonia remained constant. The difference between TKN and N-NH_4^+ allows to evaluate the concentration of organic nitrogen (N-Norg). The latter was expected due to the presence of micro-anoxic areas within the waste and suggests that denitrification occurred along with nitrification (Fig. 5 (c)). An increase of nitrate concentration (Fig. 5 (d)) was observed due to the simultaneous nitrification and denitrification processes in the aerated and anoxic landfill reactor bodies but then fell gradually along with the operation time. Finally, the concentration of nitrite was occasionally detected but was always below detection limits.

Simultaneously in situ nitrification and denitrification is attractive for waste management purposes because there is no need for additional ex situ nitrification units (Shao et al., 2007). On the other hand, it could be useful to know the optimum range of conditions that produces the best results in terms of ammonia reduction. Fig. 5 allows evaluating the feasibility of nitrogen removal in the different bioreactors:

- in the anaerobic bioreactors, the concentration of TKN was around 1,000 mg/L, consisting mainly in N-NH_4^+ since the production of organic nitrogen cannot occur due to the absence of oxygen. For the same reason, also the nitrite/nitrate concentrations were almost zero.

- in the hybrid bioreactors the trends were similar in the case of high and low air flow rate. After a ratio of liquid to solid (L/S) equal to 1.5 L/kgTS was reached, the highest values of ammonia was observed in “HFa” (around 380 mg/L) and the highest reduction in “LFb”, with values lower than half of the limit law (8 mg/L). Good results were also observed in “HFb”, with N-NH_4^+ values equal to around 65 mg/L while for “LFa” it remained around 220 mg/L. A spike trend of nitrate was observed in “HFa”, “HFb” and “LFa” during the aerobic period, but then the concentration decreased in all the columns with high values only in “HFa” (around 100 mg/L).

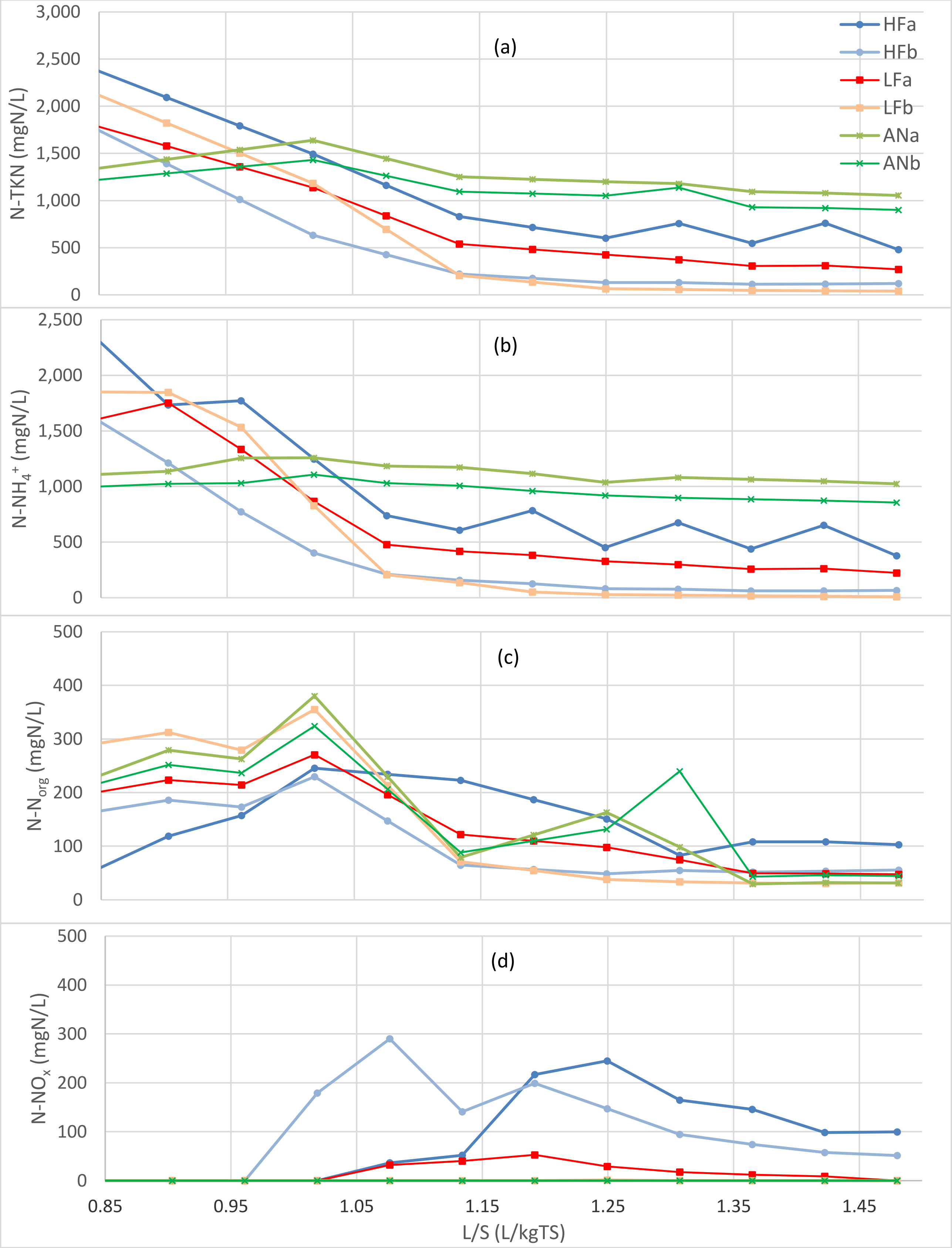

Fig. 5: Nitrogen compounds emissions trend in leachate: (a) TKN, (b) $N-NH_4^+$, (c) N-Norg, (d) $N-NO_x$. Aerobic phase

3.3 Nitrogen mass balance discussing

Ammonia nitrogen, has been indicated by the scientific community as the key parameter affecting the duration of landfill aftercare (Heyer and Stegmann, 1997) so, it should be properly monitored and reduced for example by aeration. The effectiveness of landfill in situ aeration depends mainly on three factors: I) oxygen distribution, II) temperature and III) moisture content in the landfill body (Raga and Cossu, 2012). Nitrogen mass balance could be useful tool to evaluate residual polluting potential and meet sustainability (Cossu et al., 2005). As reported in the paragraph "Nitrogen mass balance", nitrogen content in solid phase should be calculated at the beginning and the end of the given period of time, while leachate and gas should be constantly monitored. Therefore, mass balance performing will be possible only at the end of the aerobic phase when the bioreactors will be opened and the solid samples will be analysed. The difference between the initial content of nitrogen in solid phase and the final content (calculated as the sum of total nitrogen in solid phase, nitrogen calculated in the extracted leachate during all the aerobic period of time and the nitrogen stripped) will represent the missing nitrogen.

The cumulative trends of TKN, N-NH_4^+, N-Norg and N-NO_3 (mgN/kgTS) in leachate are reported in Fig. 6. The evolution of TKN (sum of ammonia and organic nitrogen) showed high values in the anaerobic bioreactors respect to the hybrid ones. After a L/S ratio equal to 1.5 L/kgTS the TKN mass was around 0.25 g/kgTS in both the anaerobic bioreactors, which represented an increase of about 1.5 times respect to the initial values in the aerobic phase. The lowest value was detected in the low flow aerated hybrid column "LFb" (0.01 gN/kgTS), with a mass reduction of about 93% respect to its initial content. The worst condition observed in the hybrid bioreactors was in "HFa" (0.14 g/kgTS) but still better than in the anaerobic ones. Moreover, it was observed that ammonia was always the major contributor to the overall nitrogen in leachate.

Fig. 6 shows that all the nitrogen cumulative trends appeared to reach a maximum level in the hybrid bioreactors, suggesting the data followed Monod kinetics, as was expected because the primary removal mechanism is biological. In this case, flushing operations could be used to optimize the removal of ammoniacal nitrogen from landfill waste (Cossu et al., 2003).

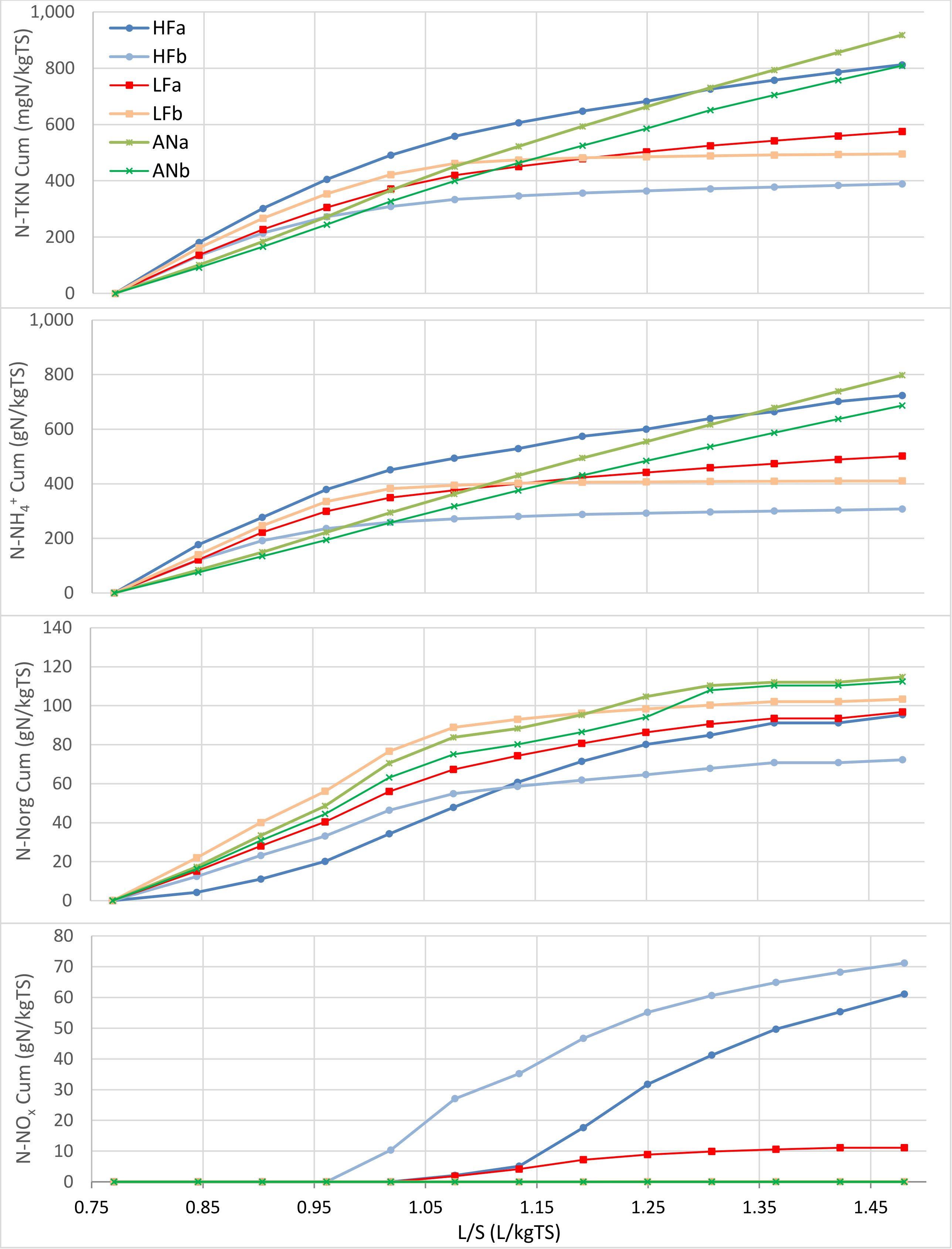

Fig. 6: Evolution of TKN, N-NH$_4^+$, N-Norg and N-NO$_x$. Aerobic phase

3.4 Gas characterization

Decomposition of organic matter under aerobic conditions results in the production of simple mineral compounds, i.e. carbon dioxide and water, but also humic-like substances (Ritzkowski et al., 2006). However, due to the waste heterogeneity, the oxygen does not reach in the same amount all the landfill parts because its concentration is determined by the waste porosity and moisture. As a result of oxygen diffusion, different processes may occur at the same time in the landfill body: methanogenesis, denitrification, sulphate reduction in the oxygen deficient spots; organic matter oxidation, nitrification, oxidation of methane in the aerated parts. The change of the conditions within the waste body, from anaerobic to aerobic, leads to a decrease in methane concentration in the landfill gas in favour of carbon dioxide (having significantly lower GWP) (Pawlowska, 2014). Prantl et al., (2006) calculated a carbon discharge approximately 5 times higher compared to anaerobic conditions and concluded that more than 90% of carbon load transformed to gas phase was discharged as CO_2. Ritzkowski and Stegmann (2007) calculated 5-10%CO_2, <1%CH_4 and 15-20%O_2 in their experimental activity on an old landfill after forced aeration. According to the results of the field study conducted by different authors (Cossu et al., 2007; Ritzkowski and Stegmann, 2007), the methane concentration lowered from about 60% to 2% and the ratio CO_2/CH_4 rose from 0.2% to 6% after the start of the aeration on an old landfill. The decreasing of methane concentration below 5%, that is the lower limit of explosive range of methane in air, is one of the advantages of aerobic conditions (Rettenberg and Schrejer, 1996). Moreover, aeration causes the decrease in the concentration of H_2S, NH_3 and other trace gases; while the CO concentrations increased with the increase of the ratio of CO_2 to CH_4. Anyway, air injection did not any noticeable influence on VOCs and N_2O concentrations (Powell et al., 2006). The results obtained in the hybrid bioreactors of S.An.A. Landfill (Table 7) confirmed the significant decrease of CH_4 and CO_2 and the gradual increasing of O_2 during the aerobic phase. The latter could be explained by the gradual decrease of waste biodegradability and the formation of preferential flow paths and drying effects in the aerated landfill (Ritzkowski and Stegmann, 2013).

Fig. 7 shows the composition trend of biogas (%) and Fig. 8 the ammonia stripping trend (mgN) in the aerobic phase. As expected, the gas composition is different due to the high and low flow rate supplied and due to the heterogeneity of the waste.

Table 7: Biogas composition in S.An.A. Landfill bioreactors. Aerobic phase

	HFa	HFb	LFa	LFb
CO_2 (%)	<1.3	<1	4-7	6-9
CH_4 (%)	<DL*	<DL	<DL	<DL
O_2 (%)	18-20	19-20	9-14	9-12

*DL: detection limit (0.02%)

Fig. 7: Biogas composition trend in the hybrid bioreactors. Aerobic phase

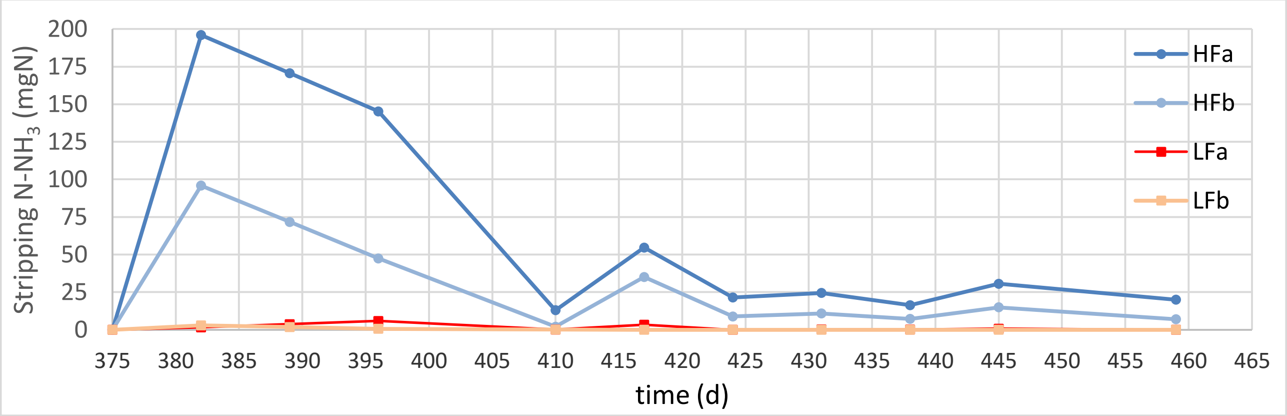

Fig. 8: Ammonia stripping trend (mgN). Aerobic phase

Fig. 9 sows the cumulated oxygen, carbon dioxide and ammonia gas discharge via the extracted gas, referred to the unit dry mass. As expected, a constant upward trend was measured for O_2, due to the continuous aeration flow in the hybrid columns: high flux (200 NL/d) in “HFa” and “HFb” and low flux (40 NL/d) in “LFa” and “LFb” reactors. The cumulative carbon dioxide increased as the organic matter degradation occurred, while the stripping of ammonia was favoured by the increasing of pH and temperature in aerobic conditions.

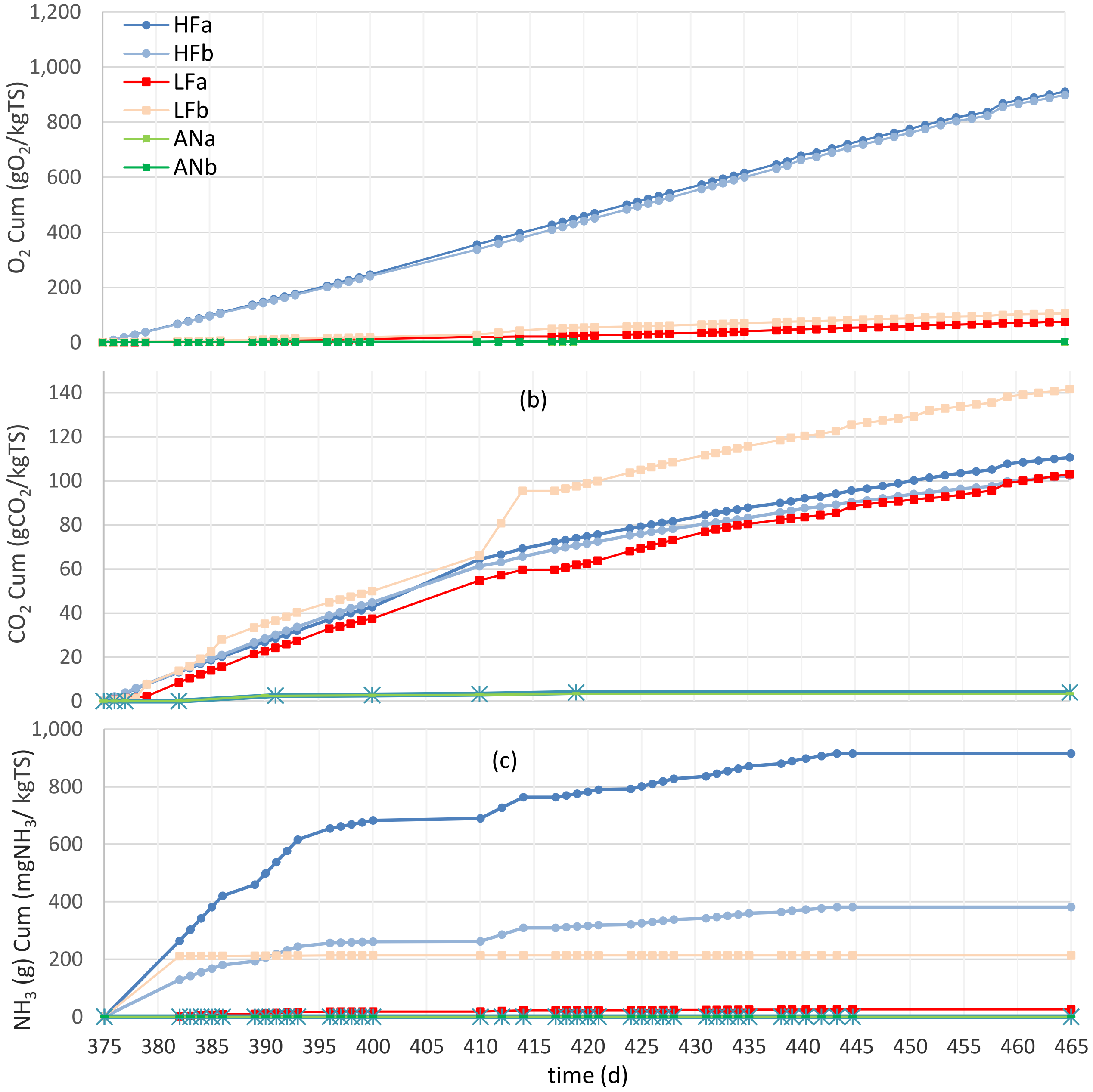

Fig. 9: Gas composition: (a) Oxygen, (b) Carbon dioxide, (c) Ammonia gas. Aerobic phase

3.5 FSQ achieving and performance

The achievement of final storage quality (FSQ) is the main goal of the modern sustainable landfilling, i.e. a situation where active environmental protection measures at the landfill are no longer necessary and the leachate is acceptable in the surrounding environment. This point in time will then mark the end of the aftercare period when the landfill can be safety abandoned (Hjelmar and Hansen, 2005). The eventual achievement of FSQ was implicitly assumed in most landfill regulations, including the EU Landfill Directive (CEC, 1999) which suggested the pre-treatment of waste and the reduction of the quantities of biodegradable municipal waste to be landfilled. However, due to the scarcity of reliable long-term observations of the development of leachate from controlled modern landfill, the strategies to move towards FSQ have not yet been included in all the existing European landfill regulations. In Italy, Lombardia Region has performed a landfill management guideline ("Linee guida regionali per la progettazione e gestione sostenibile delle discariche", 2014) which included also the admissibility criteria, in particular reporting the final storage quality in equilibrium with the environment until one generation time or anyway in a period not more than 30 years from the landfill closure. The limits suggested by the Lombardia Guidelines are: COD< 1,500 mg/L; BOD_5/COD< 0.1; ammonia-N< 50 mg/L; nitric-N< 20 mg/L; SO_4^{2-}< 1,000 mg/L; SO_3^-< 1 mg/L. The aerobic phase of S.An.A. Landfill was purposely performed to improve the quality of waste and reduce the post-closure time operation. The calculations were done to simulate 20 years in six months, improving the moisture content up to 55-60% with the leachate recirculation technique. The data obtained showed:

- a reduction of COD values below limit value in “HFb” and “LFb” after 1.3 L/kgTS, and in “LFa” after 1.4 L/kgTS; while in the remaining bioreactors the values were almost double at that time (Fig. 10 (a)).

- BOD_5/COD ratio was below the limit law in all the hybrid bioreactors still the end of the anaerobic phase; after a L/S ratio equal to 1.1 L/kgTS also in the anaerobic ones the FSQ goal was reached.

- the reaching of the FSQ of N-NH_4^+ was observed firstly in “LFb” after 1.2 L/kgTS in the aerobic phase; at 1.5 L/kgTS also in “HFb” the concentration is near the limit law but still not reached (65 mg/L); while in the remaining bioreactors remained in a range of 220-1,000 mg/L (Fig. 10 (b)). N-NO_x was negligeble in “LFb”, “ANa” and “ANb” for all the aerobic period of time; below law limit starting from 1.3 L/kgTS in “LFa” and in range of 50-100 mg/L in “HFa” and “HFb”.

- SO_4^{2-} was always below law limits in the aerobic phase in all the bioreactors, while S^{2-}, as expected, was found only in the anaerobic ones.

- Cl^- was higher than 1,500 mg/L and never reached the FSQ values until 1.5 L/kgTS (Fig. 10 (c)).

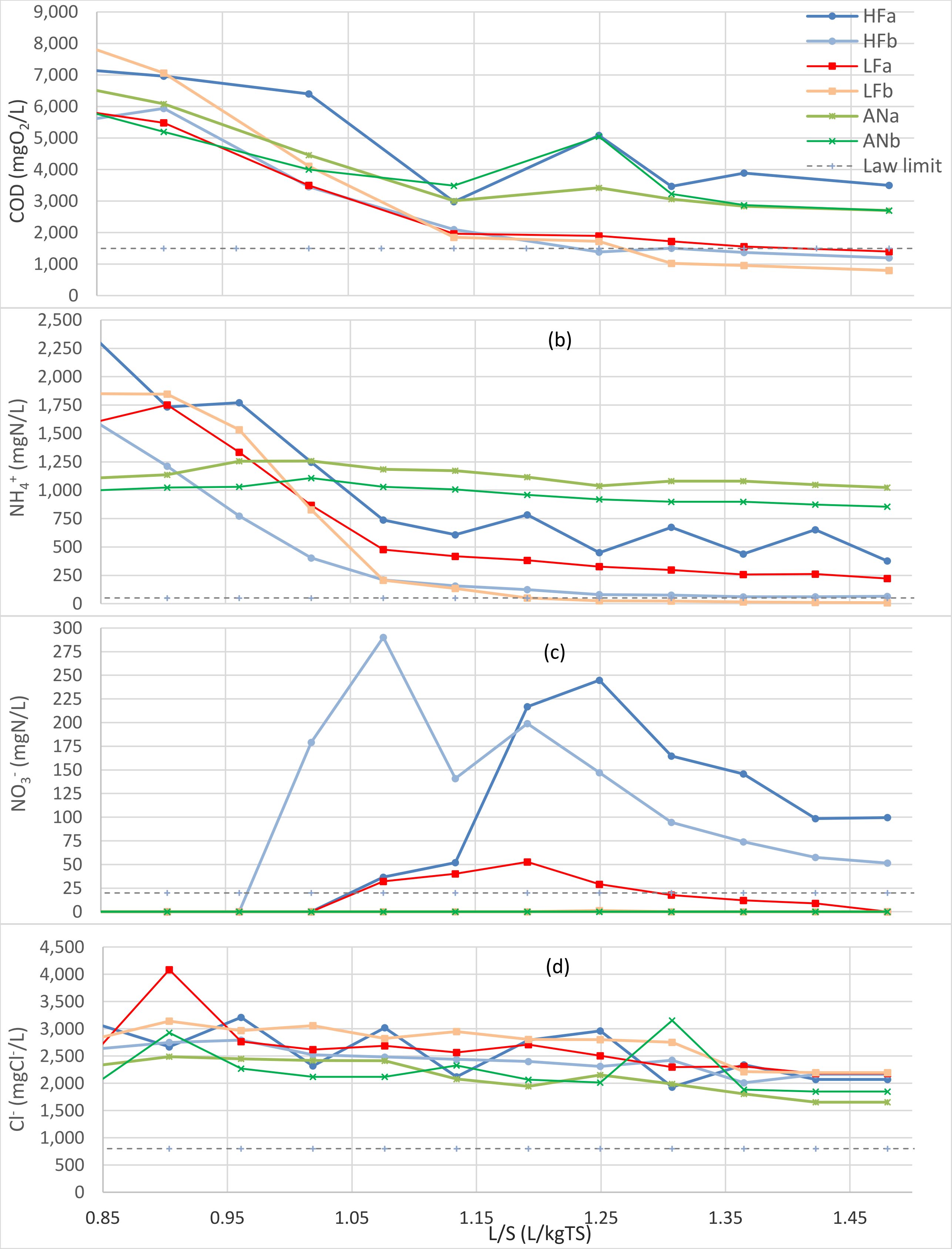

Fig. 10: FSQ performance: (a) Chemical oxygen demand, (b) ammonia-N, (c) nitric-N, (d) chloride. Aerobic phase

4. Conclusions

The main goal of the final aerobic phase was to take advantage of the increased speed of the aerobic reactions, which are generally about 10 times higher than the anaerobic ones, in order to reach faster the FSQ values. The data obtained at a time corresponding to 1.5 L/kgTS in the aerobic phase let to make the following observations:

- From the viewpoint of leachate treatment, in situ aeration was a useful tool for controlling the long term impact of landfilling as carbon and nitrogen content. As a consequence, hybrid bioreactors confirmed the advantages over traditional anaerobic ones. At the point in time corresponding to 1.5 L/kgTS the FSQ was not reached in all the hybrid bioreactors but the rate of reduction seems to predict the reaching of the goal before the end of the aerobic phase. The reaching of the FSQ at different L/S ratio could be related to the waste heterogeneity, recycled leachate and/or aeration conditions in the hybrid bioreactors;
- The continuous low aeration seemed to be better than the high aeration, showing lower COD values. Also for nitric production, the performance was better in the low aerated hybrid bioreactors;
- Data obtained for ammonia nitrogen showed that there seemed to not be any difference between high and low aeration. However, high ammonia levels reduction demonstrated the efficacy of the continuous forced aeration after an anaerobic phase in hybrid bioreactors;
- Results obtained for chloride showed that there were no differences between low and high air flow rate. In fact, aeration did not affect the content of chloride; only flushing influenced it.

The results obtained provided evidence of the effectiveness long-term pollutants degradation by reaching the FSQ in a significantly shorter time respect to the traditional landfilling. Table 8 shows L/S ratios (L/kgTS) for reach the FSQ in each bioreactor. “no” indicates that the law limit has not been yet reached until the point in time corresponding to 1.5 L/kgTS in the aerobic phase. The test is still going on.

Table 8: L/S ratio in which FSQ performance was reached in each bioreactor. Aerobic phase

FSQ (mg/L)	HFa (L/kgTS)	HFb (L/kgTS)	LFa (L/kgTS)	LFb (L/kgTS)	ANa (L/kgTS)	ANb (L/kgTS)
COD< 1,500	no	1.3	1.5	1.3	no	no
NH_4^+< 50	no	no	no	1.2	no	no
Cl^-< 1,000	no	no	no	no	no	no

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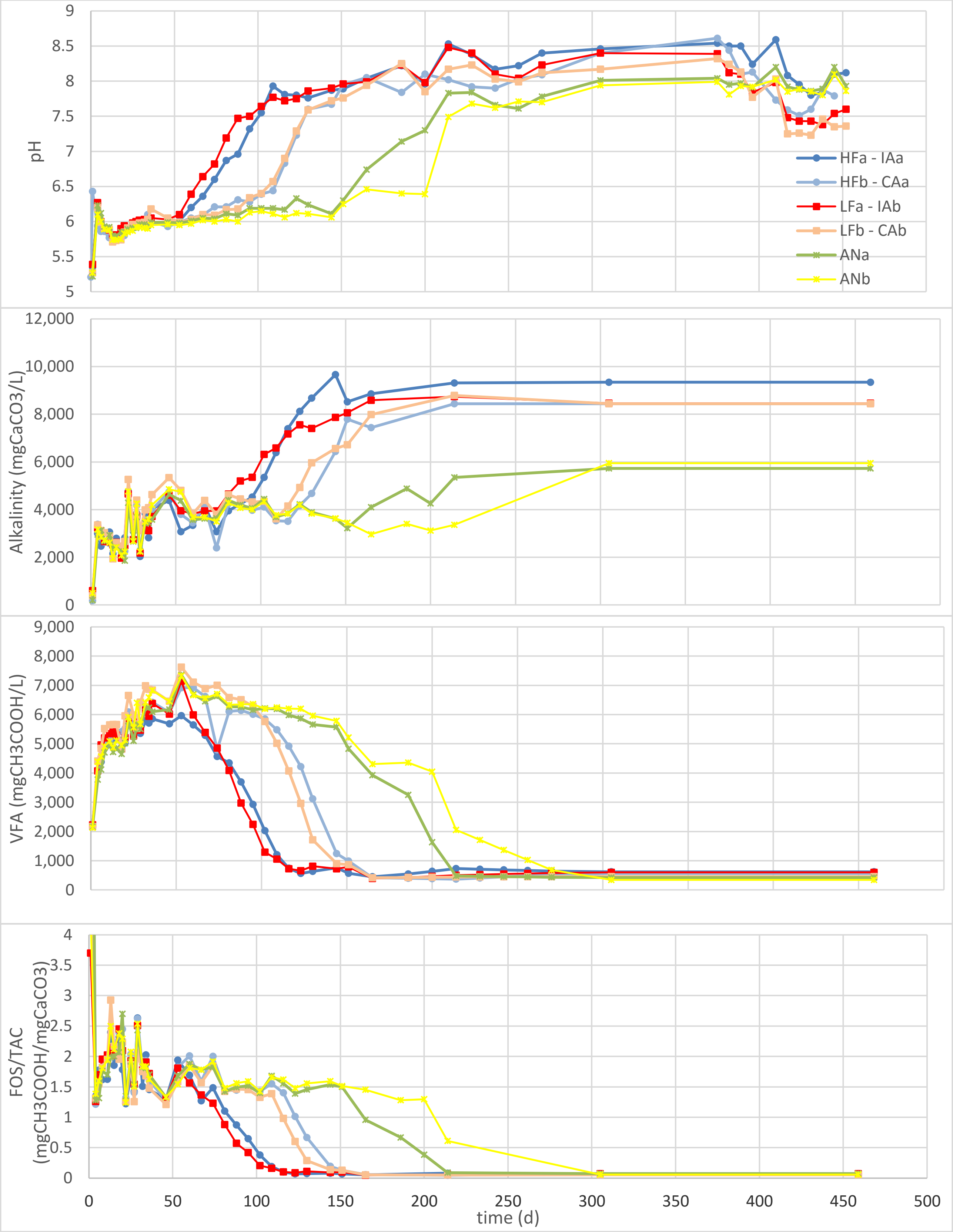
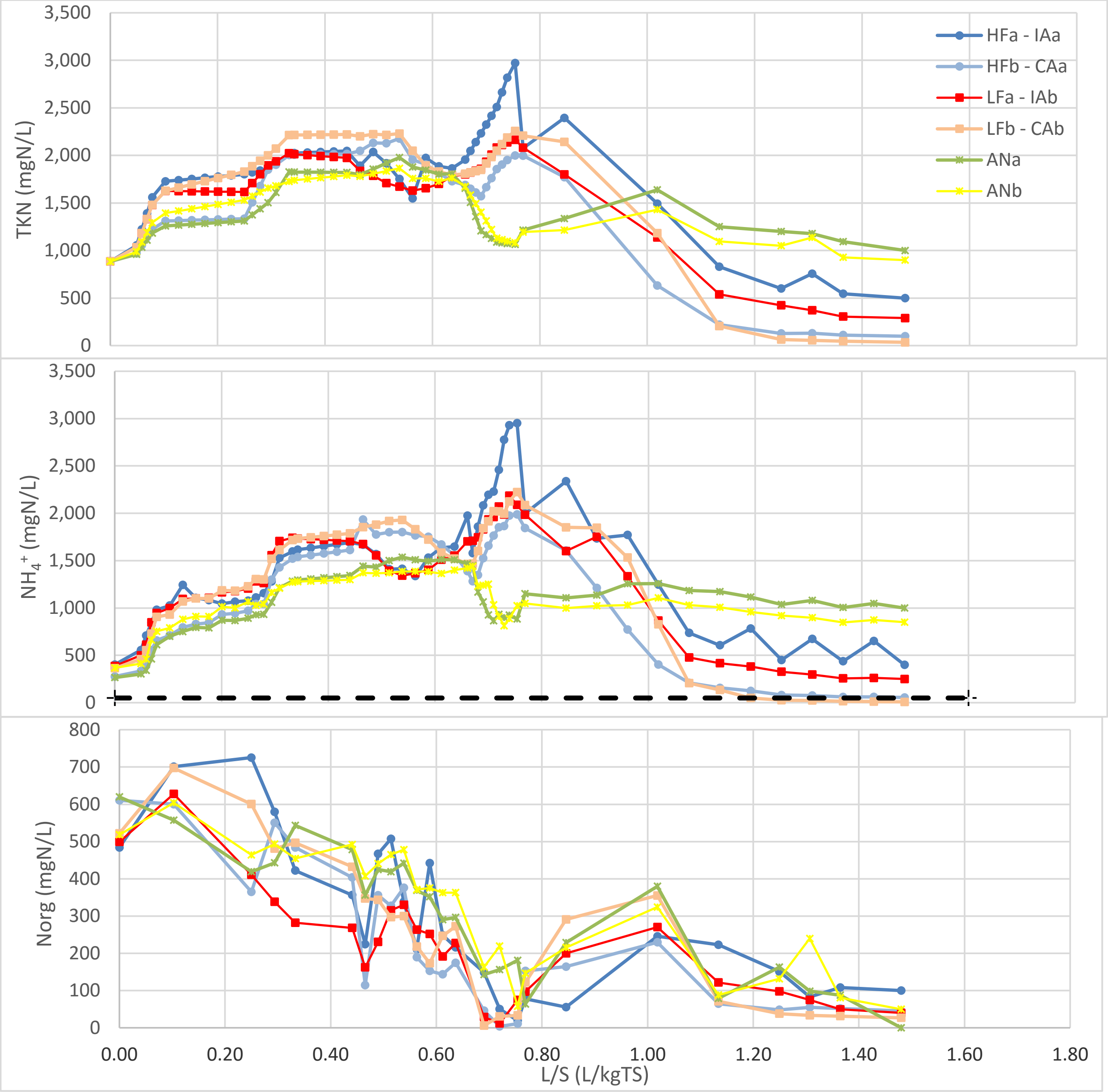
III) ANNEXES

pH, Alkalinity, VFA and FOS/TAC trend:

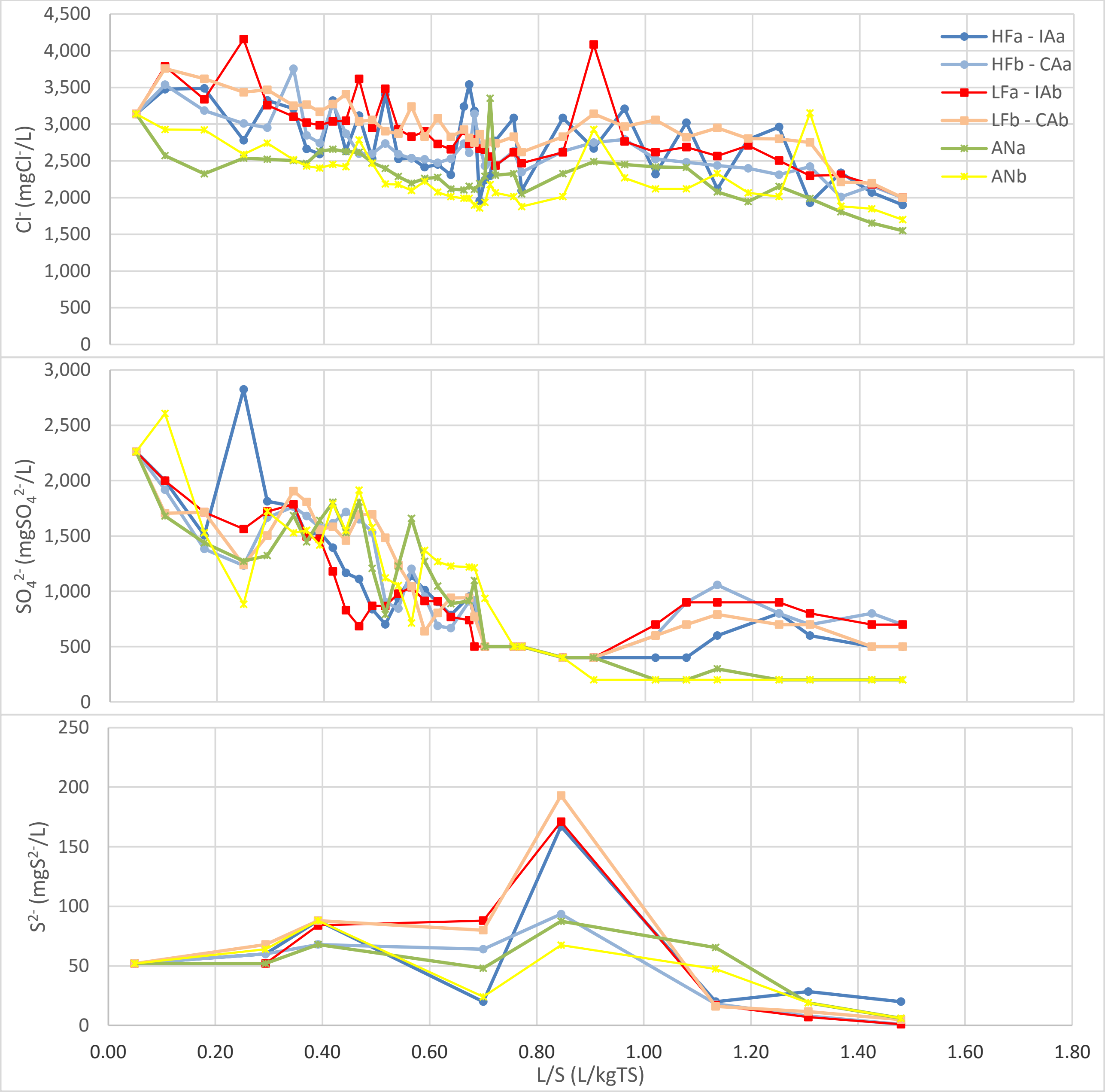


TOC, COD, BOD_5, BOD_5/COD trend:

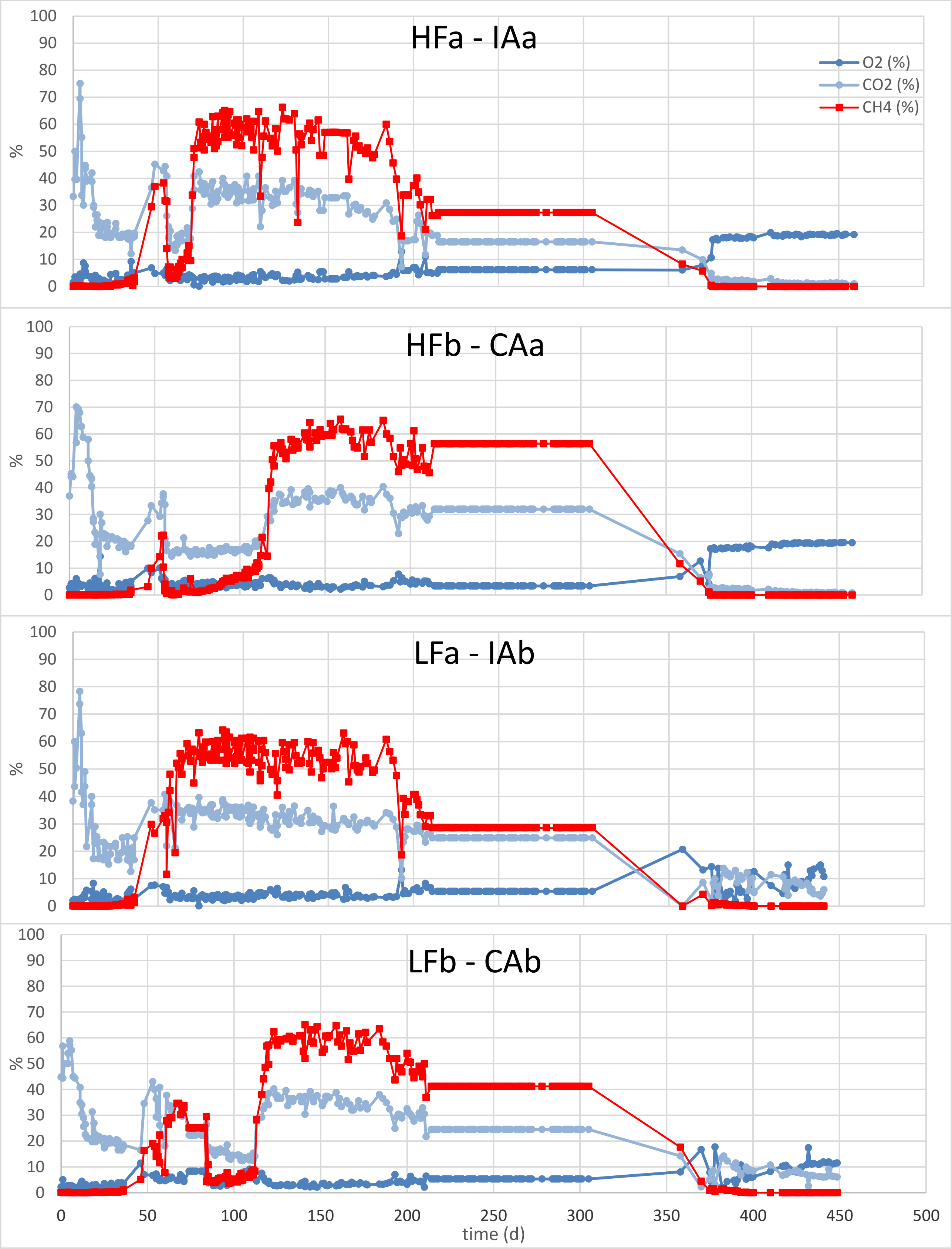
TKN, NH_4^+, Norg trend:

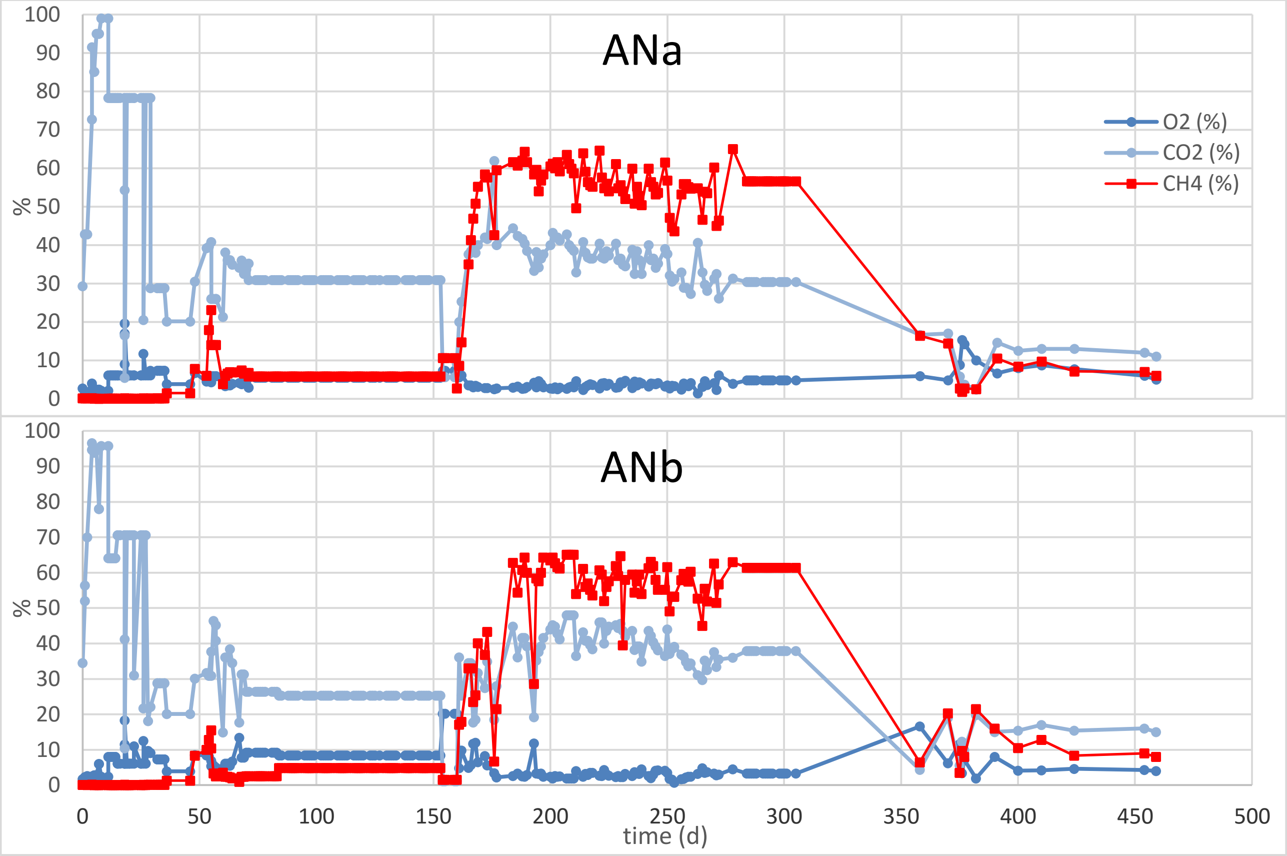


Cl^-, SO_4^{2-}, SO_3^- trend:

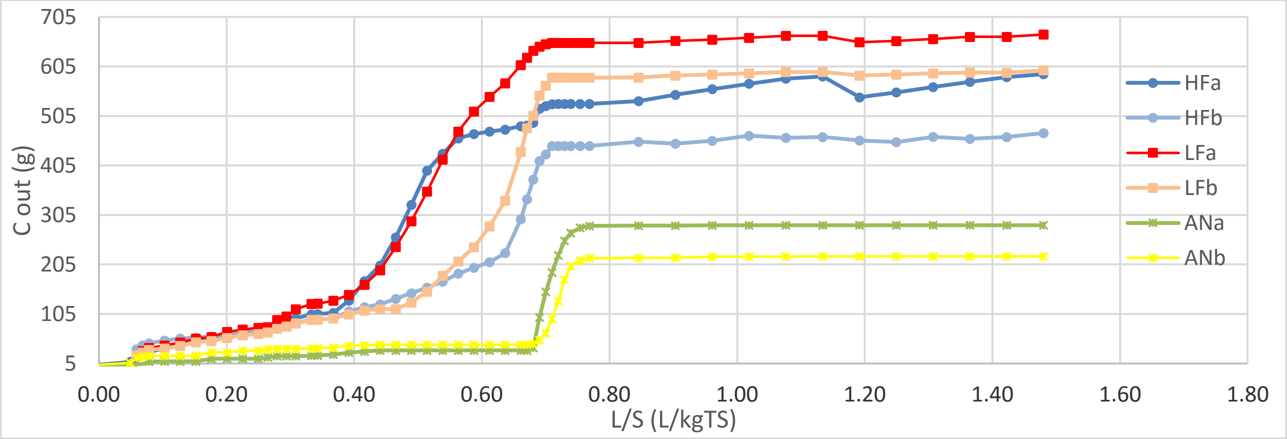


Gas composition in each bioreactor:

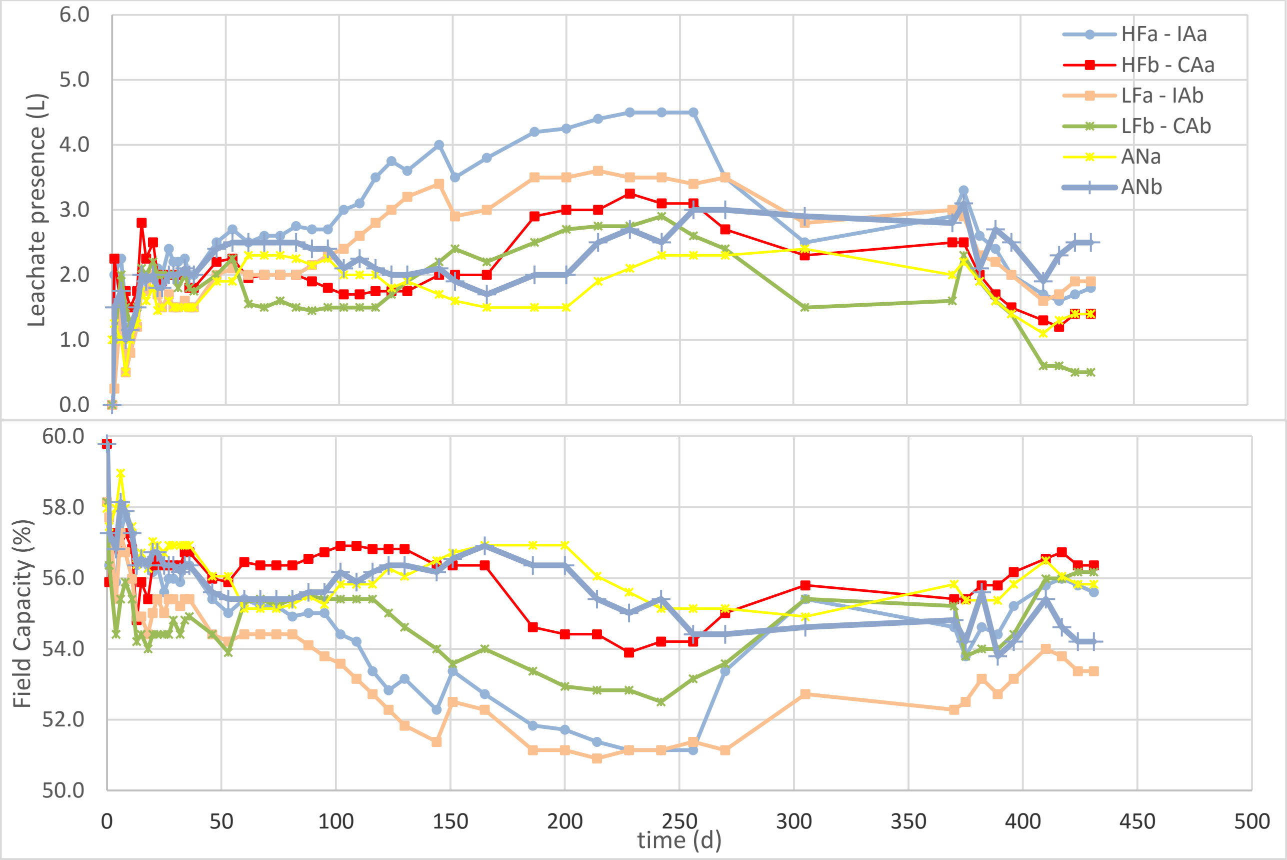




Carbon content (CH_4, CO_2) exiting:



Leachate amount and field capacity:



Reference analytical methods and equipment used:

Analytical standards for **liquid** samples

Parameter	Reference method/ equipment	Description
Ammonia (NH_3-N)	IRSA CNR 29/03 vol.2 n°4030 C	Spectrophotometric methods
Biochemical Oxygen Demand (BOD_5)	IRSA CNR 29/03 vol.2 n°5120 B2	
Chemical Oxygen Demand (COD)	IRSA CNR 29/03 vol.2 n°5130	Acid digestion with potassium dichromate followed by titration with Mohr's salt
Chlorides (Cl^-)	IRSA CNR 29/03 vol.2 n_4090	Direct titration with silver nitrate
Metals (Ba, Cd, Cr, Cu, Mo, Ni, Pb, Zn)	IRSA CNR 29/03 vol.1 n°3010+ 3020	Analysis of aqua regia extracts by inductively coupled plasma Liquid atomic emission spectroscopy
Nitrates (NO_3^-)	IRSA CNR 29/03 vol.2 n°4040 A1	Turbidimetric method: precipitation of barium sulfate in HCl medium
pH	IRSA CNR 29/03 vol.1 n°2060	Potentiometric method
Sulphates (SO_4^{2-})	IRSA CNR 29/03 vol.2 n_4140A	Gravimetric; Turbidimetric method
Total Organic Carbon (TOC)	Shimadzu TOC-VCSN analyzer	Infrared detection of CO_2 during dry combustion
Total Kjeldah Nitrogen (TKN)	IRSA CNR 29/03 vol.2 n°5030 A	Determination of ammonia by titration with a standard mineral acid, after conversion of amino nitrogen and free ammonia into ammonium by acid digestion followed by distillation
Total Solids (TS)	IRSA CNR 29/03 vol.1 n°2090 A	Gravimetric methods after drying at 105 _C for 12 h

Analytical standards for **solid** samples

Parameter	Reference method/ equipment	Description
Ammonia (NH_3-N)	IRSA CNR Q 64/86 vol. 3, n°7	
Metals (Ba, Cd, Cr, Cu, Mo, Ni, Pb, Zn)	EPA 1996 n_6010	Analysis of aqua regia extracts by inductively coupled plasma Liquid atomic emission spectroscopy
Respirometric Index (IR_4)	Sapromat and VoithSulzer Respiromat	Static respirometric index
Total Organic Carbon (TOC)	Shimadzu TOC-VCSN analyzer	Infrared detection of CO_2 during dry combustion
Total Kjeldah Nitrogen (TKN)	IRSA CNR Q.64/85 vol.3 n_6	Determination of ammonia by titration with a standard mineral acid, after conversion of amino nitrogen and free ammonia into ammonium by acid digestion followed by distillation
Total Solids (TS)	IRSA CNR Q.64/85 vol.2 n_2	Gravimetric methods after drying at 105 _C for 12 h
Total Volatile Solids (TVS)	Total Solids (TS)	Gravimetric methods after drying at 550 _C for 4 h

IRSA-CNR (Istituto di Ricerca sulle Acque - Consiglio Nazionale delle Ricerche)

Waste quality comparison between the initial of the experimental activity and the initial of the aerobic phase:

Solid phase

	Start	Start third phase					
	03/07/2014	08/07/2015					
	Initial waste	HFa - IAa	HFb - CAa	LFa - IAb	LFb - CAb	ANa	ANb
Weight (kg tal quale)	18.4	14.9	13.3	14.2	11.8	13.8	12.9
TS (%)	55.5	34.8	39.0	36.6	43.9	37.6	40.4
Weight (kg TS)	10.2	5.2	5.2	5.2	5.2	5.2	5.2
Waste height (m)	0.80	0.50	0.45	0.45	0.45	0.50	0.50
Waste density (kg/l)	0.5	0.65	0.65	0.7	0.6	0.6	0.6
VS (%TS)	59	41	32	39.5	31	26	44
RI_4 (mgO_2/gTS)	77	7	6.5	8	3	8	14
RI_7 (mgO_2/gTS)	79	9	9	11	4.5	12	21
TKN (mgN/kgTS)	9,701	7,596	8,013	7,317	8,498	7,683	7,586
TKN (gN)	99,1	39.5	42	38	44	40	39
TOC (gC/kgTS)	368	180	208	231	303	282	274
TOC (gC)	3,755	936	1,082	1,201	1,576	1,466	1,425
Cd (mgCd/kgTS)	0.6	20	< 1	< 1	< 1	< 1	< 1
Cr (mgCr/kgTS)	23	38	7	23	59	21	37
Cu (mgCu/kgTS)	28	69	15	57.5	40	26	46
Fe (mgFe/kgTS)	2,498	8,550	2,885	5,577	12,917	15,156	6,383
Mg (mgMg/kgTS)	72	390	73	264	291	210	252
Ni (mgNi/kgTS)	12	32	5	22	24	16	29
Pb (mgPb/kgTS)	10	393	5	12	24	7.5	29
Zn (mgZn/kgTS)	85	206	30	87	159	92	352

Eluate from leaching tests

pH	6.2	8.5	8.3	8.4	8.3	8.1	8.3
TOC (mgC/L)	3,640	1,810	1,150	1,370	1,315	845	1,040
COD (mgO_2/L)	14,682	4,939	2,939	4,791	4,836	2,889	4,834
BOD_5 (mgO_2/L)	7,504	365	308	309	337	393	477
Alkalinity (mg$CaCO_3$/L)	273.5	985	783	1,038	842	587	1,056
VFAs (mgCH_3COOH/L)	728	154	120	143	141	107	121
TKN (mgN/L)	756	490	237	406	411	131	261
N-NH_4^+ (mgN/L)	78	431	141	265	236	66	98
Norg (mgN/L)	678.5	59	95.5	141	175	65	163
Cl^- (mgCl^-/L)	619	343	233	243	362	376	324
SO_4^{2-} (mgSO_4^{2-}/L)	528	< 500	< 500	< 500	< 500	< 500	< 500
Cd (µgCd/L)	10	< 10	< 10	< 10	< 10	< 10	< 10
Cr (µgCr/L)	207	56	< 10	36	36	< 10	< 15
Cu (µgCu/L)	181	373	167	367	347	139	100
Fe (µgFe/L)	9,324	10,150	6,783	12,300	8,133	4,950	9,617
Mg (µgMg/L)	2,670.5	162	104	117	134	89	94
Ni (µgNi/L)	180.5	107	52	101	144	59	89
Pb (µgPb/L)	37.5	155	74	83	93	38	37
Zn (µgZn/L)	4,678.5	533	282	437	770	47	343

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