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SUSTAINABLE LANDFILLING:

HYBRID BIOREACTORS AND FINAL STORAGE QUALITY

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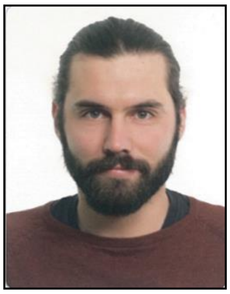

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Sustainable Landfilling: Hybrid Bioreactors and Final Storage Quality

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Summary

Modern landfilling constitutes an unavoidable final step in solid waste management. It aims to close the “Material Cycle” bringing elements back to the non-mobile state they were in before their extraction. At the same time, the application of Sustainability Principle to landfills prescribes to guarantee environmental protection and health safety, ensuring that the disposed waste will be chemically and biochemically stable within a reasonable amount of time. A “Sustainable Landfill” must combine these two fundamental purposes, balancing the efforts to obtain a “sustainable closure of material loop”.

The enhancement of biochemical processes in a landfill, with the purpose of reaching faster environmentally safe conditions and terminate the post closure care, is one of the main debated topics in waste management scientific literature. The general aim of the PhD project was giving a contribution to this debate through the lab-scale testing of systems able to simulate landfills behaviour and the analysis of the long-term expectable chemical status of waste undergone to sustainable landfilling.

The first part of the work is an overview on the basic biochemical processes in landfills and on the laboratory-scale landfill simulation tests. The approach used by the PhD student is mainly experimental, starting from the design and the management of several laboratory-scale landfill simulation tests. The elaboration of the obtained data was useful for evaluating the performances of the tested bioreactor concepts as well as for comparing the results to other scientific data derived from a thorough bibliographic research. The original work produced by the student can be subdivided in three different arguments.

The Semi-aerobic, Anaerobic, Aerated (S.An.A. ®) hybrid bioreactor is an innovative landfill concept, lab-scale run with promising results concerning the enhancement of methane production in anaerobic phase. During the third aeration phase, this system was able to reduce the long-term liquid emissions below the levels indicated in literature as targets for the biochemical stability of a landfill. The comparison with traditional anaerobic reactors showed a hypothetical reduction of the landfill active life of 25-35 %.

The recirculation of reverse osmosis leachate concentrate inside the landfill body is a practice sometimes adopted for treating and disposing this wastewater. However, the long-term effects of contaminants reinjection in the waste body are a still debated topic. Lab-scale tests showed that this practice has some positive effects, especially if combined with landfill aeration. However, some persistent compounds accumulation in the waste body can potentially make this practice unsustainable in long-term landfill management.

The Final Storage Quality (FSQ) procedure is a tool to endorse the landfill Post Closure Care termination. This procedure was applied to a long-lasting aerated and flushed reactor to quantify the residual long-term expectable emissions and compare them with a database composed by literature tests. Moreover, to check the final waste features, an in-depth chemical speciation of the main elements was performed both on the fresh sample loaded and on the stabilized waste of the reactor itself.

List of publications and contribution to conference proceedings

This PhD Thesis is based on several scientific journal articles, contribution to international conferences and books chapters prepared with the collaboration of internal and external partners. Some manuscripts has still to be submitted.

The student played a key role in all the scientific works included in the PhD thesis and contributed also to other scientific projects.

Scientific International Journal Publications and Manuscripts

Cossu R., **Morello L.**, Raga R., Cerminara G. (2015). Biogas production enhancement using semi-aerobic pre-aeration in a hybrid bioreactor landfill. Waste Management 55, pg. 83- 92.

Morello L., Cossu R., Raga R., Pivato A., Lavagnolo M.C. (2016). Recirculation of reverse osmosis concentrate in lab-scale anaerobic and aerobic landfill simulation reactors. Waste Management 56, pg. 262-270.

Morello L., Raga R., Lavagnolo M.C., Pivato A., Ali M., Yue D., Cossu R., The S.An.A.® Concept: Semi-aerobic, Anaerobic, Aerated bioreactor landfill. (Submitted to Waste Management)

Morello L., Raga R., Pivato A., Cossu R., Influence of semi-aerobic conditions and flushing on waste stabilization and long term emissions in a landfill simulation bioreactor. (Manuscript)

Morello L., Raga R., Sgarbossa P., Rosson E., Cossu R., Fate of Municipal Solid Waste main compounds undergone to a sustainable landfilling simulation. (Manuscript)

Book Contributions

Comitato Tecnico Terreni Contaminati (CTTC) (2015). Bonifica dei Siti Contaminati: osservazioni critiche, linee guida e proposte normative. Le guide del Sole 24 Ore.

Morello L., Cossu R., Stegmann R. (2017). Biochemical Processes in Landfills. The manuscript will be modified to be published in: Solid Waste Landfilling: Concepts, Processes, Technologies (2017). Cossu R. and Stegmann R.

International Conference Proceedings

Morello L., Alibardi L., Cossu R. (2014). A review on alternative energy production from landfill sites. 8th Intercontinental Landfill Research symposium (ICLRS 2014), Crystal River, Florida.

Morello L., Cossu R., Cerminara G., Raga R. (2015). The Semi-aerobic, Anaerobic, Aerobic (S.An.A) hybrid bioreactor landfill, Fifteen International Waste Management and Landfill Symposium (Sardinia 2015), Santa Margherita di Pula (Ca), Italy.

Cossu R., Lavagnolo M.C., **Morello L.**, Raga R. (2015). Reverse osmosis concentrate recirculation in lab-scale anaerobic and aerobic landfill simulation reactors, Fifteen International Waste Management and Landfill Symposium (Sardinia 2015), Santa Margherita di Pula (Ca), Italy.

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Cossu R., Carrubba P., Clò E., **Morello L.** (2015). Geotechnical and biochemical studies on pre-treated MSW produced in central Italy, Fifteen International Waste Management and Landfill Symposium (Sardinia 2015), Santa Margherita di Pula (Ca), Italy.

Morello L., Rosson E., Cossu R. (2016). Landfill mining of material from an old lab-scale lysimeter reactor, 3rd Symposum on urban mining and circular economy (SUM 2016), Bergamo, Italy.

Morello L., Cossu R. (2016). Ruolo del Final Sink nelle strategie di Circular Economy, 3rd Symposum on urban mining and circular economy (SUM 2016), Bergamo, Italy.

Cerminara G., Garbo F., **Morello L.**, Lavagnolo M.C., Cossu R. (2016). LCA approach for plasmix management, 3rd Symposum on urban mining and circular economy (SUM 2016), Bergamo, Italy.

Morello L., Rosson E., Raga R., Sgarbossa P., Cossu R. (2016). Characterization of different substances in a MSW landfill sink. 9th Intercontinental Landfill Research symposium (ICLRS 2016), Noboribetsu, Japan.

Cossu R., **Morello L.**, Yue D. (2016). Overview on Facultative-Hybrid Bioreactor Landfill. 9th Intercontinental Landfill Research symposium (ICLRS 2016), Noboribetsu, Japan.

Morello L., Cossu R. (2016). Hybrid Bioreactor Landfills: The S.An.A. Concept. 9th Intercontinental Landfill Research symposium (ICLRS 2016), Noboribetsu, Japan.

Chapter 1: Introduction

1.1 Sustainable Landfilling concept

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1.1.1 Sustainability concept applied to landfills

The Sustainability Principle is considered an international concept aiming to plan the current economic and social development with the purpose of guarantee the same possibilities of the present generation to the future ones. Society, economy and environment are to be considered as equally important in matter of sustainable development. Target that can be achieved only balancing the contribution to these three perspectives (Three Legged Stool Concept).

Many definitions have been provided to clarify this complex and all-embracing concept. Among them, the World Commission on Environment and Development (WCED), in *Our Common Future Report*, gave the first one: "The development must meet the needs of the present without compromising the ability of future generations to meet their own needs." (UN, 1987). A more recent and worldwide accepted definition is the one from the World Conservation Union (IUCN), the United Nations Environmental Program (UNEP), the World Wildlife Found (WWF) and some other international environmental associations: "Sustainable development means improving the quality of life of humans, while living within the carrying capacity of supporting ecosystems".

The European Union included the Sustainability Principle in its main driving forces and applied actively this concept to all recent regulations: approving a Sustainable Development Strategy for driving its work (EU 10917/2006).

A recent further step is the application of the action plan for the Circular Economy Strategy, consisting in "closing the loop of product lifecycles through greater recycling and re-use, and bring benefits for both the environment and the economy" aiming to "boost global competitiveness, foster sustainable economic growth and generate new jobs" (EU 416/2015). In this scenario, sustainability is the driving force to be applied to waste management (EU 275/2015) and landfilling (EU 274/2015) to reach such objectives. These European polices envisage a consistent reduction of untreated MSW deposition. However, the final disposal of waste will remain a fundamental tool for closing the material cycle: "A Circular Economy cannot exist in the absence of a sustainable closure of the material loop" (Cossu, 2016).

From this point of view, landfilling constitutes an unavoidable final step in waste management, being aimed at bringing residues back to the not-mobile state they were in before the extraction from the ground and their use as raw materials (Cossu, 2016). Moreover, modern landfilling could not overlook the application of the Sustainability

Principle, aiming to guarantee environmental protection and health safety during operations and post closure care. For this purpose, every effort has to be made for ensuring that the disposed waste will be chemically and biochemically stable within a reasonable amount of time. A Sustainable Landfill must combine these two fundamental purposes, balancing the efforts to obtain a "sustainable closure of material loop". Summarizing all the above mentioned concepts, an overall definition of Sustainable Landfill could be: "a landfill, that after being in operation, has mechanically stable structure and poses no risk for the surrounding environment" (Heimonovara et al., 2013).

In line with the above mentioned European Sustainability Principle (EU 10917/2006), reducing the duration of post operational phase towards landfill completion should be considered a priority and a driving force in waste management. For this purpose, landfills must be designed and managed to accelerate waste biochemical stabilization so as to reach the Final Storage Quality (FSQ) (Laner et al., 2012; Christensen et al., 2011). This need is related to the potential threats posed on the environment (in short and long-term) by mobile fractions present in waste, until their final stabilization in a sink (Cossu, 2016).

Landfills store huge quantities of not mobile or harmless mobile substances, not an issue from the sustainability point of view, together with some potentially dangerous chemical species, which can become contaminants in case of uncontrolled emissions in the environment (organic substances, ammonium ion, chlorine, sulphates and heavy metals above the others). In addition, some refractory organic by-products (pharmaceuticals, personal care products, hazardous, etc.) and a great number of very different "new chemicals" in small concentrations (flame retardant, stabilizers, fillers, inks, antioxydants, etc.) can be found in solid waste with increasing frequency (Bolyard and Reinhart, 2016; Pivnenko and Astrup, 2016).

The chemical speciation of each element in a landfill can be analysed with a mass balance approach applied in several moments of reactors' life (Figure 1.1.1). This tool is particularly useful so as to highlight the behaviour of potentially dangerous mobile compounds respect to not-mobile fractions, constituting the final sink for the element itself.

The elements in Raw Waste can be initially found in a not-mobile fraction as well as in a degradable one, potentially reduced by biochemical or chemical processes, and also in a mobile leachable fraction (Figure 1.1.1). The Mechanical Biological Treatment (MBT) can efficiently decrease the last two groups before waste deposition. Even though, some emissions are anyway expectable also applying strong pre-treatments. Inside a landfill, the degradable substances are progressively converted into not-mobile fractions or emissions during both routine operations (chemical reactions, biochemical degradation, biogas production and extraction, etc.) and aftercare treatments (aeration, flushing, etc.). Concomitantly, the mobile fraction keeps leaving the system as biogas and leachate, until reaching the Final Storage Quality (FSQ). As "FSQ" are defined the conditions in which landfill emissions cannot harm the environment and the human health anymore, even in case all the containment systems suddenly fail. After that, chemical and biochemical processes will continue even further, finally obtaining a not mobile final sink for the element, whose chemical characteristics can be confused with the soil ones (Figure 1.1.1).

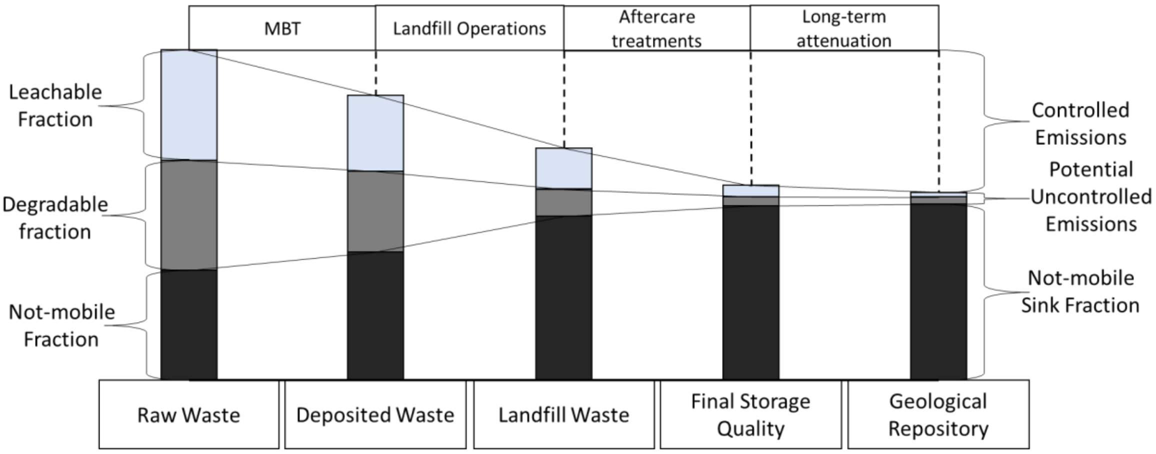

Figure 1.1.1: Sketch of the chemical speciation of the main fractions of a general element, respect to the main phases of the landfill life.

The above mentioned set of processes generally occur in a very long period, sometimes longer than a century for untreated refractory compounds, such as ammonia ion and persistent organics (Laner et al.,2012; Heimonovara et al., 2013).

The Sustainability Principle prescribes to reduce the time to reach FSQ conditions below a “generation time” (30-40 years) and, anyway, within the deadline for the containment systems failure (Cossu, 2007). This result must be achieved both increasing the pre-treatments of raw waste, in order to reduce its environmental potential dangerousness, as well as through the realization of landfills specifically designed aiming to this target since the beginning (Heimonovara et al., 2013).

Landfill construction, design and management changed consistently over time, from the 1950s until now, reflecting the different approaches and policies utilized in waste management (Christensen et al., 2011). Some general macro categories can be defined following literature descriptions. However, they do not necessary represent progressive technical evolution and this list is not stated by any legal standardization.

- *Open Dumps* are the ancient depositing system for the waste. Untreated waste (municipal as well as industrial and hazardous) is discharged in a low-value land without any design, control, monitoring and containment system for emissions (Christensen et al., 2011). The effects of this deposition are circumscribed and often tolerated by the surrounding population because of the small dimensions and the marginal location of the sites.
- *Sanitary Landfills* are designed and organized structures in which waste deposition, compaction and treatment are properly managed and where, sometimes, biogas can be collected for energy recovery. However, these sites lack in containment systems for avoiding emissions into the environment, so their potential dangerousness can be considered as relevant (Christensen et al., 2011).

- *Controlled Landfill* offers a higher level of site organization, collection and treatment systems for leachate, biogas and liners, avoiding uncontrolled emissions of contaminants. Introducing emission control systems, short-term environmental problems due to landfill emissions are generally solved, even with the not experienced technical solutions mentioned. However, these landfills have long-term problems to face, mainly related to uncontrolled emissions caused by the collection system and liners progressive usage and failure.
- *Dry Tomb*s are controlled landfills in which the water infiltration is totally prevented by means of an impermeable top cover to avoid leachate production and its consequent potential polluting problems and treatment costs. The biochemical activity in waste body is partially blocked by the absence of moisture with consequent inhibition of gas production and inferior organic compound stabilization. The efficiency of these systems is related to the maintenance of the liner systems whose failure can cause consistent environmental problems in long-term management (Christensen et al., 2011; Scharff et al., 2007).
- *Mineral Landfills* contain mainly inorganic waste (Hjelmar and Van der Sloot, 2011). This landfill environment hosts negligible quantities of biodegradable compounds. Here chemical stabilization occurs primarily by inorganics leaching. Mineral landfills have been implemented in many legislations, especially in countries in which the strategy includes the ban or the reduction of organic compounds deposition. The sustainability of these landfills is mainly due to inorganic compounds long-term residual leachability.
- *Bioreactor Landfill* is defined as: “Any landfill cell where liquid or air is injected in a controlled fashion into the waste mass in order to accelerate or enhance bio-stabilization of the waste" (EPA, 2015). These landfills are structured specifically to manage consistent quantities of biodegradable organic compounds, enhancing biochemical reactions inside with the consequent increase of methane production and reduction of the post closure care time (Townsend et al., 2015).

The sustainable landfilling concept comprises the above listed categories in which the Sustainability Principle is applied, always ensuring that emissions cannot exceed safe levels during operation. As sonsequence, despite the different characteristics (technologies, waste deposited and design), a landfill can be considered sustainable if its potential negative effect on environment, society, human health as well as economy is brought to an acceptable level within a generation time. The potential of different landfill technologies to enhance waste stabilization, as well as the long-term storage of specific compounds and elements, is currently a hot topic in scientific literature and research projects are in progress worldwide (Townsend et al., 2015; Cossu et al., 2016, Christensen et al., 2011; Laner et al., 2012; Ritzkowski et al., 2016). To this regard, the Bioreactor Landfill concept represents a valuable tool for reducing the potentially lengthy periods required to achieve sustainable conditions, even with high biodegradable organic content.

1.1.2 PhD project Outline

The overall purpose of the PhD project was contributing to the scientific discussion concerning two of the most debated aspects of the sustainable landfilling concept: the enhancement of biochemical processes and the Post Closure Care termination. These interconnected aspects were analysed designing and managing several laboratory scale landfill simulation tests that aimed to enhance the biochemical and chemical stabilization of the waste treated in several conditions. The Post Closure Care termination was faced with the Final Storage Quality approach, analysing the results of a long-term aftercare simulation, quantifying the total liquid emissions and characterizing the final stabilized material with an in deep chemical speciation of the main elements.

This thesis presents the results of the main research activity conducted by the student, organizing all the written material in three chapters.

Chapter 1 introduces the "Sustainable Landfilling" argument with an overview on the basic biochemical processes in landfills and the presentation of the laboratory-scale landfill simulation tests used for the whole PhD work. This chapter includes a contribution to a book:

- Biochemical Processes in landfills. Authors: Morello L., Cossu R., Stegmann R. The manuscript will be modified for be published in: Solid Waste Landfilling: Concepts, Processes, Technologies (2017). Cossu R. and Stegmann R.

Chapter 2 describes the bioreactor landfill systems and skills. Semi-aerobic, Anaerobic, Aerated (S.An.A.) hybrid bioreactor concept is discussed with its promising results concerning both the enhancement of methane production and the reduction of long-term liquid emissions. Moreover, a lab-scale recirculation of reverse osmosis leachate concentrate is presented. These chapter is constituted by the international journal articles:

- Biogas production enhancement using semi-aerobic pre-aeration in a hybrid bioreactor landfill. Authors: Cossu R., Morello L., Raga R., Cerminara G. Published in Waste Management 55 (2016), pg. 83- 92.
- Recirculation of reverse osmosis concentrate in lab-scale anaerobic and aerobic landfill simulation reactors. Authors: Morello L., Cossu R., Raga R., Pivato A., Lavagnolo M.C. Published in Waste Management 56 (2016), pg. 262-270.
- The S.An.A.® Concept: Semi-aerobic, Anaerobic, Aerated bioreactor landfill. Authors: Morello L., Raga R., Lavagnolo M.C., Pivato A., Ali M., Yue D., Cossu R. Submitted to Waste Management (2017).

Chapter 3 analyses the FSQ procedure, using as reference a long-term stabilized material, derived from a lysimeter test, whose emissions were monitored and quantified. These results are compared to a bibliographic database for evaluating the range of total liquid expectable emissions form an old landfill. Moreover, the chapter provides an in-deep chemical speciation of the main elements of both fresh and stabilized waste, which comparison was useful to evaluate the quality of future expectable residual emissions. These chapter is constituted by two manuscripts to be submitted to an international journal:

- Influence of semi-aerobic conditions and flushing on waste stabilization and long term emissions in a landfill simulation bioreactor. Authors: Morello L., Raga R., Pivato A., Cossu R. Manuscript (2017).
- Fate of Municipal Solid Waste main compounds undergone to a sustainable landfilling simulation. Authors: Morello L., Raga R., Sgarbossa P., Rosson E., Cossu R. To be submitted (2017).

The student played a key role in all the scientific works included in the PhD thesis, being the main actor of design, tests, bibliography, data elaboration and the preparation of the articles.

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1.2 Biochemical Processes in Landfills

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This manuscript will be modified to be published as Chapter 3.1 in the book: Solid Waste Landfilling: Concepts, Processes, Technologies. Raffaello Cossu and Rainer Stegmann (2017).

1.2.1 Introduction on biochemical processes and energetic behaviour

The landfills are huge bioreactors in which a complex system of physical, chemical and biochemical processes takes place simultaneously, transforming the initial compounds deposited, into products that can remain inside the waste body as fossil material or generate liquid and gaseous emissions. The chemical characteristics, quantity and environmental dangerousness of these emissions depends on many factors, such as initial characteristics of waste, landfill design, management, pre-treatments, in-situ treatments, etc. According with the complexity of the whole processes happening, conceptual models can be used to simulate the landfill biochemistry, subdividing the waste mass in three interacting phases: gaseous, liquid and solid. Each phase contributes and influences the biochemical processes considered in this chapter and the physical and inorganic processes too (Heimonovaara et al., 2013).

The main potentially dangerous emissions coming from the landfills are well known and, generally, controllable with modern management systems (Townsend et al., 2015; Christensen et al., 2011). Despite that, some minor compounds presence is observed with greater frequency and magnitude. Micro-contaminants presence is due to the increasing use of many new chemicals and drugs which tend to accumulate inside waste (Bolyard and Reinhart, 2016; Pivnenko and Astrup, 2016). Landfill gaseous emissions are mainly due to methane and carbon dioxide, produced during the biochemical degradation of putrescible compounds and in lower extent to sulphur compounds, CFC and trace grasses. In developed countries, the biogas coming from landfill body is collected for being energetically recovered or for being treated with bio-filters or through methane oxidation layers to avoid Green House Gasses (GHG) emissions. Concerning landfill leachate, the main source of potential contamination comes from organic putrescible compounds, ammonia-nitrogen, salts (mainly chloride), sulphates, alkaline-soil metals and Heavy Metals. In addition, there are various minor compounds which concentration depends mainly by the initial waste characteristics (Kjeldsen et al., 2002; Pivnenko and Astrup, 2016).

A useful tool for the landfill process analysis is the mass balance applied to the single macro-compound. This tool is particularly effective for performing management decisions and estimating long-term emissions. Even if the biochemical processes inside the waste body are hardly predictable with precision, the disposed waste characteristics are well known in a modern landfill, especially dealing with MSW. This starting information can be used to calibrate conceptual models with other data series, with the purpose of estimating the future life of the landfill, plan the management activity or design possible in situ treatments (Cossu et al., 2004; Christensen et al., 2011).

In this sub-chapter, the main biochemical processes of a landfill are explained. In particular, the analysis is focused on carbon, nitrogen and sulphur compounds, which are the main elements involved in the biochemical processes, all together constituting the prevalent part of organic material (Christensen et al., 2011). The other minor species or compounds present can only influence the main processes being nutrients or toxics according to their concentration (Mc Carty., 1964).

Degradation processes

The putrescible organic compounds can be used as carbon and energy source by heterotrophic microorganisms (bacteria, fungi), and as energy source by heterotrophs and chemoautotrophs (nitrifies and methanogen bacteria in a landfill). During all biochemical process inside a landfill, a redox reaction is necessary (catabolism) to gain to bacteria the necessary energy for growth (anabolism) and reproduction. The energy yield of each process depends highly on the oxidizing compound and on its availability (Table 1.2.1). However, the aerobic respiration has an energy yield much higher than methanogenesis and anaerobic processes in general. The microorganisms will always prefer the energetically favored reaction. Some of them (facultative bacteria) can also modify their catabolism according with environmental conditions, if they can freely operate. On the contrary, all the other microorganisms will enter in competition and they can be inhibited if not strong enough.

Table 1.2.1: Energetic behaviour of the main biochemical redox reactions. Modified from http://www.esf.edu/efb/schulz/Limnology/redox.html, 08/01/2016.

Biochemical REDOX Reaction Name	Oxidation	Formula	Energy Yield (kcal/mol)
Aerobic Respiration	O_2	$O_2 \rightarrow CO_2$	686
Denitrification	NO_3^-	$NO_3^- + H^+ \rightarrow N_2$	649
Iron Reduction	Fe_3^+	$Fe_2(OH)_3 + 2H^+ \rightarrow Fe_2^+$	300
Sulfate Reduction	SO_4^{2-}	$SO_4^{2-} + 2H^+ \rightarrow HS^-$	190
Methanogenesis	CO_2	$H_2 + CO_2 \rightarrow CH_4$	8.3

The waste body heterogeneity guarantees large variety of conditions and the coexistence of almost all the reactions inside a landfill is possible (Table 1.2.1, Figure 1.2.1) (Berge et al., 2013). For simplicity, the biochemical processes can be subdivided in two main conditions (aerobic and anaerobic), discriminated by the availability of oxygen the landfill body or not (Figure 1.2.1).

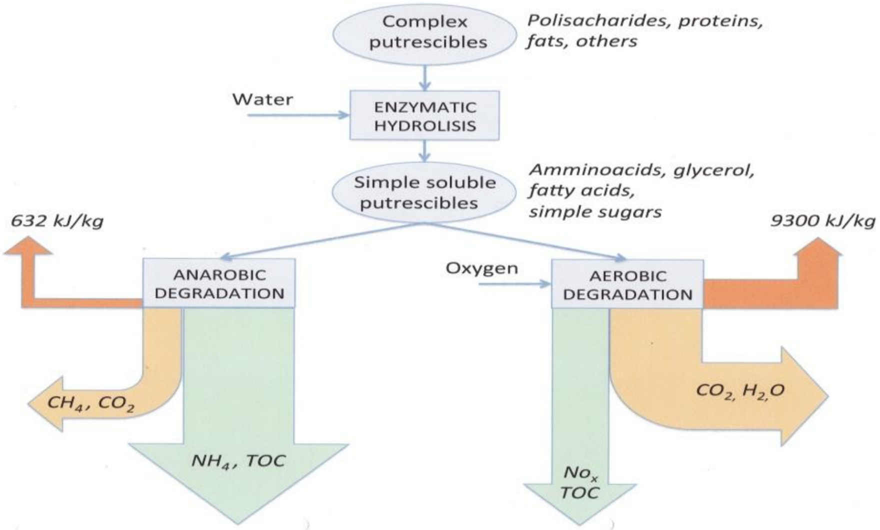


Figure 1.2.1: Landfill aerobic and anaerobic processes overview with average energy production and main catalytic products.

In the anaerobic landfills, oxygen in the interstitial pores is rapidly consumed. In short time, the energetically favor reactions become fermentation, sulphates reduction and methanogenesis. Biodegradable substances starts to be hydrolyzed and finally converted mainly into new biomass, methane and carbon dioxide. The complex organic molecules, such as lignin, cannot be degraded and ammonia-nitrogen cannot by nitrified. These persistent compounds are going to constitute the long-term leachate emissions (Berge et al., 2013; Laner et al., 2012; Brandstätter et al., 2015). The biological heat generation allows the waste body to reach and maintain the mesophilic conditions (35-45 °C). The biomass generated is less than 5% respect to initial carbon, meaning an abundant reduction of carbon compounds despite slow kinetics of degradation. In the reaction below the general formula of anaerobic digestion of glucose is reported.

$$\mathrm{C_6H_{12}C_6}\ \ (1\ \mathrm{kg}) \longrightarrow \mathrm{CH_4}\ (0.25\ \mathrm{kg}) + \mathrm{CO_2}\ (0.69\ \mathrm{kg}) +\ \mathrm{biomass}\ (0.056\ \mathrm{kg}) +\ \mathrm{Heat}\ (632\ \mathrm{kJ})$$

In the aerated Landfills, the presence of oxygen enhance biochemical reaction kinetics, fast bacteria growth and the possibility to hydrolyze some recalcitrant complex organic polymers, as well as the nitrification of ammonia-nitrogen. Methane production is totally inhibited or eventually confined in small anaerobic microenvironments. The gas produced is mainly composed by carbon dioxide, excess of oxygen, free nitrogen, water vapor and some trace compounds like gaseous ammonia. Despite aeration, some zones of the landfill body are not reached by oxygen, creating suitable places for denitrification, sulphates reduction and methanogenesis (Berge et al., 2009). Heat generation is higher respect to anaerobic digestion (50-60°C), positively influencing the activity of some microorganism (Christensen and

Kjeldsen, 1989). Biomass generation is approximately half of the initial carbon content, according to the general formula of aerobic digestion of glucose.

$$\mathrm{C_6H_{12}O_6\ (1\ kg) +\ O_2(0.64}\ kg) \longrightarrow \mathrm{CO_2\ (0.88\ kg) +\ \ H_2O\ (0.34\ kg) + biomass\ (0.4\ kg) + Heat\ (9300\ kJ)}$$

In the following sub-chapters, biochemical processes on carbon biodegradable compounds are analyzed subdivided into two macro categories (aerobic and anaerobic).

Microorganisms in landfills

Municipal Solid Waste (MSW) contains a wide range of various species of microorganisms that can proliferate, if the boundary conditions allows their growth: substrate availability, nutrient presence, absence of inhibitors, etc. Some bacteria are very specific and very sensible to changes, they can catabolize only specific substrates in very close range of pH or temperature and does not produce spores (i.e. methanogens). Some others are named "facultative" being more flexible and able to survive in a wider range of environmental conditions, from the aerobic to the anaerobic ones. In a landfill, the bacterial groups are numerous and able to interact each other forming a very complex system. In Table 1.2.2, only the key groups are listed (Sleat et al., 1989; Berge et al., 2013). The fecal bacteria and the virus are present in the fresh waste disposed in landfills but their number decreases rapidly due to the competition with other microbes and the high temperatures. In leachate, their presence is considered negligible (Andreottola and Cannas, 1992).

Table 1.2.2: Key bacterial groups involved in the biochemical processes of landfills with their main activity.

Amylolytic Bacteria	hydrolysis and degradation of starch
Proteolytic Bacteria	hydrolysis and degradation of proteins
Cellulolytic Bacteria	hydrolysis and degradation of cellulose
Hemicellulolytic Bacteria	hydrolysis and degradation of hemicellulose
Hydrogen-Oxydizing methanogenic Bacteria	Methane production from hydrogen and carbon dioxide
Acetoclastic methanogenic bacteria	Ethane and carbon dioxide production from acetic acid
Sulphate-reducing bacteria	Sulphate reduction to sulphite through acetic acid
Nitrosomonas	convert the ammonia nitrogen to nitrite.
Nitrobacter	convert nitrite to nitrate.
Thiobacillus Denitrificans	uses inorganic sulphur for reduce the nitrates in autotrophic denitrification.
Planctomycetales	ANaerobic AMMonium OXidation (ANAMMOX) which are able to oxidize ammonia nitrogen in anaerobic conditions.

1.2.2 Anaerobic degradation

The anaerobic degradation starts when oxygen is no more available inside waste mass, allowing less energetic reactions beginning. Fermentation and methanogenesis are the most commonly happening bioprocesses in the traditional landfills. Moreover, the methane production is generally encouraged for energy recovering. The set of all anaerobic processes is highly sensible to the boundary conditions: low energy yield produces less biomass and slower reaction kinetics, the pH can inhibit completely the process, nutrients and toxics presence can slow or stop the reactions, etc. The temperature is another fundamental aspect: the methanogens can be psychrophilic (15-20°C), mesophilic (33-40°C) or thermophilic (55-60°C). Out of these small temperature ranges, the methane production will be inhibited (Mc Carty., 1964). Finally, utilizable substrates are less abundant respect to aerobic conditions because the energy yield is lower and the enzymatic activity decrease as consequence.

Anaerobic digestion and methane production

The aerobic digestion processes requires the co-existence of many microbe species to finally produce methane, each one working in a specific role and with specific substrates (Senior, 1990). For this reason, the whole process is very sensible to changes of external conditions, however remaining the most important process inside the traditional landfills. The main source of potential pollution of the landfills comes from the putrescible compounds degradation and 90% of their emission into environment is due to gasification into CH_4 and CO_2 (Ehrig and Kruempelbeck, 2013). Generally, during an anaerobic process, only 5% of carbon is converted in new biomass through anabolism, while the greater part is transformed in methane and carbon dioxide with catabolism.

Anaerobic process is subdivided in four phases, carried on by different microbes, but the overall process can be synthetize by the simplified formula from Buswell and Mueller,1952:

$$\mathrm{C_nH_aO_b} \ + \ (\mathrm{n} - \frac{\mathrm{a}}{4} - \frac{\mathrm{b}}{2})\mathrm{H_2O} \longrightarrow (\frac{\mathrm{n}}{2} - \frac{\mathrm{a}}{8} + \frac{\mathrm{b}}{4})\mathrm{CO_2} \ + \ (\frac{\mathrm{n}}{2} + \frac{\mathrm{a}}{8} - \frac{\mathrm{b}}{4})\mathrm{CH_4}$$

Considering also the nitrogen, which is the main nutrient in this process, the equation becomes (Ehrig,1983):

$$\mathrm{C_nH_aO_bN_d} \ + \ \left(\mathrm{n} - \frac{\mathrm{a}}{4} - \frac{\mathrm{b}}{2} + \frac{3\mathrm{d}}{4}\right)\mathrm{H_2O} \longrightarrow \left(\frac{\mathrm{n}}{2} - \frac{\mathrm{a}}{8} + \frac{\mathrm{b}}{4} + \frac{3\mathrm{d}}{8}\right)\mathrm{CO_2} \ + \ \left(\frac{\mathrm{n}}{2} + \frac{\mathrm{a}}{8} - \frac{\mathrm{b}}{4} - \frac{3\mathrm{d}}{8}\right)\mathrm{CH_4} + \mathrm{dNH_4}$$

This formula allows to evaluate all the products and the reagents necessary for the process, with the only requirement of knowing precisely the composition of the initial substrate. Unlikely, this initial composition is generally unknown and very hard to be estimated with precision, so the formula can only have theoretical applications and no practical utility (Christensen and Kjeldsen, 1989). Generally, for the estimating the biogas production, mathematical models able to considering also the limiting factors and the control parameters are used. The heterogeneity of the waste disposed in a landfill can represent a problem for methanogens, because they need a proper moisture, specific concentrations of nutrients and micronutrients supply, substrate redistribution, dilution of toxic compounds, etc. All these requirements can be partially satisfy by the leachate recirculation that can guarantee a redistribution of compounds and humidity and more homogeneous conditions, inside the landfill body (Valencia et al., 2009). Laboratory and field scale tests proved that the leachate recirculation can increase methane yield and CH_4 concentration in biogas (Filipkowska, 2007, Chan et al., 2002, Bilgili et al., 2006). Recirculation of leachate influence positively also the carbon content of waste, which decreases due to the enhanced bio-chemical kinetics. During the anaerobic digestion, Volatile Fatty Acids (VFA) and easily degradable compounds decreases progressively respect to more refractory ones (such as lignin, cellulose and hemi-cellulose, which are the main biodegradable fraction of Municipal Solid Waste) (Bayard et al., 2013).

Anaerobic digestion can be subdivided it in four different sub sequential phases: Hydrolysis, Acidogenic fermentation, Acetogenic fermentation and Methanogenesis, plus the sulphates reduction which effects can enter in competition with the last three (Figure 1.2.2).

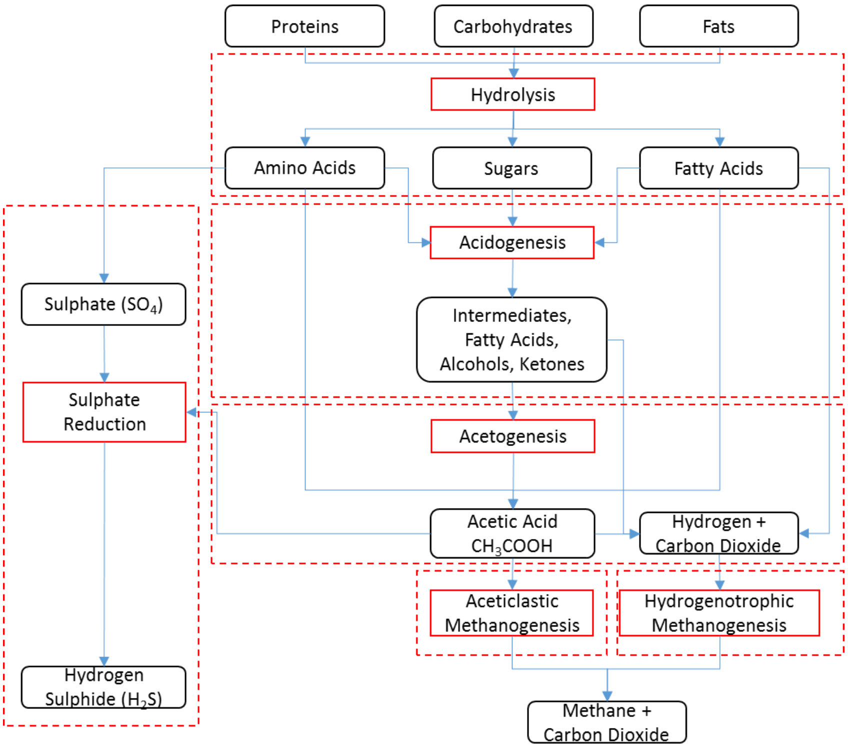


Figure 1.2.2: Anaerobic digestion processes divided into the main phases.

Hydrolysis

The first phase of every biochemical degradation is the enzymatic hydrolysis, useful for reducing the complex polymers into compounds smaller enough to penetrate the cellular membrane. For this purpose, some fermentative microbes species produce extracellular enzymes to catalyze the hydrolytical processes: cellulose, amylase, lipase and protease are the main ones (Jones et al.,1983). The main process consists in the reduction of fats, carbohydrates and proteins to fatty acids, glycerin, sugars and amino-acids (Figure 1.2.2).

$$\mathrm{Fats + nH2O} \rightarrow \mathrm{C_3H_5(OH)_3\ + R - COOH}$$
$$\mathrm{Carbohydrates\ + nH_2O} \rightarrow \mathrm{C_6H_{12}O_6}$$
$$\mathrm{Proteins\ +\ nH_2O} \rightarrow \mathrm{nR - CHNH_2 - COOH} \longrightarrow \mathrm{nRCOO^-\ +\ nNH_4^+}$$

The hydrolysis is the slowest processes of anaerobic digestion. For this reason, its kinetic governs all the following reactions slowing down the entire process. The anaerobic biochemical reactions can be modelled with Monod first order kinetic according with the substrate presence and its degradability. Water is a fundamental reagent of the reaction; as consequence, guaranteeing its abundance and its circulation inside the waste body must be a priority. In the first phases of landfill life, leachate produced will be rich of hydrolytical and of intermediate products of the process, which together can increase the acidity of the system. During this phase, the COD and BOD_5 indexes increase due to Volatile Fatty Acids (VFA) formation, pH drop down and some hydrolytical products like ammonia nitrogen and sulphates start to be produced (Figure 1.2.3).

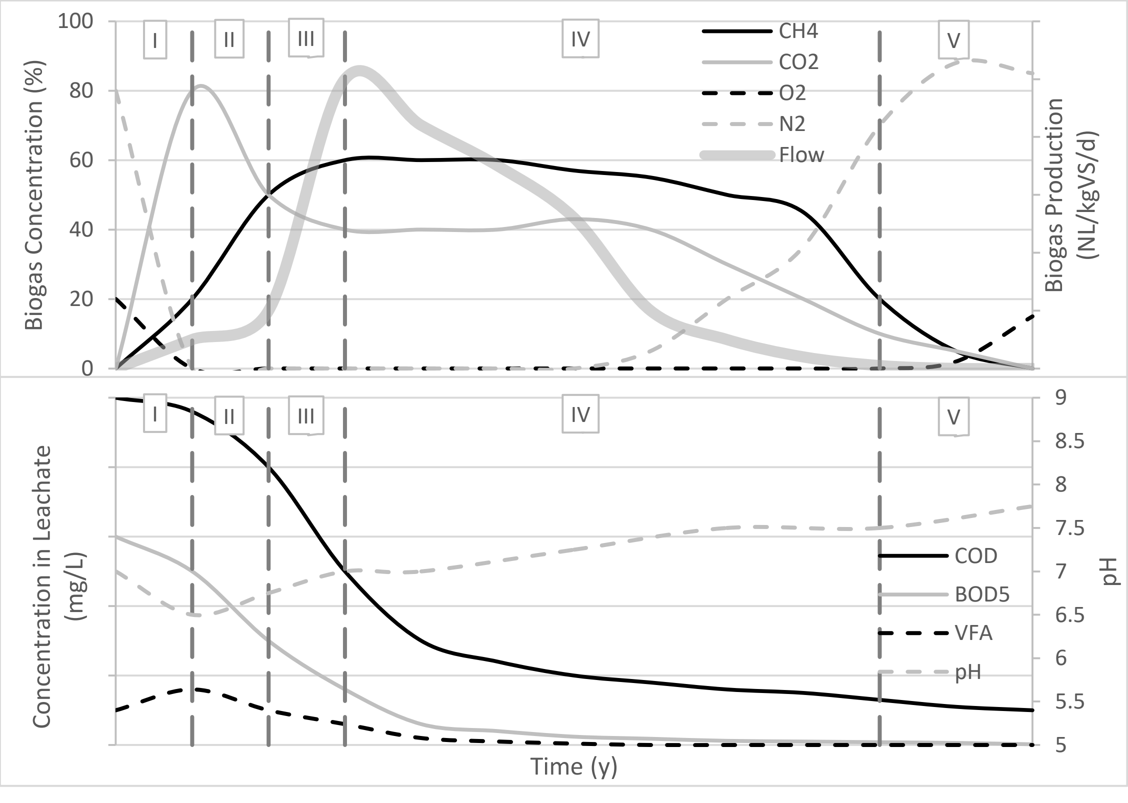


Figure 1.2.3: General biogas percentage composition, biogas flowrate and leachate biochemical characterization during the anaerobic landfill life. Behavior of concentration trend modified from Christensen and Kjeldsen, 1989; Cossu et al., 2003; Cossu et al., 2015. I: Hydrolysis, II: Acidogenesis, III: Acetogenesis, IV: Methanogenesis, V: Long term aftercare.

Acidogenesis, Fermentation

The products of the hydrolysis can be catabolized into Volatile Fatty Acids (VFA), acetic acid, alcohol, ammonia-nitrogen, hydrogen and carbon dioxide by the fermentative bacteria (Figure 1.2.2). These reactions generally happens simultaneously but the chance in some parameter equilibrium can enhance some of them respect the others.

$C_6H_{12}O_6 + H_2O \rightarrow 2CH_3COOH + H_2 + 2CO_2$
$C_6H_{12}O_6 \rightarrow C_3H_7COOH + 2H_2 + 2CO_2$
$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$

The fermentation microbe species are numerous, in particular some facultative bacteria can be favor due to their fast growth (Daverio et al., 2005). During this phase, a high presence of hydrogen producing bacteria and hydrogen consuming bacteria (like sulphates-reducing and nitrate-reducing ones) can growth (Senior, 1990). The carbon dioxide generated replaces residual oxygen and free nitrogen in the interstitial pores. Some hydrogen gas is also produced but methanogenic bacteria generally quickly consume it.

Acetogenesis, Fermentation

During the acetogenic phase, all the intermediate products coming from the acidogenesis are converted into acetic acid, hydrogen and carbon dioxide. The acidogenic bacteria seems to not be able to convert aromatic hydrocarbons into acetic acid, except if they contain oxygen (Christensen and Kjeldsen, 1989).

$C_2H_5COOH + 2H_2O \rightarrow CH_3COOH + 3H_2 + CO_2$
$C_3H_7COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2$
$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2H_2$

The conversion of all the hydrolytic compounds into acetic acid, in the fermentative phases, can cause a decrease of pH in acid conditions that can slow down the methanogenic processes. Gas produced is constituted mainly by carbon dioxide and hydrogen, like in the previous phase. The fermentation phase length can range from one to five years in a full-scale landfill; generally lasting for 2-3 years since the waste deposition (Pivato and Cossu, 2007).

Methanogenesis

The last phase of anaerobic degradation is the methanogenesis, consisting in the production of methane and carbon dioxide starting from hydrogen and acetic acid (Figure 1.2.2). The bacteria performing these reactions are very specialized, the most sensible to pH, nutrient, temperature and can use only a very specific substrate. At the beginning, the methanogenesis is an unstable process, gas composition is variable while the methanogens are adapting to the environment. Subsequently, the process becomes more stable and biogas reach the standard quality for an anaerobic process (50-60 % CH_4, 40-50% CO_2). Two main categories of methanogens can be distinguished according with the substrate utilized: hydrogenotrophic consumes hydrogen and carbon dioxide while acetotrophic uses acetic acid (Senior, 1990). Some bacteria can use also formic acid and ethanol for the methane production (Christensen and Kjeldsen, 1989). Among all the reactions of this phase, the conversion of acetic acid is the more important because 70% of methane is produced with this process (Cossu, 2001).

$CH_3COOH \rightarrow CH_4 + CO_2$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
$HCOOH + 3H_2 \rightarrow CH_4 + 2H_2O$
$CH_3OH + H_2 \rightarrow CH_4 + 2H_2O$

These reactions transforms the VFAs and the products coming from the previous phases into biogas, with the consequential dropdown of putrescible compounds in leachate. COD, BOD_5 and TOC indexes decrease immediately when stable methanogenic phase starts, until reaching values below 5000 mg/L (Figure 1.2.3). At the end of methanogenic phase, the residual carbon is mainly compose by hardly degradable humic substances. The methane and the carbon dioxide concentration in biogas remain the same until almost all the bioavailable substrate is finished. The biogas quantity has a positive peak after stable methanogenesis phase starts (due to fast degradable compounds); after that, biogas flow decreases slowly until all organic substances are finish (Figure 1.2.3).

Table 1.2.3: General composition of anaerobic digestion biogas.

Component	Symbol	Concentration Range (%vol)
Methane	CH4	50-75
Carbon Dioxide	CO2	25-45
Water Vapour	H2O	0-7
Free Nitrogen	N2	0-2
Hydrogen	H2	0-1
Hydrogen Sulphur	H2S	0.01-2
Gaseous Ammonia	NH3	0-1

During the entire traditional anaerobic landfill life, the composition of biogas produced can change consistently (Figure 1.2.3). After the short initial phase in which oxygen is consumed forming high concentrations of carbon dioxide, the methanogenic phase starts and last for all the time necessary to degrade all the putrescible matter: generally 10-20 years after the landfill closure (Ritzkowski et al., 2006). After this period, the air starts gradually to infiltrate in the waste mass generating aerobic conditions that can degrade also some complex resistant polymer. The composition of biogas during methanogenesis depends highly on initial substrate, but generally gaseous compounds concentrations are in the ranges of Table 1.2.3. Methane and carbon dioxide represent the main components and together totalize always more than 90% of biogas. Water vapor, free nitrogen and hydrogen presence depends on the process efficiency, while H_2S and NH_3(g) concentrations depends mainly on the initial waste characteristics, especially on the proteins content.

The biogas kinetic models based on the Gompertz Growth Equation are useful tools in anaerobic digestion design because they can be calibrated with real or derived biogas data to mathematically simulate the progressive Methane production. These models has sigmoid shape with a clear inflection point and the output is the cumulative volume of Methane produced from the bioreactors according to the following equation (Lay et al., 1998):

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

BG is the cumulative methane yield (mL/gVS), t is the cumulated time (d), BGP is the methane yield potential (mL/gVS), Rm is maximal daily methane yield (mL/gVS/d), λ is bacteria growth lag time (d) and e is a mathematical constant (=2.718). To calibrate this models, Bio Methane Potential (BMP) tests can be used, which consist in a lab-scale simulation of the whole anaerobic processes in a short time useful for obtaining the parameters for the Gompertz equation.

Sulphate reduction

The sulphates reduction process happens simultaneously with the fermentation and the methanogenesis process, entering in competition with the last one for the acetic acid and the hydrogen substrates and potentially causing a partial inhibition of the methane production being energetically favored (Christensen and Kjeldsen, 1989).

$2H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$
$CH_3COOH + SO_4^{2-} - \rightarrow CO_2 + HS^- + HCO_3^- + H_2O$
$2C_3H_7COOH + SO_4^{2-} + H^+ \rightarrow 4CH_3COOH + HS^-$

These reactions consumes completely the sulphates in the waste, which abundance is proportional to the initial content of proteins.

Process control parameters and nutrients

The anaerobic digestion can be highly influenced by some control parameters (pH, temperature, alkalinity, VFA, oxygen presence), by macronutrient presence (nitrogen, phosphorus, sulphur), micro nutrients availability and toxic compound concentrations (Table 1.2.4).

Temperature

The anaerobic digestion works efficiently only in three main temperature ranges: psychrophilic (15-20°C), mesophilic (33-40°C) and thermophilic (55-60°C) (Figure 1.2.4). Increasing the temperature to a higher range, get involved different microbial group activity and raise the process efficiency. However, maintaining optimal high temperature conditions can be expensive. Anaerobic digesters are artificially maintained in mesophilic or in thermophilic conditions heating the reactors, because even a small change in temperature can highly affect the methane production efficiency. In a full-scale anaerobic landfill, a heating system application is technically impossible and economically unsustainable. Anyway, the temperature inside the waste body is naturally in stable mesophilic conditions, maintained thanks to thermic characteristics of waste mass and top cover. The anaerobic digestion process produce 632 KJ, which is only the 7% respect to aerobic degradation, but it is sufficient for maintaining 35-40 °C (Christensen and Kjeldsen, 1989).

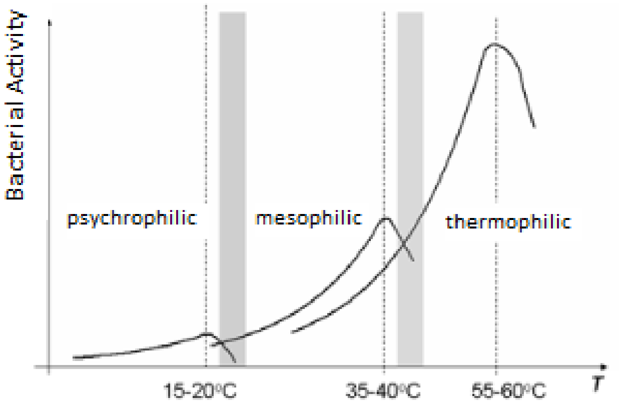


Figure 1.2.4: Optimal temperature conditions for enhancing anaerobic digestion and bacterial activity during psychrophilic, mesophilic and thermophilic conditions.

Oxygen

The oxygen presence in waste body, even in low concentrations, can inhibit completely the methane production. The aerobic bacteria are strong competitor for the same substrate used by methanogens and oxygen itself is a toxic compound for them. Methanogens does not produce spores; they probably can survive in aerobic environment thanks to the presence of anaerobic microenvironments (Christensen and Kjeldsen, 1989). However, in an anaerobic landfill the oxygen diffusion is limited to the upper layers and the top cover, not involving the waste mass.

Moisture content

The moisture content in a landfill is fundamental for enhancing biochemical processes, supporting the metabolic process, transporting nutrients, diluting toxics and allowing microorganisms to move about (Norbu et al., 2005). If the top cover does not allow fresh water to enter in waste body, the reactions will be stopped and all the potential emissions will remain inside the reactor. For this reason, guarantee the proper water supply in waste body is the priority (Ritzkowski and Stegmann, 2013) to efficiently redistributing the compounds and the necessary moisture content (Valencia et al., 2009). Moreover, the leachate recirculation can be applied for the homogenization of waste mass and can also increase the efficiency of methane production (Bilgili et al., 2006, Chung et al., 1998). Generally, a MSW contains 30-50 % of humidity, which can be increased up to field capacity (50- 60 % of total solids) for maximizing methanogenic processes efficiency. In low rainfall areas, a low water infiltration capacity or a complicate water circulation inside the landfill body make essential the control of moisture content and the recirculation becomes necessary to guarantee the biochemical processes efficiency. Forced irrigation can be a further solution, which can be made considering some infiltration windows in the top cover or building injection wells in the landfill body (Hupe et al., 2013).

Table 1.2.4: Main nutrient or inhibitor effect range for anaerobic digestion. Modified from Mc Carty, 1964.

Parameter	Positive Effect Range	Negative Effect Range
Mesophilic Temperature (°C)	30-40	
pH	6.6-7.6	< 6 and >8.2
Alkalinity (mg$CaCO_3$/L)	1000-5000	
Volatile Fatty Acids (mgCH_3COOH/L)	< 6000	> 6000
Ammonia-Nitrogen (mg/L)	40-70	>3000
Phosphorus (mg/L)	> 1 mg/l	
Sulphur (mg/L)	> 1 mg/l	
Sodium (mg/L)	100-200	>3500
Potassium (mg/L)	200-400	>2500
Calcium (mg/L)	100-200	>2500
Magnesium (mg/L)	74-150	>1000
Iron (mg/L)	10-200	>1750
Nickel (mg/L)	0.5-30	> 30
Molybdenum (mg/L)	0.1-0.35	
Tungsten (mg/L)	0.1-0.35	
Selenium (mg/L)	0.1-0.35	
Zinc (mg/L)	0.1-0.3	>400
Copper (mg/L)		>40
Chromium (mg/L)		>130
Lead (mg/L)		>340

pH

The pH highly influence the methanogens bacteria efficiency, being one of the most important parameter in anaerobic digestion processes. While fermentative bacteria can work efficiently in a wide range of pH (5-9), methanogenic bacteria operates in a more strict range: 6-8 (Zehnder et al., 1982), 6.7-7.4 (Lay et al., 1998), 6.4-7.2 (Chung et al., 1998), 6.5-8.2 (Sekman et al., 2011), 6.65-7.41 (Sandip et al., 2012) (Table 1.2.4). This index can significantly decrease during the first phases of hydrolysis and fermentation because Volatile Fatty Acids

(VFA) production. If methane production kinetics are slower respect to VFA production, the accumulation of acids can turn the pH under 6, inhibiting completely the methanogenic process (Daverio et al., 2005). In anaerobic digesters, this phenomena (named "overload") is controlled managing the feeding of the reactor; technique not applicable in a full-scale landfill. Another factor influencing the pH and contributing to acidity is the rainfall, which generally has 5.5-5.8 of pH if saturated of carbon dioxide. This pH value can decrease even more in some particular cases (Andreas, 2013).

Alkalinity

The alkalinity is the concentration of the alkali salts, indirectly indicating the buffer capacity, which is the ability to mitigate the dropdown of pH despite the generation of acids during fermentation processes. The main sources of alkalinity are the degradation of the proteins and the reduction of sulphates, while no alkalinity comes from the hydrolysis of carbohydrates, sugars, organic acids and fats (Mc Carty., 1964).

$NH_{3(g)} + H_2CO_3 \rightarrow NH_4^+ + HCO_3^-$
$4\ H_2 + SO_4^{2-} + CO_2 \rightarrow HS^- + HCO_3^- + 3\ H_2O$

This index can be universally measured as the concentration of Carbonates (HCO_3^-) inside the leachate, generating good buffer conditions (for methanogens) when reaching values upper than 1000 mg/L HCO_3^-. In the case of initial abundance of putrescible organics, mixing the waste with some buffering material can be a good practice, in particular the construction and demolition waste can both dilute the acidity and create more alkalinity (Christensen and Kjeldsen, 1989) being rich of alkaline ashes and other similar residues abundant of calcium silicates, carbonates and bicarbonates (Andreas, 2013).

VFA

The Volatile Fatty Acids (VFA) are the main contributors to the decrease of pH and the main feed for the last phases of the anaerobic digestion. The VFA are a mix of small chain acids (mainly Formic, Acetic, Propionic, Butyric, Valeric) which concentration inside a landfill can be measured referring to the acetic acid (the most common one, mgCH_3COOH/L) (Mc Carty., 1964). If VFA concentration in a landfill leachate is below 6000 CH_3COOHmg/L (Table 1.2.4), acidity will be sufficiently low to not inhibit the methanogens; however, this threshold value depends on the alkalinity concentration in the waste mass also. The VFA production progressively consumes the alkalinity of the system before affecting the pH. For this reason, the pH monitoring is not sufficient for continuously monitoring the anaerobic reactors because its changes happens only when buffer capacity is finished, being often too late for correcting the VFA content. For this purpose, ALK/VFA ratio is used in reactor management, being a more ductile index, easier to be monitored and rapidly changing with the system. ALK/VFA optimal value for an anaerobic digester is around 3.5 g HCO_3^-/gCH_3COOH. The reciprocal of ALK/VFA if the FOS/TAC: a German developed index worldwide used as controlling parameter for anaerobic digestion processes. The methane production of an anaerobic degradation system requires a ratio between VFAs and alkalinity lower than 0.8 (Farquhar et al., 1973). In a landfill, this value can be even slightly higher without affecting the methane production (Cossu et al., 2015).

Ammonia-nitrogen

The methanogenic bacteria consume ammonia-nitrogen, being it a nutrient to be present in concentration at least of 49 mg/L (Table 1.2.4), and suffers its toxicity in concentration higher than 3000 mg/L. Ammonia-ion is the main nutrient of the process and its presence is fundamental for enhancing the production of alkalinity inside the system. At pH upper than 8, the ammonium aqueous equilibrium allows the production of gaseous toxic ammonia, able to inhibit the microbes activity (Mc Carty., 1964).

Sulphates

The sulphates, originated from hydrolysis of proteins, are generally present in landfill leachate and can affect negatively the anaerobic digestion. As previously explained, their reduction process enters in competition with the methanogens for hydrogen and acetic acid substrates consumption, being the sulphates reduction energetically advantaged. Moreover, the produced H_2S is a toxic compound for methanogens in low pH environments (Mc Carty., 1964).

Nitrates

The nitrates and the nitrites have an inhibitory effect on the anaerobic digestion because denitrification bacteria enters in competition with the methanogens, which has a lower reaction yield (Filipkowska, 2007). This effect must be particularly considered in landfills with recirculation of aerobically treated leachate.

Hydrogen

The hydrogen is a secondary product of the fermentation and its pressure inside the waste mass can influence the fermentative processes itself: if the hydrogen pressure is high the main products will be ethanol, butyric and propionic acids, if it is low acetic acid will be directly produced (Christensen and Kjeldsen, 1989). Generally, the hydrogen is totally converted to methane during hydrogentrophic processes or consumed by sulphates reducing bacteria. As consequence, its concentration in biogas is virtually negligible (Table 1.2.3).

Nutrients, Micro-nutrients and Inhibitors

In anaerobic digestion, the main nutrients are nitrogen, sulphur and phosphorus. Generally, nitrogen and sulphur are abundant in waste while phosphorus may be a limiting factor. The ratio between the three macronutrients is 100 C: 0.44 N: 0.08 P, highlighting that the new biomass production is very low in percentage (Christensen and Kjeldsen, 1989; Mc Carty., 1964). In addition to main nutrients, a consistent number of other elements can be fundamental micro-nutrients or toxics for the anaerobic digestion, according with their concentration inside the landfill (Table 1.2.4). This sensibility to many elements concentration can create significant variation of kinetics inside landfill body where all these compounds are heterogeneously present. The leachate recirculation is fundamental from this point of view, mitigating this potentially negative effect (Christensen and Kjeldsen, 1989).

Carbon Emissions of an Anaerobic Landfill

The anaerobic landfill emissions are related to the waste composition, as well as to reactor characteristics and management. Generally, 90% of the emissions into the environment are due to the conversion of putrescible substances into catabolite gasses (CH_4 and CO_2) (Ehrig and Kruempelbeck, 2013). The biomass production involves less than 5% of available organic compounds and carbon emissions via leachate are an order of magnitude lower than gaseous ones, even in the anaerobic digestion phase (Lornage et al., 2013; Morello et al., 2016). The Chemical Oxygen Demand (COD) decreases faster once stable methanogenesis phase starts, reaching values even lower than 5000 mg/L, while the Total Organic Carbon (TOC) follows the same behavior. The BOD_5 concentrations decrease similarly to the COD ones, reaching values below 50 mg/L only when all biodegradable substances are finished (Figure 1.2.3).

A useful index for monitoring the biochemical status of a landfill can be the BOD_5/COD ratio, indicating the amount of biodegradable compounds still present respect to the total oxidable compounds. This index is not influenced by the leachate production quantity because is a mass ratio. BOD_5/COD values between 0.02 and 0.13 implies a low biodegradability, while between 0.4 and 0.8 shows a high biodegradability of the liquid sample (Cossu et al., 2012; Sekman et al., 2011).

In an anaerobic landfill, the majority of biogas is produced during the first 30 - 40 years, after which the gas flux will be that low that top covers or passive catching systems are generally sufficient for guaranteeing absence of uncontrolled methane emissions. Laboratory tests and model predictions suggest that long-term gas production will be negligible 20-30 years after the waste disposal (Christensen et al., 2011).

On the other hand, the long-term carbon emissions in leachate can potentially last for many more decades, being a huge problem in the landfill aftercare phases (Christensen et al., 2011; Ritzkowski et al., 2016; Laner et al., 2012). The largest part of carbon deposited in a landfill will remain stored even after centuries from deposition, being constituted by hardly biodegradable compounds (such as Cellulose, Hemicellulose, Lignin and Synthetic Organic Polymers (Manfredi and Christensen, 2009; De la Cruz et al., 2013). During the biochemical degradation of carbon, approximately 10% of it was transformed into slowly mobile forms, probably due to the formation of Humic and fulvic acids, which are the result of the conversion of biomass during degradation processes. These partially leachable compounds constitute a relevant contribution to long-term COD emissions in leachate (Brandstätter et al., 2015).

1.2.3 Aerobic degradation

The biological oxidation of putrescible compounds, as well as of refractory by-products and slowly degradable organics, is possible only in presence of sufficient free oxygen in the interstitial pores. The other requirements for performing an aerobic process are the substrate presence, the nutrients (mainly nitrogen and phosphorus) and the moisture content; last one is fundamental for both hydrolysis and compounds mobility. In these conditions, the aerobic process will have fast reaction kinetic, thanks to its high energetic yield and to the numerous groups of available aerobic microbes in waste. The aerobic degradation is partly influenced by changes of the system conditions or control parameters. Temperature in waste body is going to be high due to the powerful exothermic reactions and the pH must remain in the wide range between 4 and 9: conditions generally respected in the MSW landfills. The reactions kinetics are governed by enzymatic hydrolysis, which decompose the macromolecules and the polymers (proteins, starch, carbohydrates) into smaller compounds available to bacteria (amino-acids, sugars, fatty acids). If the oxygen presence is sufficiently high, also the nitrification process takes place, converting the ammonia-nitrogen into nitrates.

Oxidation of carbon compound

In the aerobic landfills, microorganisms progressively convert all the biologically available compounds into carbon dioxide, water and new biomass, which can be successively catabolized or converted into humic-like not degradable substances (Ritzkowski et al., 2006). This production of humic acids depends by the high energy yield of aerobic processes that allows a very fast growth rate of microbes and a consequential high production of biomass (up to 40-50% of carbon is used for anabolism and converted into new biomass). If enough oxygen is provided, all the other biological process in competition for carbon organic substrates are inhibited. The efficiency of the aerobic condition in a landfill is worldwide proved: reaction kinetics allow reducing the biological stabilization time even of ten times respect to anaerobic digestion (Cossu et al., 2008).

The main biodegradable polymeric constituents of the organic waste can be classified as follows (Senior, 1990):

- The lignocelluloses are very complex polymers with mainly structural function in plants.
- The cellulose and the hemicellulose are partially degradable in aerobic conditions: their semi-recalcitrance is mainly due to the difficult accessibility of the β-4 glucosidic bond to the hydrolytic enzymes.
- The lignin is another polymer which structure is so complex that is generally considered non-degradable at all.
- The polysaccharides are the primary foodstuff for plants and organisms. Their polymerization is easy to be broken, thanks to the hydrolysis.
- The fats are well distributed in all plants and microorganisms and they are totally biodegradable compounds.

- The proteins are amino-acids polymers, base components of cells. They are biodegradable and their hydrolysis will produce also ammonia-nitrogen and sulphur containing molecules.

When hydrolyzed, all these components can be part of the catabolic processes that happens inside the microbes cells, finally becoming carbon dioxide, water or new cell biomass during the anabolism. This process can be described by the general stoichiometric formula for the decomposition of volatile solids in the aerobic processes (Tchobanoglous et al., 1993):

$$CaHbOc + 0.5\,(ny + 2s + 0.5b - 0.5nx - c)\,O_2 \rightarrow nCwHxOy + sCO_2 + (0.5b - 0.5nx)\,H_2O$$

However, the aerobic degradation process simplification with the stoichiometric solution of this formula is considered too simplistic and potentially source of huge mistakes. Among the reactor products, there is also heat, which can grow the temperature in landfill body even to 60 - 70 °C. For this reason, even if water is produced, during the aerobic processes moisture must be supplied to the landfill, for guarantee hydrolysis as well as for temperature and fire control. The biomass produced can be further degraded during the endogenous processes, finally producing complex not-degradable compounds only partially soluble, such as humic acids (Brandstätter et al., 2015).

The carbon compounds emission of an aerobic landfill are mainly constituted by gaseous carbon dioxide, while the mass leachate emissions are more than an order of magnitude smaller (Lornage et al., 2013; Cossu et al., 2015). The presence and the circulation of water are fundamental aspects for the hydrolytic process, the redistribution of nutrients and the dilution of toxics (Valencia et al., 2009). However, aerobic processes can be equally efficient having the right moisture content inside waste (without any excess) and guaranteeing the liquid circulation (Ritzkowski and Stegmann, 2013). The aerobic conditions can increase the sulphates content inside leachate, because of the oxidation of the reduced sulphur containing molecules (Ritkowski and Stegman, 2007).

Further positive effects of aeration of landfills are the decrease of odors in biogas and the avoidance of uncontrolled methane emissions: methane is a greenhouse gas 21-25 times more powerful respect to the carbon dioxide (Dal Maso and Zanella, 2009; Tunesi, 2012).

Aerobic Landfill Systems

The aerated conditions in a landfill are generally not spontaneous, forced or natural aeration must be guaranteed with relative management and building costs. For these reason, the duration of air supply is limited at the time in which the aerobic conditions are necessary to enhance the reactions or to degrade persistent compounds. In particular, Hybrid bioreactors are systems that can operate under various combination of aerobic and anaerobic conditions to achieve the benefits of both of them (Long et al., 2009, Xu et al., 2014; Townsend et al., 2015). The use of aeration in landfills is a worldwide known option and there are many example of in-situ applications of different technologies in different countries. Aeration modality is another fundamental aspect, which can highly influence the efficiency of all in situ treatments. An intermittent aeration has been found to be more efficient because the alternation of aerobic and anaerobic conditions generates a specific microbial community, stronger respect to continuous aeration ones because able to adapt faster to any environmental change (Sang et al., 2009). As instance, the aeration can be performed with pipes excavated vertically and/or horizontally inside the landfill body, air injection can be provided from the very bottom to be more efficient, in term of organic compounds biodegradation, or only involving a vertical portion (Wu et al., 2014), etc.

The on-site aerobic leachate treatment and following treated liquids recirculation allows maintaining the landfill in a traditional anaerobic condition and simultaneously treating aerobically the leachate before reinjection. An example of this process is the Facultative Bioreactor Landfills (FBL): a category of landfill that provides an external aerobic pre-treatment of leachate prior its recirculation in an anaerobic bioreactor, to allow both the nitrification and the denitrification process for removing nitrogen compounds (De Abreu et al., 2005, US639895, 2002). Recirculation of leachate treatment products (like aerated leachate, concentrate from reverse osmosis, evaporate, etc.) can have interesting technical and economic benefits. On the other hand, this practice can cause the accumulation of persistent compounds like salts, chloride and metals (Morello et al., 2016; Robinson, 2005).

The semi-aerobic Landfill (i.e. Fukuoka Method) is a technology able to encourage the natural circulation of air inside the landfill body, using the thermic gradient between the waste mass and the surrounding environment. This method allows stimulating the biochemical degradation of organic compounds, in particular in first 5 years of application (Matzufuji et al., 2013). The airflow measured is variable according to the temperature gradient that change consistently seasonally and daily.

Hybrid system featuring an initial semi-aerobic phase to enhance methane production occurring in the subsequent anaerobic step and, finally, forced aeration for the abatement of residual emissions are also possible (Cossu et al., 2016; Repetti et al., 2013).

In modern landfilling, the most frequent use of aeration is for stabilizing old landfills, with no more methane production but which can have a negative impact on the environment due to the long-term potential leachate emissions. The target is close the aftercare of a landfill reaching the condition in which they cannot harm the environment anymore (Heyer et al., 2003) in a reasonable and sustainable time: often identify as one generation time of 30 years also by European Directive 1999/31/CE (Laner et al., 2012; Woelders et al., 2013). With the forced aeration is possible to decrease the biodegradable organic content, especially some recalcitrant compounds not hydrolysable in anaerobic conditions becomes biodegradable thanks to the higher energy yield. Moreover, the aerobic conditions can enhance the nitrification process and the abatement of the ammonia nitrogen that is a relevant problem for the old landfills (Heyer et al., 2003; Berge et al., 2013; Ritzkowski et al., 2016). Some systems foresee simultaneous air injection and gas extraction to provide a fixed pressure of air which magnitude depends according with waste density and air circulation inside the landfill body (Raga and Cossu, 2014). Another possible design methodology consist in evaluating an optimum airflow by means of lab-scale reactors to be applied later in full scale

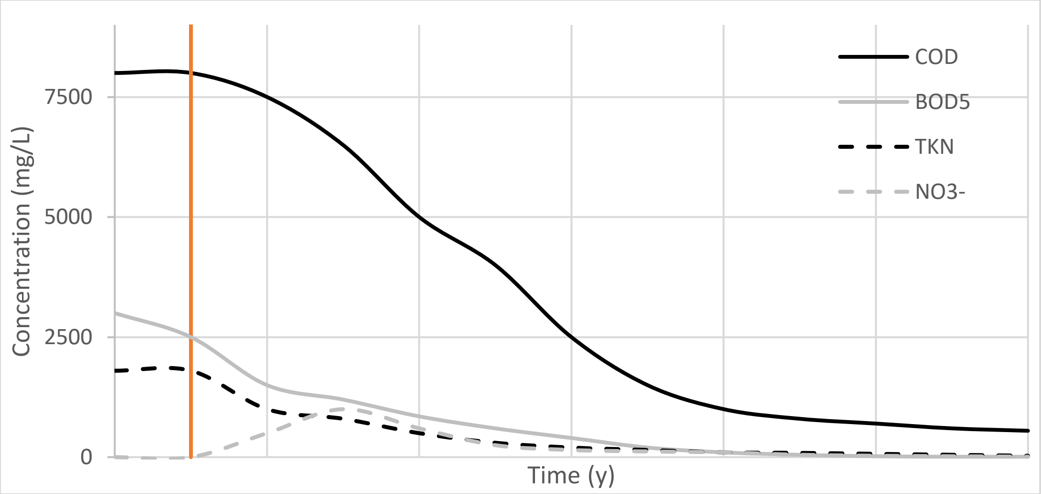
(Hrad et al., 2013). In some recent projects, the landfill is treated as a bioreactor and aeration is designed since the beginning to be adopted at the end of methane production (Some Hybrid Bioreactors) or since the beginning (semi-aerobic Fukuoka Method). In other bioreactors, the aeration is designed to be turned on periodically according with the needs of the landfill management, or in the first phases of landfill cultivation (Berge et al., 2007; Cossu et al., 2016).

Carbon Emissions of an Aerobic Landfill

The final emissions of an aerobic landfill depends highly on the initial waste characteristics, the landfill management history, the level of heterogeneity, the water circulation efficiency and many other factors. Despite that, lab- and full-scale tests show that the aerated reactors are able to guarantee lower concentrations of carbon and nitrogen compounds in leachate, in comparison with non-aerated ones (Berge et al., 2009; Cossu et al., 2002; Cossu et al., 2016; Ritzkowski et al., 2016; Raga and Cossu, 2013; Matzufuji et al., 2013; Wu et al., 2014, Hrad et al., 2013; Eres et al., 2008). In lab-scale tests, the effect of aeration can be appreciated immediately in carbon and nitrogen compound concentrations, in real-scale landfills this process requires longer time, which is hardly predictable because depends on many technical specific factors (Hrad et al., 2013; Ritzkowski et al., 2006).

During aeration, the gaseous emissions are mainly composed by carbon dioxide, free nitrogen and residual oxygen, with low content of other trace gasses, in concentrations depending by air flux and other technical aspects. Since the beginning of the aeration, the carbon emissions in leachate (COD, BOD_5) rapidly decrease until reaching concentration low and stable, in long-term comparable with river discharging law limits (Figure 1.2.5).

Figure 1.2.5: General behaviour of Carbon (COD and BOD_5) and Nitrogen (TKN and NO_3^-) compounds after aeration start up in a landfill. Aeration started from with the vertical line.



Laboratory and field scale tests proved that the COD concentrations could be decreased to values below 1000 mg/L (Laner er al., 2012; Ritzkowski and Stegmann 2013). However, the residual carbon emissions are mainly due to humic and fulvic acids: slowly mobile organic forms resulting from the conversion of biomass during degradation processes (Brandstätter et al., 2015). The efficiency of the aeration in decreasing carbon compound is visible also analyzing the stability indexes: the BOD_5/COD ratio in leachate can reach values under 0.01 (Cossu et al., 2012; Sekman et al., 2011), respiration indexes can reach values under 2.5 mgO2/kgTS (Laner et al., 2012) and Gas formation potential GP21 can reach values under 3.2 L/kgTS (Ritzkowski et al., 2016) in solid waste sample. The aeration has also a potentially negative effect increasing sulphates concentration and inhibiting their reduction to H_2S.

1.2.4 Nitrogen Biochemistry

In the solid waste samples, the nitrogen is mainly trapped into organic substances, which can be partially mobilized through ammonification during the hydrolysis of proteins. The ammonia-nitrogen produced can be volatilized, flushed away or nitrified-denitrified to free nitrogen gas (Figure 1.2.6).

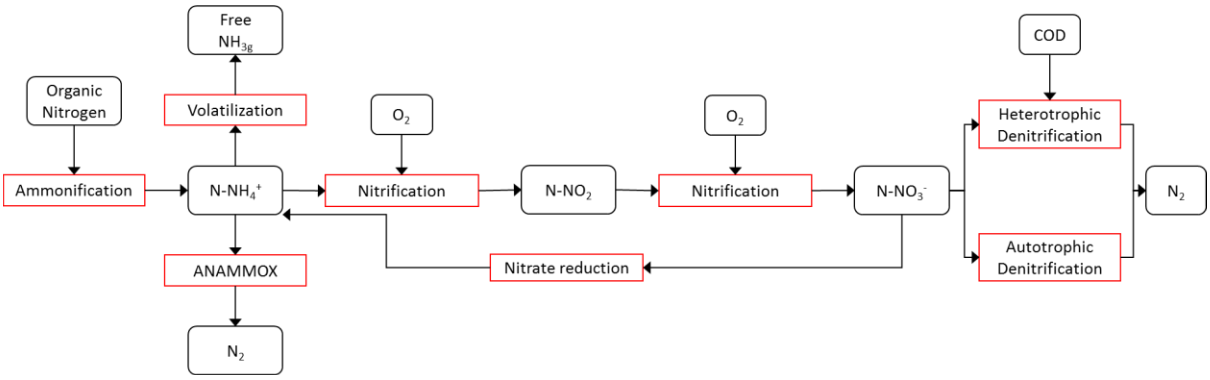


Figure 1.2.6: Principal pathways of nitrogen transformation in a landfill. Modified from Berge et al., 2013.

Concerning the nitrogen mass balance, there are strong differences between the anaerobic and the aerated landfill. With a sufficient air supply, the nitrification-denitrification can start, converting the ammonium ion into free nitrogen. This is the most efficient and feasible way to remediate the nitrogen pollution in the landfill leachate.

Ammonification

The most abundant nitrogen compound in leachate is ammonia-nitrogen, coming mainly from the hydrolysis of proteins (yard and food wastes) in a process named Ammonification. This process takes place both with the biological aerobic and anaerobic degradation and stops when all the available organic nitrogen is consumed (Figure 1.2.6). The ammonia nitrogen in acqueous environment is in equilibrium between ammonium ion form (NH_4^+) and gaseous ammonia form ($NH_{3(g)}$): the second one starts forming only with pH higher than 8. Generally, in a landfill the pH is always lower than 8.5 and the majority of ammonia nitrogen is in ion form as consequence (Berge et al., 2013). Once produced, the NH_4^+ can be taken up by other organic compounds, can be nitrified (and consequently denitrified) in presence of oxygen, can be volatilize if the pH is high enough and can be progressively flushed away with the leachate.

In an anaerobic landfill, the absence of oxygen does not allow the nitrification to happened, so the only way for nitrogen to be emitted remains flushing. In old traditional anaerobic landfills, the ammonia nitrogen concentration is the main problem for the leachate pollution and toxicity, even after decades (Heyer et al., 2003). On the contrary, in the aerated landfills nitrification and volatilization processes freely occurs, contributing to decrease the total nitrogen content.

Volatilization

The volatilization processes happens when free ammonia is present in leachate and pH is higher than 8. In these conditions, the production of gaseous $NH_{3(g)}$ is possible. The increase of temperature and the gas circulation are the other factors that can positively influencing the ammonia volatilization (Berge et al., 2013). In a traditional landfill, this process is generally negligible due to pH inhibition and also unwanted because $NH_{3(g)}$ is a toxic and corrosive compound.

Nitrification

The nitrification is an autotroph process which happens only in strong presence of oxygen; it is the first fundamental step for the nitro-denitro process useful for biologically removal the nitrogen (Figure 1.2.6). Ammonia-nitrogen presence in a waste is generally abundant and the possibility of convert this compound into an inert gas is the most sustainable remediation system. If the oxygen supply is sufficient for enhance the nitrification, the benefits on the nitrogen content are visible both pre-aerating the waste before landfilling it (Lornage et al., 2013), and aerating the waste during the aftercare (Ritzwoski et al., 2006). The nitrification is able to reduce the ammonia-nitrogen concentration until reaching values below 50 mg/L, starting from values sometimes over 3000 mg/L. The simultaneously produced nitrites and nitrates can be denitrify in the landfill anoxic zones, maintaining their concentration sufficiently low to not become an environmental problem (Figure 1.2.7).

Nitrification consists in a two-step process, the first one converts ammonia nitrogen into nitrite thanks to Nitrosomonas bacteria, the second step transforms nitrite into nitrate thanks to Nitrobacter (Berge et al., 2013).

$HH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O$
$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$

Both the reaction require abundant oxygen presence and consume alkalinity forming nitrous acid. The first reaction is generally the limiting one because the higher energy required and the consequential slower bacteria growth (Tchobanoglous et al., 2003). The nitrification autotrophs bacteria need presence of a carbon source for their biomass growth and also the oxygen can become a limiting factor in case of abundant presence of organics because of the competition with the heterotrophs. The temperature is another limiting factor being

Nitrosomonas thermal death around 54-58 °C, temperature easily reachable in an aerated landfill with fresh MSW. Considering all these technical contains, the nitrification can be applied with better results in old landfill cells, respect to younger ones (Berge et al., 2013).

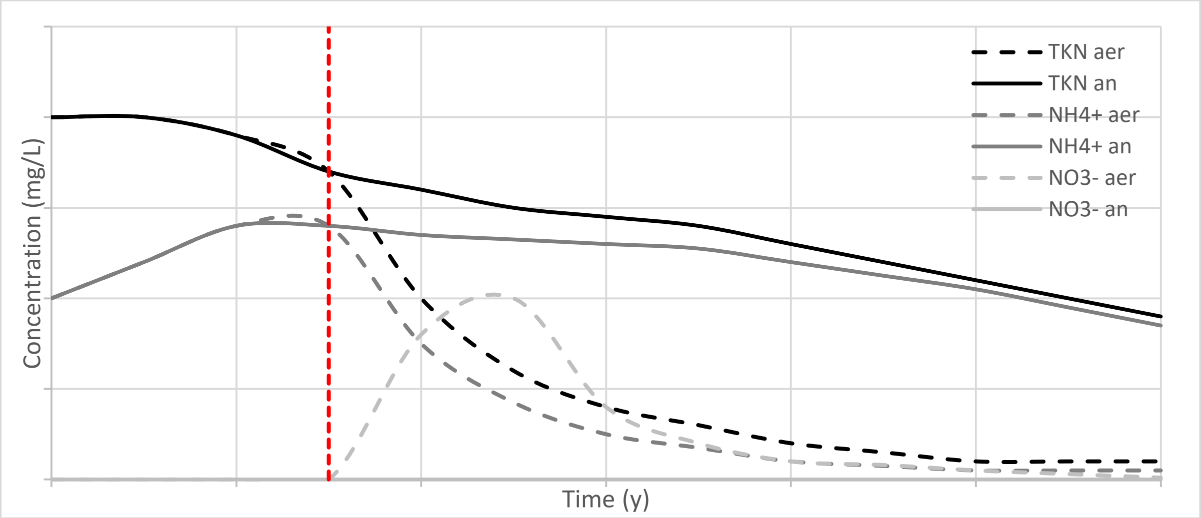


Figure 1.2.7: Ammonia and nitrates trend during an in situ aeration process in a landfill, compared with a non aerated one. Modified from Ritzkowski et al., 2006.

Denitrification

The denitrification is an anoxic process, which uses the nitrates and nitrites to oxidize the organic matter and produce energy with a yield slightly lower than aerobic respiration. The absence of oxygen and the presence of a biodegradable organic source are fundamental requirements for the process. In wastewater treatment plants, the denitrification processes is commonly applied prior to the aerobic treatment and the nitrification, for guaranteeing a low oxygen content and an abundant presence of fresh organic matter to be used (Tchobanoglous et al., 2003). In aerated landfills, the denitrification is possible in all the zones not directly reached by the airflow or in specific portions of waste mass purposely not aerated for guaranteeing the anoxic conditions.

The denitrification is a heterotrophic process provided by the facultative aerobes bacteria that, in absence of oxygen, uses the nitrates or the nitrites as electron acceptor (Berge et al., 2013) according with following reactions:

$NO_3^- + 2\,e^- + 2\,H^+ \rightarrow NO_2^- + H_2O$
$NO_2^- + e^- + 2\,H^+ \rightarrow NO + H_2O$
$2NO + 2\,e^- + 2\,H^+ \rightarrow N_2O + H_2O$
$N_2O + 2\,e^- + 2\,H^+ \rightarrow N_{2(g)} + H_2O$

This process produce free nitrogen gas that escapes from the system; However, NO and N_2O are middle way products detectable in very low negligible quantities. These gasses can increase greenhouse effect and are potentially dangerous for the environment, but their conversion process into free nitrogen is sufficiently fast to avoid their uncontrolled emission from the system.

The Autographic denitrification has generally a lower magnitude respect to heterotrophic one but contributes consistently to the nitrates depletion not requiring easily degradable carbon substrates. The Thiobacillus Denitrificans uses inorganic sulphur for reduce the nitrates, producing sulphates starting form HS^- (Berge et al., 2013):

$$2\ NO_3^- + 1.25\ HS^- + 0.75\ H^+ \rightarrow N_{2(g)} + 1.25\ SO_4^{2-} + H_2O$$

This mechanism is possible only in presence of inorganic sulphur. Despite that, in old landfills, in case of low carbon content, the autotrophic denitrification is favored over the heterotrophic one and can be responsible of 15 – 55 % of the total denitrification process (Onay and Pohland, 2001).

Anammox

ANaerobic AMMonium OXidation (ANAMMOX) is the process by which the ammonia nitrogen can be oxidize also in anaerobic conditions by some groups of bacteria like Planctomycetales (Berge et al., 2013):

$$NH_4^+ + 1.26\ NO_2^- + 0.085\ CO_2 + 0.02\ H^+ \rightarrow N_{2(g)} + 0.017\ H^+ + 0.24\ NO_3^- + 1.95\ H_2O$$

This process is very complex, sensible to environment conditions and enters in competition with denitrifies for the nitrites conversion. Moreover, the Anammox bacteria grow rate is very low so they requiring high retention times and a very stable system for surviving. Generally, Anammox processes are rarely observed in full-scale landfills and their contribution to the nitrogen pollution depletion is considered negligible.

Long-term nitrogen emissions

The long-term nitrogen emissions typology and quantity depends strongly by the landfill management choices; in particular, the aeration will strongly modify the biochemical conditions, allowing the nitrification and changing consistently the nitrogen compounds concentrations in leachate (Townsend et al., 2015; Ritzkowski et al., 2016). However, the majority of the initially present nitrogen (60-85%) will remain stored in the landfill body, unable to be ammonified, bounded to complex not-degradable polymers and organic matter (Manfredi and Christensen, 2009).

In anaerobic landfills, the ammonification produces ammonia ion in huge quantities, decreasing soluble organic nitrogen content (Figure 1.2.7). the NH_4^+ cannot be biologically converted in anaerobic conditions anymore and its emissions by stripping are generally negligible in a traditional MSW landfill; as consequence, ammonium ion concentrations grow up to values even higher than 3000 mgN/L constituting one of the main problems in long-term landfill management (Ritzkowski and Stegmann, 2013). The progressive leaching of the ammonia ion will reduce its concentration in leachate but reaching the environmental acceptable levels requires decades in these conditions (Christensen et al., 2015).

In the aerated landfills, the nitrification-denitrification processes allows abatement of nitrogen persistent emissions of ammonia ion, potentially reaching the environmentally safe conditions in a sustainable time (Berge et al., 2005; Ritzkowski et al., 2006). The nitrate produced can be monitored in leachate emissions but the denitrification will maintain their concentration low enough to not become an issue, even during the peak generally monitored after aeration start (Figure 1.2.7).

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1.3 Laboratory-scale landfill simulation tests

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1.3.1 Laboratory scale landfill simulation tests

Landfills are huge heterogeneous reactors hosting several chemical and biochemical processes inside which result is hardly controllable and hardly monitor-able with precision. Their complexity is mainly due to their long lifespan (some decades), to the several simultaneous biochemical reactions happening and to the heterogeneity of the materials deposited inside. All these factors increase the variability in humidity content, hydraulic conductivities and density, causing the formation of several interconnected microenvironments in the waste body. Despite all these complications, landfills require a periodical analysis of emissions, a continuous monitoring of internal conditions for their management and some prevision tools for their initial design and for calibrating possible in situ interventions.

Emissions monitoring is the general way to control landfill running conditions. In some cases, probes are installed inside the landfill body to have a continuous check of the processes of interest. Intense constant monitoring is particularly useful having ongoing processes or treatments, like biogas production and extraction, leachate recirculation, air injection, etc., which requires to be periodically calibrated according with the reactor performances. In particular, oxygen, methane and carbon dioxide in biogas are frequently analyzed, being the faster and the most abundant emissions of a Municipal Solid Waste (MSW) landfill. The evaluation of this compounds reciprocal percentages in biogas can immediately clarify macroscopically the landfill biochemical status. Similarly, leachate analysis are useful for monitoring biochemical processes in landfill: their trend gives information regarding the efficiency of the treatments, the residual substrates and nutrients presence in the waste body. Uncontrolled emissions monitoring is made sampling groundwater from wells placed around the landfill, according with groundwater flows itself.

While landfill routine management needs a constant monitoring of the parameters of concern, its design and the in-situ intervention calibration requires more sophisticated tools. Lab-scale simulators are able to run the whole landfill life in a highly controllable reactor and in a “laboratory” time. These reactors are commonly used tools in chemical engineering and can be efficiently used for landfill simulation: they have different dimensions, operation time and design according with the aspect they want to simulate. Only some of these tests have a standard routine or an associated international method to be follow; however, some macro categories can be distinguished.

- Leaching tests consists in several methodologies used for estimating the potential mobility of compounds in a solid sample. Each test is calibrated specifically on the phenomena to simulate or to the compound to search for. Leaching test are very fast analysis, useful for evaluating macroscopically the total potential liquid emissions of a solid material. Biochemical processes are not so fast to be appreciable with these methods. The most used in waste management is an international standard methodology (UNI EN 12457-2) where the sample is milled at 4 mm diameter, distilled water is added until L/S reached 10 L/kgTS, the produced mix is turned for 24 hours and then filtered at 0.45 µm.
- Batch biochemical tests are a huge category of laboratory scale tests studied for evaluating the biochemical characteristics of the sample in a short time. Among them, respiration tests are focused on estimating the biochemical potential activity, measuring the oxygen consumed by a sample in a fixed amount of time. Anaerobic fermentation tests are used for lab-scale simulating the methane and the hydrogen production, evaluating the total convertible fraction of a sample and the kinetics of the process (Table 1.3.1).

Table 1.3.1: Stability Indexes overview.

Biological Stability Index	**Characteristics**
BOD_5 – Biological Oxygen Demand	BOD_5 is a static biochemical index for liquid samples, worldwide used. It measures the oxygen consumed by the sample in 5 days at the standard temperature of 20°C (Cossu et al., 2012).
BOD_5/COD ratio	BOD_5/COD is a stability index for liquid samples derived from the BOD_5. The advantage is that the ratio with COD is not influenced by the dilution effect (Cossu et al., 2012). In a landfill leachate, a $BOD_5/COD < 0.1$ means an advanced methanogenic phase with low residual biodegradable matter content (Van Vossen et al., 2013; Sekman et al., 2011)
SRT – Static Respiration Test	SRT are respiration indexes commonly used for checking the residual biodegradability of compost or other solid samples. SRT measures the oxygen consumed by the sample without replacing it once consumed (STATIC) (Komilis and Kletas, 2012).
RI_4 – Respiration Index	IR_4 measures the oxygen consumption of a sample in 4 days, replacing the oxygen once consumed for maintaining its concentration constant for the whole test (SEMI-DYNAMIC). It is used for both solids and liquids. In a waste sample, $IR_4 < 2.5$ $mgO_2/kgTS$ means low biodegradability (Laner et al., 2012).
DRI – Dynamic Respiration Index	DRI test measures the oxygen consumption of a solid sample continuously injecting new air for the whole test (DYNAMIC) (Cossu et al., 2001). This system has the advantage to be able to use up to some kilos of sample for decreasing the heterogeneity effect.
GB_{21} – Gas Generation Sum	GB_{21} index measures the anaerobic biogas production of a mud sample in 21 days at the standard condition of 40 °C. The index results can be correlated with the respiration test ones (Cossu and Raga, 2008).
BMP – Bio Methane Potential	BMP tests measures the total methane production of a sample, until reaching the endo of biochemical process (Esposito et al., 2012). This test is longer than GB_{21} but can supply data useful for the evaluation of the reaction kinetics and the total methane expectable.

- Columnar reactors (Figure 1.3.1) are useful for simulating the whole landfill life as well as a single part of it or an in situ treatment. According with the initial project, a test can be run in some months (Cossu et al., 2003) or require many years to be completed (Hrad et al., 2013; Ritzkowski et al., 2006; Cossu et al., 2016). Reactor body is a sealed cylinder generally made of steel, glass or plastic, which can contain 10-50 kg of waste depending on compaction. The laboratory dimensions allow to place them directly inside a building and to achieve a high control level on processes and emissions. In particular, water and air injection or extraction can be efficiently managed, as well as the temperature. This tool is described in Chapter 2.
- Large lysimeters (Figure 1.3.6) are reactors conceptually similar to columnar ones but working with more than 500 kg of waste. This increased dimension is useful to simulate the phenomena influenced by waste heterogeneity inside waste body: water flow preferential paths, impermeable lens, effects of deepness as well as differences in compaction, interstitial gas diffusion, oxidative conditions and internal concentration of compounds. These systems have the disadvantage to increase the run time to even to a decade. This tool is described in Chapter 3.

Leaching and biodegradability test outputs generally are “maximum potential values” useful for calibrating mathematical models and comparable directly to other test results or real landfills monitoring data. Columnar reactors and lysimeter tests are complete simulations of landfill processes so their timescale must be readapted to the real application one to have a correct interpretation of the results obtained. This operation is complicated by the order of magnitude of difference (in both dimensions and time) between the real landfill and the laboratory equipment. The main control variables of any landfill process are time and leaching, which are only partially correlated while acting simultaneously on the same substrates (Hjelmar O. and Van der Sloot H., 2011). As consequence, one factor cannot be freely substituted by the other, without consistent uncertainty: leachate emissions remove substrates otherwise available to microorganisms while biological processes cannot overlook liquid movements to work properly (Ritzkowski et al., 2013). The lag-factor between lab and field performance depends also on the differences between calculated and real parameters, systems efficiency, temperature, moisture and the higher heterogeneity of landfill respect to a laboratory equipment (Hrad et al., 2013).

The easiest linking method consists in progressively calibrate the reactor timescale with the real landfill time. However, generally, better comparison results are obtained working with the liquid variable instead of the time variable.

The probably most used methodology is the Liquid-Solid (L/S) ratio (L/kgTS) where: “L is the cumulated amount of water that at any given time has percolated through the system and S is the dry weight of waste that has been percolated” (Hjelmar O. and Van der Sloot H., 2011). L/S scale is build “confusing” the time with the corresponding L/S and using it for compare different reactors and/or real landfills too. This tool is also used backwords for laboratory scale tests design (Cossu et al., 2016; Morello et al., 2016). In mathematical models, more complicate equations are used, correcting directly the time with a factor influenced by L/S (Hjelmar O. and Van der Sloot H., 2011).

A tracer in leachate (Chloride as instance) can be used to normalise liquid emissions both in real landfill and in lab-scale equipment. In this case, timescale is change with the correspondent tracer emission scale (Fellner et al., 2009). Similarly, rationalise a generic compounds concentration with the tracer one is a procedure used for comparing leaching status of the landfill (Ritzkowski et al., 2016).

Whatever method is chosen, the direct comparison between lab-tests and field data must be always managed with caution and experience. In addition, data obtained from these tests can be elaborated for closing a mass balance, testing the efficiency of a new concept and used for evaluating kinetics to design pilot scale applications.

1.3.2 Columnar Reactor Equipment

The experiments in Chapter 2 were carried out by using six identical lab-scale columnar reactors (Figure 1.3.1). The equipment body is a Plexiglass® (polymethyl methacrylate) transparent pipe height 106 cm, with a diameter of 24 cm and a thickness of 0.5 cm; the total internal volume amounts to 48 L. The bottom of each reactor is pasted to a HDPE trolley support and the top is closed with two sealing rings fixed to a HDPE cap, screwed to the main Plexiglas body (Figure 1.3.2). The reactor loading can be done from the upper side, manually compacting the waste.

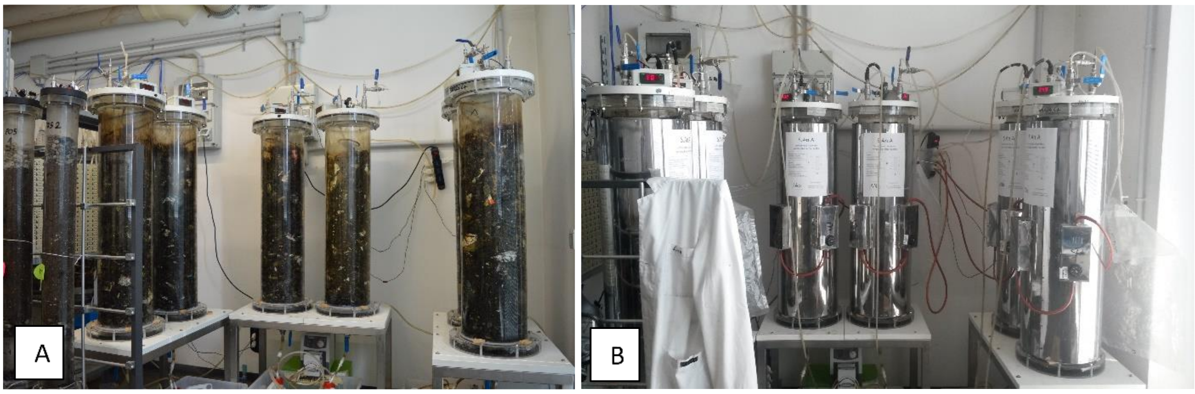

Figure 1.3.1: Picture of columnar reactor equipment with thermo-regulation suits (B) and without (A).

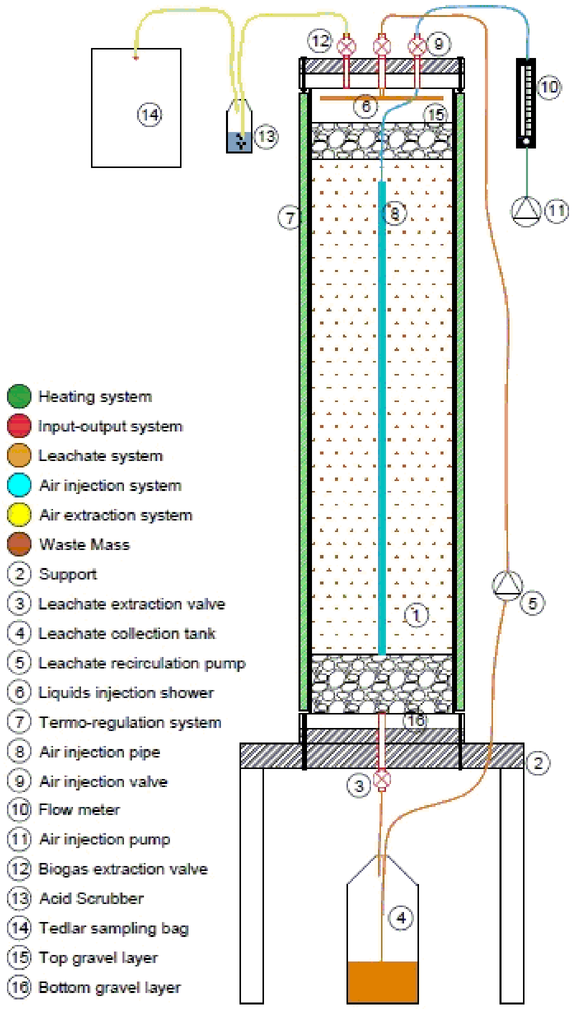

Figure 1.3.2: Technical sketch of columnar reactor equipment with graphical description of the regulation systems.

A 10 cm thick gravel layer (Ø 20-30 mm) is placed at the bottom of each reactor as a drainage layer to facilitate the extraction of leachate. Another 8 cm gravel layer is placed at the top of each column to increase the distilled water and recirculated leachate distribution (Figure 1.3.2). Leaving 5 cm of headspace between the cap and the top gravel layer, the height available for waste sample is 83 cm and the maximum waste volume is reduced to 38 Litres. For guaranteeing structural integrity of the Plexiglas pipe, the sample compaction cannot exceed 0.8 kg/L; as consequence, this kind of reactor can contain at maximum 30 kg of wet waste.

The reactors allows a high control level of the process utilizing a heating system for temperature control, a leachate system for moisture management, a gas extraction system and an air injection one. All these tools can be facultative used in line with test design and process necessities. The upper cap of the reactor body is equipped with three valves providing for the introduction of air, sampling and extraction of gas as well as the introduction of liquids, while under the bottom another valve is placed for leachate extraction, by gravity.

Heating system

The exothermic biological processes happening inside a landfill generate sufficient heat to maintain mesophilic conditions (35-45 °C) during the anaerobic phases and to reach even 60-70 °C during the aeration of the waste body. In lab scale, even if biological process are faster than in real sites, the generated temperature is dispersed into the environment because the specific heat exchange surface is too high.

Figure 1.3.3: Picture of columnar reactor equipment with Tedlar bags for biogas collection and leachate recirculation system.

A constant temperature in laboratory test is also preferred for excluding its variation effect in the monitored processes. For these reasons, temperature is maintained constant at 38 - 40°C by means of a thermo-regulated insulation system covering all the reactor lateral surfaces (Figure 1.3.1, 1.3.2 and 1.3.3). Another used system comprises a spiral circuit of silicon pipes placed around the columns with circulating hot water at 40°C and a bubble-wrap cover as insulation. The internal temperature was monitored with Thermo Systems TS100 temperature probes or PT 100 (Endress+Hauser) probes installed inside the core of the reactor. The reactors were placed in a room in which the temperature is maintained constantly around 20 °C.

Leachate system

The reactors can be equipped for not only leachate extraction and distilled water injection; a temporized leachate recirculation can be adopted for better control the humidity inside and for guaranteeing a homogeneous distribution of nutrients, microorganisms and substrates. The leachate collection port is located at the bottom of each column and the liquid extracted falls directly into a collection tank of 5 L capacity (Figure 1.3.4, B). The recirculation of leachate is carried out using programmable peristaltic pumps (Heidolph PD 5001), which automatically pump up leachate form the tank to the introduction of liquids valve, placed in the top of the reactor (Figure 1.3.2). Flowing into the valve, leachate is uniformly distributed in the entire sample surface by means of a shower, placed into the internal part of the cap (Figure 1.3.4, A). The leachate collection as well as the recirculation system are built with the purpose to avoiding any leakage of leachate and any loss of gas in the circuit.

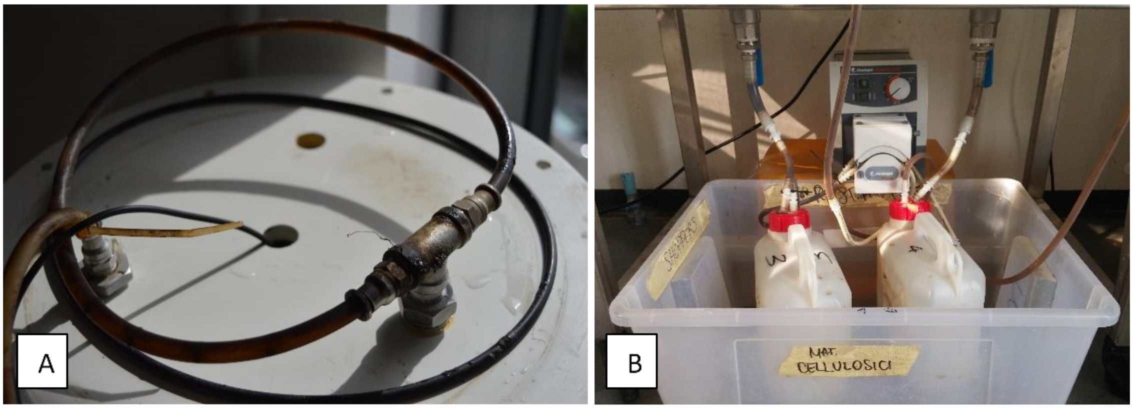

Figure 1.3.4: Particular of the leachate distribution shower placed in the internal top part of the reactor (A) and of the leachate collection tanks placed under the reactors, with leachate recirculation pumps (B).

Gas extraction system

The gas generated from each column can freely exit form a valve placed in the top cap and flow into a Tedlar® sampling bag (Figure 1.3.3). The gas volume is calculated measuring the time necessary to empty the bag at the constant flow of 200 L/h, regulated by means of a volumetric flow meter. This methodology reliability has been certified by comparing it with a direct volumetric measurement. If the volume exceed the Tedlar bag capacity during aeration, an emergency system will discharge away the gas to not generate excessive pressure in the reactors. A portable analyser (Eco-Control LFG20) measures oxygen, carbon dioxide and methane concentrations. Stripped N-NH_3(g) can be caught through an acid scrubber, placed immediately after the off-gas valve of each reactor (Figure 1.3.2). Boric acid 0.5 M was used as scrubber and the gaseous ammonia emission results were periodically compared with a portable gas analyser (Analitica Strumenti LFG 2000).

Air injection system

To channel air into the waste body, a vertical PVC pipe with side perforations was installed at the centre of the reactor (Figure 1.3.2). This system was designed to guarantee the uniform distribution of air throughout the reactor and to simulate a vertical well injection. The injection of air from the bottom of the reactor is possible, but not compatible with continuous leachate extraction. A Prodac Air Professional pump 360 provides for airflow generation, while a Sho-Rate GT1135 flow meter regulates the flow quantity (Figure 1.3.5). The air injection is possible only if gas extraction system avoids the increase of pressure in the column. Fundamental for air distribution efficiency is considering the effects of waste compaction due to the biochemical processes happening in the waste mass. In particular, compaction must be made avoiding voids in waste mass and holes in the air distribution pipes has to remain under the minimum height reached by the waste volume reduction.

Figure 1.3.5: Particular of the air injection pumps and flow meters. The temperature monitoring equipment is visible on the bottom left side of the picture.

1.3.3 Lysimeter equipment

The experiments in Chapter 3 were carried out by using a large lysimeter in which the waste sample was stored and treated for a decade (Figure 1.3.6). The reactor body is constituted by a Plexiglas column of 3 m height with a square base of 0.8 m side, resulting in a total volume of approximately 2 m^3. This particular lysimeter is arranged to simulate a semi-aerobic landfill, enhancing natural air circulation, and with the possibility to create anaerobic conditions.

The top of the reactor is hermetically closed by a Plexiglas cap, with the except for an opening which is useful for liquid injection and gas circulation. A gravel layer (Ø 16-32 mm) is placed at the bottom of the reactor, contained by a plastic grid (# 5 mm) to prevent waste sample to enter in. A holed HDPE pipe (diameter 300 mm) is horizontally inserted into the gravel layer until the opposite side, exiting from the reactor for 60 cm (Figure 1.3.6). Thanks to the pipe, the air can freely enter into the gravel layer, pass through the waste body and exit from the opening in the cap, encouraged by the thermic gradient existing between the biodegradable waste mass and the external environment. This process can be stopped closing the pipe and the opening in the cap, creating an anaerobic environment. All the sides of the lysimeter are thermal insulated by means of polystyrene foils: this system guarantees temperatures of 5-10°C higher respect to the external environment. The temperature is monitored from three positions on the side of the reactor (T1, T2, T3: Figure 1.3.6)

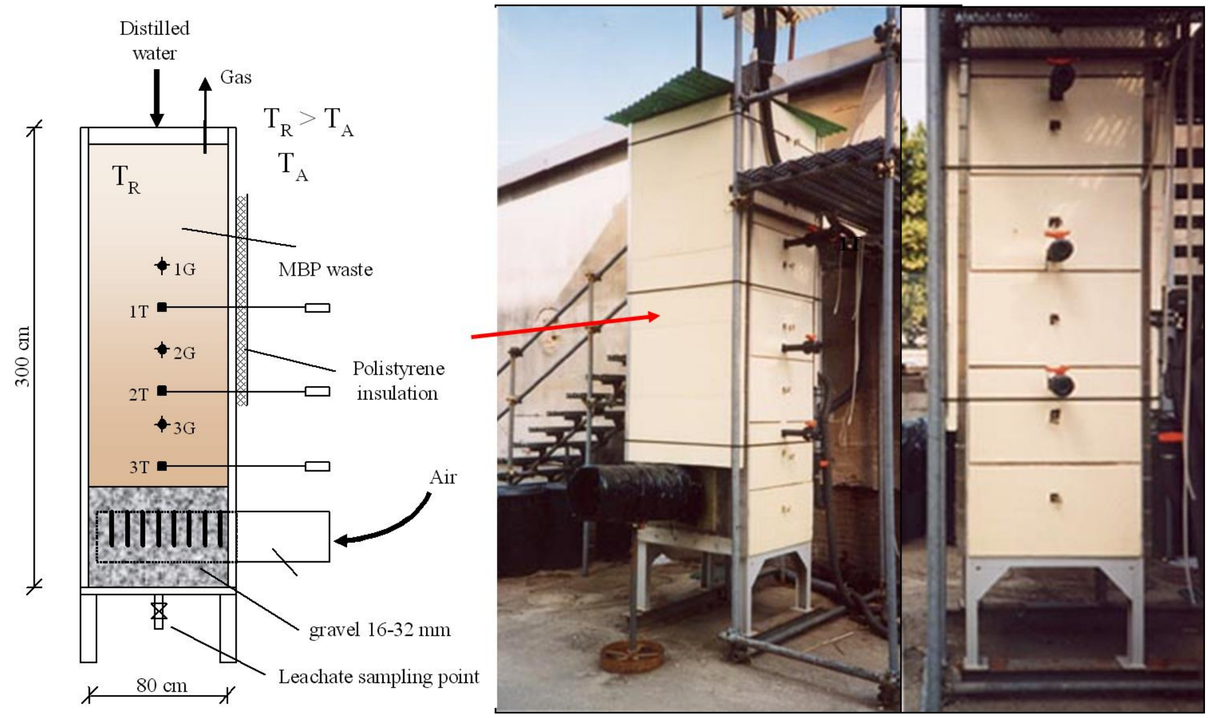

Figure 1.3.6: Sketch and picture of the lysimeter equipment with the thermal insulation cover.

The bottom of the reactor is equipped with five valves for leachate exit, all of them connected to a system discharging the liquid in a collection tank (Figure 1.3.7). Leachate sampling is done from the tank and recirculation can be performed manually, reinjecting the liquid from the cap. Accumulation of an excessive quantity of leachate inside the reactor is not possible due to the Pipe placed 15 cm over the bottom.

The biogas sampling can be performed both from the cap and the sides of the reactor by means of the same temperature monitoring positions. Solids sampling is also possible both from three side openings (G1, G2, G3: Figure 1.3.6) and excavating the reactor from the top.

Figure 1.3.7: Picture of the lysimeter equipment without frontal thermal insulation cover.

1.3.4 Analytical methods

Sampling

The collection and the analysis of gas composition during anaerobic processes was made directly from the Tedlar sampling bags, evaluating the general composition of biogas emissions. While gas circulation is active (during methane production phases and aeration), results of this methodology are consistent with a direct sampling from interstitial pores. On the contrary, if gas flow is negligible (during semi-aerobic phases and anaerobic aftercare), analysis on Tedlar bag gas can be slightly affected by possible intrusion of oxygen from the connection pipes. In this case, for avoiding uncertainty, sampling was made directly form the headspace of reactor.

Leachate sampling was always made from the collection tanks (Figure 1.3.8, C). If the reactor management comprises a daily leachate recirculation, sampling was made immediately after the recirculation and prior to the new fresh distilled water injection.

The solid waste sampling was a tricky operation, affecting consistently the analytical results obtained. Take samples only from the upper part of reactors is never suitable because the extracted material will not be representative for the whole waste. Moreover, the small dimensions of the lab scale equipment (Figure 1.3.8, B) will probably complicate the operation. Opening the reactor with ongoing processes can consistently disturb the processes itself so this operation must be avoided, if possible. For the experiments carried out in the following chapters, solid waste samples was taken at the beginning and at the end of the test and managed with the same methodology.

The initial solid waste prior to be loaded into reactors and the treated waste, fully extracted at the end of the test, was disposed in a tank and manually mixed (Figure 1.3.8, A). After that, for obtaining a homogeneous sample with dimensions consistent with lab-scale analytical methods, 2-3 kg of the material were milled at 10 mm and mixed again. The milling procedure at 10 mm does not change chemical characteristics of the sample or its humidity. The produced material constituted the final matrix to be used for the analysis.

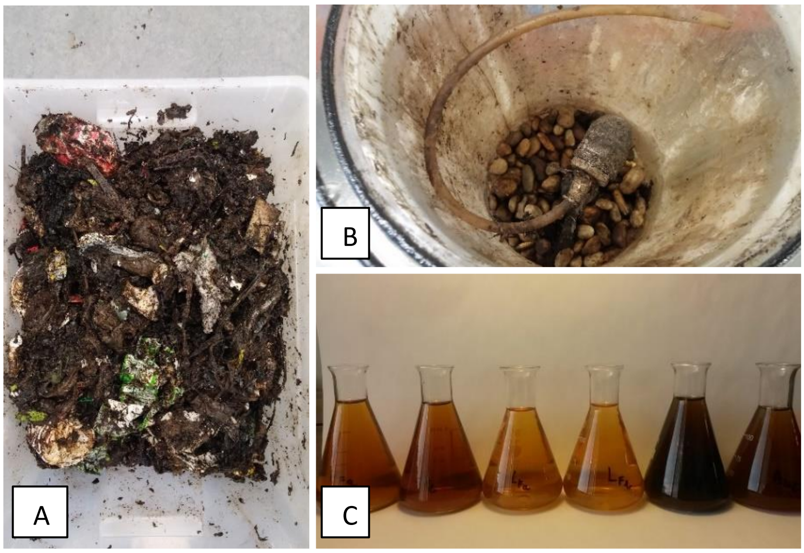

Figure 1.3.8: Waste samples extracted from a lab-scale reactor, after methane production end (A). Internal view of a columnar reactor at the end of the test (B). Leachate samples collected (C).

Analytical methods

International standard methods were used for the analysis of all samples (solid, liquid and gaseous) in order to allowing a precise comparison with other scientific tests in literature. In particular, chemical analysis followed Italian official procedures, derived from international certified standards (CEN, 2002).

A portable analyser (Eco-Control LFG20) were used for measure carbon dioxide, methane and oxygen concentrations in the biogas. The LFG20 was calibrated with normal air before every use, with a standard gas mixture (50% CH_4, 50% CO_2) once a week and the results were periodically compared with an LFG 2000 analyser and with a micro Gas Chromatography. Stripped $N\text{-}NH_{3(g)}$ could be measured through an acid scrubber placed immediately after the off-gas valve of each reactor. A solution of boric acid (0.5 M) trapped the gaseous ammonia, retaining it in solution as ammonium ion. Periodically, the scrubbing solution was titrated with sulfuric acid (0.01 M) to evaluate the amount of $N\text{-}NH_3$(g) exiting from the reactor. This measurement system for the gaseous ammonia emissions was periodically checked with the portable gas analyser (Analitica Strumenti LFG 2000).

Chemical and biochemical analysis on liquid samples were made in a laboratory without the support of ready to use kits. The routine analysis performed on leachate were pH, COD, TOC, BOD_5, TKN, $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, SO_4^{2-}, Cl^- and Heavy Metals (Cr, Cu, Fe, Mn, Ni, Pb, Zn). In particular, routine procedures were the following ones:

- pH and conductibility are measured directly with specific probes.
- Chemical Oxygen Demand (COD) analysis starts with an acid digestion at 150°C with a strong chemical oxidizer (potassium dichromate). The oxygen chemically consumed is stoichiometric calculated by means of a titration with Mohr salt.

- Total Organic Carbon (TOC) is measured directly with the “TOC-V CSN” analytical equipment.
- Biological Oxygen Demand (BOD_5) is a batch test quantifying the oxygen biologically consumed by the sample in 5 days.
- Total Kjeldahl Nitrogen (TKN) is evaluated with the standard Kjeldahl methodology. The sample is digested with acid at 350°C for destroying all the organic bonds. After that, soda is added to increase pH over 10 and stripping of gaseous ammonia is enhanced by distillation. The extracted $N\text{-}NH_3(g)$ is caught in boric acid and the solution is titrated with sulfuric acid (0.01 M) to evaluate the amount of nitrogen present in the initial solution.
- Ammonia ion ($N\text{-}NH_4^+$) is analysed as TKN, without the initial digestion.
- Nitrates ($N\text{-}NO_3$) and Sulphates (SO_4^{2-}) are evaluated by means of a spectrophotometer.
- Chloride (Cl^-) concentration is quantified after a titration with argent nitrate 0,1 M.
- Heavy Metals (HM) are analysed by means of an Inductively Coupled Plasma (ICP) after an acid digestion of the sample.

The analysis on solid samples were performed both on the material as it is, to evaluate the massive compounds concentrations (TS, VS, TOC, TKN, and HM) and on the eluate from a standard leaching test, to evaluate the emission potential of some mobile species (pH, COD, TOC, BOD_5, TKN, $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, SO_4^{2-}, Cl^- and HM). To decrease the analytical uncertainty due to waste heterogeneity, all the tests on solid samples were performed at least in duplicate:

- Total Solid (TS) quantifies the dry mass of a sample (in percentage respect to the wet mass), heating the sample at 105 °C for 24 hours, evaporating the interstitial pores water.
- Total Volatile Solids (VS) quantify the mass of the volatile compounds present in a sample (in percentage respect to the dry mass), heating the sample at 550 °C for 4 hours, burning all combustible volatile substances.
- TOC on solid sample is directly measured with the “TOC-V CSN” analytical equipment plus the burning chamber for solid samples.
- TKN and HM are evaluated with the same methodology used for leachate samples.

The leaching test used for evaluating the emission potential of soluble compounds present in solid waste is the international standard methodology (UNI EN 12457-2). The solid sample was milled at 4 mm diameter, the dust was mixed with distilled water for reaching a liquid to solid ratio of 10 L/kgTS, the mix was turned for 24 hours at 20 °C and, finally, filtered at 0.45 µm. The eluate obtained with this procedure can be analysed with the same methods used for liquid samples.

Dealing with degradable substances, some biological tests are particularly useful for understanding potential methane production or residual degradability of a sample:

- BOD_5, as explained before, quantifies the oxygen consumption due to the aerobic degradation processes that happens in a batch liquid test. This index is presented as a concentration and can be evaluated for either leachates and eluates from leaching tests. To evaluate the biodegradability of a sample avoiding dilution effect present in any concentration, BOD_5/COD ratio can be estimated (Cossu et al., 2012). This index can assume values ranging between 0.02 and 0.13 for low biodegradability and values greater than 0.4 for high biodegradability (Sekman et al., 2011).
- Respiration Index (RI_4) is a German developed tool (AT_4) internationally certified as a biological stability index for solid waste samples (ANPA 3/2001 n.12.1.2.3). RI_4 is a respiration test in which cumulative oxygen consumption in 4 days is measured under the controlled standard conditions of "SAPROMAT" equipment (H+P Labortechnik, Germany). The aerobic microorganisms in the sample consume oxygen producing carbon dioxide, which is caught by soda, generating a negative pressure in the system. Sapromat automatically registers this pressure difference and inject new oxygen in the batch system. The oxygen consumption is progressively measured respect to the dry mass of sample.
- Biological Methane Potential (BMP) is an anaerobic batch test lasting until the methane production becomes negligible. Sample is loaded in a bottle at 40°C with sufficient headspace to store the gas produced, which has to be emptied at least daily. This test is useful to calculate the theoretical maximum production of methane in optimum conditions and some kinetic parameters useful to design other laboratory tests.

During the aftercare phases, more than 10% of the organic carbon initially present in the samples was transformed into not mobile forms, probably due to the formation of humic substances (Brandstätter et al., 2015). The determination of humic and fulvic acids in the eluate form leaching tests can be made following the procedure proposed by Baddi et al. (2004). Some mL of eluate sample undergo to a double step centrifugation (7000 rpm for 25 min) with subsequent distilled water washing in order to remove any particulate matter in solution. The pH of the supernatant was decreased below 2 with a sulfuric acid solution (2 M) to enhance humic acids precipitation. The mixture is settled (24 h at 4 °C) for a complete coagulation. Subsequently, a second double step centrifugation was performed and the precipitate was dried under vacuum. The obtained residue represented the amount of humic acids. The supernatant coming from centrifugation is collected and dialyze through Spectra/Por® Dyalysis Membranes (3500 Da). The amount of eluate retained is dried to evaluate the fulvic acids content of the sample.

Heavy Metals speciation can be performed on solid samples through the multistep procedure proposed by Krishnamurti et al. (2002). This method allowed to separate eight different forms under which Heavy Metals could be found: ion exchangeable, carbonate-bound (adsorbed), as metal-organic complexes (associated with humic and fulvic acids), as easily reducible metal-oxides, bound to organic matter (other than humic and fulvic acids), in amorphous mineral colloids, as crystalline iron-oxides and bound to aluminum-silicate minerals. Every step of the procedure require a precise mixing time, temperature, pH and reagent. After each step, a double centrifugation (at 10500 rpm for 20 min) with distilled water washing is necessary to separate the supernatant which is analysed with ICP.

1.3.5 Reactor management

Columnar reactors and lysimeters can simulate several processes happening in landfills and their management has to be specifically designed for recreate these situations in laboratory time. Working with lab-scale reactors requires some good practice adoption for obtaining results comparable to field scale ones, especially when the simulation include biological processes.

Filling and start-up

The solid waste sample must be carefully selected in line with the test purposes and the reactor requirements. If the test includes anaerobic biological processes, the organic content of waste cannot be excessive for being able to controlling the acidity of the system. For avoiding this problem, the sample can be mixed with some buffering material (i.e. construction and demolition waste) to increase the alkalinity and better control the pH (Christensen and Kjeldsen, 1989). Another solution consists in the aeration of the reactor during start-up phase for decreasing the VFA and the acidity, as consequence (Cossu et al., 2016).

The sample selected is well mixed before being loaded into reactor; sharpened objects, dangerous materials and intruders are removed. In lab-scale equipment, pieces greater than 60 mm of diameter must be avoided to guarantee a sufficient homogeneity of the sample. The compaction density is choose before of the loading procedure, in line with the resilience of the reactor. In Plexiglas columns with a thickness of 0.5 cm, the maximum reachable density for not breaking the reactor body is 0.8 kg/L. Compacting sample in layers of 10-20 cm is a good practice to have a homogeneous density and avoid preferential ways for liquid circulation or voids caused by the pipes inserted in waste body.

At start-up, the moisture content inside the reactors is adjusted to 40-50% with deionized water, in order to ensure a sufficient initial humidity to reach the field capacity and promote leachate formation. Recirculate several time the first leachate produced (until the exiting quantity is constant) will ensure a uniform distribution of moisture inside the reactor, useful for biological processes launch.

Leachate management

Injection of new demineralized water, recirculation of leachate and moisture accumulation in the reactor depend mainly on the test design and purposes.

The simulation of specific biological processes does not require constant leachate extraction. As consequence, new water additions can be only related to the replacement of the liquid samples taken for the analysis in order to maintain constant the moisture content of the reactor (Cossu et al., 2016).

A complete landfill simulation is designed with respect to the characteristics of the simulated landfill. Generally, the test length is chosen according with the reactor dimensions, compared with the real landfill time estimation and water injection is calculated with respect to the rainfall entering in the waste body. Leachate produced can be continuously extracted or accumulated for short periods.

Lab-scale reactors can also simulate a Flushing Bioreactor with a “flushing tests”, which consist in a significant increase of water injection for monitoring the effect of an enhanced solubilization of contaminants (Bolyard and Reinhart, 2016).

Aeration

Laboratory scale reactors can be equipped for the simulation of semi-aerobic conditions as well as forced aeration ones. The natural circulation of air can be enhanced by the reactor design (lysimeter) or simulated by a forced aeration; in both cases, continuous monitoring of gas quality and temperature is necessary. In Cossu et al. (2016), airflow was set at a low regime and incremented until oxygen was detectable in the off gasses ($O_2 > 1\text{-}2$ %), resulting in 50 L/d at 20 °C, which in the specific case corresponds to 5 NL/d/kgTS, TS being the dry matter content (Total Solids) in the reactor. The decision of the airflow amount can be based on a series of lab-scale experiments carried out on landfill bioreactors in conditions similar to the simulated ones (Cossu et al., 2016; Sun et al., 2013; Wu et al., 2014).

The forced aeration can be made injecting air from a central holed pipe (i.e. columnar reactor) as well as from the bottom or in specific horizontal layers. The injection pressure has to be calibrated in situ, according with the waste density and the well influence radius. In lab-scale test design, the air flux can be chosen comparing results with full scale ones or evaluating the treatment efficiency by measuring oxygen concentration in off gas (Chapter 2.3). In Low Air Flow reactors, the air injection was calibrated for maintaining oxygen in off gas detectable but lower than 4%; consequently, the air injection was 5 - 10 NL/kgTS/d. The High Air Flow simulations was made with the purpose of having more than 14% of oxygen in off gas, exceeding the real-scale standards, thus limiting the risk of poorly aerated zones in the reactor; consequently, the air injection was 40 - 60 NL/kgTS/d (Cossu et al., 2016; Morello et al., 2016).

1.3.6 Elaboration of results

Liquid-Solid ratio calculation

The liquid-solid ratio (L/S) express the total volume of liquid passed through a certain quantity of solid dry sample, indicated as L/kgTS (Hjelmar O. and Van der Sloot H., 2011).

$$L/S = \frac{Cumulative\ liquid\ percolated\ throught\ the\ system}{Dry\ waste\ mass\ that\ has\ been\ percolated}$$

The total volume of liquid output accounted in the L/S formula is the one leaving definitively the system, containing the compounds emitted and not recirculated anymore. This number is constantly growing since the liquid extracted is cumulative in time. The solid mass accounted in the formula represent the initial Total Solid mass content.

L/S can be particularly useful for understanding the washing state of a reactor, for evaluating the past and future possible emissions of a sample and for standardize the leaching tests. As explained before, the time is not directly correlated with the amount of water passing through a reactor. However, the time can be confused with the liquid-solid ratio in laboratory scale tests in which water inputs are regularly performed. Starting from this assumption, different scale reactors can be compared each other's changing their timescale with L/S scale.

Adding water to a reactor will not produce leachate since the field capacity of the reactor is not saturated (without considering the preferential pathways for water movement). Moreover, leachate recirculation requires an accumulation of process liquids to be performed. Both these aspects can cause an initial delay in which the L/S ratio can remain null despite the time and the liquid injection are running.

Kinetic calculation

Landfill numerical simulation can be done through a large quantity of mathematical derived models fitting the single data-series or simulating the whole processes (Jorgensen et al., 2001). Potentially, the entire reactor can be simulated numerically. In this work, the biogas production kinetics and the leaching rates are particularly useful for numerically expressing the data collected and for making a mathematical comparison between the performances of different reactors. The calibration of the necessary parameters is carried out by minimizing the mean square deviation of the values measured and calculated.

The biogas production is simulated by means of a kinetic model derived from the Gompertz Growth Equation, calibrated with biogas daily data (Cossu et al., 2016). This model has a sigmoid shape with an inflection point, it requires the calibration of three physical friendly parameters (BGP, Rm, λ) and its output is the cumulative volume of methane produced from the bioreactors and (Lay et al., 1998).

$$BG = BGP * \exp\left\{- \exp\left[\frac{Rm * e}{BGP} * \ (\lambda - t) + 1\right]\right\}$$

BG is the cumulative methane yield (mL/gVS), t is the cumulated time (d), BGP is the methane yield potential (mL/gVS), Rm is the maximal daily methane yield (mL/gVS/d), λ is the bacteria growth lag time (d) and e is a mathematical constant (equal to 2.718).

The emission rates of some slowly degradable compounds (i.e. COD, NH_4^+, Cl^-) can be numerically simulated by means of a simple first order kinetic Equation (Jorgensen et al., 2001).

$$C_t = C_0 * \ e^{-k*t}$$

C_t is the concentration at time t, C_0 is the initial concentration and k (t^{-1}) the kinetic constant. If the compound mobility is related only to solubilization and leaching (i.e. chloride), the L/S ratio can be efficiently used instead of the time.

Mass Balance

The mass balance is a primary principle for modelling chemical and biochemical processes happening inside a reactor. This tool is the application of the mass conservation principle to the space surrounded by an arbitrary boundary. The fate of substances entering, leaving or changing inside can be analysed in several ways (Jorgensen et al., 2001). In a landfill, the mass balance can be mainly used for estimating not monitored emissions or checking the analysis reliability. Carbon and nitrogen balances are particularly interesting being the most environmentally relevant compounds of a landfill.

The general mass balance formulation can be summarized as:

$$\text{Accumulation} = \text{Input} - \text{Output} + \text{Production} - \text{Consumption}$$

In a landfill, Accumulation consist in compounds still remaining inside after a time t; Input are compounds in the initial waste deposited, Output are the wanted or unwanted emissions of leachate and biogas, Production and Consumption derives from the reaction happening inside the waste body. The formula can be rewritten as follows:

$$\frac{dx}{dt}notmob + \frac{dx}{dt}mob = \sum_i (Xsi * Qsi) \ - Xl * Qlc - Xl * Qlu - Xg * Qgc - Xg * Qgu - rV$$

Where:

- $\frac{dx}{dt}notmob$: is the compounds still present in not-mobile form after the time t
- $\frac{dx}{dt}mob$: is the compound still present in mobile form after time t
- $\sum_i (Xsi * Qsi)$: Is the initial waste input evaluated as the sum of the mass of each trade category (Qsi) multiplied by the specific compound content of each one (Xsi).
- $Xl * Qlr$: is the mass of the compounds emitted by leaching in a controlled way, evaluated as the flux of leachate (Qlr) multiplied by the compounds fraction in leachate (Xl).
- $Xl * Qlu$: is the mass of the compounds emitted by leaching in an uncontrolled way, evaluated as the flux of leachate uncontrolled emitted (Qlu) multiplied by the compound fraction in leachate (Xl).

- $Xg * Qgc$: is the mass of the compounds emitted in biogas in a controlled way, evaluated as the flux of biogas collected (Qgc) multiplied by the compound fraction in biogas (Xg).
- $Xg * Qgu$: is the mass of the compounds emitted in an uncontrolled way by gas, evaluated as the flux of biogas that escape the gas collection systems (Qgu) multiplied by the compound fraction in biogas (Xg).
- rV: is the mass converted by a reaction, evaluated as the volume of reactor multiplied by the kinetic parameter (r). According with the compound characteristics and with the reaction conditions the kinetic constant can be positive or negative.

$\sum_i (Xsi * Qsi)$, $\frac{dx}{dt} notmob$ and $\frac{dx}{dt} mob$ in a reactor can be evaluated analysing the initial and the final solid samples. In these terms are contained the great part of the mass balance uncertainty because the heterogeneity of solid samples increases consistently the analytical mistake. The biogas and leachate controlled emissions are monitored, sampled and analysed with more reliable methods. In lab-scale reactors the uncontrolled emissions can be considered negligible while in the field scale test leakages must be periodically investigated.

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Chapter 2: Bioreactor Landfills

2.1 Bioreactor Landfill Concept

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Based on:

Cossu R., Morello L., Yue D. (2016). Overview on Facultative-Hybrid Bioreactor Landfill. 9th Intercontinental Landfill Research symposium (ICLRS 2016), Noboribetsu, Japan.

Cossu R., Morello L., Yue D. (2015). Hybrid bioreactor landfill: a review of the possible systems, Fifteen International Waste Management and Landfill Symposium (Sardinia 2015) , Santa Margherita di Pula (Ca), Italy.

2.1.1 Bioreactor landfill concept

Solid Waste Association of North America (SWANA) defined as Bioreactor Landfill “Any landfill cell where liquid or air is injected in a controlled fashion into the waste mass in order to accelerate or enhance bio-stabilization of the waste" (EPA, 2015). Other similar descriptions can be read in scientific literature, referring to lab- pilot- and full-scale tests or to existing bioreactor landfills (Townsend et al., 2015; Erses et at., 2008; Berge et al., 2009; Price et al., 2003; Xu et al., 2014; Christensen et al., 2011, b). These definitions highlight the fundamental role of water and/or air injection, leachate recirculation, enhanced cultivation and other combinations of in situ treatments designed for allowing biochemical kinetics control, nitrification, pH, redox conditions and moisture content adjustment. The final purpose of all these treatments is to create a more suitable environment for biochemical processes, which is fundamental for increasing energy recover, enhancing biodegradation of slowly degradable compounds and decreasing the time necessary for landfill completion. Modern landfilling must consider the economic aspects, simultaneously respecting the sustainability principle, which prescribes to reach low pollution conditions (Final Storage Quality) in a “reasonable” time (Erses et at., 2008). Refuse settlement, higher waste compaction, savings in long-term leachate treatment cost and less post closure operations are further advantages derived from enhancing biochemical kinetics by means of bioreactors (Price et al., 2003; Berge et al., 2005).

In a general reactor, chemical processes can be efficiently controlled managing loads, mixing, temperature, pressure, additions of reagents and many other factors. In a landfill, almost all these actions are not feasible or hardly controllable mainly because of the waste mass heterogeneity, the pulse initial loads and the huge dimensions of the reactor. Consequently, taking care of initial cultivation, controlling extraction of leachate and gas, managing moisture content, recirculating process liquids and injecting air in waste body are the only active actions efficiently applicable. Injection of reagents is technically possible but often not economically feasible, because of the huge bioreactor dimensions.

Landfill cultivation has a fundamental role for bioreactors; in particular, the deposition of incoming waste according with its biochemical characteristics can create a more homogeneous substrate since the beginning of the landfill life. Highly degradable material can favour acidic conditions inhibiting some biochemical processes, as Methanogenesis. In this case, mixing the waste with some buffering material is a good practice for landfill cultivation. Remarkable results can be achieved adding materials like construction and demolition waste that can dilute the acidity and create more alkalinity at the same time (Christensen et al., 2011, a). Compaction of waste during deposition until a density of 0.8 – 1.2 kg/L must be a priority both to save volumes, reduce interstitial pores in landfill body, and prevent preferential pathways of leaching or impermeable lens.

The moisture control in a bioreactor is fundamental for supporting the metabolic processes, the nutrients transport and the microorganisms movement (Bolyard and Reinhart 2016; Norbu et al., 2005; Berge et al., 2005). Presence of 30-60 % of moisture in waste mass is essential for guaranteeing hydrolysis of organic compounds, which is the first step of any kind of biochemical degradation. For this reason, hydraulically seal a landfill is never convenient and the top cover must be engineered for allowing the inlet of the necessary quantity of rainwater. In some developed countries legislative regulations, leachate accumulation in the bottom of the landfill is forbidden to avoid the increase of uncontrolled leaching of potential polluting compounds. However, liquids extracted can be partially recirculated for enhancing nutrient transport and microorganisms movement (Sandip et al., 2012; Norbu et al., 2005). This practice is particularly useful to homogenize the reactor, control pH, redox conditions and its application is proved to have positive effects in degradation kinetics and methane production capacity. Moreover, leachate recirculation can increase waste settlement, recovering airspace and saving treatment costs (Berge et al., 2009). In a bioreactor landfill, the injection of treated leachate fractions, wastewaters and wastewater treatment sludge is theoretically possible (EPA, 2015). The challenge of this practice is creating a biochemical synergy between the treatment of waste and wastewaters. As instance, reinjection of leachate reverse osmosis concentrate in waste body is proved to have both positive and negative effects on leachate characteristics (Morello et al., 2016). Increase further the water injection for producing more leachate, with the consequent enhancement of the extraction of soluble compounds is a treatment named “Flushing”. This practice can be useful for leaching out inorganic compounds, being very effective also with biodegradable components of waste and refractory organic by-products (ammonia-nitrogen, pharmaceuticals personal care products and heavy metals) (Bolyard and Reinhart, 2016). However, this process increase drastically leachate production and related treatment costs, even considering the use of internal leachate treatment plants.

The air injection in landfill body can consistently speed up the biological processes, reducing the long-term slowly degradable compounds and allowing nitrification and nitrogen compounds removal (Ritzkowsky et al., 2013; Morello et al., 2016; Berge et al., 2006). The presence of oxygen in interstitial pores causes the inhibition of methane production and the creation of a completely different biochemical environment in the waste body, involving different microorganisms and kinetics. Aeration can be naturally enhanced or forced through injection systems (Ritzkowski et al., 2016; Price et al., 2003; Sekman et al., 2011). Generally, this treatment is expensive and used only for limited periods, as consequence.

The bioreactor landfill can also have some disadvantages mainly derived from the enhancement of biochemical processes: increased odours, physical instability of waste mass due to increased moisture and density, instability of liner systems, surface seeps, and landfill fires.

According with EPA (2015) definition, there are three main types of landfill bioreactors:

- Anaerobic bioreactors, similarly to traditional landfills, are managed under anaerobic conditions for recovering methane, however causing consistent emissions and ammonium ion accumulation in leachate during long-term management. Most of bioreactor landfills discussed in literature were operated under anaerobic conditions (Price et al., 2003; Valencia et al., 2011; Vigneron et al., 2007; Christensen et al., 2011, b).
- Aerated bioreactors are system in which air circulation is promoted, increasing biochemical degradation kinetics of organic substances and inhibiting methane generation. The oxygen presence allows also nitrification process, which can contribute to biological ammonium ion reduction.
- Hybrid bioreactors operate under various combination of aerobic and anaerobic conditions to achieve the benefits of both of them (Cossu et al., 2016; Long et al., 2009, Xu et al., 2014; He et al., 2011). In particular, the air circulation can be controlled both enhancing energy recovery due to methane production and allowing nitrification-denitrification processes, while treating persistent nitrogen compounds.
- As extension to this classification, Flushing Bioreactors are landfills in which moisture addition is increased for enhancing biochemical processes and favouring emission of soluble compounds (Bolyard and Reinhart, 2016; Christensen et al., 2011, b). This systems can be anaerobic, aerated or hybrid. Moisture added can be fresh water (increasing rainwater infiltration or irrigating the top cover) or recirculated process liquids, after an in site or on site treatments (Bolyard and Reinhart, 2016; Morello et al., 2016).

The bioreactor landfill applications are consistently increasing nowadays, both in laboratory tests, in pilot-scale tests (with research purposes) and in full-scale landfills. Results presented in scientific literature often highlight successful increase of kinetics and chemical stabilization of organic compounds, reduction of nitrogen emissions, enhancement of waste mass compaction and limitation of long-term leachate pollution potential (Cossu et al., 2016; Sun et al., 2013; Erses et at., 2008; Sekman et al., 2011; Sandip et al., 2012; Xu et al., 2014; Shao et al., 2008; He et al., 2011; Townsend et al., 2015). A bioreactor landfill can be comparable to a traditional one, from an economically point of view; in some cases it can be even more advantageous (Berge et al., 2009).

2.1.2 Anaerobic bioreactors

The anaerobic bioreactors main purpose is to maximize energy recovery coming from methane utilization, enhancing CH_4 production from biodegradable substrates of waste. For this purpose, cultivation of landfill is planned for having the necessary quantity of putrescible material, without causing acidity problems. Leachate extraction and recirculation is managed with performance-based systems aiming to guarantee a sufficient moisture in the landfill body, maintaining simultaneously the organic compounds inside the system. The optimum humidity for biological processes is generally around 40-60% of weight respect to dry mass, approximately corresponding to the field capacity of compacted waste. However, the key factor for enhancing methane production is the constant liquids movement inside the landfill body, instead of having a static accumulation of water in the interstitial pores (Valencia et al., 2009). To increase the methane extraction, gas vacuum system can be installed since the sector cultivation in full-scale anaerobic bioreactors, considering also the possibility to use horizontal pipes systems.

The anaerobic bioreactor technology is successfully applied both in small pilot plants and in field scale landfills (Townsend et al., 2015). Lab-scale test by Erses et at. (2008) showed that anaerobic bioreactors were able to degrade the putrescible organic substances only when methanogenesis starts. During the first management phases, COD concentration remained over 50000 mg/L, dropping suddenly down at the methanogenic phase start and reaching 1000 mg/L at the end of methane production. BOD_5/COD ratio, initially higher than 0.6, decreased under 0.1, which can be considered a target value for biochemical stabilization of a leachate (Cossu et al., 2012; Seckmann et al., 2011). Other comparable pilot tests showed similar results and methane production yield of bioreactors was always higher than comparison reactors managed as traditional landfills. Methane production in full scale anaerobic bioreactor can start even after some months; on the other hand, active catching of biogas in traditional landfills generally starts after the complete filling of the landfill cell, which often means years later. As consequence, in many bioreactor applications, biogas extraction systems were placed during cultivation to catch also initial methane production (Berge et al., 2009). If operated as a bioreactor, the anaerobic landfill has many proved advantages but the remediation of nitrogen pollution in leachate remains the major challenge (Long et al., 2008; Berge et al., 2006; Price et al., 2003). The problem of ammonium ion persistence in leachate will influence also the post-closure management and the aftercare leachate treatment. For this reason, an aerobic treatment is frequently applied after the methane production end. Another considered solution, tested in pilot scale, is the complete excavation of the waste after methane production end, the subsequent thermal treatment for the extracted material and the reuse of bioreactor cell for depositing new fresh substrates. Anaerobic bioreactors are able to save some leachate treatment cost thanks to recirculation mainly but, on the other hand, the continuous pumping of leachate can be expansive (Berge et al., 2009).

2.1.3 Aerated bioreactors

Aerated Bioreactors are systems in which air is naturally or artificially channelled inside the waste mass with the purpose of promoting oxygen diffusion and allowing aerobic biological processes. A bioreactor aerated since the beginning of its life promotes a fast reduction of biodegradable compounds and allows nitrification process, while the methane generation for energy recovery is totally inhibited (Berge et al., 2009). During aeration, carbon indexes reduction amount is comparable with the anaerobic processes one, even if the reaction lag time and the whole process duration are more than halved (Erses et at., 2008; Morello et al., 2016). Despite the higher ammonification due to aerobic processes, NH_4^+ concentration in leachate decreases constantly due to nitrification process, reaching values potentially lower than 10 mg/L in laboratory scale tests (Erses et at., 2008; Ritzkowski et al., 2016). Aeration is probably the most cost-effective methodology for nitrogen compounds remediation in landfills, whether if performed on extracted leachate or inside the waste body through forced aeration (Berge et al., 2006). To complete nitrogen removal, after nitrification process denitrification is useful for transform nitrates into inert free nitrogen gas. Requiring an anoxic environment, theoretically the denitrification process is inhibit in aerated reactors. However, in a real-scale landfill the two processes happens simultaneously even under low biodegradable matter conditions because heterogeneity of waste mass guarantee always anoxic microenvironments (Berge et al., 2006, Shao et al., 2008; Morello et al., 2016).

Injecting air in landfills and creating fast exothermic reaction kinetics can rise up the temperature to values higher than 60 °C, resulting in a high evaporation of water and causing lower leachate production as consequence (Berge et al., 2005). For this reason, water supply during aeration processes must be increased to guarantee a sufficient moisture to mitigate the effect of the improved evaporation. Creating aerobic conditions in a bioreactor landfill proved to be economically comparable and in some cases even more advantageous, respect to the traditional anaerobic management, if the duration of the treatment is limited (Berge et al., 2009). For this reason and for avoiding problems related to high temperatures, aeration is applied to landfill only for a limited amount of time.

The semi-aerobic landfill concept can be applied also to Bioreactors, allowing controlled natural circulation of air, instead of forcing it. This technology proved to be efficient both in lab- and in full-scale applications, increasing the degradation of carbon compounds, and allowing nitrification-denitrification process in case of low degradable organic content (He et al., 2012; Kawaguchi et al., 2013; Christensen et al., 2011, b). However, with natural circulation, air distribution in the waste body is hardly controllable, nitrification process is generally less efficient because of the very low oxygen concentrations and waste excessive density can totally stop the airflow (Wu et al., 2014).

2.1.4 Hybrid bioreactors

Hybrid bioreactors are managed with a sequence of aerobic and anaerobic conditions, studied with the purpose of achieving the benefits of both of these two states; many of these systems have been tested in lab or full-scale with promising results (Berge et al., 2005; Townsend et al., 2015). These bioreactors are designed since the beginning with the possibility to change between the aerated and the anaerobic conditions following a fixed schema (one after the other, sequences, short-term cycles, etc) or according with the performances of the reactor itself (Xu et al., 2014; Long et al., 2008; Cossu et al., 2016). This alternation of chemical oxidative conditions, in synergy with moisture control, enhanced cultivation and other specific bioreactor characteristics, can be used to achieve different purposes. Among them, speed up biochemical stabilization of waste with nitrogen removal from leachate and enhance simultaneously the methane production for energy recover are the targets of many laboratory and field scale test in literature. Despite the listed advantages, hybrid bioreactors are expensive tools, because of their building, management and running costs respect to traditional systems. Moreover, their management requires specialized technical personal. In particular, air injection-extraction plant running is expansive; this is the main reason why aeration is applied only for limited periods. However, part of these costs are generally covered by the methane energy recovery and by the leachate treatment savings due to recirculation and aeration themselves (Berge et al., 2009).

Anaerobic-Aerated

A hybrid bioreactor can be managed anaerobically until the methane production is effective for the energy recovery; after that, aeration can be applied with the purpose of reducing residual biodegradable fraction and the ammonia content of leachate. The aeration of old landfills can be considered a first application of the hybrid bioreactor concept, even if the sectors were not properly designed for bioreactor systems and air injection since the beginning. Despite that, this practice proved to be efficient in remediation of persistent organic compounds and nitrogen removal (Ritzkowski and Stegmann, 2013). In recent landfills, hybrid technology is planned since the design, consequently biogas extraction, top cover and leachate recirculation systems are made considering the synergy with aeration (Christensen et al., 2011, a; Townsend et al, 2015). Air injection enhance an efficient nitrification both with very old waste and with partially stabilized one; as consequence, aeration can be applied also during the last methanogenic phases of a sector (Ritzkowski and Stegmann, 2013; He et al., 2011; Berge et al., 2006; Sun et al., 2013). Laboratory tests were made to fix hybrid landfill technology to specific waste compositions and environmental conditions, trying to maximize methane production and reduce air injection for saving money (Berge et al., 2009). As instance, aeration of waste was find to be more efficient (in terms of biochemical degradation of carbon and nitrogen compounds) if the air is injected from the bottom of the reactor, allowing a better distribution (Wu et al., 2014).

Aerated-Anaerobic

Aeration can be also used as a pre-treatment for reducing biodegradability or humidity of waste and for enhancing methane production, consuming the initial acidity due to Volatile

Fatty Acids presence. This practice is worldwide used as a treatment applicable in specific plants before the waste deposition in landfill. On the contrary, the injection of air in the waste mass during cultivation of real bioreactor is technically difficult and requires the building of specific in situ systems (Repetti et al., 2013). Despite the technical difficulties, lab-scale tests proved that pre-aeration has beneficial effects on methane production respect to immediate anaerobic conditions. In particular, 70 days of pre-aeration were able to increase pH over 7 in leachate, showing a higher production of methane and higher consumption of organic compounds (Xu et al., 2014). In a lab-scale test by Sandip et al. (2012), pre-aeration in combination with leachate recirculation and/or inoculum injection could increase the methane production even of 30%. Finally, Cossu et al. (2016) tested pre-aeration in several operative conditions, confirming an increase of methane production of more than 50% and better performances regarding production velocity and lag phase. Anyway, pre-aeration is not sufficient for solving the problem of nitrogen persistency in leachate and this type of hybrid bioreactor has the same long-term management problems that anaerobic one has.

S.An.A.

S.An.A. (Semi-aerobic, Anaerobic, Aerated) concept is a more complex system consisting in a first semi-aerobic phase to enhance the methane production occurring in the following anaerobic step and a final forced aeration for the abatement of the residual emissions (Repetti et al., 2013). Cossu et al. (2016) tested this concept in lab scale achieving an increase in methane production performances and the reduction of long-term potential pollution emissions of hybrid reactors. However, this hybrid bioreactors require a performance based management and a constant monitoring of the system which is expensive and need high level technical workers (Cossu et al., 2016).

Multiple stages

Another Hybrid bioreactor concept consists in the subdivision of the process in two or more stages to be performed simultaneously in different reactors. Long et al. (2008) proposed a hybrid bioreactor subdivided in two stages, one anaerobic with methane production and one aerobic, to enhance the nitrification and the hydrolysis. Leachate outputs were crossing recirculated cyclically every day. This system was able to nitrify-denitrify more than 70% of the initial content of nitrogen in the waste sample, producing methane for energy recovery and dropping down main organic pollutants concentration to low levels.

External leachate treatment

Aeration can be also made through an external leachate treatment, maintaining the bioreactor in stable anaerobic conditions and partially recirculating the aerobic liquid products into waste body. The Facultative Bioreactor Landfill (FBL, United States patent US639895, 2002) is an example of this concept, laboratory and full scale applied. The system aims to enhance methane production by maintaining the whole landfill in anaerobic conditions, stimulating simultaneously the hydrolysis and the nitrification in the aerobic leachate treatment. Subsequent threated leachate reinjection inside waste body is useful both in denitrification of produced nitrates and in maintaining moisture, microorganisms, organic substrates and nutrients inside the reactor (De Abreu et al., 2005; Price et al., 2003; Berge et al., 2005). FBL has been tested in laboratory and field-scale to verify the concept efficiency and results shows that the system allows ammonia and organic compounds reduction in the landfill without building and maintaining in situ aeration systems. On the other hand, building and maintaining an in situ biological leachate treatment plant will be necessary for the whole landfill life and recirculated leachate can introduce in landfill also oxygen and nitrates, disturbing methanogenic activity (Price et al., 2003).

2.1.5 Flushing Bioreactors

Flushing bioreactors are structured for increasing the moisture content, in comparison with normal landfill management, with the purpose of enhancing biochemical processes and favouring emission of soluble compounds (Bolyard and Reinhart, 2016; Christensen et al., 2011, b). This practice is one of the most effective system for removing soluble inorganic compounds and refractory organic by-products (ammonia-nitrogen, pharmaceuticals, personal care products and heavy metals), avoiding their future long term emissions (Bolyard and Reinhart, 2016).

Fresh water addition can be made designing the top cover for increase the water inlet or injecting water purposely by means of an irrigation system. Frequently, landfill irrigation is forbidden by law or not authorised by public authorities, which consider this practice an unsustainable contamination of clean liquids. For this reason, Flushing is generally allowed only with process liquids that never leave the system. Leachate recirculation is very useful in enhancing biochemical processes (as explained before) but does not increase significantly solubilization and extraction of compounds. On the contrary, treated leachate fractions can be used as flushing liquid, being the extracted compounds removed from the system by the treatment. These Bioreactors are highly complex and expansive, requiring a synergy between the leachate treatment plant and the bioreactor landfill. However, effectiveness of these solutions has been tested in laboratory and full scale and adopted for recirculation of various leachate treatment products, like reverse osmosis concentrate and oxidised leachate (Morello et al., 2016; Bolyard and Reinhart, 2016; Calabrò et al., 2010; He et al, 2015; Talalaj and Biedka, 2015).

Generally, this process increase drastically leachate production and related treatment costs, even considering internal treatment plant and recirculation. Another negative aspect is the possible unsustainability of the process if the leachate treatment causes some kind of persistent compounds accumulation in the waste body (Morello et al., 2016).

2.1.6 Qualitative comparison between bioreactors

The macro categories of Bioreactor Landfills concepts considered in the previous sub-chapters, with their main characteristics, are listed in Table 2.1.1. A comparison between them can only be conceptual and qualitative because some technologies have not been full-scale tested, the performance of each bioreactor depends highly on the waste characteristics and site conditions, costs and technological complexity change from country to country, etc. For the same reasons, one technology can be preferred to the others according to the characteristics of each waste management system.

Table 2.1.1: Qualitative comparison between the main categories of Bioreactors and Hybrid Bioreactors. (HM: Heavy Metals, Ni-Den: Nitrification and denitrification processes, LR: Leachate recirculation, ---: Depends on specific bioreactor technology)

Bioreactor Typology	**Methane production**	**Biochemical Kinetics**	**Nitrogen Treatment**	**Persistent Emissions**	**Technological Complexity**	**Maintenance Costs***	**Leachate Treatment Costs**
Traditional Landfill	Traditional	Slow	Flushing only	COD, NH_4^+, Salinity, HM	Gas collection, sometimes LR	Low	High
Anaerobic Bioreactor	Enhanced	Medium	Flushing only	COD, NH_4^+, Salinity, HM	LR, Gas collection	LR	LR Savings
Aerobic Bioreactor	No	Fast	Ni-Den	Salinity, HM	LR, Aeration	LR, Aeration	LR, Aeration Savings
Semi-aerobic	No	Medium	Partial Ni-Den	Salinity, HM	Natural Aeration	LR	Aeration Savings
Hybrid Ana-Aer	Traditional	Fast	Ni-Den	Salinity, HM	LR, Aeration	LR, Aeration	LR, Aeration Savings
Hybrid Aer-Ana	Enhanced	Fast	Flushing only	COD, NH_4^+, Salinity, HM	LR, Gas collection, Aeration	LR, Aeration	LR savings
Hybrid S.An.A.	Enhanced	Fast	Ni-Den	Salinity, HM	LR, Aeration, Natural Aeration	LR, Aeration	LR, Aeration Savings
Hybrid Multiple Stages	Enhanced	Fast	Ni-Den	Salinity, HM	Two reactors, Crossed LR, Aeration	LR, Aeration, two reactors	LR, Aeration Savings
External Leachate Treatment	Traditional	Fast	Ni-Den	Salinity, HM	Leachate treatment facility, LR, Aeration	LR, Aeration, Leachate plant	Internal plant
Flushing Bioreactor	---	Fast	---	Null	---	---	Very High

** except for leachate treatment*

Summarizing literature evidences, bioreactors have a higher management level respect to traditional landfills, useful for better controlling reactor performances, reaching faster sustainable conditions and enhancing specific biochemical processes.

Leachate recirculation is a practice utilized worldwide with positive results both in bioreactors and in traditional landfill. Recirculation of other process liquids or wastewaters can be a promising tool for their treatment in synergy with landfill waste; however, sustainability principle prescribes to avoid some persistent compounds accumulation in the waste body (Morello et al., 2016).

Aeration demonstrates to be very useful for enhancing degradation kinetics and allowing nitrification process, having the great disadvantage to inhibit the methanogenesis and the correlated energy recovery. For this reason, many hybrid systems are developed with the purpose to avoid or reduce negative effects on methane production or even to stimulate it. Almost all considered bioreactor concepts promote nitrification-denitrification processes with different methodologies, being the ammonium ion recognised as the main long-term potential pollutant compounds in leachate. These results are obtained increasing progressively the technological complexity and the maintenance costs.

Summarizing, carbon and nitrogen emissions can be reduced with biological treatment applied to bioreactor landfills. However, leachate generally contains relevant concentrations of saline compounds (Fellner et al., 2009), refractory organic by-products (Bolyard and Reinhart, 2016) and Heavy Metals, which are impossible to be removed biologically. Flushing bioreactors can represent a solution for treating this particular long-term emissions and reducing post closure care. Concerning HM, even if their presence in MSW is relevant, their mobility is low and their emissions in leachate are generally considered not to be of environmental interest (Qu et al., 2008).

Applying leachate recirculation, aeration and other technologies is expensive, especially in the first cultivation phase of the landfill; however, consistent reductions in leachate treatment costs are observed in long-term management (Berge et al., 2006). From this point of view, investing money in technology and modern systems management can be repaid with savings in leachate treatment and post-closure care duration.

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2.2 Biogas production enhancement using semi-aerobic pre-aeration in a hybrid bioreactor landfill

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Abstract

Landfilling continues to be one of the main methods used in managing Municipal Solid Waste (MSW) worldwide, particularly in developing countries. Although in many countries national legislation aims to reduce this practice as much as possible, landfill is a necessary and unavoidable step in closing the material cycle (Cossu, 2009). The need for innovative waste management techniques to improve landfill management and minimize the adverse environmental impact produced has resulted in an increasing interest in innovative systems capable of accelerating waste stabilization. Landfill bioreactors allow decomposition kinetics to be increased and post-operational phase to be shortened; in particular, hybrid bioreactors combine the benefits afforded by both aerobic and anaerobic processes. Six bioreactor simulators were used in the present study: four managed as hybrid, with an initial semi-aerobic phase and a second anaerobic phase, and two as anaerobic control bioreactors. The main goal of the first aerated phase is to reduce Volatile Fatty Acids (VFA) in order to increase pH and enhance methane production during the anaerobic phase; for this reason, air injection was stopped only when these parameters reached the optimum range for methanogenic bacteria.

Biogas and leachate were constantly monitored throughout the entire methanogenic phase with the aim of calibrating a Gompertz Model and evaluating the effects of pre-aeration on subsequent methane production. The results showed that moderate and intermittent pre-aeration produces a positive effect both on methane potential and in the kinetics of reaction.

Keywords

Landfill emissions, Landfill pre-aeration, Bioreactor landfill, Hybrid landfill, Methane production enhancement.

2.2.1 Introduction

Landfilling continues to be one of the main methods used in managing Municipal Solid Waste (MSW) worldwide, particularly in developing countries. Although in many countries national legislation aims to reduce this practice as much as possible, landfill is a necessary and unavoidable step in closing the material cycle (Cossu, 2009). The need for innovative landfill management techniques to better minimize their adverse environmental impact, has led to an increasing interest in bioreactors, capable of accelerating the decomposition of Municipal Solid Waste (MSW) and reducing the post-operational phase of a landfill (Price et al., 2003; Xu et al., 2014).

Bioreactor landfills are characterized by use of a series of technologies including water and/or air injection, leachate recirculation, and other combinations of in situ treatments to allow adjustment of pH, redox conditions and moisture content with the aim of creating a more suitable environment for degradation processes. Moisture control is required to support metabolic processes, transport of nutrients and microorganisms (Norbu et al., 2005), while air injection speeds up degradation processes (Cossu et al., 2003; Ritzkowski and Stegmann, 2013).

In recent years, it has been demonstrated that bioreactor landfill technology promotes the decomposition and stabilization of biodegradable organic waste, through water addition, leachate recirculation or air injection (Sun et al., 2013; Erses et at., 2008; Sekman et al., 2011; Sandip et al., 2012; Xu et al., 2014; Shao et al., 2008; He et al., 2011). In particular, as far as the metabolic pathway is concerned, three main types of landfill bioreactors are currently considered: anaerobic, aerobic and hybrid, the latter providing for a sequence of aerobic and anaerobic conditions (EPA, 2015). Most of the bioreactor landfills discussed in literature were operated under anaerobic conditions (Price et al., 2003; Valencia et al., 2011; Vigneron et al., 2007), causing ammonia accumulation and at times a partial or complete inhibition of methane production. On the contrary, a system operated solely under aerobic conditions may increase the degradation kinetics of organic substances but inhibits completely methane generation and renders energy recovery impossible. Hybrid bioreactors operate under various combinations of aerobic and anaerobic conditions to achieve benefits from both (Long et al., 2009, Xu et al., 2014). The facultative landfills bioreactor is another type of Hybrid bioreactor which provides external aerobic pre-treatment of leachate prior to its recirculation in an anaerobic bioreactor, to allow both the nitrification and denitrification process to remove nitrogen compounds (De Abreu et al., 2005, US639895, 2002).

The test proposed in this study takes into consideration six landfill simulating bioreactors: four hybrid bioreactors with a first semi-aerobic phase prior to a second anaerobic phase and two anaerobic control bioreactors. During the semi-aerobic phase, air was injected into the waste mass to simulate natural convection caused by the temperature gradient between the external environment and the landfill body, with the goal of Volatile Fatty Acids (VFA) reduction and pH increase to enhance methane production in the next anaerobic phase. The effects of continuous and intermittent aeration were compared, the latter appearing beneficial for accelerating waste stabilization and reducing the acid formation, based on the outcomes of previous experiments (Sang et al., 2009). This hybrid system also provided for leachate recirculation to ensure better nutrient distribution and appropriate moisture content.

This test is based on S.An.A Landfill model, a Hybrid system featuring an initial semi-aerobic phase to enhance methane production occurring in the subsequent anaerobic step and, finally, forced aeration for the abatement of residual emissions (Repetti et al., 2013).

The change from semi-aerobic to anaerobic conditions was challenging: no aeration time was decided a priori, as this was highly dependent on the initial waste characteristics, but was selected with the aim of monitoring specific chemical parameters capable of guaranteeing optimal conditions for methanogenic bacteria.

The aim of the present study was to apply the hybrid waste management system, in order to combine the previously demonstrated advantages of leachate recirculation and aeration, with a greater methane production. In line with the mode of aeration and with air flow in each bioreactor at the moment of change from semi-aerobic to anaerobic operating conditions, an association with the characteristic parameters of methane generation (production rate, cumulative volume produced and lag phase) were observed. This analysis is of use in determining the optimum air injection method and airflow range to both stimulate methane production and increase degradation kinetics.

2.2.2 Materials and methods

Waste samples

The waste used for the experiment was the residual fraction of Municipal Solid Waste sampled after source segregation and provided by a public waste management company operating in thirteen municipalities of Livorno Province, Tuscany (Italy). A 200 kg sample was sieved with an 80 mm mesh and then analyzed by different waste fractions (Table 2.2.1); the undersieve (<80 mm fraction) was loaded into bioreactors. The waste composition was characterized by high amounts of food waste, plastic, paper and fines. Minor quantities of green waste, metals, glass, wood and textiles were detected (Table 2.2.1).

Table 2.2.1: Fractional composition of raw waste and undersieve (<80 mm), i.e. the fraction used to fill the reactors.

Trade Class	Raw waste (%)	Undersieve <80 mm (%)
Food Waste	14.0	17.4
Green Waste	6.1	6.0
Paper	22.9	10.5
Plastic	18.4	12.6

Metal	5.2	6.2
Glass and Inert	3.5	3.2
Wood	0.4	0.3
Textiles	8.5	5.1
Undersieve #20 mm	20.9	38.8

Equipment

The experiments were carried out by using six Plexiglass® (polymethyl methacrylate) columns (height 106 cm, diameter 24 cm). Each reactor was filled with the aim of reaching a density of 0.5 t/m3, resulting in 18.4 kg MSW placed in each reactor. A 10-cm thick gravel layer (Ø 20-30 mm) was placed at the bottom and the top of each column as a drainage layer to facilitate the distribution of recirculated leachate (Figure 2.2.1).

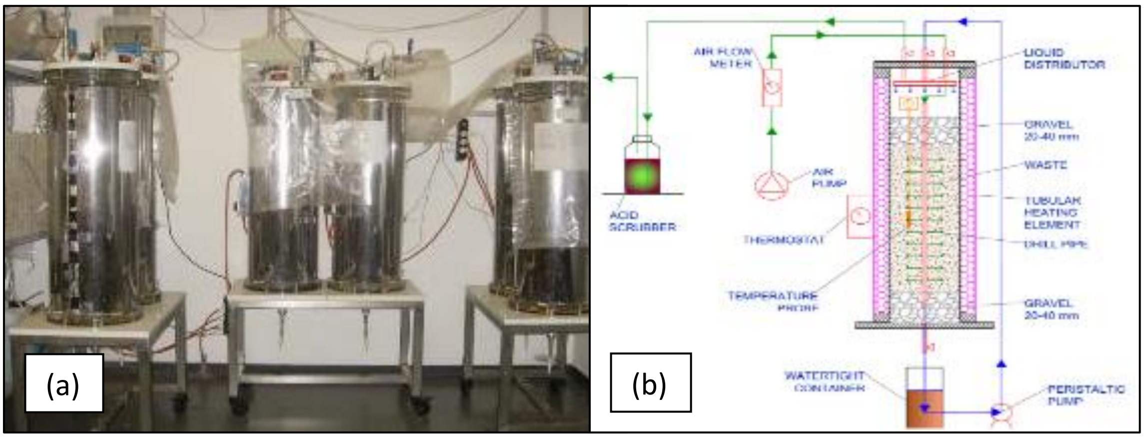

Figure 2.2.1: Reactor setup: (a) view and (b) sketch.

The upper end of reactor body was equipped with three valves providing for the introduction of air, sampling and extraction of gas as well as introduction of water and leachate recirculation. Recirculation was carried out from the top of the reactor using peristaltic pumps (Heidolph PD 5001). A leachate collection port was located at the bottom of each column for leachate extraction.

To channel air into the waste body, a vertical PVC pipe with side perforations was installed at the center of the waste layer; this system was designed to guarantee the uniform distribution of air throughout the reactor. The pumping equipment was a Prodac Air Professional pump 360 and inlet airflow was regulated by a Sho-Rate GT1135 flow meter. Biogas generated from each column was collected by a Tedlar® sampling bag connected to the upper gas port and its volume and quality were measured daily (Figure 2.2.1).

Temperature monitoring was performed by means of Thermo Systems TS100 temperature probes installed inside the reactor and the temperature was maintained constant at 39 - 42°C by means of a thermo-regulated insulation system covering all reactor lateral surfaces.

Methodology

The test was divided into three distinct main phases: Semi-aerobic, Anaerobic and Aerobic. The first phase was meant to enhance biogas production in the following anaerobic phase; the third one was functional to the complete stabilization of residual contaminants by means of aeration and flushing. In this paper, only the first two phases have been taken into consideration.

Six column reactors were filled with the same quantity of waste and managed under identical hydraulic conditions to obtain a clear comparison of results. Four reactors were Hybrid (IAa and IAb with intermittent aeration; CAa and CAb with continuous aeration); the remaining two were anaerobic (ANa and ANb) and used as control bioreactors. After filling and startup, aeration was commenced according to the scheme in Figure 2.2.2, to simulate semi-aerobic conditions. Daily air flux was the same for all pre-aerated reactors (Figure 2.2.2) and equal to 50 L/d at 20°C, that in our specific case corresponds to 5 NL/d/kgTS, TS being the dry matter content (total solids) in the reactor. Intermittent aeration was turned on for twelve hours a day (4.1 L/h), while continuous aeration was provided all day long, seven days per week (2.1 L/h). Daily air flux was chosen on the basis of a series of lab-scale experiments carried out on landfill bioreactors in semi-aerobic conditions: these ranged from 0.7 NL/d/kgTS (Wu et al., 2014) to 32.0 NL/d/kgTS (Cossu et al., 2003) with average values between 4-10 NL/d/kgTS (Cossu et al., 2005; Sun et al., 2013;). At test start up, airflow was set at a low regime and incremented until oxygen was detectable in the off gasses (O2 > 1-2 %).

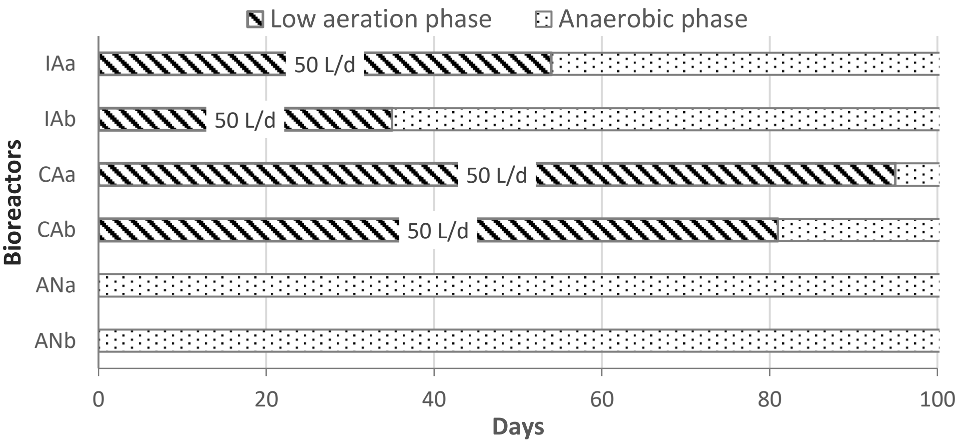

Figure 2.2.2: Operative conditions observed over time in the different experimental columns. IA: intermittent aeration, CA: continuous aeration, a, b double series of columns. Daily aeration was the same for all pre-aerated columns (50 L/d at 20°C and 1 atm).

At the beginning of the test, 5 L of distilled water were introduced into each reactor to adjust moisture content to around 55-60% and guarantee leachate production; leachate recirculation was carried out daily throughout the entire test. Leachate samples (0.1 - 0.5 L) were collected weekly for analysis. Fresh water was injected to replace the leachate sampled for testing and to maintain a constant moisture content, fundamental for biochemical processes (Valencia et al., 2009); this represented the sole contribution to the increase of Liquid-Solid ratio (L/S).

The transition from the semi-aerobic phase to the anaerobic one was based on the observation of parameters of concern in leachate. In particular, pH steadily increased and reached values above 6 after four weeks of aeration. It was then decided to interrupt aeration in column IAb at day 35, the pH being equal to 6.25 and within the optimal range (6-8) suggested by Zehnder et al. (1982), although VFA concentration was approximately equal to 7100 mgCH_3COOH/L, still above the optimal value for starting methanogenesis (6000 mgCH_3COOH/L) recommended in Table 2.2.2. For comparison, column IAa was turned anaerobic 20 days later than IAb, the pH value being at 6.46 and VFA concentration equal to approximately 5300 mgCH_3COOH/L, within the optimal value in Table 2.2.2.

The transition into anaerobic conditions was postponed for columns CAa and CAb, until the pH in leachate reached values steadily above 6. Column CAb was turned anaerobic at day 81 (the pH being equal to 6.34), although VFA concentration was approximately equal to 6300 mgCH_3COOH/L, still above the optimal value in Table 2.2.2. For comparison, column CAa was turned anaerobic two weeks later than CAb, the pH value being at 6.46 and VFA concentration equal to approximately 5500 mgCH_3COOH/L, within the optimal value in Table 2.2.2 (see Table 2.2.4).

Table 2.2.2: Operative parameters and range of values selected in defining the length of the pre-aeration phase.

Parameter	Values Range	References
Temperature (°C)	30-40	Christensen et al., (1996)
	35-40	Yuen et al., (1995)
	35	Cossu et al., (2005)
pH	6-8	Zehnder et al., (1982)
	6.7-7.4	Lay et al., (1998)
	6.4-7.2	Chugh et al., (1998)
	6.5-8.2	Sekman et al., (2011)
	6.65-7.41	Sandip et al., (2012)
Alkalinity (mg$CaCO_3$/L)	1000-5000	Agdag et al., (2005)
	2000-3500	Sekman et al., (2011)
Volatile Fatty Acids (mgCH_3COOH/L)	< 6000	Wang et al., (1999)

A kinetic model derived from the Gompertz Growth Equation, calibrated with biogas data, was used to mathematically simulate Methane production. This model has a sigmoid shape with a clear inflection point and its output is the cumulative volume of methane produced from the bioreactors according to the Equation 1 (Lay et al., 1998; Sandip et al., 2012).

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

BG is the cumulative methane yield (mL/gVS), t is the cumulated time (d), BGP is the methane yield potential (mL/gVS), Rm is maximal daily methane yield (mL/gVS/d), λ is bacteria growth lag time (d) and e is a mathematical constant (=2.718). The calibration of Gompertz Equation was carried out by minimizing mean square deviation of the values measured and calculated.

Analytical methods

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

A portable analyzer (Eco-Control LFG20) was used for periodic measurements of CO_2, CH_4 and O_2 concentrations in biogas collected in the bags.

Leachate samples were analyzed periodically for pH, VFA, alkalinity, COD, TOC, BOD5, TKN, $N\text{-}NH_4^+$, SO_4^{2-} and Cl^-. The ratio between VFA and alkalinity was calculated to obtain the so called FOS/TAC (Voss et al., 2009). FOS/TAC is an index developed in Germany as a control parameter for anaerobic digestion processes, yielding a rapid indication as to the status of the system in relation to buffer capacity and VFA content. For this reason, FOS/TAC was monitored frequently during the first phase of the test.

Waste was thoroughly mixed before filling the reactors, in such a way that the same material was used in each test; waste samples were taken for characterization before filling the reactors. Waste characterization at the end of the anaerobic phase involved the complete extraction of the waste from each reactor and the mixing in a tank to increase the homogeneity; after this procedure, a sample of 500 g was taken and analyzed for each column. Solid samples were milled to 4 mm prior to determination of TS, VS, TKN, $N\text{-}NH_4^+$, TOC, IR_4 and IR_7. TOC on solid samples was measured by means of a TOC-VCSN Shimadzu Analyzer. Respiration Index (RI_4 and RI_7 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 waste samples (L/S was brought to 10 L/kgTS, mixing for 24 hours and filtration at 0.45 µm). The eluate obtained was analyzed to evaluate the emission potential of the same contaminants considered in leachate (pH, VFA, alkalinity, COD, TOC, BOD_5, TKN, $N\text{-}NH_4^+$, SO_4^{2-} and Cl^-. All tests on solid samples were performed in duplicate.

2.2.3 Results

Solids

The results of waste characterization at the beginning of the test as well as at the end of the anaerobic phase are reported in Table 2.2.3. Waste mass decreased in 305 days from the initial value of 18.4 kg per column, to values between 14.7 and 16.9, indicating a drop between 8 and 20% in each reactor.

Total Solids (TS) content in the waste decreased from 55% to 35-45%; Volatile Solids (VS) displayed a similar trend due to the degradation processes. TKN content slightly decreased (15-18 %) in all columns; nitrogen emissions occurred only via leaching and no nitrification was detected, even during the semi-aerobic phase. TOC decreased about 30% from the beginning of the test, mainly due to biogas emissions.

The leaching test on solid samples showed a significant decrease of all parameters affected by the biochemical processes taking place during the 305 test days, with the exception of ammonium, which was produced by hydrolysis from organic nitrogen and an increase was observed in the solid phase compared to initial values. Chloride emission potential was halved from the beginning to the end of the test due to fast dissolution into leachate, as reported in other similar landfill simulation experiments (Fellner et al., 2009).

Table 2.2.3: Quality parameters of waste sample at the beginning of the test (Initial Waste) and at the end of the anaerobic phase (IAa, IAb, CAa, CAb, ANa, ANb): concentrations in the solid phase and in the eluate of a standard leaching test (UNI EN 12457-2).

		Initial waste	**IAa**	**IAb**	**CAa**	**CAb**	**ANa**	**ANb**
Solid phase	Waste Mass (kg)	18.4	14.9	15.5	15.3	14.9	14.7	16.9
	TS (%)	55.5	39.4	35.7	47.9	44.1	61.4	41.3
	VS (%TS)	58.9	40.6	39.5	32.4	31.0	25.8	44.2
	IR$_4$ (mgO$_2$/gTS)	76.9	7.2	8.3	6.5	2.8	8.1	13.9
	IR$_7$ (mgO$_2$/gTS)	79.3	9.3	11.4	8.9	4.5	11.8	20.8
	TKN (mgN/kgTS)	9700	7596	7317	8013	8498	7683	7586
	TOC (gC/kgTS)	368	180	231	208	303	282	274
Eluate from leaching test	pH	6.2	8.5	8.4	8.3	8.3	8.1	8.3
	COD (mg/L)	14682	4939	4791	2939	4836	2889	4834
	BOD$_5$ (mg/L)	7504	365	309	308	337	393	477
	Alkalinity (mgCaCO$_3$/L)	274	985	1038	783	842	587	1056
	VFA (mgCH$_3$COOH/L)	728	154	143	120	141	107	121
	TKN (mgN/L)	756	490	406	237	411	131	261
	N-NH$_4^+$ (mg/L)	78	431	265	141	236	66	98
	Organic nitrogen (mg/L)	679	59	141	96	175	65	163
	Cl$^-$ (mg/L)	619	343	243	233	362	376	324

Waste respiration index (RI$_4$) dropped significantly from the initial value in all reactors. However, except for CAb, final RI$_4$ values in all reactors were higher than the reference limit of 5 mgO$_2$/gTS indicated for waste acceptance in landfills in the German regulation (Ritzkowski et al., 2006).

Despite all analyses being performed in triplicate, the variation of analytical values was strongly influenced by heterogeneity of the solid sample, thus resulting in the lack of any evident distinction due to the diversity of management of the reactors (Table 2.2.3).

Leachate

The evolution of the main parameters monitored in leachate samples extracted from the reactors during the test is visible in Figures 2.2.3 to 2.2.5.

The beneficial effect of pre-aeration on pH increase in the subsequent anaerobic phase is clearly visible. Actually, pH increase did not start until 3 weeks after aeration was stopped in

IAb. Conversely, pH increase was observed just a couple of days after IAa (where aeration lasted 20 days longer than in IAb) was turned anaerobic (Table 2.2.4).

The evolution of VFA in IAa and IAb is similar and it is consistent with pH results. The same behavior was observed for continuously aerated reactors.

In anaerobic reactors a steady pH increase and concomitant VFA decrease appeared after 6 months of test only.

Table 2.2.4: Values of the operative parameters (listed in Table 2.2.2) monitored in the pre-aerated columns at the end of the semi-aerobic phase.

	Aeration time (d)	**pH**	**VFA (mgCH_3COOH/L)**	**Alkalinity (mgCaCO3/L)**	**FOS/TAC**	**N-NH4+ (mg/L)**	**COD (mg/L)**
IAa	55	6.46	5287	4163	1.27	1597	34778
IAb	35	6.25	7144	3953	1.81	1557	51465
CAa	95	6.46	5479	3533	1.55	1766	44764
CAb	81	6.34	6283	4321	1.45	1918	54344

The evolution of alkalinity was very similar in all reactors over the first 3 months of test. A clear increase trend was observed in IA reactors 2 months after aeration was stopped; the same increase pattern is visible in CA reactors from approximately 40 days after the end of aeration.

A behavior very similar to VFA was observed for COD and TOC also.

BOD_5/COD ratio is an important parameter that indicates the amount of biodegradable compounds still present in a liquid (Cossu et al., 2012). According to Sekman et al., (2011), BOD_5/COD ratio between 0.02 and 0.13 implies a low biodegradability, while according to Kjeldsen et al., (2002), a ratio between 0.4 and 0.8 implies high biodegradability. During the test, BOD_5/COD ratio decreases in all reactors starting couple of weeks after the beginning of methanogenic phase and reaching values under 0.1 (Figure 2.2.4).

The results of monitoring of nitrogen compounds are reported in Figure 2.2.5. Nitrification processes may occur in aerobic bioreactors and allow the conversion of ammonium into nitrites and nitrates. During the first semi-aerobic phase of this test however, no nitrates were found in the leachate samples and no ammonium decrease was detected, probably due to the low quantity of air injected. Ammonium nitrogen concentration accumulated in all bioreactors due to hydrolysis of organic nitrogen and in IAa, CAa, IAb, CAb reached values of almost 2000 mgN/L during the first months of test. An unexpected increase trend was observed in aerated reactors after day 150, with values up to 3000 mgN/L in IAa. Concentrations were below 1500 mgN/L in ANa and ANb due to slower ammonification processes under anaerobic conditions.

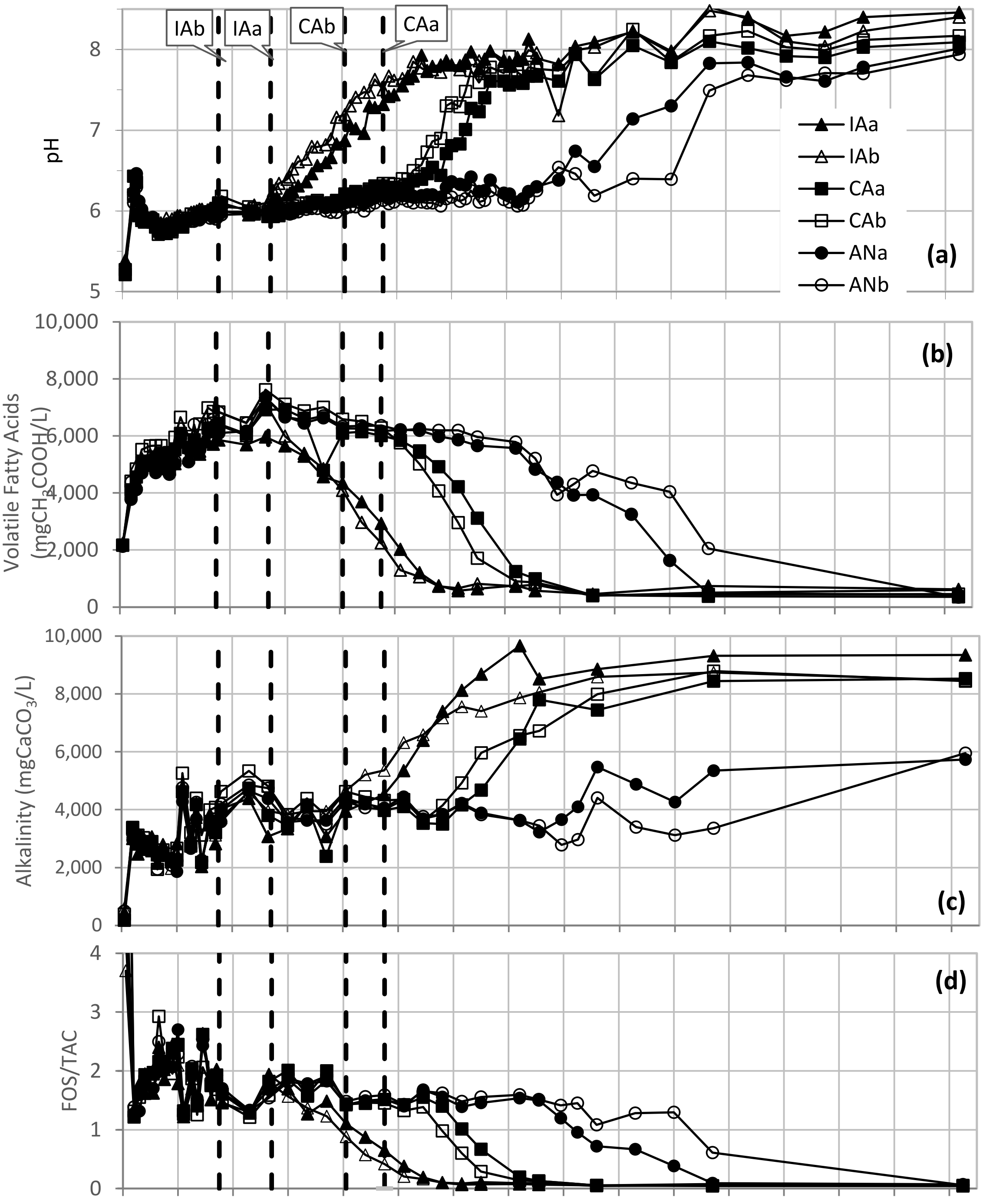

Figure 2.2.3: Monitoring of control parameters in leachate, useful in selecting the appropriate time to turn off aeration and start the second phase of the test: (a) pH, (b) Volatile Fatty Acids (VFA), (c) Alkalinity, (d) FOS/TAC ratio. Dotted vertical lines indicate the passage form the first to the second phase of hybrid reactors.

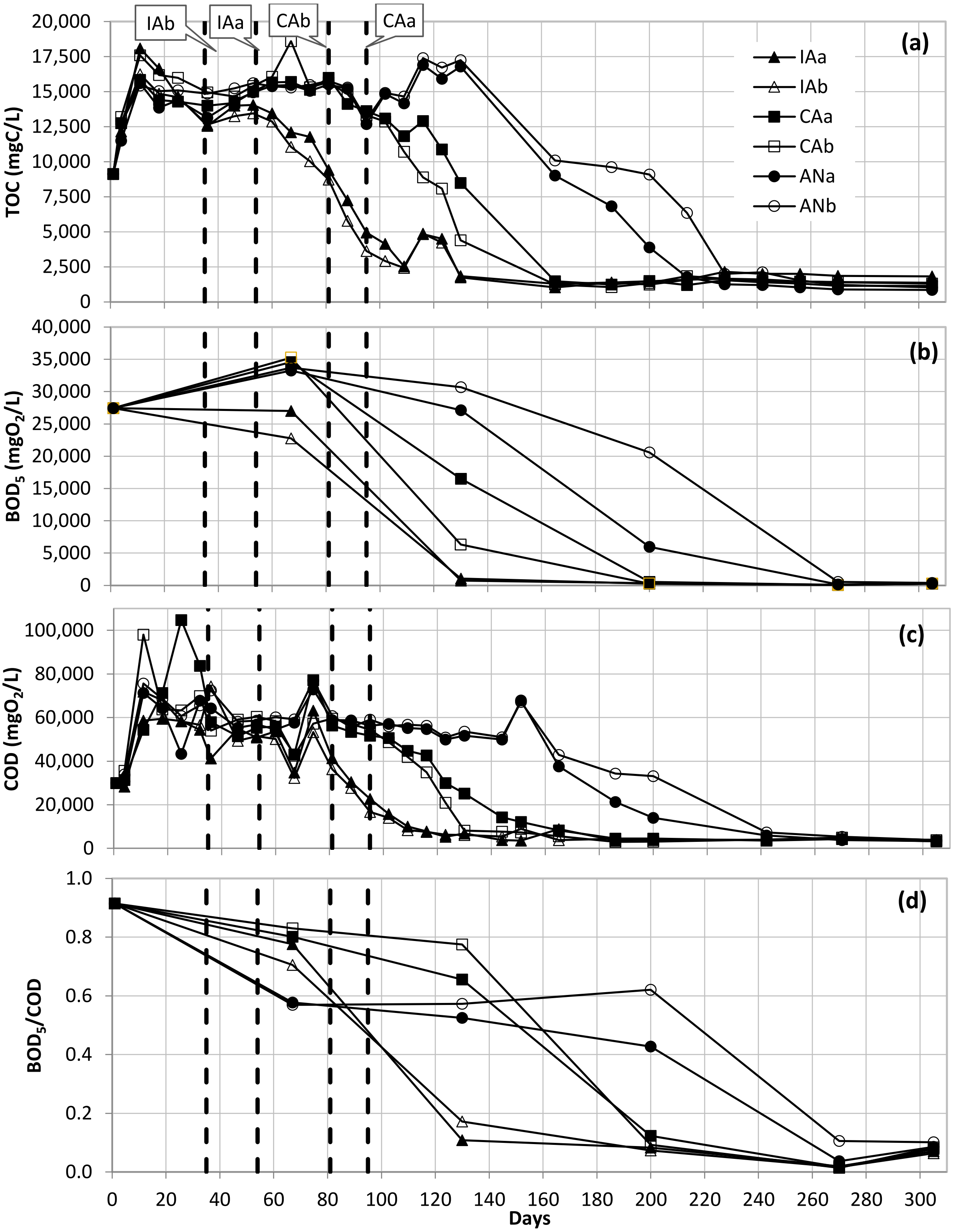

Figure 2.2.4: Carbon indexes monitoring in leachate: (a) TOC, (b) BOD$_5$*, (c) COD, (d) BOD*$_5$*/COD ratio. Dotted vertical lines indicate the passage form the first to the second phase of hybrid reactors.*

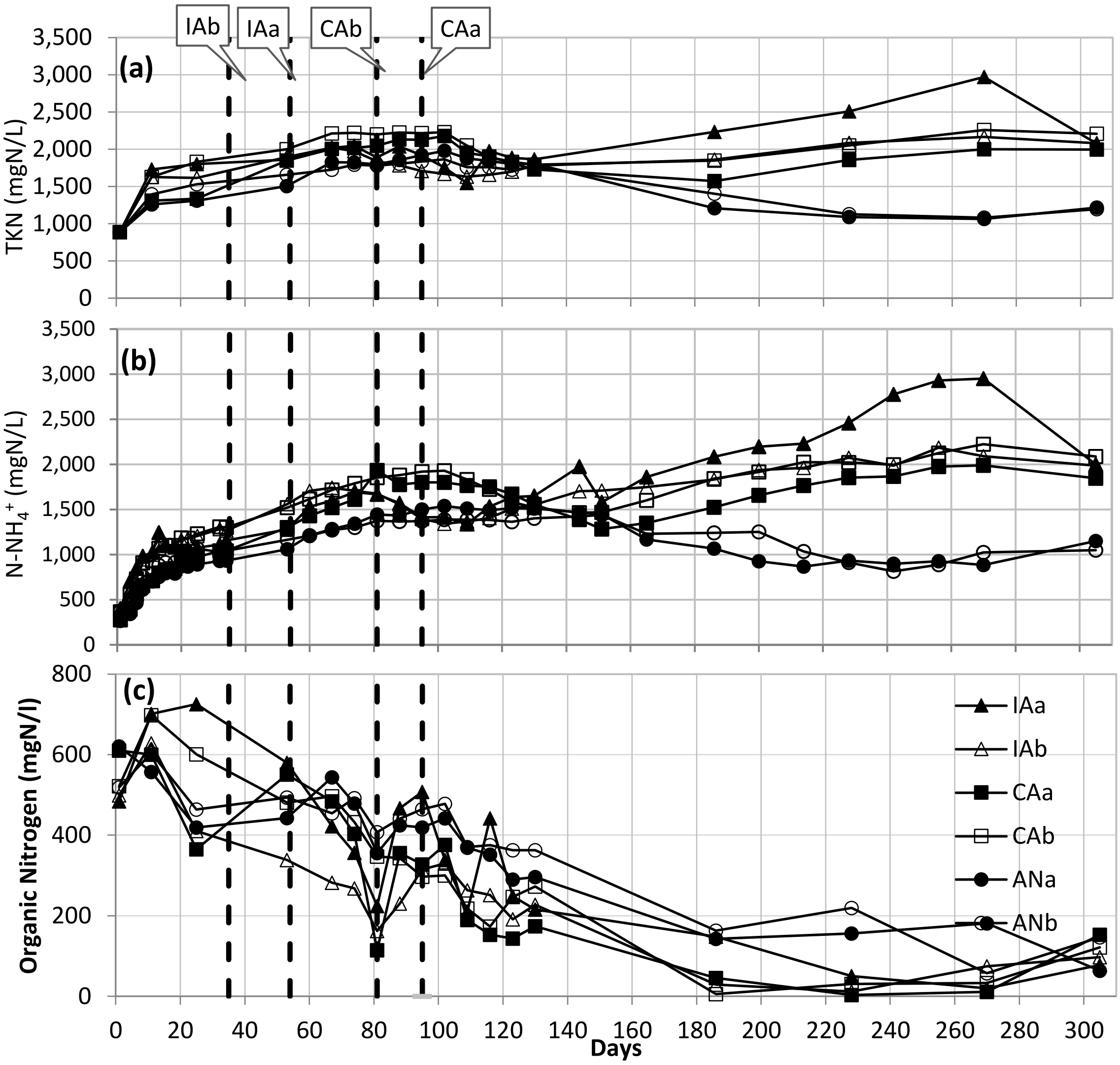

Figure 2.2.5: Nitrogen parameters monitoring in Leachate (a) TKN, (b) N-NH$_4^+$, (c) Organic Nitrogen. Dotted vertical lines indicate the passage form the first to the second phase of hybrid reactors.

Biogas production

The evolution of cumulative methane production is reported in Figure 2.2.6. In hybrid reactors, methane production started within the first 5-7 days under anaerobic conditions, reaching a peak after 2 weeks; in control bioreactors ANa and ANb methane production started after 5 and 6 months respectively, from the beginning of the test.

Cumulative methane produced in the whole test in reactors IAa and IAb was 75 and 102 NL/kgVS respectively; the lower value recorded for IAa is most probably due to the higher amount of organic material oxidized during the longer pre-aeration phase. Values between 54 and 80 NL/kgVS were obtained for continuous reactors, between 31 and 55 NL/kgVS for control bioreactors (Table 2.2.5). The highest methane production rate was recorded in intermittent reactors IAa and IAb, where a peak was observed on day 86 at 2.9 NL/d/kgVS for IAa and on day 96 at 2.8 NL/d/kgVS for IAb (Table 2.2.5).

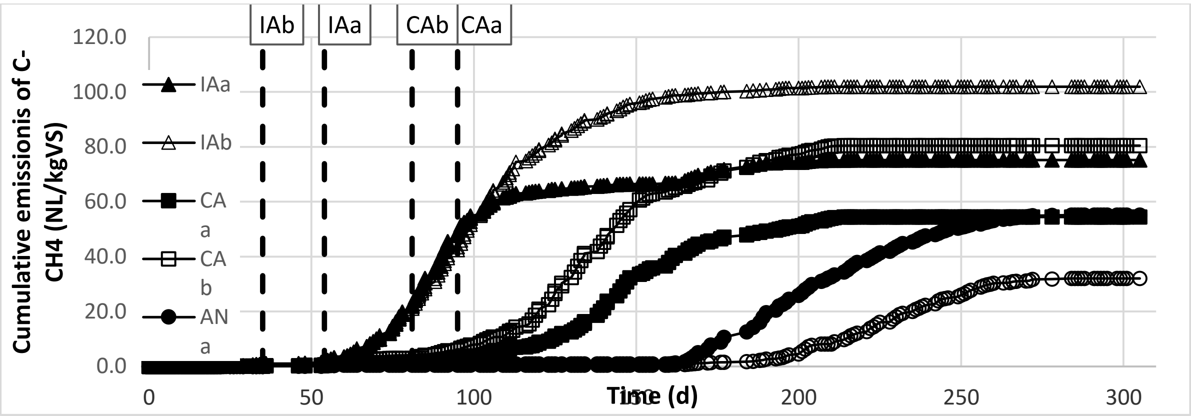

Figure 2.2.6: Cumulated volume of methane produced in time. Dotted vertical lines indicate the passage form the first to the second phase of hybrid reactors.

Table 2.2.5: Methane production observed at the end of the anaerobic phase in the experimental columns, according to the different aeration conditions adopted. Values of the Gompertz parameters calculated for the different columns are also reported.

	Experimental Data				**Gompertz Model parameters**			
	Total volume of injected air (NL/kgVS)	**Pre-aeration time (d)**	**Maximum daily methane Production (NL/d/kgVS)**	**Cumulative methane production (NL/kgVS)**	**BGP (NL/kgVS)**	**R_m (NL/d/kgVS)**	**λ (d)**	**Standard Deviation**
IAa	357	55	2.9	75.2	72.7	1.6	12.3	6.9
IAb	210	35	2.8	101.9	102.3	1.7	34.2	0.8
CAa	675	95	2.3	54.4	55.5	0.8	15.7	3.2
CAb	566	81	2.5	80.5	81.3	1.2	21.5	5.8
ANa	0	0	1.6	54.7	55.8	0.8	168	1.0
ANb	0	0	1.2	31.2	34.8	0.5	192	1.4

2.2.4 Discussion

Mass Balance

Carbon and nitrogen mass balances were built considering the TOC and TKN content in the solid sample at the beginning of the test and at the end of the anaerobic phase, the cumulative emissions in leachate and biogas (Table 2.2.6).

Carbon mass balance evidenced a difference between the analysed and the calculated final content of TOC of up to 35%, with a relative error of 19%: this was probably due to waste heterogeneity rather than system losses. Liquid emissions totalled approximately 2 - 3 % of the initial carbon content with no evident differences between pre-aerated and control reactors. On the contrary, gaseous emissions varied from 12 - 17% of initial TOC in pre-aerated reactors and only 6 – 8% in control ones, indicating the effectiveness of pre-aeration in methane generation enhancement, as already observed by other authors (Sekman et al., 2011; Sang et al., 2009; Erses et al., 2008). These data also confirmed that carbon emissions via leachate are generally an order of magnitude lower than those emitted in biogas (Lornage et al., 2013).

Table 2.2.6: Carbon mass balance based on TOC content detected at the beginning and at the end of the test in solid samples, TOC emissions via leachate and via biogas. Nitrogen mass balance based on TKN content detected at the beginning and at the end of the test, nitrogen emissions via leachate and via biogas. All values are expressed as g/kgTS, with percentages respect to initial content reported in brackets.

Carbon Balance

gC/kgTS and (%)	IAa	IAb	CAa	CAb	ANa	ANb
Initial content	368 (100)	368 (100)	368 (100)	368 (100)	368 (100)	368 (100)
Final content (305 d)	181 (49.2)	232 (63.0)	208 (56.7)	303 (82.5)	282 (76.8)	274 (74.6)
Leachate Emissions	7.4 (2.0)	6.9 (1.9)	9.0 (2.4)	9.1 (2.5)	9.8 (2.7)	10.3 (2.8)
Biogas Emissions	52 (14)	64 (17)	44 (12)	57 (16)	28 (8)	21 (6)
Methane Emissions	24 (6)	32 (9)	17 (5)	25 (7)	15 (4)	10 (3)
Missing (%)	34.74	17.73	29.06	-0.48	13.06	16.77

Nitrogen Balance

gN/kgTS and (%)	IAa	IAb	CAa	CAb	ANa	ANb
Initial content	9.70 (100)	9.70 (100)	9.70 (100)	9.70 (100)	9.70 (100)	9.70 (100)
Final content (305 d)	8.48 (88.4)	8.38 (86.4)	8.63 (89.0)	9.00 (92.8)	8.01 (82.5)	8.08 (83.3)
Leachate Emissions	1.45 (14.9)	1.34 (13.8)	1.30 (13.4)	1.46 (15.1)	1.16 (12.0)	1.19 (12.3)
Nitrates Emissions	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Gaseous Emissions	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Missing (%)	-2.3	-0.2	-2.4	-7.9	5.5	4.4

Nitrogen emissions were all associated to TKN in leachate; no N-NOx were detected during the test and denitrification was supposed to be negligible as well. Liquid emissions ranged from 12 - 15 % of the initial nitrogen content. No gaseous ammonia was emitted via biogas, although pH achieved values higher than 8 at the end of the test. The difference between the analysed and calculated final nitrogen content was approximately (-8) - 5 %, with a relative error of 3.8%, probably mainly due to heterogeneity of the waste samples. Dissolved nitrogen increased due to ammonification process that took place mainly in pre-aerated reactors; this was confirmed both by concentration evolution (Figure 2.2.5) and by total nitrogen emissions, which were higher in all hybrid reactors in comparison with control ones (Table 2.2.6).

Influence of pre-aeration on methane production

Acidity was the main inhibition factor for methanogenic bacteria; they work efficiently only in a small range (6.5-8.0) of pH values (Sekman et al., 2011). VFA constitute the feed for methanogens, although, if concentrations are too high (upper than 6000 mg/L), pH decreases excessively resulting in inhibition of methanogenic activity. This “excess of loading” may potentially occur in all anaerobic digesters, although can be controlled through the FOS/TAC, the ratio between VFA and alkalinity. According to Farquhar and Rovers (1973), the methane production of an anaerobic degradation system requires a ratio between VFA and alkalinity lower than 0.8. In our reactors methanogenesis started with an even higher value (1.25), but FOS/TAC decreased rapidly once methane production was established (Figure 2.2.3).

After a pre-aeration period, total methane production in hybrid reactors was greater than that obtained from control anaerobic bioreactors, confirming that pre-aeration improves methane generation and increases the production rate.

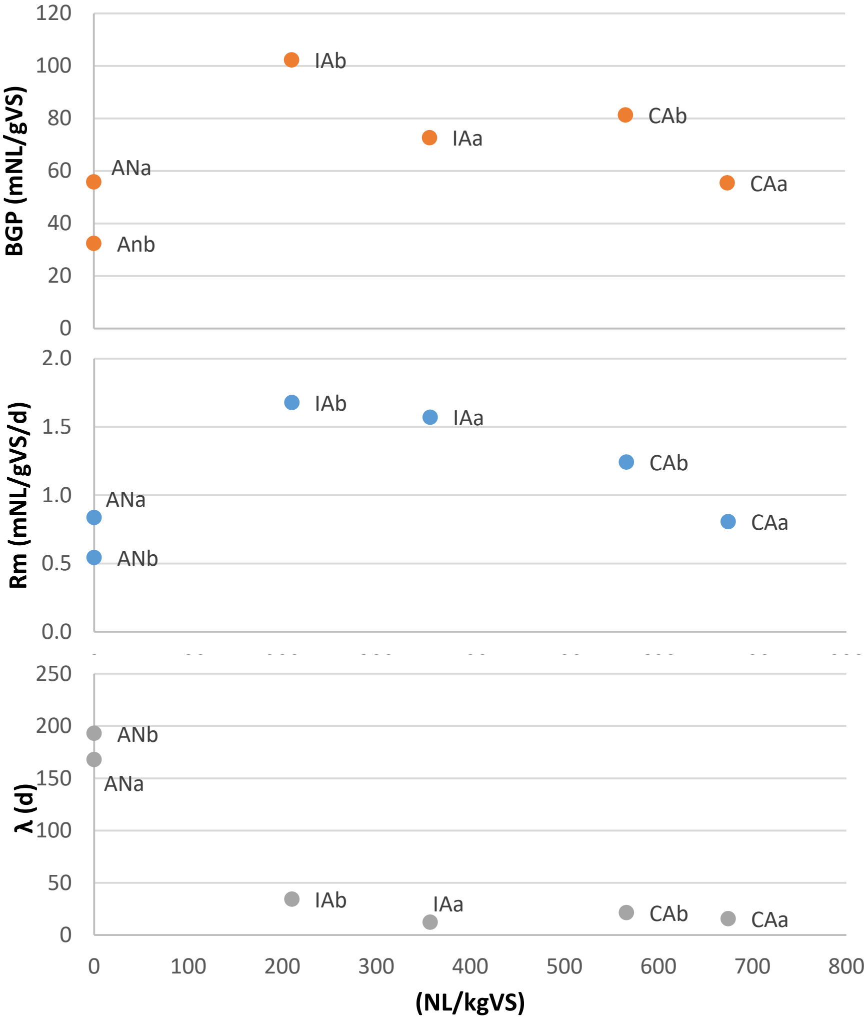

Figure 2.2.7: Gompertz Model parameters (BGP, Rm, λ) respect to total air volume injected. BGP is the methane yield potential (mL/gVS), Rm is maximal daily methane yield (mL/gVS/d), λ is bacteria growth lag time (d).

Acidic conditions were influenced by aeration mode: intermittent aeration speeded up pH increase, shortening the first phase and anticipating methane generation (Figure 2.2.3). The alternation of aerobic and anaerobic periods renders the transition from an aerobic to an anaerobic microbial population more dynamic, thus forming a diversified microbial community. Sang et al. (2009) carried out tests on landfill bioreactors under both anaerobic and aerobic conditions, with aeration supplied both continuously and intermittently. They found a very rich bacterial population within the reactor characterized by intermittent aeration: in particular methanogens, such as Methanobacteriales (H_2-utilizing groups) and Methanosarcinales (acetate-utilizing group) were detected. During the test

Methanobacteriales were gradually replaced by Methanosarcinales, suggesting that the main degradation pathway was acetotrophy for methanogenesis. Aerobic bacteria were found to be subjected to stressful conditions due to the presence of anaerobic periods, therefore, during aerobic conditions the degradation process progressed at a faster rate.

Excessive pre-aeration should be avoided to limit the oxidation of organic substance and the subsequent decrease of methane production potential. As an example, IAa was aerated to a slightly greater extent than IAb (Figure 2.2.2): this resulted in a faster transition to methanogenesis in IAa after the end of the aeration phase, but the total methane generation was negatively affected and a lower yield compared to IAb was observed (Figure 2.2.6).

The Gompertz Equation proved suitable to model biogas production during the test. The results of model calibration carried out by minimizing mean square deviation of the values measured and calculated are reported in Table 2.2.5; standard deviation between real data and the model was lower than 7%. Gompertz model parameters are reported in Figure 2.2.7 also, where they are plotted versus the total injected air.

2.2.5 Conclusions

Pre-aeration was effective in reducing the organic content of reactors, increasing degradation kinetics, controlling the concentration of VFA and stimulating methanogenesis. Moreover, air injection was found to increase total methane production in the subsequent anaerobic phase in comparison with control bioreactors where acid conditions endured for a longer time.

Intermittent aeration proved to be more efficient than continuous aeration, promoting faster reaction kinetics for methane production.

The highest methane yield was recorded in intermittent reactor IAb, where the aeration was stopped earlier (day 35) than other reactors, although the low pH value (6.25) and the still high VFA content (above 7100 mg/L) in the leachate caused a higher lag phase and a slightly slower biogas generation rate than in IAa. However, despite the better start, the longer pre-aeration in IAa caused a cumulative methane production 25% lower than in IAb.

Pre-aeration of a bioreactor landfill proved effective in promoting and speeding up methane production; the process should be carefully monitored and air injection carried out and eventually interrupted based on the biochemical performance of the reactor.

Carbon mass balance evidenced a significant difference between the analysed and the calculated final content of TOC, probably due to waste heterogeneity rather than system losses. Carbon emissions via leachate were approximately 2 - 3 % of the initial TOC content in the solid waste, with no evident differences between pre-aerated and control reactors; conversely, carbon emissions via process gas were enhanced in pre-aerated reactors (12-17% of the initial TOC) compared to control ones (6-8% of the initial TOC).

Ammonia nitrogen concentration in leachate from all reactors remained above 1000 mgN/L at the end of the test; a subsequent aeration phase, as foreseen in the S.An.A. landfill concept, is required for ammonia removal and would be beneficial for the completion of waste biological stabilization.

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2.2 The S.An.A.® Concept: Semi-aerobic, Anaerobic, Aerated bioreactor landfill

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Abstract

Hybrid Bioreactor Landfills are designed to enhance and speed up biological processes, aiming at reducing the duration of post operational phase until landfill completion. S.An.A.® (Semi-aerobic, Anaerobic, Aerated) concept consists in a Hybrid Bioreactor featuring a first semi-aerobic phase to enhance the methane production occurring in the following anaerobic step and a forced aeration for the abatement of the residual emissions. At the end of the last step, semi-aerobic conditions are restored and flushing applied for leaching residual non-biodegradable compounds. Results of the application of S.An.A.® concept to a lab scale bioreactor system showed that pre-aeration was effective in controlling the concentration of VFA, increasing pH and stimulating methane production during anaerobic phase; in particular with intermittent airflow the methane potential was 50% higher respect to control reactors. Forced aeration reduced organic compounds and nitrogen concentration in leachate of an order of magnitude, better performing in low airflow reactors. S.An.A.® Hybrid bioreactors proved to be an efficient system both for increasing methane production and reaching landfill completion in shorter time, suggesting that with proper landfill management, the duration of post-closure care might be reduced by 25-35%.

Keywords

Bioreactor landfill; Hybrid landfill; Landfill aeration; Long-term landfill emissions; Landfill methane production.

2.2.1 Introduction

Landfilling constitutes an unavoidable final step in waste management, being aimed at returning residues to the non-mobile state they were in prior to extraction from the ground and use as raw materials (Cossu, 2016). Although European policies envisage a consistent reduction of untreated MSW deposition (EU 2015), the final disposal of waste will remain a fundamental tool for closing the material cycle. “A Circular Economy cannot exist in the absence of a sustainable closure of the material loop” (Waste Management Editorial, 2016).

In line with the European sustainability principle (EU 2006), reduction of the duration of post operational phase towards landfill completion should be considered a priority and a driver in the proper management and design of landfills. This is currently a heavily debated topic in scientific literature (Laner et al., 2012; Ritzkowski et al., 2016), with local authorities, such as the Lombardy Region (Italy), starting to include this concept in their guidelines (Deliberation of the Regional Council 2461/14). Some authors report that landfills can be safely closed by enhancing the biochemical processes occurring inside and thus guaranteeing environmental acceptability of future emissions. To this regard, the Bioreactor Landfill concept represents a valuable tool for use in reducing the potentially lengthy periods required to achieve these conditions.

Bioreactor Landfills are designed to accelerate waste stabilization processes and several examples of lab and full-scale applications are available (Price et al., 2003; Xu et al., 2014; Berge et al., 2009; Townsend et al., 2015; Cossu et al., 2016). Bioreactors are defined by use of a series of technologies including water or wastewater injection (Cossu et al., 2003; EPA, 2015; Morello et al., 2016), forced or natural aeration (Ritzkowski et al., 2016; Price et al., 2003; Sekman et al., 2011; Raga et al., 2015), leachate recirculation (Sandip et al., 2012; Morello et al., 2016) and other combinations of in situ treatments (Townsend et al., 2015). These options facilitate the control of pH, redox conditions, moisture content, distribution of nutrients and microorganisms (Norbu et al., 2005), oxygen supply for nitrification process, and leaching of inorganics, among others (Shao et al., 2008; He et al., 2011; Erses et at., 2008; Xu et al., 2014). Three main types of landfill bioreactors are commonly considered as far as the metabolic pathway is concerned: anaerobic, aerobic and hybrid bioreactors, the latter providing for a sequence of aerobic and anaerobic conditions (EPA, 2015; Townsend et al., 2015). In particular, Hybrid Bioreactors operate under a series of combinations of aerobic and anaerobic conditions to achieve benefits from both, potentially enhancing biochemical processes and allowing methane production as well as nitrification-denitrification of ammonium ions (Long et al., 2009, Xu et al., 2014; Townsend et al., 2015).

This paper presents an application of the S.An.A.® (Semi-aerobic, Anaerobic, Aerated) Landfill concept (Repetti et al., 2013), which consists in a hybrid bioreactor featuring an initial semi-aerobic phase to enhance methane production occurring in the subsequent anaerobic step and, finally, forced aeration for the abatement of residual emissions (Cossu et al., 2016). At the end of the last step, naturally occurring semi-aerobic conditions will be restored and flushing can be applied for the leaching of residual non-biodegradable compounds.

The aim of the present study was to apply the S.An.A.® concept to four lab-scale landfill simulation reactors, analysing different management options and comparing final results with two traditional anaerobic reactors. Phase 1 was designed to combine the demonstrated advantages of leachate recirculation and landfill pre-aeration, with a greater methane production monitored during Phase 2. Preliminary results were presented in Cossu et al., 2016. This paper reports the results of the full experiment in which the anaerobic Phase 2 was followed by forced aeration in Phase 3, with the aim of completing biological stabilization processes and a final optional Phase 4 involving flushing of inorganics. Flushing is an efficient technology, able to leach out the soluble fractions of landfill contaminants until reaching low concentrations (Bolyard S.C. and Reinhart D.R, 2016); however, it is generally too expensive to be used in real landfills.

In this paper, the results of the entire test were taken into consideration; in particular, final quality of waste, degradation kinetics and comparison between reactor performances were analysed.

2.2.2 Materials and methods

Waste samples

Waste used for the lab-scale test was the residual fraction of Municipal Solid Waste after source segregation, provided by a public waste management company operating in thirteen municipalities of Livorno Province, Tuscany (Italy). A 200 kg sample was sieved using an 80 mm mesh and the fractional composition analysed (Table 2.3.1); the under-sieve (<80 mm fraction) was loaded into bioreactors (Cossu et al., 2016).

Table 2.3.1: Fractional composition of raw waste and undersieve (<80 mm), i.e. the fraction used to fill the reactors. Modified from Cossu et al., (2016).

Trade Class	Raw waste (%)	Undersieve <80 mm (%)
Food Waste	14.0	17.4
Green Waste	6.1	6.0
Paper	22.9	10.5
Plastic	18.4	12.6
Metal	5.2	6.2
Glass and Inert	3.5	3.2
Wood	0.4	0.3
Textiles	8.5	5.1
Undersieve <20 mm	20.9	38.8

Equipment

The experiments were carried out using six Plexiglass® (polymethyl methacrylate) columns (height 106 cm, diameter 24 cm), each filled with 18.4 kg MSW. A 10-cm thick gravel layer (Ø 20-30 mm) was placed at the bottom of each reactor as a drainage layer to facilitate the extraction of leachate. Another similar gravel layer was placed at the top of each column to increase the distribution of distilled water and recirculated leachate (Figure 2.3.1).

The upper end of the reactor body was equipped with three valves providing for the introduction of air, sampling and extraction of gas as well as introduction of liquids. A leachate collection port was located at the bottom of each column and leachate extracted fell directly into a collection tank (5 L capacity). Recirculation of leachate was carried out using programmable peristaltic pumps (Heidolph PD 5001), which automatically pump up leachate from the tank to the liquids introduction valve placed in the top of the reactor. The leachate collection and recirculation system was built to avoid any leakage of leachate and any loss of gas in the circuit (Figure 2.3.1).

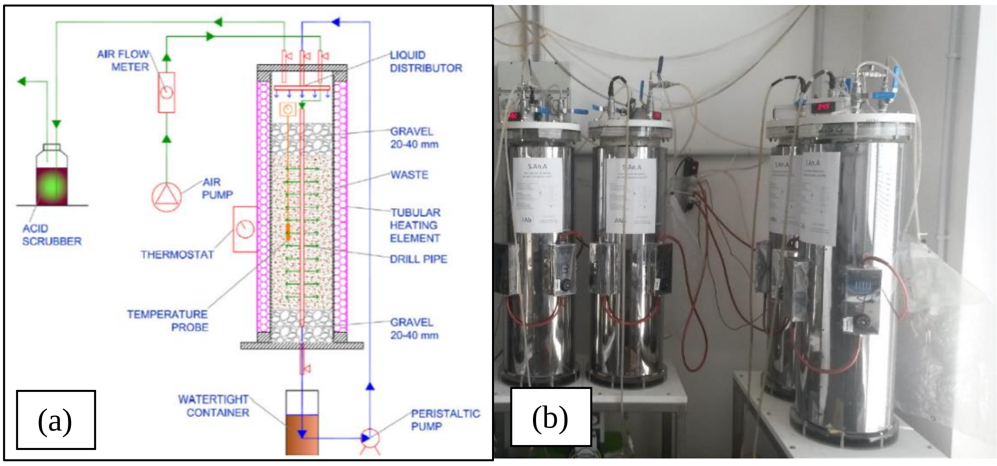

Figure 2.3.1: Reactor setup: (a) sketch and (b) view

To channel air into the waste body, a vertical PVC pipe with side perforations was installed at the centre of the waste layer; this system was designed to guarantee the uniform distribution of air throughout the reactor. Air injection was provided by Prodac Air Professional pump 360, and airflow was regulated by a Sho-Rate GT1135 flow meter. Biogas generated from each column was collected by a Tedlar® sampling bag connected to the upper gas port and its volume and quality were measured by means of a volumetric flow meter.

Temperature monitoring was carried out using Thermo Systems TS100 temperature probes installed inside the reactor and the temperature maintained constant at 38 - 40°C by means of a thermo-regulated insulation system covering all lateral surfaces of the reactor (Figure 2.3.1).

Test Setup

The experiment was divided into three distinct main phases: Semi-aerobic, Anaerobic and Aerobic, in line with the S.An.A.® concept introduced by Repetti et al. (2013) and tested for the first two phases as described in Cossu et al. (2016). Phase 1 was intended to enhance biogas production in the subsequent anaerobic Phase 2. Phase 3 was functional to complete waste stabilization by means of forced aeration. Phase 4 with flushing under semi-aerobic conditions was aimed at removing residual salts and heavy metals (HM).

The six column reactors were filled with the same quantity of waste and run under identical hydraulic conditions for the whole test. Two reactors (ANa and ANb) were run under anaerobic conditions and used as control. Hybrid bioreactors were managed under different conditions as represented in Figure 2.3.2 and described below:

- Reactor HF-I: Intermittent semi aerobic Phase 1 and High Air Flow rate during forced aeration.
- Reactor HF-C: Continuous semi aerobic Phase 1 and High Air Flow rate during forced aeration.
- Reactor LF-I: Intermittent semi aerobic Phase 1 and Low Air Flow rate during forced aeration.
- Reactor LF-C: Continuous semi aerobic Phase 1 and Low Air Flow rate during forced aeration.

At the beginning of the test, 5 L of distilled water were introduced into each reactor and recirculated several times to saturate waste field capacity and produce 2-3 L of process water for sampling and recirculation. Leachate samples (0.1 - 0.25 L) were collected periodically for analysis and replaced each time with the same amount of distilled water.

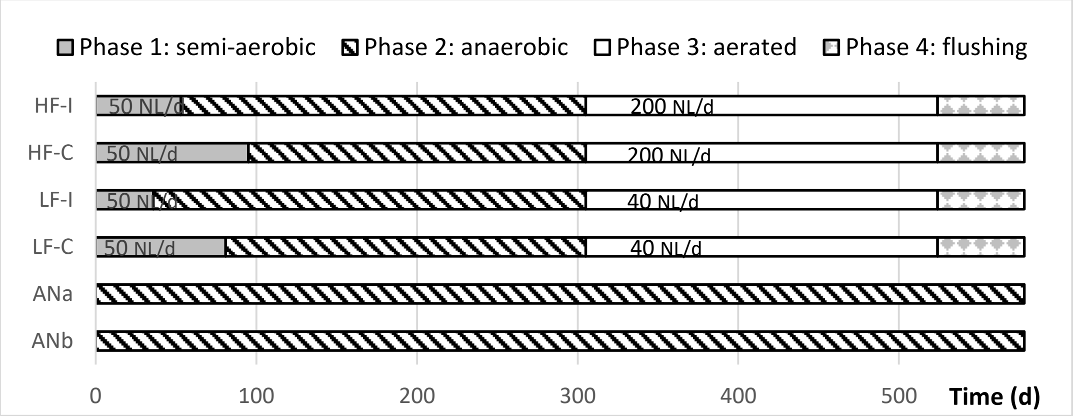

Figure 2.3.2: Lab-scale reactor air management. AN control reactor operated solely in anaerobic conditions while S.An.A.® reactors were subjected to four different phases.

After filling, aeration was commenced in hybrid reactors to simulate semi-aerobic conditions (Figure 2.3.2). At test start up, airflow was set at a low regime and incremented until oxygen was detectable in the off gasses (O_2 > 1-2 %). Daily air flow was the same for all pre-aerated reactors (50 L/d at 20°C) which, in our specific case, corresponded to 5 NL/d/kgTS, TS being the dry matter content (Total Solids) in the reactor. As described by Cossu et al. (2016), this air flow was chosen on the basis of a series of lab-scale experiments carried out on landfill bioreactors in semi-aerobic conditions (Cossu et al., 2003; Sun et al., 2013; Wu et al., 2014). Intermittent aeration (-I reactors) was turned on for 12 hours a day (air flow approximately equal to 0.42 NL/h/kgTS), while continuous aeration (-C reactors) was provided 24 hours a day, seven days per week (air flow equal to 0.21 NL/h/kgTS).

Transition between the different phases was carried out by means of a performance-based method consisting in continuous monitoring of specific parameters in leachate (Table 2.3.2). In particular, the transition between semi-aerobic Phase 1 and the subsequent anaerobic Phase 2 was conducted by monitoring specific chemical parameters capable of guaranteeing optimal conditions for methanogenic bacteria (Cossu et al, 2016).

Anaerobic Phase 2 lasted until methane production was no longer detectable for all reactors; biogas was monitored constantly throughout the whole period and temperature maintained at 38-40°C.

During subsequent Phase 3, air was channelled continuously into S.An.A.® reactors to simulate forced aeration and thus enhance biological degradation processes and promote nitrification for ammonium depletion (Townsend et al., 2015, Berge et al., 2006; Ritzkowski et al., 2016). In Low Air Flow (LF) reactors, air injection was calibrated to maintain oxygen in off gas detectable but lower than 4% (LF-I and LF-C). Consequently, air injection was 40 NL/d, corresponding to approximately 7.7 NL/kgTS/d (Figure 2.3.2). In High Air Flow (HF) reactors, air injection was carried out with the purpose of achieving oxygen levels of more than 14% in off gas (HF-I and HF-C), thus limiting the risk of poorly aerated zones in the reactor (Ritzkowski and Stegmann, 2013; Morello et al., 2016). Air injection in HF reactors was 200 NL/d, corresponding to approximately 38.5 NL/kgTS/d (Figure 2.3.2).

Table 2.3.2: Performance-based parameters and values for leachate samples used to determine the transition between phases and the end of the test.

	Parameter	Values Range	References
Transition from Phase 1 to 2	pH	6.7-7.4	Lay et al., (1998)
		6.4-7.2	Chugh et al., (1998)
		6.5-8.2	Sekman et al., (2011)
		6.65-7.41	Sandip et al., (2012)
		6.25 - 8.00	Cossu et al., (2016)
	Alkalinity (mg$CaCO_3$/L)	1000-5000	Agdag et al., (2005)
		2000-3500	Sekman et al., (2011)
	Volatile Fatty Acids (mgCH_3COOH/L)	< 6000	Wang et al., (1999)
		< 7100	Cossu et al., (2016)
Transition from Phase 2 to 3	Area-specific methane production (L_{CH4}/d/m^2)	< 0.5	Detection Limit
		< 0.1 - 0.5	Laner et al., (2012)
Stop of forced aeration	COD (mgO_2/L)	< 1500	D.G.R. 2461/14
	BOD_5/COD	< 0.1	D.G.R. 2461/14
		< 0.13	Sekman et al., (2011)
	Ammonium (mgN/L)	< 300	Laner et al., (2012)
		< 50	D.G.R. 2461/14
	RI_4 (mgO_2/gTS)**	< 2,5	Laner et al., (2012)
Test end	Nitric nitrogen (mgN/L)	< 20	D.G.R. 2461/14
	Sulfates (mg/L)	< 1000	D.G.R. 2461/14
	Chloride (mgN/L)	< 1200	D.G.R. 2461/14

**Methane was monitored in biogas emissions.*

***RI_4 was monitored in solid samples.*

Forced aeration was stopped once waste and leachate characteristics in all S.An.A.® reactors featured values constantly below those illustrated in Table 2.3.2. Among them, BOD_5/COD ratio below 0.1, ammonium below 50 mg/L and respiration index in solid waste

(RI_4) under 2.5 $mgO_2/kgTS$ were recommended to reach biochemical stability of waste (Laner et al., 2012; Sekman et al., 2011; D.G.R. 2461/14).

After aeration stop (day 524), reactors were again managed under semi-aerobic conditions, with natural air circulation enhanced by opening the top and the bottom valves of reactors, increasing water supply to simulate flushing (Figure 2.3.2). Leachate production was increased to 1 L/w to stimulate the dilution and leaching of inorganic compounds (sulphates, chloride, nitric nitrogen and heavy metals). This Phase 4 lasted for 7 weeks, starting from L/S ratio = 2.19 L/kgTS, reaching 3.35 L/kgTS, when all target values illustrated in Table 2.3.2 were achieved.

At the end of the test, all monitored parameters in hybrid reactors reached values listed in Table 2.3.2; in the anaerobic control reactor ammonium leaching was not sufficient to reach a concentration lower than 50 mgN/L, even after flushing.

At the end of the test, monitoring data were used to evaluate total compound emissions for each column (carbon, nitrogen, chloride and HM), and estimate the quantity of compounds still present in the waste.

Reaction kinetics and leaching rates were evaluated to allow a mathematical comparison to be made between performances of S.An.A.® reactors and controls. Biogas production during Phase 2 was simulated by means of a kinetic model derived from the Gompertz Growth Equation, calibrated with biogas daily data (Cossu et al., 2016). This model has a sigmoid shape with a clear inflection point and its output is the cumulative volume of methane produced from the bioreactors according to Equation 1 (Lay et al., 1998; Sandip et al., 2012).

$$BG = BGP * \exp\left\{-\exp\left[\frac{Rm * e}{BGP} * (\lambda - t) + 1\right]\right\} \tag{1}$$

BG is cumulative methane yield (mL/gVS), t is cumulated time (d), BGP is methane yield potential (mL/gVS), R_m is maximal daily methane yield (mL/gVS/d), λ is bacteria growth lag time (d) and e is a mathematical constant (=2.718). Calibration of the Gompertz Equation was carried out by minimizing mean square deviation of the values measured and calculated.

COD and ammonium ion consumption during Phase 3 were simulated by means of a first order kinetic Equation (2): C_t is concentration at time t, C_0 is the initial concentration and k (t^{-1}) the kinetic constant. Similarly, chloride leaching in Phases 3 and 4 was simulated with a first order equation calibrated on L/S ratio as control variable, instead of time.

$$C_t = C_0 * e^{-k*t} \tag{2}$$

Calibration of the single kinetic constant was carried out by minimizing mean square deviation of the values measured and calculated.

Analytical methods

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

A portable analyser (Eco-Control LFG20) was used to measure CO_2, CH_4 and O_2 concentrations in biogas, collected in the Tedlar bags, on at least a weekly basis. Stripped N-$NH_{3(g)}$ was measured through an acid scrubber placed immediately after the off-gas valve of each reactor (Figure 2.3.1). Boric acid 0.5 M was used as scrubber and emission results were periodically compared with a portable gas analyser (Analitica Strumenti LFG 2000).

Leachate samples were analysed periodically for pH, COD, TOC, BOD_5, TKN, N-NH_4^+, N-NO_3^-, SO_4^{2-}, Cl^- and Heavy Metals (Cr, Cu, Fe, Mn, Ni, Pb, Zn) according to the prescribed Italian standards, derived from international certified procedures (CEN, 2002).

Waste was sampled for characterization prior to reactor filling and at the end of the test, following complete extraction of the material and mixing in a tank to increase homogeneity.

Waste characterization at the end of the anaerobic phase comprised complete extraction of the waste from each reactor and mixing in a tank to increase homogeneity. Following this procedure, solid samples were milled to 4 mm prior to determining TS, VS, TOC, TKN, Cl^-, RI_4 and heavy metals. TOC on solid samples was measured using a TOC-VCSN Shimadzu Analyser. Respiration Index (RI_4 and RI_7 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 waste samples (L/S was brought to 10 L/kgTS, mixed for 24 hours and filtered at 0.45 µm). The eluate obtained was analysed to evaluate the emission potential of some contaminants considered in leachate (COD, BOD_5, N-NO_3^-, and Cl^-). BOD_5/COD ratio is a parameter capable of indicating the amount of biodegradable compounds still present in a liquid (Cossu et al., 2012), assuming values between 0.02 and 0.13 for low biodegradability (Sekman et al., 2011) and values exceeding 0.4 for high biodegradability (Kjeldsen et al., 2002).

All tests on solid samples were performed at least in duplicate.

2.2.3 Results

Solids

The fractional composition of waste loaded into reactors was characterized by high amounts of food waste, plastic, paper and fines. Minor quantities of green waste, metals, glass, wood and textiles were detected (Table 2.3.1).

The results of waste characterization at both the beginning and the end of the test are reported in Table 2.3.3. Waste wet mass decreased from the initial value of 18.4 kg per column (Total Solids TS = 55.0%), to values between 12 and 13 kg in the different reactors at the end of the test (TS = 37.1-43.2), indicating a significant drop in waste dry mass. Concomitantly, Volatile Solids (VS) displayed a similar trend, starting from 58.9 %TS and decreasing to 22.8 – 44.0 %TS, due to degradation processes. TOC decreased by about 30% during Phases 1 and 2 (Cossu et al., 2016) and by about 60% throughout the whole test.

During the test, BOD_5/COD ratio decreased from an initial value of 0.51 to reach values below 0.06 in all reactors (Table 2.3.3). RI_4 and RI_7 Respiration Indices confirmed the low residual degradability of samples. From initial values of 76.9 mgO_2/gTS, RI_4 decreased to reach values of less than 2.5 mgO_2/gTS (Table 2.3.3), the target value indicated by Laner et al. (2012) in Table 2.3.2.

Table 2.3.3: Solid waste characterization in initial and final samples (Average ± SD).

	Initial Sample	Final Samples					
	All Reactors	HF-I	HF-C	LF-I	LF-C	ANa	ANb
TS (%)	55.0 ± 1.0	37.0 ± 0.1	40.9 ± 0.1	41.4 ± 0.5	43.2 ± 1.6	40.1 ± 2.7	40.9 ± 0.3
VS (%TS)	58.9 ± 1.1	36.1 ± 0.1	32.5 ± 1.6	28.4 ± 2.7	22.8 ± 2.4	44.0 ± 0.4	36.5 ± 0.1
TOC (gC/kgTS)	368 ± 10	217 ± 38	197 ± 44	220 ± 47	216 ± 20	221 ± 12	226 ± 39
TKN (gN/kgTS)	9.7 ± 0.5	7.1 ± 0.4	7.0 ± 0.5	7.2 ± 0.1	7.3 ± 0.1	7.6 ± 0.6	7.6 ± 0.2
Cl^- (gCl-/kgTS)*	7.2 ± 0.1	1.5 ± 0.1	1.1 ± 0.2	1.0 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	1.1 ± 0.2
RI_4 (mgO_2/gTS)	76.9 ± 2.4	2.4 ± 0.2	2.1 ± 0.1	2.2 ± 0.2	2.3 ± 0.1	6.2 ± 0.8	6.0 ± 0.2
RI_7 (mgO_2/gTS)	79.3 ± 4.4	4.5 ± 0.3	4.3 ± 0.2	3.9 ± 0.3	3.8 ± 0.1	9.4 ± 1.3	9.4 ± 0.2
BOD_5/COD*	0.51 ± 0.2	0.04 ± 0.1	0.04 ± 0.1	0.06 ± 0.1	0.04 ± 0.1	0.04 ± 0.1	0.04 ± 0.1
$N\text{-}NO_3^-$ (mg/L)*	< 10	< 1	< 1	< 1	< 1	< 1	< 1

**Obtained thoughout analysis on eluate of a standard leaching test UNI EN 12457-2.*

TKN content in solid samples decreased slightly in all columns during Phases 1 and 2 (Cossu et al., 2016) as nitrogen emissions occurred only via leaching and no nitrification was detected. On the contrary, during forced aeration in Phase 3, the presence of oxygen promoted the nitrification process, which consumed efficiently ammonia ion. TKN content in solid waste was reduced by 24% in S.An.A.® reactors, whilst only an 18% reduction was detected in anaerobic control reactors (Table 2.3.3).

Chloride emission potential decreased by 79 - 85% from the beginning to the end of the test due to rapid dissolution into leachate, as reported in other similar landfill simulation experiments (Fellner et al., 2009).

Leachate

Evolution of the main parameters of carbon, nitrogen, sulphates and chloride, monitored in leachate samples extracted from the reactors throughout the test, is reported in Figures 2.3.3 and 2.3.4.

Effect of pre-aeration on pH increase due to VFA consumption is clearly visible in Figure 2.3.5. As illustrated in Table 2.3.2, pre-aeration in S.An.A.® reactors was stopped after reaching a pH of 6.25 and 7100 $mgCH_3COOH$/L VFA, corresponding to 35 d (LF-I) and 55 d (HF-I) in intermittent reactors, and 81 d (LF-C) and 95 d (HF-C) in continuous ones. These test phases have been discussed in Cossu et al. (2016), reporting a beneficial effect of pre-aeration, especially with intermittent airflow (HF-I and LF-I).

At the beginning of Phase 2, methane production started and COD dropped from about 70000 mg/L to less than 5000 mg/L and BOD_5/COD ratio decreased from 0.8 to 0.1 (Figure 2.3.3), reaching biochemically-stable conditions (Sekman et al., 2011).

Ammonium ion concentrations remained higher than 1000 mgN/L throughout Phases 1 and 2, in which ammonification increased NH_4^+ content and the only possible emission was solubilization and leaching. During Phase 3, forced aeration allowed nitrification processes, consuming ammonia ion until the established target value of 50 mg/L was reached (Figure 2.3.3).

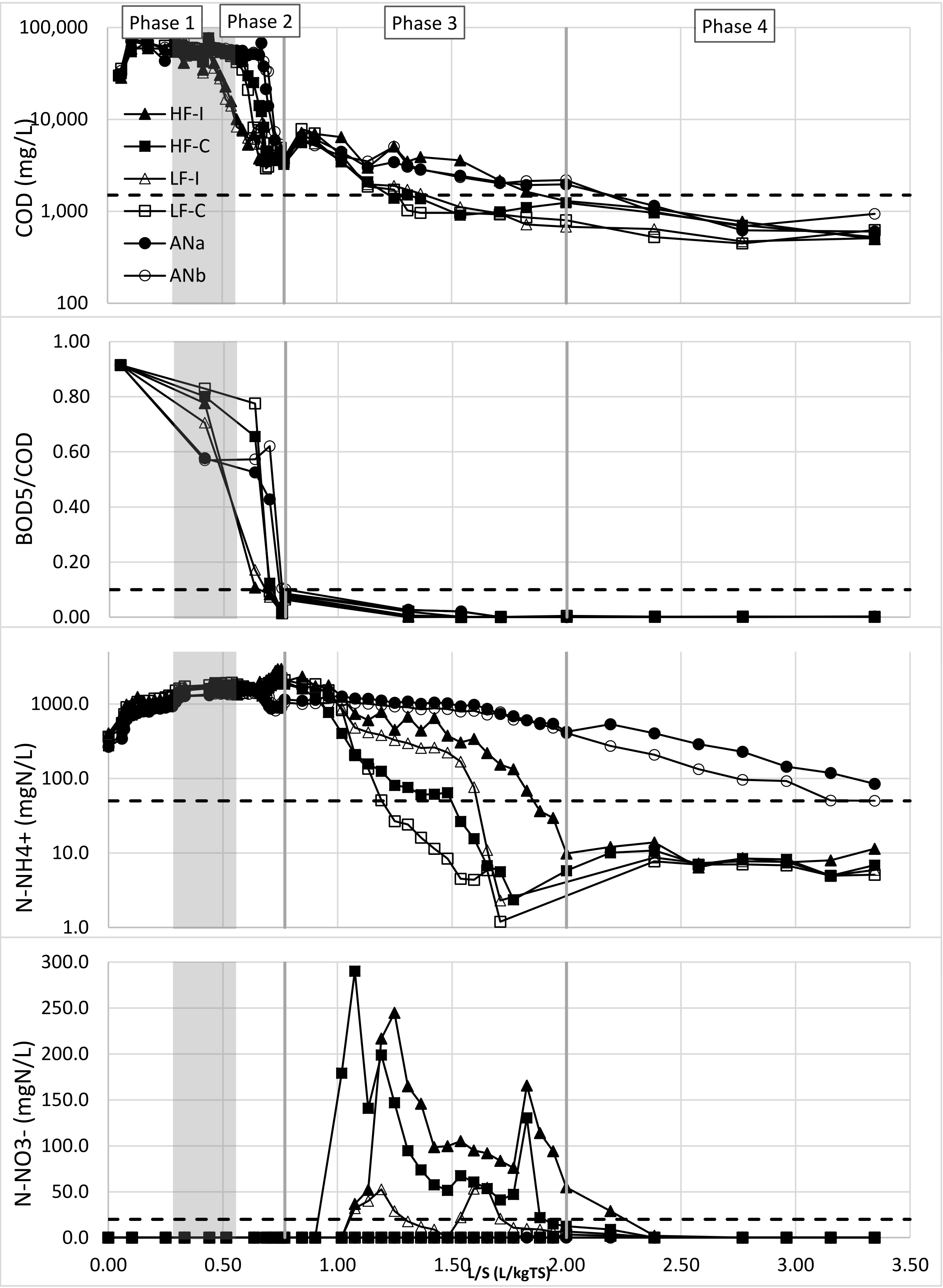

Figure 2.3.3: Carbon and Nitrogen index monitoring in leachate (COD, BOD_5/COD, N-NH_4^+, N-NO_3^-). Grey vertical lines indicate the passage between the four phases while the dotted horizontal line indicates the performance-based limits of Table 2.3.2. COD and N-NH_4^+ are reported in logarithmic scale.

As observed by other authors (Berge et al., 2006; Raga and Cossu 2013) denitrification is likely to occur in anoxic zones of aerated reactors. During aerobic Phase 3, lower NO_3^- concentrations than those expected from stoichiometry calculations for nitrification were detected, suggesting the possible development of simultaneous denitrification processes. NO_3^- concentrations up to 300 mg/L were observed in HF reactors; lower values, always below 50 mg/L, were measured in LF reactors where the lower air flow probably caused the presence of more extensive anoxic zones suitable for denitrification than in HF reactors (Figure 2.3.3).

Sulphate concentrations decreased constantly during Phases 1 and 2, from an initial 2250 mg/L, to 500 mg/L. During aeration in Phase 3, the opposite process happened due to high oxygen availability, with sulphate concentrations once again increasing in S.An.A.® reactors only (Figure 2.3.4). Finally, in Phase 4, all remaining sulphates were removed by flushing and final concentrations below the target value of 1000 mg/L were reached.

Cl^- emissions were dependent only on solubilization and leaching. From initial values of up to 4000 mg/L, chloride concentration decreased to below the target value of 1200 mg/L in the same way in all reactors (Figure 2.3.4).

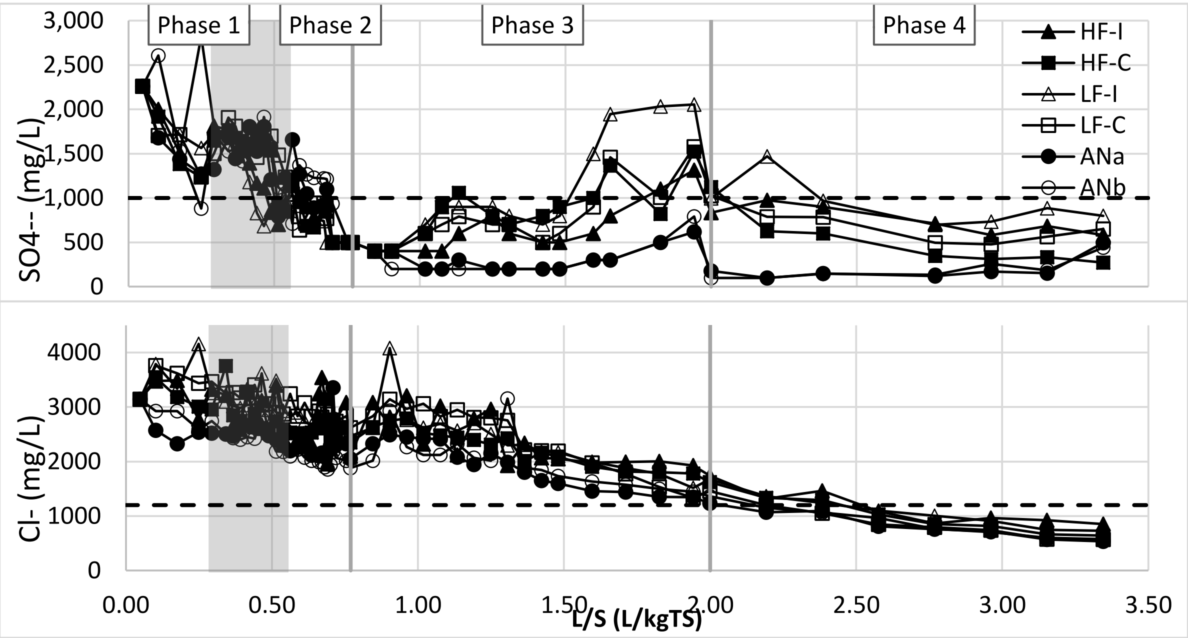

Figure 2.3.4: Sulphates and chloride monitoring in leachate. Grey vertical lines indicate the passage between the four phases while the dotted horizontal line indicates the performance-based limits of Table 2.3.2.

Biogas

The evolution of cumulative gaseous emissions is reported in Figure 2.3.5. Methane, carbon dioxide, oxygen and stripped ammonia were all closely monitored.

Methane emissions were limited to anaerobic Phase 2 and influenced by pre-aeration mode: intermitted reactors emitted up to 32 gC/kgTS of methane, performing better than continuous reactors and consistently better than control reactors, which produced less than 15 gC/kgTS of methane (Cossu et al., 2016).

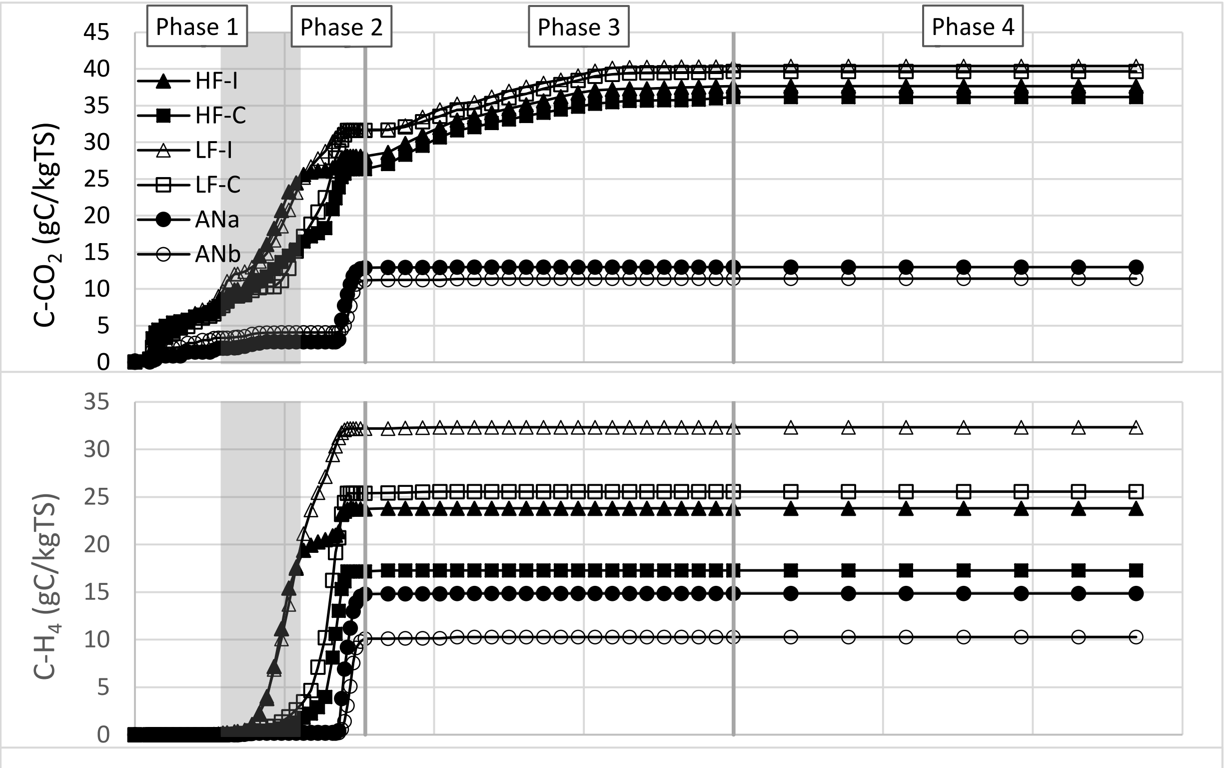

Figure 2.3.5: Carbon dioxide, methane and stripped ammonia monitoring in gaseous emissions and pH monitoring in leachate. Grey vertical lines indicate the passage between the four phases.

Carbon dioxide emissions in hybrid reactors were registered throughout the test period, in concentrations up to 70% during Phase 1 and around 40% during anaerobic Phase 2; subsequently, these percentages progressively decreased to zero. Massively higher emissions were detected during Phase 2, concomitant with methane production, and during aeration in Phase 3 (Figure 2.3.5). At the end of the test, S.An.A reactor emitted 35 – 40 gC/kgTS, while control columns emissions were below 12 gC/kgTS.

Stripped ammonia volatilization was only observed during Phase 3 in aerated reactors, although pH values were slightly below 8 (Figure 2.3.5). HF reactor emitted a total of 0.17 - 0.20 gN/kgTS, LF-I reactor emitted 0.04 gN/kgTS, while no emissions were detected in LF-C and anaerobic reactors.

2.2.4 Discussion

Emissions evaluation

Total emissions percentages, respect to initial content of each compound in the waste sample, are reported in Table 2.3.4.

Table 2.3.4: Percentages of carbon, nitrogen, chloride and heavy metal emissions respect to initial compound content in solid waste sample.

Emissions (%)			HF	LF	AN
Carbon	Leachate	TOC	2.6 ± 0.1	2.4 ± 0.4	3.1 ± 0.1
		VFA	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.1
	Gas	$C\text{-}CH_4$	5.4 ± 1.2	7.7 ± 1.3	3.3 ± 0.9
		$C\text{-}CO_2$	9.8 ± 0.3	10.6 ± 0.1	3.2 ± 0.3
Nitrogen	Leachate	$N\text{-}NH_4^+$	16.9 ± 4.3	16.4 ± 0.4	22.6 ± 2.3
		N-Norg	5.0 ± 1.2	4.3 ± 0.6	5.6 ± 0.2
		$N\text{-}NO_3^-$	1.1 ± 0.1	0.2 ± 0.1	0.0 ± 0.0
	Gas	$N\text{-}NH_{3g}$	1.9 ± 0.2	0.3 ± 0.2	0.0 ± 0.0
Chloride	Leachate	Cl^-	88.6 ± 3.6	90.4 ± 2.2	73.8 ± 1.9
Heavy Metals	Leachate	Cr	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.3
		Cu	2.9 ± 0.3	2.1 ± 0.2	1.6 ± 0.1
		Fe	1.3 ± 0.1	1.3 ± 0.2	1.2 ± 0.1
		Mn	7.8 ± 2.2	7.9 ± 2.4	10.0 ± 0.8
		Ni	6.5 ± 0.2	6.9 ± 2.0	8.5 ± 0.7
		Pb	1.2 ± 0.8	0.7 ± 0.1	0.8 ± 0.1
		Zn	4.4 ± 0.5	3.4 ± 0.4	3.6 ± 0.2

TOC emissions in leachate totalled 2.4 - 2.6 % respect to initial content in solid samples in S.An.A.® reactors, and were a little higher (3.1 %) in control ones in which the concentrations of organic compounds in leachate remained higher. Total methane production (5.4 – 7.7 % of initial content in solid samples) was lower than carbon dioxide production (9.8 - 10.6 % of initial content in solid samples) due to the forced aeration performed during Phase 3 (Table

2.3.4). These data also confirm that carbon emitted via leachate in aerated bioreactors is generally one order of magnitude lower than carbon emitted in biogas; this finding is in agreement with the observations of other authors (Lornage et al., 2013). Monitoring of control reactors highlighted a fifty percent reduction in carbon gaseous emissions compared to hybrid reactors, confirming the effectiveness of pre-aeration in methane generation enhancement (Cossu et al., 2016; Sang et al., 2009; Erses et al., 2008), and the need for aerobic treatment to achieve a persistent depletion of organic compounds (Heyer et al., 2013; Raga and Cossu, 2013; Ritzkowski and Stegmann, 2013).

Nitrogen emissions in leachate were mainly due to ammonium ions and, to a lesser extent, to organic nitrogen, which had been ammonified almost completely during Phases 1 and 2, and nitrates, which had been produced during forced aeration in Phase 3 (He et al., 2011; Ritzkowski et al., 2006). Cumulative emissions of ammonium ions were found to be higher in control (22.6 % of initial content in solid samples) than in S.An.A.® reactors (16.4 – 16.9 %) because nitrification-denitrification was not possible in AN columns, and because the fact that high NH_4^+ concentrations in leachate persisted until the end of the test (Table 2.3.4). Nitrate emissions were monitored only in aerated reactors, particularly in HF (1.1 % of initial content in solid samples) in which denitrification was slowed down by the excess of oxygen. Stripped ammonia emissions were monitored only in S.An.A.® reactor, in particular in HF (1.9 % of initial content in solid samples), enhanced by excess of air circulation and slightly favourable pH conditions (Morello et al., 2016).

Total chloride emissions were 90.4 – 88.6 % respect to initial content in solid samples in hybrid reactor and slightly lower in controls (73.8 %), depending on solubilization conditions, pH and leaching processes. These emission percentages were comparable with data present in literature (Fellner et al., 2009; Raga and Cossu, 2013).

Heavy metal emissions in leachate are generally not considered to be of environmental interest due to their low mobility (Qu et al., 2008), although they are often present at considerably high levels in solid waste (Oygard et al., 2004). The emission of heavy metals is influenced by pH and other complex chemical equilibriums depending on HM form: ion exchangeable, carbonate-bound (adsorbed), as metal-organic complexes (associated with humic and fulvic acids), as easily reducible metal-oxides, bound to organic matter (other than humic and fulvic acids), in amorphous mineral colloids, as crystalline iron-oxides and bound to aluminium-silicate minerals (Krishnamurti et al., 2002). In this test, total HM emissions did not exceed 10% of initial presence in solid waste, in particular Mn and Ni were more mobile than others, and Fe concentrations remained high until the end of the test (Table 2.3.4). A decrease of Mn and Ni emissions was observed in S.An.A.® reactor compared to control reactors, while a small increase was detected for Cu.

Kinetic performances

Reactor performances were mathematically evaluated calibrating the Gomperts model (Equation 1) for methane production during Phase 2, the first order kinetic model (Equation

2) for COD, ammonia ion depletion during Phase 3, and for chloride solubilization throughout the entire test (Table 2.3.5).

Table 2.3.5: S.An.A.® performance evaluation through calibration of Gompertz model for methane production in Phase 2, first order kinetic model for COD and ammonium ion depletion during Phase 3, and first order kinetic model for chloride leaching throughout the whole test. Duration of single phase was calculated with the calibrated limits model illustrated in Table 2.3.2.

Reactor	Phase 1	Phase 2					Phase 3				Entire Test		
	Duration (d)	Duration (d)	Gompertz model Parameters				COD		N-NH4+		Total Duration (d)	Cl-	
			pH	BGP (NL/ kgVS)	Rm (NL/d/ kgVS)	λ (d)	Duration (d)	Kc (d^{-1})	Duration (d)	Kn (d^{-1})		Total L/S (L/kgTS)	Kcl (KgTS/L)
HF-I	55	147	6.46	72.7	1.6	12.3	119	0.010	133	0.025	321	2.58	0.27
HF-C	95	119	6.46	55.5	0.8	15.7	70	0.019	91	0.054	284	2.58	0.31
LF-I	35	166	6.25	102.3	1.7	34.2	91	0.019	105	0.027	292	2.58	0.27
LF-C	81	133	6.34	81.8	1.2	21.5	63	0.028	56	0.041	277	2.38	0.27
ANa	0	270	--	55.8	0.8	168	161	0.011	>203	0.005	431	2.19	0.45
ANb	0	270	--	34.8	0.5	192	161	0.009	>203	0.005	431	2.19	0.45

As discussed in Cossu et al., (2016), pre-aeration was effective in controlling the concentration of VFA, decreasing pH, stimulating methanogenesis and reducing lag time (λ). In S.An.A.® reactors, total methane potential (BGP) and a higher increase in production kinetics (Rm) was observed than in control columns (Table 2.3.5). The duration of Phase 1 was equal to the time required to reach optimum conditions for methanogenesis, while the duration of other phases was calculated as the time required to reach conditions illustrated in Table 2.3.2, using the kinetic models calibrated with data from actual reactors.

During forced aeration Phase 3, COD depletion kinetics were generally increased in hybrid reactors, particularly LF. Concomitantly, nitrification-denitrification facilitated ammonia ion depletion, which was consumed 5 – 10 times kinetically faster than in control reactors, in which leaching effect alone contributed to NH_4^+ attenuation (Table 2.3.5).

Chloride leaching kinetics were evaluated in comparison with L/S ratio, not depending directly on biological processes. The results obtained show that 2.19 L/kgTS were sufficient to achieve the target value in anaerobic control reactors, performing better than hybrid columns, which required 2.38 - 2.58 L/kgTS to achieve the same result (Table 2.3.5).

Taking into account all the results obtained, the best performing reactor was LF-I, characterized by low air flow aeration during Phase 3 (7.7 NL/kgTS/d), and by intermittent pre-aeration during Phase 1 (5 NL/kgTS/d, 12h/d). These conditions were conducive to requiring only 35 days of pre-aeration, a higher production of methane (102.3 NL/kgVS) with faster kinetic (1.7 NL/d/kgVS), and to reaching target conditions illustrated of Table 2.3.2 over a period of 105 days, in line with other S.An.A.® reactors.

2.2.5 Conclusions

The S.An.A.® bioreactor landfill concept proved to be an efficient system both in increasing methane production and achieving sustainable conditions over a 25 – 35 % lower time frame compared to traditional anaerobic systems.

Pre-aeration was effective in controlling the concentration of VFA, increasing pH and stimulating methanogenesis during the anaerobic phase. S.An.A.® concept proved capable of increasing BGP and kinetics velocity, particularly applying intermittent aeration (5 NL/d/kgTS, 12 h/d).

Forced aeration performed during Phase 3 successfully increased COD depletion kinetics in LF reactors by more than 67 %. Moreover, air supply promoted the nitrification process, consuming ammonium ions ten times faster than the leaching effect observed in control columns. By guaranteeing the presence of approx. 4 % of oxygen in off gas, reactors with low air flow aeration (7.7 NL/kgTS/d) performed better than those with high air flow, showing faster kinetics, stimulating nitrification and simultaneous efficient denitrification of nitrates produced, with a lower energy consumption.

Chloride leaching was more efficient in control respect to S.An.A.® reactors, reaching target concentrations after L/S = 2.19 L/kgTS, and emitting 73.8% of initial chloride content. Flushing was also the sole means of achieving long-term depletion of ammonium ions and persistent organic compounds in anaerobic control reactors, although less efficient respect to aeration.

The S.An.A.® concept performed best in the presence of intermittent pre-aeration (5 NL/d/kgTS, 12h/d) during Phase 1, and low air flow forced aeration following methane production during Phase 3.

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2.4 Recirculation of reverse osmosis concentrate in lab-scale anaerobic and aerobic landfill simulation reactors

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Abstract

Leachate treatment is a major issue in the context of landfill management, particularly in view of the consistent changes manifested over time in the quality and quantity of leachate produced, linked to both waste and landfill characteristics, which renders the procedure technically difficult and expensive. Leachate recirculation may afford a series of potential advantages, including improvement of leachate quality, enhancement of gas production, acceleration of biochemical processes, control of moisture content, as well as nutrients and microbe migration within the landfill. Recirculation of the products of leachate treatment, such as reverse osmosis (RO) concentrate, is a less common practice, with widespread controversy relating to its suitability, potential impacts on landfill management and future gaseous and leachable emissions. Scientific literature provides the results of only a few full-scale applications of concentrate recirculation. In some cases, an increase of COD and ammonium nitrogen in leachate was observed, coupled with an increase of salinity; which, additionally, might negatively affect performance of the RO plant itself. In other cases, not only did leachate production not increase significantly but the characteristics of leachate extracted from the well closest to the re-injection point also remained unchanged. This paper presents the results of lab-scale tests conducted in landfill simulation reactors, in which the effects of injection of municipal solid waste (MSW) landfill leachate RO concentrate were evaluated. Six reactors were managed with different weekly concentrate inputs, under both anaerobic and aerobic conditions, with the aim of investigating the short and long-term effects of this practice on landfill emissions. Lab-scale tests resulted in a more reliable identification of compound accumulation and kinetic changes than full-scale applications, further enhancing the development of a mass balance in which gaseous emissions and waste characteristics were also taken into consideration. Results showed that RO concentrate recirculation did not produce consistent changes in COD emissions and methane production. Simultaneously, ammonium ion showed a consistent increase in leachate (more than 25%) in anaerobic reactors, free ammonia gaseous emissions doubled with concentrate injection, while chloride resulted accumulated inside the reactor.

Keywords

Landfill leachate treatment; Recirculation of reverse osmosis concentrate in landfill; Persistent emissions in landfill; Injection of wastewaters in landfills; Bioreactor landfill

2.4.1 Introduction

Leachate emissions are one of the main sources of environmental risks originated by landfills, especially in case of uncontrolled leakages during aftercare period. This environmental dangerousness comes from the leachate content of inorganic salts, heavy metals, persistent organic matter, xenobiotic compounds, microorganism, etc., which can be monitored in consistent concentrations also during long-term phases (Kjeldsen el al., 2010; Zhang et al., 2013). For this reason, leachate treatment is a major issue in the context of landfill management: treatment design should take into account not only quantity and quality but also variation over time, in line mainly with landfill age (Brennan et al., 2015). Amongst the various forms of leachate treatment, membrane filtration consists in a physical process that separates wastewater into two different fluxes through use of a membrane; this in turn results in the production of a filtrate capable of crossing the membrane, and a concentrate in which compounds not able to cross the membrane accumulate. Membrane processes are generally classified as microfiltration (MF), ultrafiltration (UF) or reverse osmosis (RO), according to the decreasing dimension of membrane pores (Renou et al., 2008; Zhang et al., 2013). Filtration efficiency is related not only to pore dimension but also to the type of membrane material, the nature of the driving force, the separation mechanism and the nominal size of the separation achieved (Metcalf & Eddy, 2004; Subramani and Jacangelo, 2014). Treating leachate, RO is the membrane treatment with the highest removal efficiency: retention of 80-95% organic substances and 60-70% inorganic compounds in a single membrane process; if stages further down the line are taken into consideration these percentages increase to more than 99% (Hunce et al., 2012; Renou et al., 2008; Henigin, 1993; Eipper and Maurer, 1999). The semipermeable RO membrane has a porosity of several nanometers in which a pressure higher and opposite than osmotic one is applied, thus enhancing separation of permeate and concentrate. The main issues encountered with this technology are the high membrane and management costs and membrane fouling that requires periodic cleaning (Metcalf & Eddy, 2004; Talalaj and Biedka, 2015). Concentrate-permeate ratio ranges from 1:4 to 1:5 in a reverse osmosis treatment, depending on the treatment plant and wastewater characteristics; this ratio is generally respected also with leachates (Henigin, 1993). At the end of the process, the remaining concentrate (20-25% the initial wastewater volume) requires further treatment. The most effective treatments for leachate concentrate include incineration in an appropriate facility, solidification with materials such as fly ashes, mixing with sludge from municipal wastewater treatment, dewatering-disposal in industrial landfills and recirculation into the landfill body (Peters, 1998; Subramani and Jacangelo, 2014). The latter procedure is a cheaper and more easily implementable option; however, results found in literature are still conflicting since success and issues with the effects of concentrate recirculation have been reported (Talalaj and Biedka, 2015).

Rainwater and occasionally recirculated leachate are the sole contributors to moisture management in conventional landfills, whilst in bioreactor landfills injection of storm water, wastewater, and wastewater treatment sludge may be implemented (EPA, 2015). Bioreactor landfills are characterized by the use of technologies such as water and/or air injection, leachate recirculation and other combinations of in-situ treatments that facilitate biochemical kinetic control, nitrification, pH adjustment, control of redox conditions and moisture content to create a more suitable environment for the enhancement of degradation processes (Berge et al., 2009; Townsend et al., 2015). Recirculation of concentrate therefore is in line with the bioreactor concept. This practice affords similar advantages to leachate recirculation, redistributing moisture and nutrients inside the landfill body and promoting biochemical processes. MSW can act either as compounds source and as storage, having relevant water sorption capacity, effectively entrapping metals and consuming easily biodegradable substances. However, waste capacity of attenuating ammonia and chloride coming from recirculated leachate was found to be negligible (Calabrò and Mnacini, 2012).

Field experiments have shown contradictory results: in Italy, the recirculation of concentrate is a practice commonly adopted in a series of old landfills where this type of wastewater is viewed as a process liquid. According to Calabrò et al. (2010), the reinjection of RO concentrate does not affect leachate quality, due to an apparent buffer capacity of the waste mass on ammonium (NH_4^+) and chloride (Cl^-). On the contrary, according to other authors, concentrate reinjection is not deemed to be sustainable in the long term due to a persistent accumulation of pollutants (Henigin, 1993; Talalaj and Biedka, 2015) which exerts an immediate effect on leachate characteristics, increasing COD and ammonium concentration (Robinson, 2005; He et al, 2015). In field-scale also hydraulic consideration must be taken into account since dried wastes has a high capacity of retaining waters before reaching field capacity.

The purpose of this paper was to investigate the effects of concentrate reinjection in an MSW landfill using lab-scale simulation reactors, contributing to the debate concerning sustainability of RO concentrate recirculation, engaged by many literature studies (Calabrò et al., 2010; Robinson, 2005; He et al, 2015; Talalaj and Biedka, 2015). Lab-scale tests could provide more precise evidence of compound accumulation than full-scale applications in which the heterogeneity of waste may buffer accumulation effects. The management of reactors foreseen different weekly concentrate inputs and a constant monitoring of leachable and gaseous emissions, useful for a subsequent elaboration of data for clarifying the short and long-term effects of this practice. Monitoring of emissions was focused on three specific components: carbon and nitrogen compounds, plus chloride as salinity index tracer. In particular, salts are not biodegradable, can accumulate inside solid mass (Zhang et al., 2013) and affect negatively RO membrane performances (Talalaj and Biedka, 2015). Aeration was applied to half of reactors, in order to identify whether the proven efficiency of aeration techniques in remediating the persistence of carbon and nitrogen compounds in leachate (Ritzkowski et al., 2006; Calabrò anc Mancini, 2012) might also mitigate the possible accumulation of these compounds following injection of concentrate. Literature evidenced that recirculation of aerobically treated concentrate inside an anaerobic lab scale reactor could have positive effects on leachate quality (He et al., 2015). Finally, a mass balance was developed for carbon, nitrogen and chloride, based on the results obtained from monitoring of the liquid and gaseous emissions.

2.4.2 Materials and methods

Equipment

Experiments were carried out using six plastic columns (height 106 cm, diameter 24 cm) filled with 14.7 kg of MSW compacted to reach a density of around 0.5 t/m^3. A 15-cm thick gravel layer (20-40 mm) was placed at the bottom and a 5-cm layer at the top of each column as drainage to facilitate the distribution of moisture and concentrate (Figure 2.4.1).

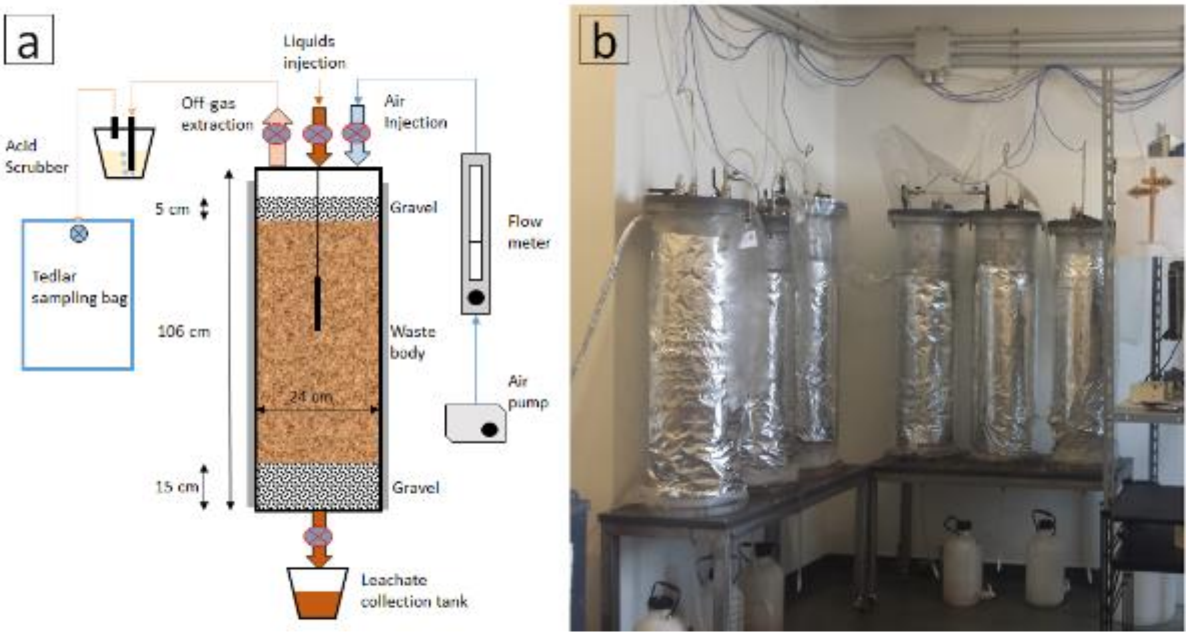

Figure 2.4.1: Sketch (a) and picture (b) of reactor setup at the beginning of the test.

Leachate extraction was carried out through a valve on the bottom of the reactor, connected directly with an accumulation tank to ensure against loss of biogas. A further three valves were used for air injection, gas extraction and liquid input from the top of the lab-scale equipment. Liquid distribution inside the reactor was sufficiently homogeneous thanks to a shower system distribution and the top gravel layer. Injected air was channeled into a vertical pipe with side perforation placed inside the waste body to promote a uniform distribution of air throughout the reactor. A Prodac Air Professional pump 360 was used, and inlet airflow was regulated by means of a Sho-Rate GT1135 flow meter (Figure 2.4.1). Biogas generated from each column was collected using a Tedlar® sampling bag connected to the upper gas port and biogas volume and quality were measured daily by means of a volumetric flow meter (Cossu et al., 2016).

Temperatures were monitored using six probes PT 100 (Endress+Hauser) placed in the core of the waste body. Reactors were thermo-regulated by means of a heating system comprising a spiral circuit of silicon pipes placed around the columns in which circulating hot water ensured a constant temperature of 33-35°C.

Waste and concentrate samples

RO concentrate used for the test was sampled from the leachate treatment plant of an old Italian MSW landfill which had been closed in 2004 and is currently in the aftercare phase. The plant comprised an UF prior to a four step RO (Figure 2.4.2): samples were obtained at the end of the whole process. The main biochemical characteristics of concentrate, measured for the whole test period, were reported in Table 2.4.1.

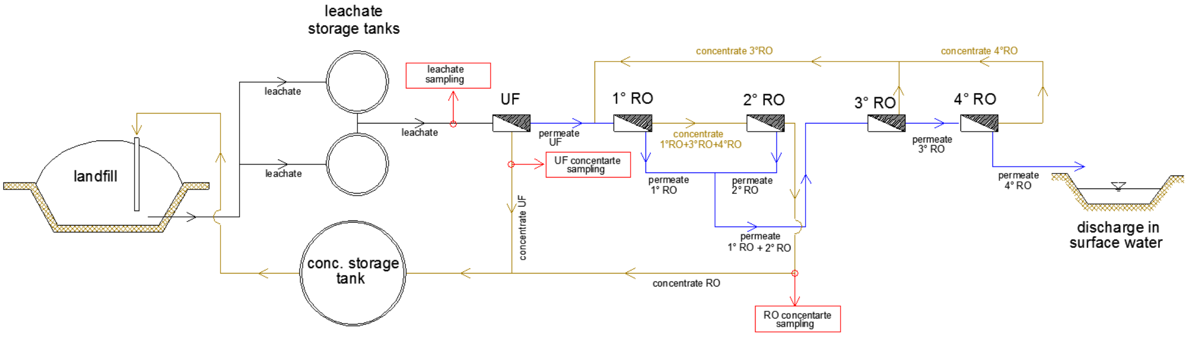

Figure 2.4.2: Flowsheet of the reverse osmosis (RO) leachate treatment plant. Leachate collected from the landfill is treated by ultrafiltration prior to a four step RO.

Table 2.4.1: Concentrate samples characterization during the test. In each column, average, minimum, maximum value and standard deviation of all analysis are reported.

	AVERAGE	**MIN**	**MAX**	**ST. DEVIATION**
pH	7,52	7.40	7.66	0.09
COD (MG/L)	2198	1957	2417	196
N-NH$_4^+$ (MGN/L)	2388	2240	2532	123
CL$^-$ (MG/L)	1823	1721	2013	101

Waste used to fill the reactors was obtained from MSW collected in a municipality in Northern Italy and was aerobically treated before filling the reactors. Aerobic treatment was made for enhancing natural air circulation into waste deposited in windrows and completely turned daily for two months. Solid sample was constituted mainly by undersieve 20 mm (51.5 %) and small fractions between 80 and 20 mm (46.7 %); only 1.8% of the material was bigger than 80 mm. Apart from the undersieve 20mm, the sample was largely made up of plastics, paper and putrescible matter; minor quantities of textiles, glass, inert material and metals were detected (Table 2.4.2). Kitchen residues, small pieces of paper or plastic film and dust visually mainly composed undersieve 20mm fraction. Total Solids (TS) and Volatile Solids (VS) measured on undersieve 20 mm were slightly higher than the total waste ones (TS = 72.1%, VS = 79.3 %TS), confirming what visually seen.

Table 2.4.2: Fractional composition of waste used to fill the reactors in percentage by mass.

	> 80 mm	80 - 40 mm	40 - 20 mm	Total per category
Paper	0.5	4.7	4.1	9.3
Textiles	0.7	1.6	1.8	4.1
Glass and Inerts	0.0	0.2	2.4	2.6
Plastics	0.6	11.3	11.8	23.7
Metals	0.0	0.4	0.5	0.9
Putrescible	0.0	3.0	4.9	7.9
Undersieve 20 mm*	0.0	0.0	0.0	51.5
Total per sieve	1.8	21.2	25.5	100.0

*Undersieve TS = 72.1%, VS = 79.3 %TS, visually mainly putrescible paper, plastic and dust

Test setup

Six lab-scale column reactors were filled with the same quantity of waste to obtain identical startup conditions to allow clear comparison of results. In order to evaluate the effects of concentrate recirculation, in the landfill body, three cases were compared: distilled water (W- reactors, W-an and W-ae), a mix of distilled water and concentrate (CW- reactors, CW-an and CW-ae) and concentrate only (C- reactors, C-an and C-ae) were injected in the reactors (Table 2.4.3). Concentrate only injection and mid- term conditions were used for evaluating numerically the effect of concentrate injection at the endo of the test. One triplet of reactors were managed as a traditional anaerobic landfill (-an reactors) and the other three were aerated from the outset to investigate the effects of air injection during concentrate input (-ae reactors).

Table 2.4.3: Reactors management scheme. Input subdivision, recirculation modality and airflow rate for the six lab-scale bioreactors.

			C-an	CW-an	W-an	C-ae	CW-ae	W-ae
First Phase	67 d, L/S = 0.85-0.95 L/kgTS	Water input (L/w)	0	0.5	1	0	0.5	1
		Concentrate input (L/w)	1	0.5	0	1	0.5	0
		Input Frequency	daily	daily	daily	daily	daily	daily
		Leachate Recirculation	no	no	no	no	no	no
		AirFlow (L/d 20°C)	0	0	0	50	50	50
Second Phase	56 d, L/S = 1.4-1.7 L/kgTS	Water input (L/w)	0	0.5	1	0	0.5	1
		Concentrate input (L/w)	1	0.5	0	1	0.5	0
		Input Frequency	Weekly	Weekly	Weekly	Weekly	Weekly	Weekly
		Leachate Recirculation	daily	daily	daily	daily	daily	daily
		AirFlow (L/d 20°C)	0	0	0	600	600	600

At startup, moisture content inside the reactors was adjusted to 50% with deionized water, in order to ensure a sufficient initial humidity to reach field capacity and promote leachate formation (Kjeldsen et al., 2010).

The test was divided into two different phases, devised for the purpose of enhancing differences between a daily concentrate input with free leachate exit and a controlled input with leachate recirculation typical of a bioreactor (He et al., 2015; Manzur et al., 2016). The first phase lasted 67 days during which reactors reached a Liquid Solid ratio (L/S) of 0.85 - 0.95 L/kgTS. Weekly liquid input was subdivided for being injected every day (0.15 L/d), no recirculation was performed and the leachate produced was able to freely exit the system once produced. This phase was planned in order to enhance the effect of continuous concentrate input in a traditional landfill without leachate recirculation and to highlight possible clogging effects due to the difference in viscosity of concentrate compared to demineralized water. The length of the second phase was 56 days during which L/S ratio was increased to 1.4 - 1.7 L/kgTS. Liquid was injected once a week (1 L/w); produced leachate was recirculated daily to maintain the moisture inside the reactor and totally extracted only at the endo of the week, immediately prior to the new liquid input (Table 2.4.3). This phase was devised to simulate a bioreactor landfill in which moisture control is fundamental in enhancing biochemical processes, and where injection of wastewaters can be better controlled (Berge et al., 2006; Bigili et al., 2008; Cossu et al., 2016; Manzur et al., 2016). Totally, the injection in each reactor amounted to 10 L during the first phase and 7 L during the second one.

Daily air injection was applied continuously for all three aerated bioreactors. During the first phase, air flux was established at 50 L/d (20°C), which in this specific case corresponded to 5 NL/d/kgTS. This value was selected on the basis of a series of lab-scale experiments carried out under semi-aerobic or low pressure flowrate conditions ranging from 0.7 to 32.0 NL/d/kgTS with average values around 4-10 NL/d/kgTS (Cossu et al., 2003; Cossu et al., 2016; Wu et al., 2014; Sun et al., 2013). In the second phase, air-flow was increased to 600 L/d (20°C), corresponding to 60 NL/d/kgTS, to simulate a strong forced aeration in which the percentage of oxygen in off gas exceeded 14% (Ritzkowski and Stegmann, 2013), as the rate previously adopted was considered not sufficient for ammonium control.

The main emissions produced by a landfill are biogas (mainly methane, carbon dioxide) and leachate (mainly carbon compounds, ammonium ions, organic nitrogen, nitrates, chlorides, sulfates and heavy metals) (Kjeldsen et al., 2010). Monitoring of gaseous emissions also took into account carbon compounds (methane and carbon dioxide) and stripping of ammonium, a process that occurs when pH increases beyond a value of 8 (Berge et al., 2005). Leachable carbon was monitored by means of Chemical Oxygen Demand (COD), which takes into account both biodegradable and persistent compounds (humic and fulvic acids): this is an index widely used in long-term monitoring for landfill aftercare termination (Laner et al., 2012). The main nitrogen compounds present in leachate are ammonium ion, organic nitrogen, as well as nitrates formed during nitrification if the reactor is aerated. The most abundant and persistent nitrogen compound, ammonium ion, increases following ammonification of organic nitrogen and can only be removed by leaching, if aeration is not performed (Berge et al., 2005). For this reason, and due to the fact that organic nitrogen in both concentrate and initial leachate was less than 50 mg/L, ammonium ion was chosen for the monitoring of nitrogen compounds. Lastly, chloride, a salinity index scarcely influenced by biochemical conditions, was used to effectively highlight the possible accumulation of salts.

The six different reactors were compared to evaluate numerically the potential positive or negative effects of concentrate injection on the following aftercare life of the landfill, especially after the main biochemical reactions end. In particular, a mass balance was developed taking into account the quality of solid waste at the start and end of the process, as well as gaseous and liquid injection or emissions. Moreover, mass balance was capable of revealing the effects produced by injection of new compounds into the reactor under both aerobic and anaerobic conditions. To conclude, evaluation of the fate of carbon, nitrogen and chloride was made calculating the difference between the cumulative emissions in reactors with concentrate injection (C- and CW-) and emissions in reactors without (W-).

Analytical methods

Standard international methods were used for the analysis of solid samples, leachate and biogas.

A portable analyser (Eco-Control LFG20) was used to measure CO_2, CH_4 and O_2 concentrations in biogas collected in the Tedlar bags on an at least weekly basis. Stripped $N\text{-}NH_{3(g)}$ was measured through an acid scrubber placed immediately after the off-gas valve of each reactor (Figure 2.4.1). Boric acid 0.5 M was used as scrubber and the emission results were periodically checked through a portable gas analyser (Analitica Strumenti LFG 2000).

Leachate samples were taken weekly from the collection tanks and analysed for pH, COD, $N\text{-}NH_4^+$ and Cl^- following international certified procedures (CEN, 2002). In particular, titration methodologies were used for COD, $N\text{-}NH_4^+$ and Cl^-, a pH probe for pH measurement and no ready to use kits were utilized.

Wastes were sampled for characterization before reactor filling and at the end of the test following complete extraction of the waste and mixing in a tank to increase homogeneity. Solid samples were milled to 4 mm prior to determination of TS, VS, TKN and TOC. TOC on solid samples was measured using a TOC-VCSN Shimadzu Analyser, TKN was measured with the standard Kjeldahl method. A leaching test was carried out according to the standard UNI EN 12457-2 on waste samples (L/S ratio of 10 L/kgTS was obtained, which was mixed for 24 hours and filtered at 0.45 µm). The eluate obtained was analysed to evaluate the total initial and final presence of nitrates and chlorides. All tests on solid samples were performed at least in duplicate.

2.4.3 Results

Solid samples

In all columns, initial humidity of solid waste was 33 % (by mass), due to high content of volatile compounds respect to Total Solids (TS). At the end of the test all biochemical indices had decreased respect to initial values, indicating no over-accumulation of carbon, nitrogen or chloride compounds (Table 2.4.4). Numerical evaluation of compound accumulation is possible only once a complete analysis and in-depth comparison of emissions, achievable through mass balance, has been performed.

Table 2.4.4: Physical-chemical characterization (Average ± SD) of waste samples at the beginning of the test (Start 1st phase) and at the end (End 2nd phase).

	Start 1st phase	End 2nd phase					
	All reactors	C-an	CW-an	W-an	C-ae	CW-ae	W-ae
TS (%)	67.0 ± 0.8	37.8 ± 0.6	60.3 ± 1.5	53.7 ± 2.8	53.9 ± 2.4	45.3 ± 2.6	51.7 ± 2.7
VS (%TS)	78.3 ± 0.4	41.5 ± 1.0	66.9 ± 0.4	68.4 ± 1.2	54.0 ± 0.8	56.3 ± 0.7	70.2 ± 1.1
TKN (mg N/kg)	7.9 ± 0.6	5.3 ± 0.4	6.3 ± 0.3	4.9 ± 0.4	3.9 ± 0.1	3.6 ± 0.3	3.5 ± 0.3
TOC (gC/kgTS)	445 ± 27	409 ± 11	439 ± 2	433 ± 1	372 ± 8	416 ± 1	420 ± 3
Cl- (gCl/kgTS)	9.7 ± 0.1	6.3 ± 0.1	6.5 ± 0.1	6.8 ± 0.1	7.7 ± 0.3	6.8 ± 0.3	6.2 ± 0.3

TS values decreased from an initial 67% to values ranging between 38 - 60 % due to the injection of liquids, which increased moisture content until field capacity was reached and ensured a sufficient leachate production. Volatile Solids (VS) decreased from 78% to 41 - 67% in reactors with concentrate injection due to leaching and biochemical processes, while a lower reduction (68 – 70%) was observed in control reactors (W-). Total Organic Carbon (TOC) decreased from 444.7 gC/kgTS to 372 - 439 gC/kgTS, corresponding to a reduction of 1 – 16%, with no evident differences due to reactor management. Total Kjeldahl Nitrogen (TKN) levels were initially 7.9 gN/kgTS, subsequently reaching values in the range of 3.5 – 3.9 gN/kgTS in aerobic columns (51- 56 % reduction). This decrease in nitrogen concentration demonstrated the efficiency of aeration in remediation of nitrogen persistent compounds even in the case of concentrate injection. On the contrary, in anaerobic reactors TKN decreased to 4.9 - 6.3 gN/kgTS (20 - 38% reduction) due to the sole presence of leaching and free ammonia stripping as nitrogen emissions. The initial concentration of chlorides in solids was 9.7 $gCl^-/kgTS$; at the end of the test, values had fallen to 6.2 – 7.7 $gCl^-/kgTS$ (20 – 35% reduction) with no evident differences due to reactor management.

Leachate emission monitoring

The evolution of main parameters monitored in leachate samples, extracted weekly from reactors, is illustrated in Figure 2.4.3. Although a uniform initial waste mass was used (including initial humidity) and the quantity of liquid injected was identical for each reactor, the quantity of leachate produced, and as a consequence, L/S ratio, differed slightly. At the end of the test, L/S ratio reached values ranging between 1.6 and 1.8 L/kgTS in anaerobic reactors, and between 1.4 and 1.6 L/kgTS in aerobic reactors. This difference was due to the air flux in aerobic columns that enhanced water evaporation. No differences in leachate quantity due to concentrate injection were detected.

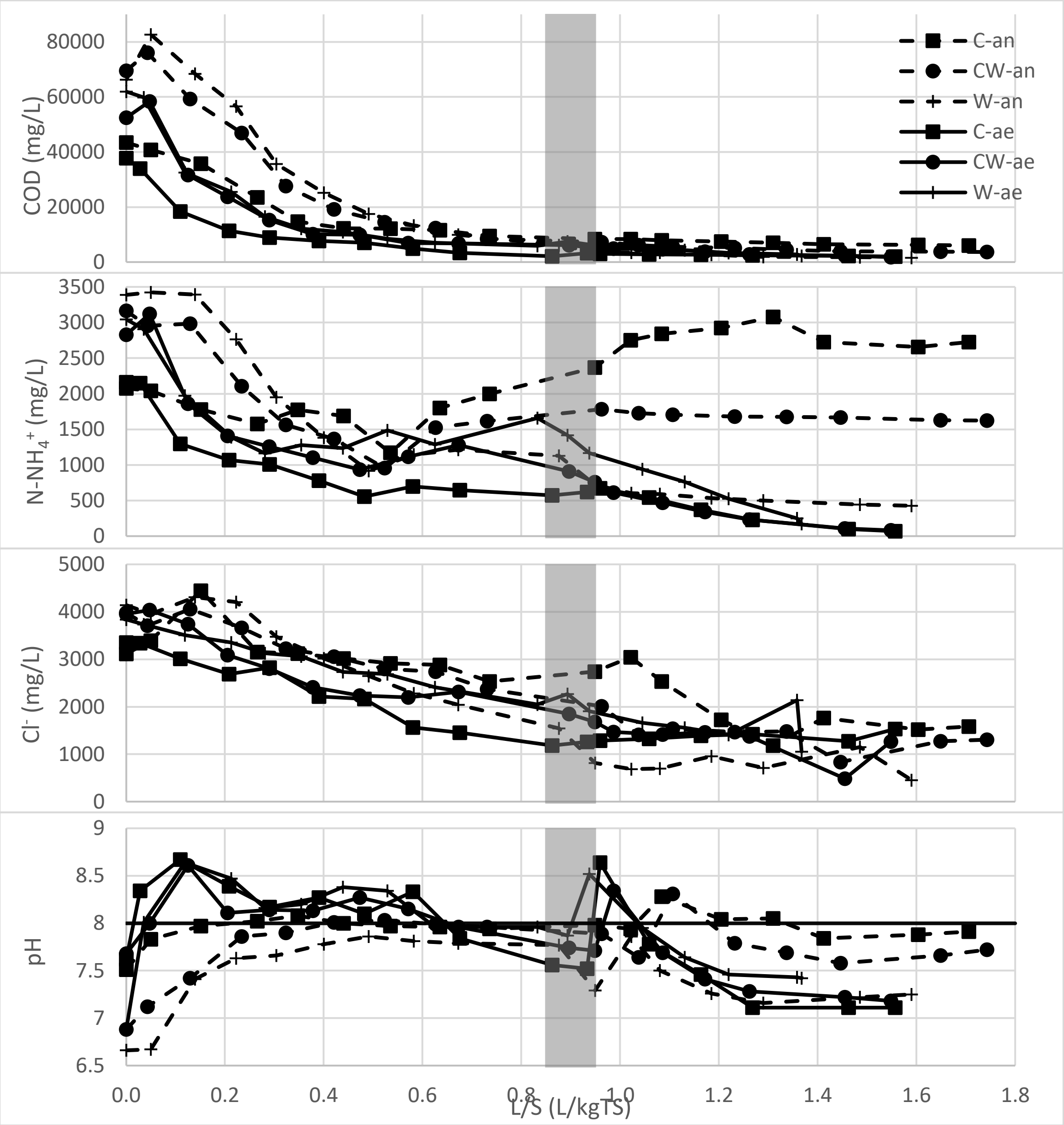

Figure 2.4.3: Leachate emission concentration of monitored indices (COD, NH_4^+, Cl^- and pH) respect to liquid solid ratio (L/S). A vertical grey column indicates the passage between first and second phase.

Chemical Oxygen Demand (COD) in leachate decreased during the first phase, from initial concentrations exceeding 40000 mgO2/L (up to 70000 mgO2/L) to values below 10000 mgO2/L, with no evident effects ascribable to concentrate injection (Figure 2.4.3). Reaction kinetics in aerated reactors were faster than in anaerobic reactors, thus producing a more rapid decrease in COD . During the second phase, weekly residual carbon emissions of C-columns were invariably below 0.3 gC/kgTS, despite the weekly injection of 0.08 gC/kgTS with concentrate, showing no evident accumulation.

Evolution of ammonium ion emissions was strongly influenced by the nitrification-denitrification process, enhanced by oxygen availability in aerobic reactors (Berge et al., 2006; Ritzkowski et al., 2006). In aerobic columns, NH_4^+ concentration decreased from 2000 mgN/L to less than 200 mgN/L at the end of the test (Figure 2.4.3). Biochemical use of NH_4^+, due to nitrification, also consumed the ammonium injected with concentrate in C reactors (0.37 gN/kgTS per week); no effect of accumulation was therefore observed. Curiously, the aerobic column with concentrate injection (C-ae) was the best performing reactor in terms of ammonium ion depletion.

NH_4^+ evolution in anaerobic reactors was strongly affected by concentrate injection (Figure 2.4.3), showing a clear accumulation of ammonium ion, proportional to input quantity. Monitored ammonium content decreased until L/S was equal to 0.6 L/kgTS, reaching values around 1000 mgN/L, probably due to NH_4^+ utilization in biochemical processes and/or dilution into waste mass. Once this limit had been exceeded, in control reactor (W-an), ammonium content continued to decrease until levels of 500 mgN/L (0.05 - 0.10 gN/kgTS per week) were reached. In C-an reactor, with a weekly NH_4^+ injection of 0.27 gN/kgTS, ammonium ion started to accumulate up to concentrations of more than 2500 mgN/L (0.30 - 0.40 gN/kgTS per week). Finally, in CW-an reactor, with a weekly NH_4^+ injection of 0.14 gN/kgTS, ammonium ion concentration stabilised around 1500 mgN/L (0.15 - 0.25 gN/kgTS per week).

Chloride emissions in leachate decreased from 3000 - 4000 mg/L to 500 – 1500 mg/L with no differences due to aerobic or anaerobic conditions; moreover, no accumulations could be ascribed to concentrate injection (even if concentrate Cl^- content was more than 1800 mg/L).

pH was monitored for the entire test for checking methanogenic and ammonium stripping processes. In anaerobic reactors, pH stood always between 7.5 and 8.2.

Biogas

The evolution of cumulative gaseous emissions produced by carbon compounds (carbon dioxide, methane) and nitrogen compounds (stripped $NH_{3(g)}$) are reported in Figure 2.4.4. Monitoring of N_2 concentration in biogas from the aerated reactor was not technically feasible due to a high air flux.

In anaerobic columns, methane production started after a lag phase lasting approximately two weeks and was completed after six weeks only (L/S equal to 0.7 L/kgTS), due to the limited residual degradability of the waste, reaching a plateau that remained constant throughout the second phase. Concentrations of carbon emissions from aerated reactors remained substantially constant throughout the entire test, generating a constantly growing cumulative emission curve, despite the different aeration rate between the two phases. At the end of the test, -ae reactors emitted two-three fold more gaseous carbon than -an reactors. In both aerated and anaerobic reactors, an increase of emissions in C versus control columns was observed, indicating that carbon compounds in concentrate had been partially degraded and transformed into CO_2 and/or CH_4 (Figure 2.4.4).

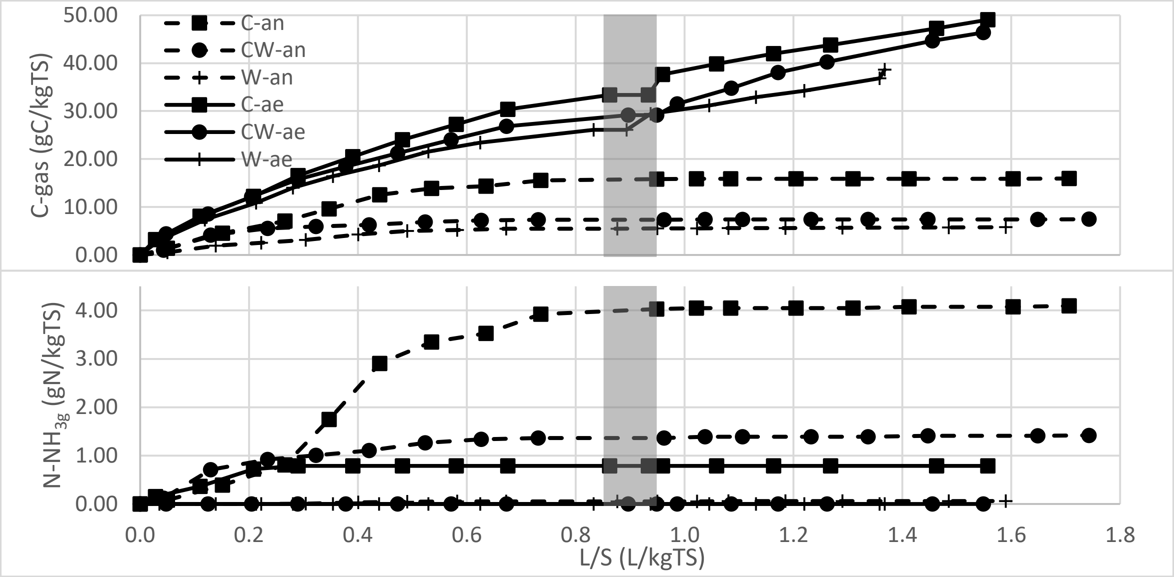

Figure 2.4.4: Cumulative gaseous emissions of carbon (C-CH4 plus C-CO_2) and stripped free ammonia (N-NH_{3g}) respect to liquid solid ratio (L/S). A vertical grey column indicates the passage between first and second phase.

The presence of stripped free ammonia in biogas was detected only in reactors with concentrate injection, particularly under anaerobic conditions. Throughout the entire test, C-an column emitted 4.1 gN/kgTS of $NH_{3(g)}$, twice the amount emitted by all other reactors, corresponding to less than 2 gN/kgTS of $NH_{3(g)}$ (Figure 2.4.4). Ammonia stripping was detected mainly during the first phase, this behaviour was caused by pH that was slightly below 8, inhibiting the stripping process (Figure 2.4.3).

2.4.4 Discussion

Reinjection of RO concentrate produced no effect on the amount of leachate emission: the sole difference detected in L/S ratio was likely elicited by the injection of air and consequential higher evaporation of water in ae reactors (Figure 2.4.3). Likewise, the different hydraulic management between the two phases of the test, in particular daily recirculation of all leachate produced, failed to modify leachate quantity. The higher air injection provided during the second phase only slightly influenced gaseous carbon emissions in aerated reactors and did not affect leachate quality.

Leachate and biogas monitoring results shows that, if a difference ascribable to concentrate injection was recorded, C reactors concentration increased consistently respect to W columns and CW reactors concentrations were found to be in mid-term conditions. This behaviour was clear with ammonium ion in anaerobic reactors (Figure 2.4.3) and with carbon and nitrogen gaseous emissions (Figure 2.4.4), confirming that increase of concentration of these compounds in landfill’s emissions were due to concentrate injection.

Mass Balance

Carbon, nitrogen and chloride mass balances were developed taking into account initial and final content of each compound in the solid sample, cumulative emissions in leachate and biogas (not for chloride) and cumulative concentrate input (Table 2.4.5).

Table 2.4.5: Carbon (C), Nitrogen (N) and Chloride (Cl^-) mass balance in all six lab-scale reactors. All values are expressed in grams of compound respect to total dry mass in the initial solid sample. “Missing” represents the difference between inputs and outputs.

(*) Nitrogen mass balance missing for aerobic reactors included also free nitrogen produced by nitrification-denitrification process.

Carbon Balance (gC/kgTS)		**C-an**	**CW-an**	**W-an**	**C-ae**	**CW-ae**	**W-ae**
Inputs	Solid in	445	445	445	445	445	445
	Concentrate	1.3	0.6	0.00	1.3	0.6	0.00
Outputs	Solid out	409	439	433	372	416	420
	Leachate	5.8	7.2	7.4	2.4	4.1	4.2
	C-CH_4 + C-CO_2	15.9	7.5	5.8	49.0	46.4	38.6
Missing		15.3	-8.3	-1.5	22.6	-21.2	-18.1

Nitrogen Balance (gN/kgTS)		C-an	CW-an	W-an	C-ae	CW-ae	W-ae
Inputs	Solid in	7.9	7.9	7.9	7.9	7.9	7.9
	Concentrate	4.6	2.3	0.0	4.6	2.3	0.0
Outputs	Solid out	5.3	6.3	4.9	3.9	3.6	3.5
	Leachate	3.9	3.0	1.9	0.9	1.3	1.7
	N-$NH_{3(g)}$	4.1	1.4	0.1	0.8	0.0	0.0
Missing		-0.8	-0.6	1.0	6.9*	5.3*	2.7*

Chloride Balance (gCl-/kgTS)		C-an	CW-an	W-an	C-ae	CW-ae	W-ae
Inputs	Solid in	9.7	9.7	9.7	9.7	9.7	9.7
	Concentrate	3.3	1.6	0.0	3.3	1.6	0.0
Outputs	Solid out	6.3	6.5	6.8	7.7	6.8	6.2
	Leachate	4.3	3.8	3.1	2.7	3.0	3.3
Missing		2.4	1.0	-0.2	2.5	1.5	0.3

Total concentrate injection generated a cumulative input of carbon compounds equal to 1.29 gC/kgTS in C- reactors and 0.64 gC/kgTS in CW reactors. Liquid emissions totalled less than 2% respect to initial carbon content in solid samples with a clear difference between aerated (2.38 – 4.16 gC/kgTS) and anaerobic (5.74 – 7.37 gC/kgTS) reactors. Carbon emissions in biogas were higher in aerated than in anaerobic columns. Moreover, C- reactors emitted more carbon than CW- and W- reactors, indicating an increase elicited by concentrate injection (Table 2.4.5). Mass balance for carbon highlighted a relative error of 3.7 %, probably due to waste heterogeneity rather than system losses.

Nitrogen emission monitoring was not technically able to measure free nitrogen gaseous emissions; therefore, N_2 production was considered null in anaerobic reactors in which no nitrates were detected (no nitrification). For these reason, in aerobic reactors, free nitrogen produced was accounted in the missing fraction. Relative error committed totalled 7.3 %, not considering aerobic reactors. A huge difference was observed in total nitrogen emissions between aerated and anaerobic reactors due to nitrification - denitrification processes, which occurred in aerated reactors (Berge et al., 2005). In anaerobic reactors, the influence of concentrate injection in nitrogen emissions was clearly evident (Talalaj and Biedka, 2015): leachate NH_4^+ had doubled in C- columns (3.88 gN/kgTS) respect to control columns (1.89 gN/kgTS), and stripped free ammonia was 4.09 gN/kgTS in C- columns respect to 0.06 gN/kgTS in control columns (Table 2.4.5). Moreover, final nitrogen emissions remained extremely high in leachate: up to 2500 mgN/L in C-an (Figure 2.4.3). Concentrate injection did not affect negatively nitrogen emissions in aerobic reactors as the nitrification-denitrification process had efficiently transformed all the ammonium ion present into free nitrogen: at the end of the test, NH_4^+ was found to be below 200 mgN/L in all aerated reactors (Figure 2.4.3). For this reason, no nitrogen accumulation effect was detected in leachate from aerated reactors (Table 2.4.5).

With regard to chlorides, leaching represents the sole possible means of emission, with solubilisation being mainly related to pH alone (Fellner et al., 2009). Cumulative emissions of chloride in leachate appeared to range between 28 and 44 % the initial content in solids, without any visible trend related to aeration or concentrate injection. Taking into account final content in solids, a lack of Cl^- of 24.6 – 26.0 % in C- reactors, 10.0 – 15.7 % in CW- and -2.0 – 2.6 % in control reactors was highlighted. This missing appeared to be directly related to the quantity of concentrate injection: 33.7 % in C reactors, 16.8 % in CW- and 0.0 % in controls (Table 2.4.5). This effect was likely due to an accumulation of chloride in solid waste that is not detectable by means of routine analysis, but remains present inside the reactor and requires further investigation.

Fate of concentrate contaminants

Evaluation of percentage emission difference between C- or CW- and control (W-) reactors, may reveal the fate of carbon, nitrogen and chloride compounds. Fate of compounds in C reactors was evaluated by calculating the difference between emissions from the reactor itself and the control; the same procedure was also applied to obtain CW values. In Figure 2.4.5, results were plotted for both CW- and C- columns to highlight whether accumulation was proportional to compound injection quantity. If a positive change was obtained, an accumulation in the specific matrix (biogas, liquid or solid waste) was deemed to have occurred.

Carbon compound difference ranged between -2 and 3 % for all three matrixes, in particular a biogas increase of approx. 2.5 % was detected, and leachate change was considered null (Figure 2.4.5). This behavior provides confirmation that, in this test, concentrate addition produced no appreciable influence on lab-scale emissions of carbon from the reactors.

Concentrate injection strongly affected gaseous emissions of free ammonia, which increased by 51.12 % in anaerobic reactors (Figure 2.4.5). Particularly, gaseous ammonia emissions were monitored only with concentrate injection, both in anaerobic and aerobic reactors. NH_4^+ emissions in leachate remained unchanged in aerobic reactors, thanks to nitrification-denitrification process efficiency, but were a huge problem in all anaerobic reactors, where concentrate injection increased values by more than 20% throughout the test.

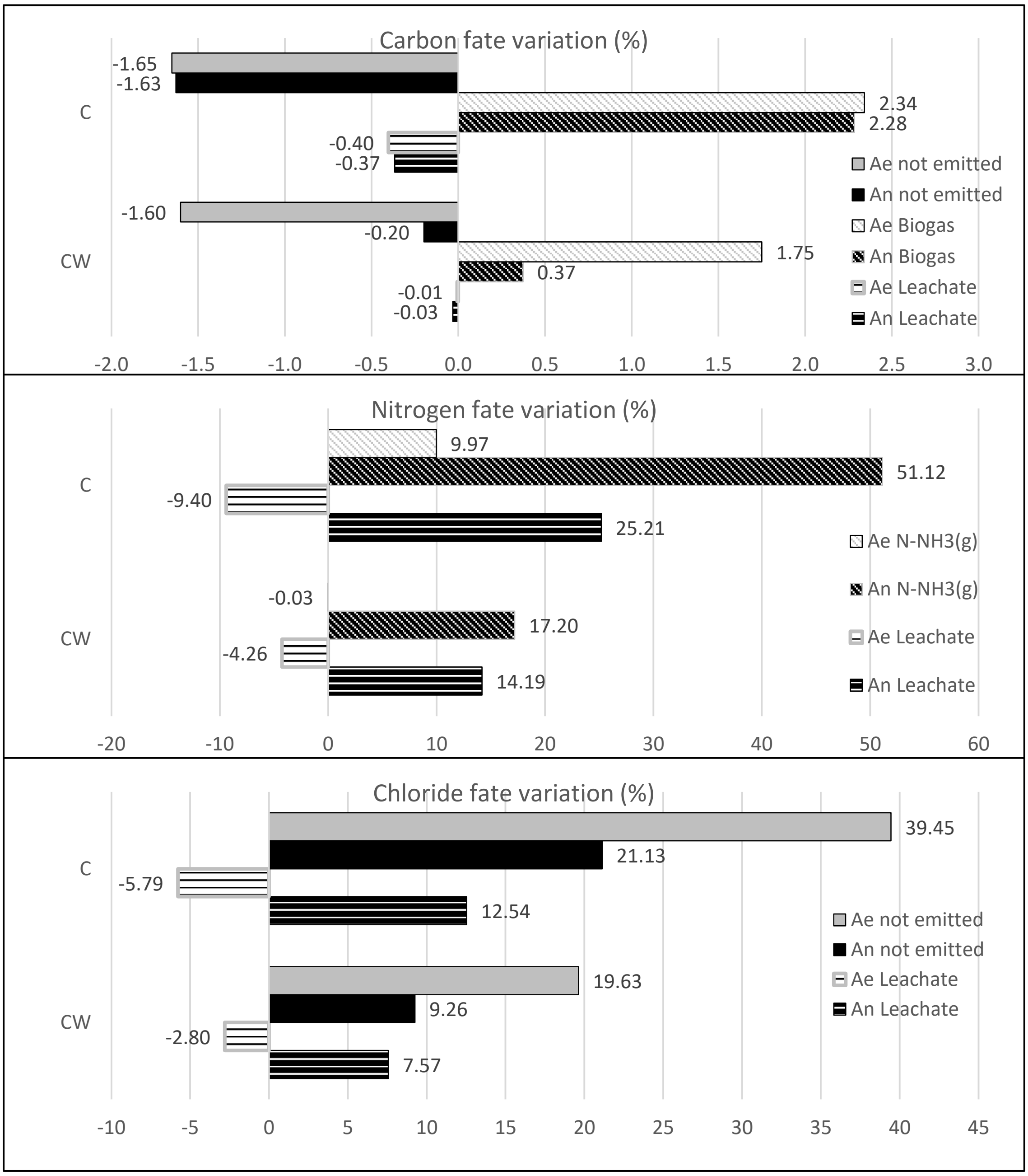

Figure 2.4.5: Fate of Carbon, Nitrogen and Chloride in C- and CW- columns versus control W-reactors (based on solid samples, leachate and total biogas emissions). Biogas emission of carbon compounds takes into account both methane and carbon dioxide, while gaseous nitrogen emissions relate solely to gaseous ammonia volatilization.

Change of chloride compounds presence in leachate highlighted an accumulation only in anaerobic reactors (10%); a more abundant increase of Cl^- in solid waste was observed (20 – 40 %) (Figure 2.4.5). This accumulation in reactor was driven by not sufficient leaching of these compounds; as consequence, increase further L/S ratio could be a solution to prevent chlorides accumulation in solids and the possibility of the latter becoming a long-term uncontrolled emission in leachate.

2.4.5 Conclusions

The effects of RO concentrate recirculation were evaluated in lab-scale reactors under anaerobic and aerobic conditions.

Leachate production was not influenced by concentrate injection and no clogging was observed in the collection systems; L/S ratio was only influenced by air injection and the consequential higher evaporation of water in aerated reactors.

Injection of carbon compounds into reactors produced no consistent change both in gaseous and leachate emissions.

RO concentrate recirculation caused an increase of ammonium ion concentration in leachate in anaerobic reactors; as consequence, increase of $N\text{-}NH_{3(g)}$ generation due to stripping process was observed.

In lab-scale reactors, aerobic conditions enhanced the nitrification-denitrification processes, thus promoting the complete degradation of ammonium both produced by the waste and present in the concentrate injected. Concentrate recirculation caused an increase of $N\text{-}NH_{3(g)}$ stripping in this case also.

Upgrade to full scale needs to be evaluated by means of specific field scale test. By implementing an effective aeration process, the addition of nitrogen compounds to a landfill bioreactor could represent an environmentally sustainable technique.

The reinjection of chloride did not seem to produce any immediate effect on leachate emissions, although the fate of this compound remains to be clarified due to possible Cl-accumulation in waste mass that may therefore represent a future potential source of emissions.

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Chapter 3: Final Storage Quality

3.1 Aftercare termination and Final Storage Quality concept

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Morello L., Rosson E., Cossu R. (2016). Landfill mining of material from an old lab-scale lysimeter reactor, 3rd Symposum on urban mining and circular economy (SUM 2016), Bergamo, Italy.

3.1.1 Landfill Aftercare Completion

Landfill aftercare completion nowadays is a worldwide debated topic in scientific community and in local legislative authorities, boosted by the necessity of a standard procedure to definitively and safely close a landfill. Despite this topic has been faced with many different approaches (Laner et al., 2012), more research experience is required to understand which level of chemical stabilization is effectively reachable at the end of the post closure care and which long term emissions are tolerable for the environment surrounding a landfill (Christensen et al., 2011; Hjelmar et al., 2011; Knox et al., 2013). In line with the European sustainability principle (EU 2006), the duration of the post operational phase towards landfill completion should be reduced as much as possible (Chapter 1.1). In addition, the role of a modern landfill should include the closure of many material cycles, bringing back to earth and storing definitively all the elements coming out form the Circular Economy (Cossu, 2016). Considering all these aspects, the ultimate goal in aftercare completion will be achieve the landfill closure in a “sustainable” time, after reaching conditions in which the potential uncontrolled emissions cannot harm the environment anymore. Moreover, develop a clear standard procedure utilizable by the public control authorities as well as the stakeholders is an unavoidable and fundamental requirement.

The scientific community and the public authorities faced the problem of aftercare termination in different ways during the last 30 years. The time based aftercare termination is a commonly used methodology prescribing to terminate the aftercare (and the landfill owner duties) after a specified amount of years. This system does not guarantee that the landfill has reached environmentally acceptable conditions and the possible long-term pollution is going to be faced by the local administrations, in absence of a legal responsible (Laner et al., 2012). On the contrary, with perpetual Post Closure Care system, the landfill owner duties never ends. However, perpetual care is rarely applied because endless responsibility does not fit with the economic and insurance systems that need to fix a deadline for its products. The aftercare termination methodologies developed nowadays are based on the environmental protection and on the sustainability principle. Among them, three main macro approaches can be recognized (Laner et al., 2012):

- Target values approach prescribes to terminate aftercare when the landfill reach a chemical specified endpoint. Control authorities must define a set of indexes able to describe the landfill status and the relative threshold values to be reached for ensuring environmental safety. Reaching these limits in a sustainable time constitutes part of the landfill owner responsibility. This approach is simple and law friendly, not requiring highly professional figures to be certified, but it does not consider site-specific constraints. The definition of all-embracing indexes and threshold values remains the main problem to be faced by the public authorities and scientific community (Laner et al., 2012; D.G.R. 2461/14). Moreover, a list of landfill pollutants can be not sufficient for guaranteeing environmental protection because of the increasing presence of new chemicals in MSW (Pivnenko and Astrup, 2016).
- Impact/risk assessment approach uses the backwards risk analysis to evaluate the conditions in which the landfill must be for not harming the surrounding targets. These systems follow the same concept developed for the evaluation of the Risk Contaminants Concentration (RCC) in the European approach for the remediation of contaminated sites and the results obtained are site-specific for each landfill. The assessment considers a large set of values, evaluates the ones potentially harming the environment and specifies the concentration value to be respected to declare the aftercare end. The procedure needs a professional figure to be implemented and it becomes similar to the target values approach, once this set of parameter is evaluated. However, the definition of the groundwater criteria are often highly uncertain, the points of compliance for human and environmental targets are complicate to be fixed in long time and the flow of contaminants through the failed geological barrier is really hard do be successfully modelled. As consequence, the evaluated target values can result so prescriptive to be unrealistic.
- Performance-based approach is based on a site specific mathematical model constantly uploaded with monitoring data for the evaluation of future emissions and of the risks associated to a landfill, starting from the performance of the reactor itself. This system can balance the actual potential performances of the reactor with the environmental constraints coming from a risk assessment. The main disadvantage of these approaches is the necessity of hiring highly professional personal for the whole landfill life and the constant expensive monitoring of reactor performances.

These three different approaches aimed to define, in different ways, the chemical conditions in which the landfill can be considered “safe” and released by control measures as consequence: this overall condition is named Final Storage Quality (FSQ).

3.1.2 Final Storage Quality conditions

The “Final Storage” term was coined in the middle eighties by the Swiss working group on landfills for indicating the situation in which the quality of waste is the same of the surrounding geological strata and the flux of elements is that low to not be able to harm the environment (Cossu et al., 2007; Christensen et al., 2011). Results obtained by the team were focused on leachate emissions and the criteria assumed were similar to the Swiss limits for discharging liquids in surface waters.

Nowadays, Final Storage Quality (FSQ) is defined as the chemical status in which a landfill cannot harm the environment and the human health anymore, allowing the safe removal of all the emission control and monitoring measures. Despite the concept is worldwide accepted (Christensen et al., 2011; Cossu et al., 2007; Knox et al., 2013; Hjelmar et al., 2013), its practical definition is one of the most debated topic in waste management scientific literature, as explained before (Laner et al., 2012). An all-embracing numerical description is hardly achievable because the landfill characteristics, the groundwater criteria and the point of compliance for environmental targets location will drive the FSQ definition to site-specific characteristics. The common traditional landfill design and operations are often likely to increase time for FSQ achievement, rather than decrease it. As consequence, the conditions in which landfill emissions are reduced to levels acceptable for the surrounding environment is hard to be technically fulfilled (Hjelmar et al., 2013).

3.1.3 Final Storage Quality methodology

The Final Storage Quality is the previously introduced chemical status in which a landfill must be for safely removing the emission control measures and a methodology for assessing the aftercare termination, purposed by Cossu et al. (2007). FSQ methodology is a middle way between a target values and a risk based approach, the last one useful for considering site-specific features of the landfills (Figure 3.1.1). As previously explained, the target values methodology has the advantage to be law-friendly and technically simple to be applied but the development of an all-embracing set of indexes and targets which are valid for all the circumstances is complex. This methodology uses several international standard indexes, worldwide used as reference for guaranteeing chemical and biochemical stability of waste. These indexes are chosen also to be easily analysable and technologically available at an acceptable cost. The monitoring of each phase (biogas, leachate and solid waste) is made sequentially, starting from the easier and cheaper (biogas), stopping and restarting the procedure if a threshold value is not respected. FSQ threshold values are chosen according with literature and real landfill experiences; comparing them with law limits for discharging liquids in surface water-bodies, which can be considered an environmentally acceptable condition. This choice must also include performance based aspects, simultaneously respecting environmental constrains and technical feasibility. Finally, the site-specific conditions are taken into consideration at the beginning of the procedure with a risk assessment able to modify the FSQ threshold values, if necessary (Figure 3.1.1).

The FSQ methodology procedure starts only once a landfill is geotechnically stable, condition necessary also for the placement of the final top cover without the risk of damaging it. In particular, general and localized settlements must be negligible (Scheutz and Kjeldsen, 2011; Scharff, 2011). The first step is the risk assessment for accounting potential site-specific constraints and precautionary adjust the general FSQ threshold values. The result of this analysis will be the list of site-specific FSQ values to be respected by the landfill (Cossu et al., 2007).

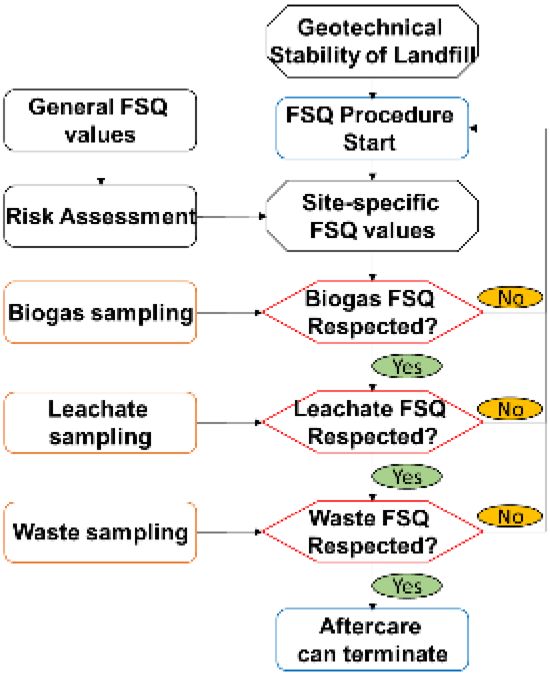

Figure 3.1.1: Sketch of the Final Storage Quality procedure for approving the termination of the post closure care of a landfill. Modified from Cossu et al. (2007).

The first analysis are carried out for the biogas indexes, which is the easiest phase to be monitored. Samples can be taken both form the extraction system as well as from different wells or superficial points all around the landfill (Figure 3.1.1). The biogas composition is a routine analysis for an open plant and the probes installed to continuously register these values can be maintained during the aftercare phase for the long-term monitoring. Once biogas FSQ threshold values are respected, leachate indexes are considered. Also for leachate, periodical analysis are an administrative routine prescribed by the law. This is probably the most tricky step because the long-term potential pollution of a general landfill comes mainly form persistent compounds presence in leachate, which can escape the containment systems, in case of liner failures caused by aging (Christensen et al., 2011). Persistent compounds in leachate can last for centuries, if not biologically degraded or flushed away with leaching (Hall et al., 2013). As consequence, for efficiently respecting FSQ limits, in situ treatments for enhancing biochemical processes must be plan since the design of the landfill. The last procedure step includes a waste sampling proportional to the landfill dimensions, aiming to collect a statistically solid number of samples. FSQ indexes in solid material are mainly useful to quantify the possible presence of still biologically active compounds, in zones not reached by humidity for years. This problem can be faced managing moisture access, compacting homogeneously the material and avoiding excessive hydraulic conductivity differences in the waste body. When all the FSQ values are respected, the FSQ methodology can be considered finished and the aftercare can safely terminate, releasing the owner of the landfill form its legal and economical duties.

Defined the methodology, the choice of all-embracing indexes and threshold values remains the most challenging problem to face. As previously explained, the indexes must be able to describe the whole landfill status, they must be worldwide known and applicable and their number cannot be excessive for maintaining a procedural simplicity. Simultaneously, the threshold values chosen for the indexes have to guarantee the environmental protection, contemporary respecting the landfill performance constraints related to the Best Available Technology (BAT) utilization. Many authors faced the problem of Final Storage Quality definition, contributing to the ongoing debate on landfill closure and suggesting some targets to reach (Laner et al., 2012; Cossu et al., 2007; Hall et al., 2011; Knox et al., 2013) and some regional authorities started to implement this concepts into their technical guidelines (D.G.R. 2461/14).

Table 3.1.1: Performance-based parameters and values used in S.An.A. test to determine the transition between phases and the end of the test.

	Parameter	Values Range	References
Stop of anaerobic conditions	Methane Production (L_{CH4}/d)*	< 0.5	Detection Limit
		< 0.54	Laner et al., (2012)
Stop of forced aeration	COD (mgO_2/L)	< 1500	D.G.R. 2461/14
	BOD_5/COD	< 0.1	D.G.R. 2461/14
		< 0.13	Sekman et al., (2011)
	Ammonium (mgN/L)	< 300	Laner et al., (2012)
		< 50	D.G.R. 2461/14
	RI_4 (mgO_2/gTS)**	< 2,5	Laner et al., (2012)
Test end	Nitric nitrogen (mgN/L)	< 20	D.G.R. 2461/14
	Sulfates (mg/L)	< 1000	D.G.R. 2461/14
	Chloride (mgN/L)	< 1200	D.G.R. 2461/14

The biogas production during the aftercare phase is generally too low to be energetically recoverable. Despite that, its production in still active, lasting until slow degradable organic substances are available. The total gas production (Nm^3/d) or the Areal biogas production (Nm^3/d/m^2) are useful indexes able to quantify the residual gaseous emissions and their threshold value can be clearly established (Laner et al., 2012) (Table 3.1.1). In particular, the superficial biogas can be monitored by means of static or dynamic chambers, building a monitor grid for ensuring that the top cover methane oxidation capacity is enough to avoid uncontrolled leakages in the atmosphere (Cossu et al., 1997; D.G.R. 2461/14) (Table 3.1.2).

The long-term leachate emissions monitoring is generally focused on the indexes able to estimating the presence of compounds potentially dangerous for the environment, if released. In particular, organic biodegradable compounds, ammonia nitrogen, chlorides, sulphates, Heavy Metals and other substances like pesticides, hydrocarbons and solvents (Table 3.1.1 and 3.1.2). The total organic carbon content can be estimated through Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Dissolved Carbon (DOC), while the Biodegradable Oxygen Demand (BOD_5) can measure its biodegradability. The ratio BOD_5/COD is a valuable tool for establishing the residual putrescible organic content, the landfill age and its biochemical status, being not affected by dilution effects (Cossu et al., 2012). Generally, a BOD_5/COD ratio under 0.1 highlights a sufficient stabilization degree of the leachate sample (Sekman et al., 2011). Humic and fulvic persistent substances often constitute the higher contribute to long-term organic compounds emissions, causing a residual COD emissions while having a BOD_5 virtually negligible (Bolyard and Reinhart, 2016).

Table 3.1.2: Final Storage Quality values purposed by Lombardia Region (Italy) for landfill cost closure care termination. Modified from D.G.R. 2461/14.

Sample	Parameter	FSQ value	Unit of measure
Leachate	COD	1500	mg/L
	BOD_5/COD	0.1	adm
	Ammonia	50	mg/L
	Al	1	mg/L
	As	0.5	mg/L
	B	2	mg/L
	Cd	0.02	mg/L
	Cr	2	mg/L
	Cr (VI)	0.2	mg/L
	Cu	1	mg/L
	Fe	2	mg/L
	Hg	0.005	mg/L
	Mn	2	mg/L
	Ni	2	mg/L
	Pb	0.2	mg/L
	Se	0.03	mg/L
	Sn	10	mg/L
	Zn	3	mg/L
	CN^-	0.5	mg/L
	SO_4^{2-}	1000	mg/L
	SO_3^-	1	mg/L
	F^-	6	mg/L
	Nitric nitrogen	20	mg/L
	Total hydrocarbon	5	mg/L
	Phenols	0.5	mg/L
	Aromatic organic solvents	0.2	mg/L
	Nitrogenous organic solvents	0.1	mg/L
	Phosphorous pesticides	0.1	mg/L
	Total pesticides (excluding phosphorous pesticides)	0.05	mg/L
	Chlorinated solvents	1	mg/L
Biogas	Surface emission with extraction plant off	0.5	NL $CH_4/(m^2h)$
Solid	IR_4	2	mgO_2/gTS
	IRD	100	$mgO_2/kgVS/h$
	GP_{21}	5	NL/kgTS

Nitrogen emissions in a traditional landfill are commonly due to ammonia ion and organic nitrogen, both measurable with Total Nitrogen (TN) and Total Kjeldahl Nitrogen (TKN). In addition to these indexes, nitrates are a by-products of nitrification-denitrification process, which must be monitored if the aeration treatment is applied. Chloride and sulphates are often present in high quantities in all the landfill long-term emissions. Finally, Heavy Metals, pesticides, solvents, hydrocarbons, etc. are found with frequency especially in recent wastes (Pivnenko and Astrup, 2016). The environmental protection and the sustainability principle application prescribe to fix a limit even for their emission; however, their monitoring is not technically simple, their presence is generally low or negligible and only flushing can theoretically decrease their content. As consequence, a FSQ limits for these compounds can be fixed only if a risk assessment display the environmental necessity to control them, as consequence of their potential mobility in aqueous solution.

The last part of FSQ methodology consists in the analysis of a quantity of solid sample statistically representative for the whole landfill, to investigate possible localized potential residual emissions. The residual biodegradability can be evaluated by means of respiration and fermentation tests (Respiration Index RI_4, Dynamic Respiration Index DRI, Fermentation Test GB_{21}, Biological Methane Potential BMP, etc.) (Table 3.1.2). In addition, the residual potential leachable emissions can be evaluated by means of a standard leaching test of the solid sample (UNI EN 12457-2), estimated the same parameter considered for leachate.

This procedure needs to be further investigated by researchers both for the site-specific evaluation of natural attenuation capacity of uncontrolled emissions from the landfill to the target, as well as for establishing achievable long-term compounds reduction applying the best technologies available. These two aspects will necessarily meet each others to find Final Storage Quality conditions for the landfill. In this chapter, the total emissions of an aerated and flushed reactor are analysed for understanding which long-term concentrations are expectable. Moreover, a chemical speciation of the main landfill compounds was made to characterize the final state of stabilized material and identify which emissions can potentially occur after the FSQ conditions achievement.

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3.2 Influence of semi-aerobic conditions and flushing on waste stabilization and long-term expectable emissions from a landfill simulation bioreactor

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3.2.1 Introduction

The current approaches of the scientific community to the long term management of municipal solid waste (MSW) landfills can be classified in categories of increasing complexity, from the simple target value approach, based on the definition of legislation limits to be met to complete aftercare (Cossu et al., 2007), to the risk-based approaches, where site specific conditions are taken into account (Laner et al, 2012). As consequence, the Final Storage Quality of solid waste and the leachate long-term potential emissions become relevant issues in the scientific literature. Final Storage Quality (FSQ) is defined as the chemical status in which a landfill cannot harm the environment or the human health anymore and all the emission control measures can be safely removed (Christensen et al., 2011). However, the FSQ chemical definition is still debated in the scientific community because the environmental risk of a general landfill is hardly definable, being also influenced by site-specific constrains. On the contrary, the expected future residual emissions of a landfill can be easily quantified and used for contributing to the definition of Final Storage Quality conditions.

Landfills store a huge quantity of not mobile or harmless mobile substances, which are not an issue for environmental or healthcare safety and constitute a final sink for closing material cycles (Cossu, 2016). Concomitantly, carbon, nitrogen, chlorine, sulphur and Heavy Metals (HM) are compounds consistently present in a Municipal Solid Waste (MSW) landfill which can potentially become contaminants in case of uncontrolled emissions into the environment, especially during long-term aftercare (Christensen and Kjeldsen, 1989). In addition to them, also some refractory organic by-products and new chemicals are met with increasing frequency in long-term leachate emissions and solid waste, in particular pharmaceuticals, flame retardant, stabilizers, fillers, inks, antioxydants, personal care products, etc (Bolyard and Reinhart, 2016; Pivnenko and Astrup, 2016). For reaching FSQ safe conditions and terminate the aftercare phase, the biodegradable compounds must be biologically stabilized and the leachable ones must be extracted, aiming to reach the conditions in which the related concentration in leachate becomes environmentally acceptable and the potential emissions become negligible, as consequence.

Many authors proposed different solutions for accelerating the biochemical stabilization processes and finally reaching FSQ conditions (Townsend et al., 2015; Cossu et al., 2016, Christensen et al., 2011; Ritzkowski et al., 2013; Ritzkowski et al., 2016; Fellner et al., 2009; Wu et al., 2014; Ritzkowski and Stegman, 2013). Landfill aeration and Hybrid bioreactor demonstrated to be valuable tools for decreasing the long-term organic compounds and ammonia nitrogen in leachate (Townsend et al., 2015; Ritzkowski et al., 2016). Flushing was also fundamental for the abatement of not degradable compounds until reaching the acceptable concentrations (Bolyard and Reinhart, 2016).

Following this route, the further step could be estimate statistically the total emissions of a MSW landfill for knowing the maximum expectable emission value potentially reachable. This result is obtained analysing the long-term biochemical and chemical features of a large-scale landfill simulation reactor, maintained for a decade in semi-aerobic conditions. In particular, the long-term compounds concentration in leachate and the total emissions potential were analysed by means of two flushing test conducted on the reactor until reaching a Liquid Solid (L/S) ratio higher than 2.7 L/kgST. The test was constituted by long aftercare simulations, alternated with flushing tests, for highlighting the different effects of leaching and aeration in compounds long-term emissions. Finally, the total emissions potential of the reactor were compared with the data elaboration of other lab-scale tests found in literature and re arranged in a landfill potential emissions database.

3.2.2 Materials and methods

Equipment

The landfill simulation test was carried out in a large lysimeter reactor constituted by a Plexiglas column of 3 m height with a square base of 0.8 m side, resulting in a total volume of approximately 2 m^3. This particular lysimeter is arranged to simulate a semi-aerobic landfill, enhancing natural air circulation, with the possibility to create anaerobic conditions too (Figure 3.2.1).

The top of the reactor is hermetically closed by a Plexiglas cap, with the exception for an opening which is useful for liquid injection and gas circulation. A gravel layer (Ø 16-32 mm) is placed at the bottom, contained by a plastic grid (# 5 mm) to prevent waste sample to enter in. The reactor was equipped with a holed HDPE pipe (diameter 300 mm) horizontally installed into the bottom gravel layer for allowing natural air flow driven by the temperature gradient between the waste body and the external environmental temperature (Matsufuji et al., 2013) (Figure 3.2.1). All the sides of the lysimeter are thermally insulated by means of polystyrene foils; this system guarantees temperatures of 5-10°C higher respect to the external environment. The air circulation can be stopped closing the pipe and the opening in the cap, creating an anaerobic environment as consequence.

The bottom of the reactor is also equipped with five valves for leachate sampling. The accumulation of an excessive quantity of leachate inside the reactor is not possible due to the pipe placed 15 cm over the bottom. The temperature is monitored from three positions on the side of the reactor (T1, T2, T3: Figure 3.2.1). The biogas sampling can be performed both from the cap and the sides of the reactor by means of the same temperature monitoring positions. Solids sampling is also possible both from three side openings (G1, G2, G3: Figure 3.2.*1*) and excavating the reactor from the top.

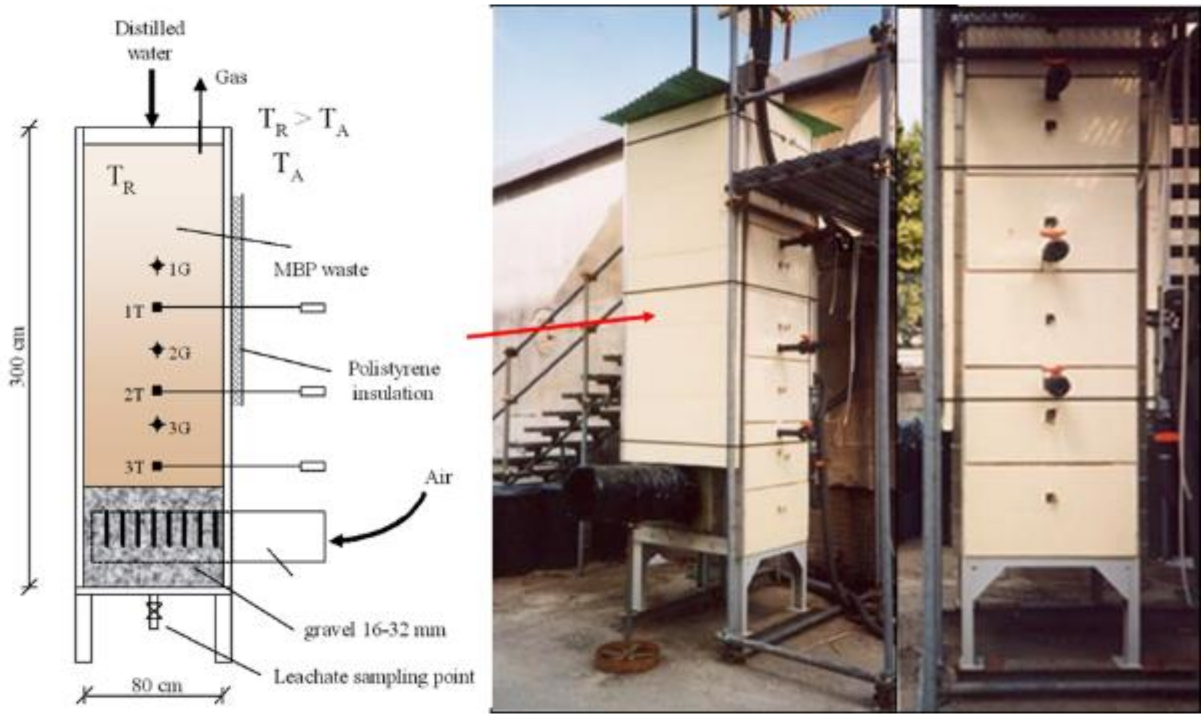


Figure 3.2.1: Sketch and picture of the lysimeter reactor used for the test.

Table 3.2.1: Fractional composition of the waste loaded into reactor, in percentage by mass.

	>100 mm	**100 - 60 mm**	**60 - 20 mm**	**Class Total**
Plastic	0.0	5.8	14.3	20.1
Paper & Cardboard	0.0	6.0	12.1	18.1
Kitchen Residues	0.0	2.9	0.9	3.8
Green waste	0.0	1.6	2.7	4.3
Textiles	0.0	0.4	4.0	4.3
Metals	0.0	0.5	4.5	5.1
Glass & Inherts	0.0	0.4	4.0	4.3
Under-sieve <20 mm				39.9
Sieve Total	0.0	17.6	42.6	100.0

Waste sample

The solid waste sample was 750 kg of mechanically treated Municipal Solid Waste (MSW), taken from a Mechanical Biological Treatment (MBT) plant, located in Northern Italy. This starting material was specifically the same generally deposited in the landfill, without performing the aerobic stabilization. The granulometric distribution of the waste size was influenced by the mechanical treatments; as consequence, more than 80% of the sample was constituted by pieces smaller than 6 cm (Table 3.2.1). The fractional composition was the typical one of MSW: the under-sieve was the main fraction (39.9% by mass), plastic and paper were also abundant (more than 18 %), while other classes totalized under the 5 %.

Test Setup

The experiment was divided into 5 different phases, for a whole length of 3250 d, corresponding approximately to 108 months (Table 3.2.2) (Vettorazzi, 2005; Piovesan, 2007; Morello, 2013). The test was constituted by an initial anaerobic start up and two long aftercare simulations (totally representing more than the 90% of the test duration), alternated with flushing tests. As previously explained, the purpose of the flushing test was to evaluate the total liquid emission potential of the reactor, while the alternation with aerated aftercares aimed to highlighting the different effects of leaching respect to aeration.

The test start-up was made of an Anaerobic Phase in which a constant water supply of 10 L/week allowed the establishment of stable methanogenic conditions, lasted for 174 days, reaching a Liquid to Solid ratio (L/S) of 0.74 L/kgTS (Table 3.2.2). This water input was chosen to simulate the standard precipitation of the northern part of Italy in the top surface of the reactor. The second and fourth phases were long Aftercare Simulations with no water supply and in which the natural air circulation was enhanced by the reactor design creating a semi-aerobic bioreactor landfill (Matsufuji et al., 2013). The first Flushing was performed from day 968, adding the triple of the standard precipitation on a week bases for two months, in order to simulate an absence of the top cover over the landfill. The second, more abundant, Flushing phase started at the day 3154 and lasted for three months with a total injection of 750 L of water, finally reaching a L/S of 2.76 L/kgTS (Table 3.2.2).

Table 3.2.2: Management of the reactor subdivided into five different phases.

	Phase	Duration (d)	Final L/S (L/kgTS)	Aeration
Anaerobic phase	1	174	0.74	Anaerobic
Aftercare simulation 1	2	794	0.82	Natural-circulation
Flushing 1	3	60	1.07	Natural-circulation
Aftercare simulation 2	4	2126	1.14	Natural-circulation
Flushing 2	5	96	2.76	Natural-circulation

Leachate and gaseous emissions were monitored on week bases during the Anaerobic Phase and the Flushing tests; no sampling of leachate was performed during the long-term aftercare simulation because the absence of water injection did not allow leachate production. Solid waste analysis were performed on the initial sample as well as on samples taken from the lysimeter at the end of Flushing 1 and Flushing 2.

The data collected allow to build a mass balance, evaluating the liquid emissions of the reactor at the end of Flushing 1 and Flushing 2 phases. The gaseous emissions could only be estimated from the mass balance itself being technically impossible to quantitatively measure them without influencing the natural circulation of air.

For comparing this experimental results with the literature ones, a database of lab-scale tests was assembled. The comparison factor chosen was the compound cumulative liquid emission percentage respect to its initial content in the solid waste sample loaded into the reactor. This choice was driven by the necessity to have a normalized massive index instead of the concentration of a compound, which is highly influenced by the dilution effect and by the management of the landfill itself. This comparison is made for both the anaerobic and the aerated tests, to highlight the differences among these operative conditions. The elements chosen are Carbon, Nitrogen and Chloride, whose monitoring data are abundant in literature tests, being they universally recognised as the main environmentally relevant compounds of a MSW landfill (Christensen and Kjeldsen, 1989; Morello et al., 2016; Fellner et al., 2009).

The database is constituted by lab-scale landfill simulation test, each of them dealing with Mechanical Biological Treated (MBT) Municipal Solid Waste (MSW), until reaching an estimated Liquid Solid ratio (L/S) higher than 0.8 L/kgTS and until the reactor's emissions were considered sufficiently stable. The biological stability was stated by the authors themselves or accepted if concentrations of carbon and nitrogen compounds were considered sufficiently low and constant in time, also according with FSQ values found in literature (D.G.R. 2461/14, Laner et al., 2012). Moreover, each test was loaded into the database only if the L/S ratio could be estimated, the leachate data collection was possible with sufficient precision and the analysis of the chosen compounds in the initial solid waste were available. The data considered into the database were given directly by the authors as well as evaluated or estimated from the information being available in the published articles.

The database totally comprised 60 lab-scale landfill simulations: Cossu et al., 2003; Raga and Cossu, 2014; Manfredi and Christensen, 2009; Ritzkowski et al., 2006; Ritzkowski and Stegmann, 2013; Wu et al., 2014; Fellner et al., 2009; Valencia et al., 2009; Sandip et al., 2012; Sang et al., 2009; Lornage et al., 2013; Matsufuji et al., 2013; Cossu et al., 2016; Morello et al., 2016; Bolyard and Reinhart, 2016. For creating a sufficiently large record, the test used included 35 fully anaerobic landfill simulations, 21 aerated reactors and 4 semi-aerobic reactors. Among them, 2 were open dumps simulations, 5 were Hybrid bioreactors, 2 had a pre-aeration phase and 3 were flushed until reaching a L/S higher than 3 L/kgTS.

Analytical Methods

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

A portable analyser (Eco-Control LFG20) was used to measure CO_2, CH_4 and O_2 concentrations in biogas from the side openings of the lysimeter equipment, the results were periodically compared with another portable gas analyser (Analitica Strumenti LFG 2000). The quantification of the gaseous emissions was not technically possible for avoiding interferences with the natural circulation of air, as already explained.

Leachate samples were periodically analysed for pH, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Biological Oxygen Demand(BOD_5), Total Kjeldahl Nitrogen (TKN), Ammonium Nitrogen ($N\text{-}NH_4^+$), Nitric Nitrogen ($N\text{-}NO_3^-$), Sulphates (SO_4^{2-}), Chlorides (Cl^-) and

Heavy Metals (Cr, Cu, Fe, Mn, Ni, Pb, Zn) according to the prescribed Italian standards, derived from international certified procedures (CEN, 2002). The BOD_5/COD ratio is a parameter capable of indicating the amount of biodegradable compounds still present in a liquid (Cossu et al., 2012), assuming values between 0.02 and 0.13 for low biodegradability and values exceeding 0.4 for high biodegradability (Sekman et al., 2011).

The solid waste was sampled at the beginning as well as at the end of the test, extracting completely all the material. Only at the end of the Flushing 1, the solid waste collection was made excavating the waste inside the reactor and taking samples at different deepness. The extracted material was thoroughly mixed in a tank to increase homogeneity and the material greater than 6 cm was removed before the analytical determination of Total Solids (TS), Volatile Solids (VS), TOC TKN and Respiration Index (RI_4). All tests on solid samples were performed at least in duplicate.

TOC on solid samples was measured using a TOC-VCSN Shimadzu Analyser. The Respiration Index (RI_4 mgO_2/gTS) was determined by means of Sapromat apparatus (H+P Labortechnik, Germany).

3.2.3 Results

Solid samples

The massive concentration of Total Organic Carbon (TOC) and Total Nitrogen (TN) significantly decreased to 55 % and to 59 % respectively, from the beginning (Start) until the end of the test (Flushing 2). However, the most consistent reduction occurred within the end of Flushing 1 (Table 3.2.3).

Table 3.2.3: Solid waste analysis (Average value ± Stgandard Deviation) from the beginning of the test (Start) to the end of Phase 3 (Flushing 1) and until the end of the whole test (Flushing 2).

	TOC (gC/kgTS)	**TN (gN/kgTS)**	**IR4 (gO2/kgTS)**	**TS (%)**	**VS (%TS)**
Start	311 ± 24	15.0 ± 1.3	66.4 ± --	44.5 ± 1.3	48.5 ± 8.7
Flushing 1	190 ± 7	9.8 ± 1.0	0.7 ± --	41.4 ± 1.0	26.1 ± 5.0
Flushing 2	172 ± 30	8.9 ± 0.9	0.7 ± 0.2	52.3 ± 2.4	27.5 ± 6.9

Similar results can be observed also for the volatile solids, representing the potential organic carbon content, and for the Respiration Index, stating the biodegradable residual fraction of the solid material. In particular, RI_4 decreased to 0.7 $gO_2/kgTS$ since the end of the Flushing 2, being lower than 2.5 mgO_2/gTS, which is the target value indicated by Laner et al. (2012) to establish the biochemical stability of the landfilled waste.

The final waste sample chemical stability, as well as long-term leachability of compounds, were evaluated to be below the threshold values suggested by literature (D.G.R. 2461/14; Laner et al., 2012) and below the Italian soil contamination law threshold limits, also (D.Lgs 152/06).

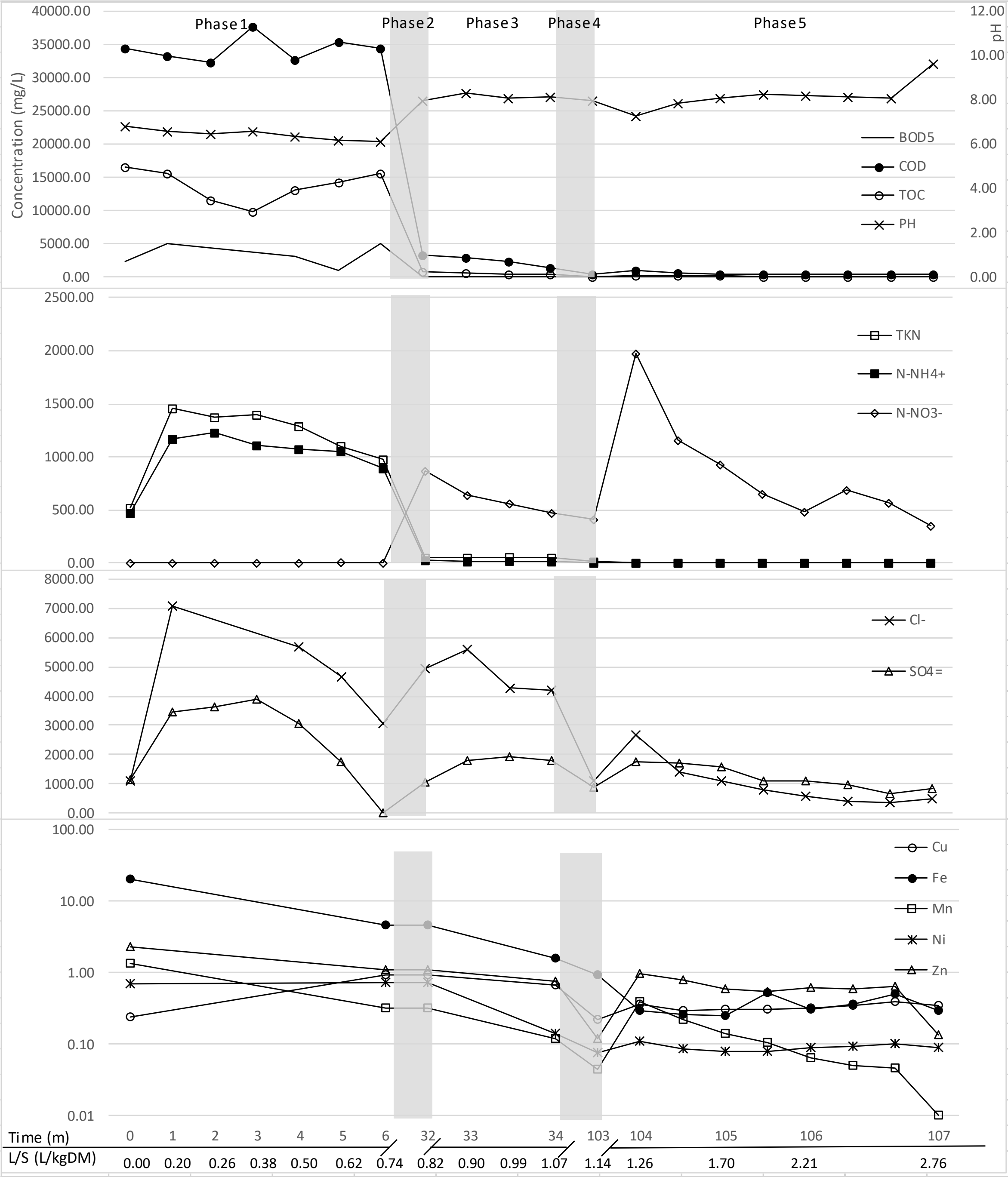


Figure 3.2.2: Concentration of the main monitored compounds in leachate for carbon, nitrogen, chloride, sulphates and Heavy Metals. A Logarithmic scale is used for Heavy Metals concentration. Cd and Cr concentration were always under the detection limit.

Leachate monitoring

Figure 3.2.2 shows the evolution of the main parameters monitored in the leachate samples extracted from the reactors throughout the test (carbon, nitrogen, sulphates, chloride and Heavy Metals). The results are plotted respect to the L/S ratio for highlighting the effect of leaching in comparison with the long aftercare simulation phases, which are represented by the grey vertical lines.

The carbon compounds concentration remained stable for the entire anaerobic phase, decreasing of an order of magnitude only during the Phase 2 (Figure 3.2.2). At the beginning of the first Flushing test, the COD concentration was below 4000 mg/L and further decreased finally reaching values under 500 mg/L, due to the leaching of the persistent not degradable compounds (Bolyard and Reinhart, 2016). Simultaneously, the BOD_5 concentration was reduced from 5000 mg/L to values below 50 mg/L since the beginning of Phase 3. As consequence, the BOD_5/COD ratio in leachate, at the beginning of the Phase 3, was far below 0.01, reaching the values certifying the biochemically stable conditions for the reactor (Sekman et al., 2011).

The nitrogen emissions in a landfill are mainly due to ammonia ion which is recognised as one of the most persistent compounds in the long-term leachate emissions (Morello et al., 2016). The aeration of the reactor since the Phase 2 allows the nitrification of almost all the ammonia ion produced by the ammonification of organic nitrogen compounds, demonstrating to be a valuable method to treat this long-term potential pollution (Ritzkowski et al., 2016). Subsequently, denitrification is likely to occur in anoxic zones of aerated reactors for converting the nitrates in free nitrogen gas (Berge et al., 2005; Raga and Cossu 2014). However, the high concentrations of oxygen in the reactor (over 15% since Phase 2) partially inhibit the denitrification process, causing nitrates accumulation in the solid waste and their subsequent release by leaching during the Flushing Phases (Figure 3.2.2). The sudden introduction of water in the reactor washed out the nitrates showing a peak concentration of 2000 mg/L during the Flushing 2. At the end of the test, TKN concentration was below 5 mg/L.

Chloride and sulphates concentrations decreased according with the L/S ratio, showing a rebound at the start of every Flushing phase, probably due to the sudden increase of water content (Figure 3.2.2). At the end of the test, monitored chlorides and sulphates concentrations were both below 1000 mg/L.

The Heavy Metals (HM) leachate concentration in MSW landfill has not great environmental interest due to their low mobility (Qu et al., 2008). This test confirmed this sentence, being the HM emissions over 2 mg/L only for Iron during the Anaerobic Phase (Figure 3.2.*2*).

The comparison of the final compounds concentrations in leachate with the FSQ indexes available in literature (D.G.R. 2461/14; Laner et al., 2012) showed that every compound present in the reactor, with the exception for Nitric Nitrogen, reached chemical and biochemical stabile conditions.

The leachate concentration behaviour confirmed that the aeration was effective in reducing the organic compounds concentration and contemporary in allowing complete nitrification of ammonia ion. On the other hand, the flushing treatment was efficient in extracting the more soluble compounds (such as chlorides, sulphates, nitrates) and the low quantities of Heavy Metals.

Gas Monitoring

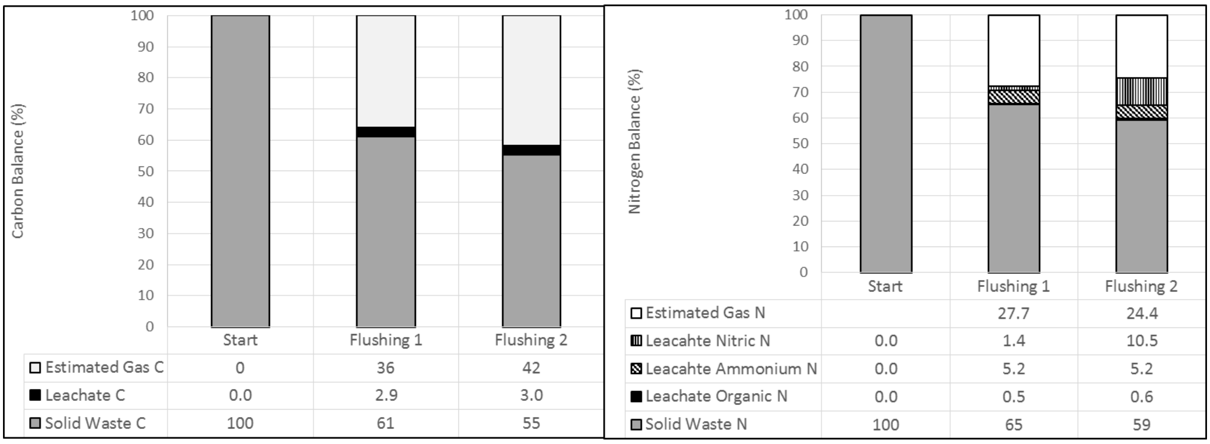
The gas in the waste interstitial pores, as well as the headspace one, was periodically monitored for the entire duration of the test. For the whole Anaerobic Phase 1, the residual oxygen in the reactor was rapidly consumed producing CO_2, which reached concentrations of 25-35%. After 2 months, some methane started to be produced until the beginning of the Aftercare simulation (Phase 2), in which oxygen presence totally inhibit the CH_4 production. During the first aftercare, the natural airflow guaranteed a significant presence of O_2 in the reactor, with very variable concentrations in time and in the different sampling points located all over the reactor. However, since the end of Phase 2 and for all the following phases, the interstitial gas composition was the same of external air, meaning that the aerobic biochemical processes in the lysimeter becomes negligible.

3.2.4 Discussion

Mass Balance

The mass balance for carbon and nitrogen was calculated starting from the solid waste analysis and the leachate emissions monitoring. The gaseous emissions were estimated through the balance itself; however, being in line with the gas quality monitored (Figure 3.2.3). The results obtained in Figure 3.2.*3* can be considered reliable concerning liquid emissions; the main source of mistake is the analysis of solid sample, even if performed in triplicate, as shown in Table 3.2.3.

At the end of Flushing 1, approximately 39 % of the initial carbon has leaved the reactor, while this quantity increased to 45 % at the end of the entire test. Almost all the carbon emissions in leachate happened within the Flushing 1 (2.9 %), while only a small increase was monitored after that phase. Concomitantly, the final gaseous emissions were estimated to be approximately 42 % of the initial carbon, confirming that in a landfill the gaseous emissions are an order of magnitude higher than the liquid ones (Morello et al., 2016, Lornage et al., 2013; Fellner et al., 2009). These data highlighted also that the majority of the biochemical degradation processes happened within the Flushing 1 (Phase 2), as stated also by the BOD_5/COD ratio (Figure 3.2.2) and by the RI_4 index (Table 3.2.3). Some long-term reaction involving the slowly degradable persistent organics (such as cellulose, polymers, humic substances, etc) kept on until the end of the test and their effect is visible in the increase of gaseous emissions between the two Flushing phases. At the end of the test, the not mobile compounds contributing to finally sink the carbon were calculated to be the 55 % respect to the initial content (Figure 3.2.3).



	Start	Flushing 1	Flushing 2
□ Estimated Gas C	0	36	42
■ Leachate C	0.0	2.9	3.0
▒ Solid Waste C	100	61	55

	Start	Flushing 1	Flushing 2
□ Estimated Gas N		27.7	24.4
▥ Leacahte Nitric N	0.0	1.4	10.5
▧ Leacahte Ammonium N	0.0	5.2	5.2
■ Leachate Organic N	0.0	0.5	0.6
▒ Solid Waste N	100	65	59

Figure 3.2.3: Carbon and Nitrogen mass balance evolution from the beginning of the test (Start) to the end of Phase 3 (Flushing 1) and until the end of the whole test (Flushing 2). The gaseous emissions are estimated through the balance itself. The results are given in mass percentage respect to the initial content of compound in the fresh waste loaded into the reactor.

The nitrogen balance showed that about the 60 % of the initial nitrogen remained stored inside the solid waste in a not mobile form, constituting a final sink for that element (Figure 3.2.3). Similarly to carbon leachable compounds, the ammonia ion and the organic nitrogen leachate emissions entirely happened before the Flushing 1 Phase, resulting negligible for the rest of the experiment. This behaviour confirm the efficiency of the landfill aeration in nitrification of the ammonia ion (Berge et al., 2005; Ritzkowski et al, 2016). The nitrates emissions remained consistently high, even in long-term, amounting to more than 10 % of the initial nitrogen, at the end of the test (Figure 3.2.3). This behaviour confirmed the inefficiency of denitrification process probably inhibited by the excessive oxygen presence and by the absence of readily degradable organic substrates. Moreover, the increase of nitrates in Flushing 2 (Figure 3.2.3) was probably caused also by an increased solubilization of these compounds due to the heavy flushing applied, which redistributed the moisture content in the whole reactor, removing the negative effects of the preferential pathways for water movement.

Comparison with a Literature Database

The mutual comparison between the leachate emission for carbon and nitrogen compounds was made by assembling a lab-scale landfill simulation database, whose statistical elaboration results are reported in Figure 3.2.4 (the X is the average sample value and the O is the lysimeter test result). The data elaboration was performed considering only the values comprised between percentiles 10 and 90, for excluding extreme cases. The average L/S of the tests sample was 2.40 L/kgTS and the 80% of L/S values were comprised between 0.92 and 3.36 L/kgTS, corresponding to the percentile 10 and 90.

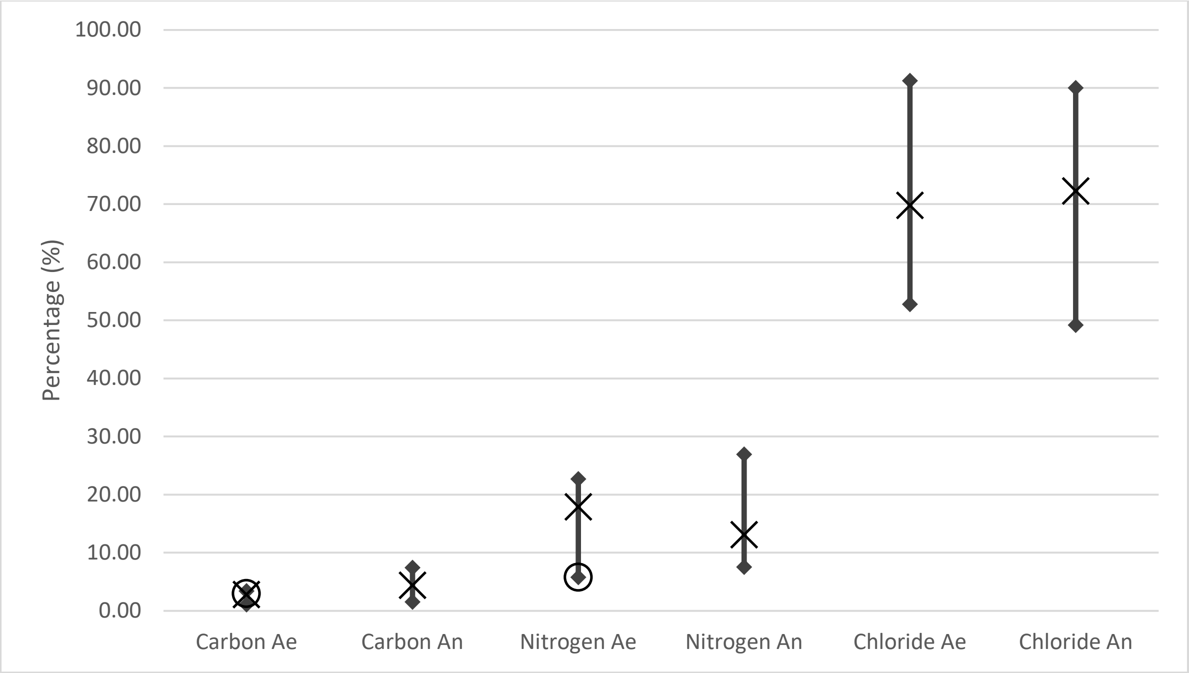


Figure 2.3.4: Carbon, Nitrogen and Chloride percentage (%) liquid emissions statistic, elaborated from the lab-scale test database for both aerated (Ae) and anaerobic (An) reactors. X represent the average value, O is the lysimeter result and the range considered is comprised between the percentile 10 and 90.

The carbon leachate total emissions, respect to the initial concentration in the solid waste, remains always below 8 % in the considered tests. In particular, the aeration proved to be a valuable solution to decreasing the carbon liquid emissions even under 4 %, as demonstrated by the elaborations as well as by the lysimeter test results (Figure 3.2.4).

The nitrogen total liquid emissions ranged between 8 % and 28 % respect to the initial concentration in solid waste (Figure 3.2.*4*). The aeration only slightly decreased the nitrogen liquid emissions, even if the dropdown of ammonia final concentration was undeniable and verified in all aerated reactors. As consequence, even if the nitrogen total emission quantity was similar in all tests, residual emission potential remained much higher is the anaerobic reactors. The database analysis results confirmed that the aeration was a valuable method for decreasing nitrogen persistent pollution, as stated by Ritzkowski et al., 2016.

The chloride total emissions respect to the initial concentration in solid waste were always higher than 50%, sometimes reaching values over 90% (Figure 3.2.4). Negligible differences caused by the different landfill treatments are registered, being chloride influenced almost only by solubilization and by the L/S ratio reached (Fellner et al., 2009).

3.2.5 Conclusions

The aeration and the flushing applied to landfill simulation reactors were able to chemically and biochemically stabilize the waste as well as to reduce the long-term leachate emissions far below the target values suggested by D.G.R. 2461/14 and Laner et al., 2012. In particular, the leachate concentrations of organic and nitrogen compounds at the end of the test were consistently reduced.

The leachate concentration behaviour showed that aeration was effective in reducing the organic compounds concentration and contemporary in allowing the complete nitrification of ammonia ion. On the other hand, the flushing treatment was efficient in extracting more soluble compounds (such as chlorides, sulphates, nitrates) and Heavy Metals. As consequence, the biochemical and chemical stability of the potential polluting elements of a landfill can be reached by balancing the efforts of both the two treatments.

The mass balance confirmed that the MSW deposited in a landfill is a good final sink for the carbon (55 % stored respect to the initial content) as well as for the nitrogen (60 % stored respect to the initial content). The comparison with database highlighted that the expectable total landfill liquid emissions are generally below 8 % (respect to the initial content) for carbon, range between 8 % and 28 % for nitrogen and are higher than 50 % for chlorides.

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3.3 Fate of Municipal Solid Waste main compounds undergone to a sustainable landfilling simulation.

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Abstract

Modern landfilling should not overlook the application of the sustainability principle, which prescribes to guarantee environmental protection within a reasonable amount of time. Solid waste contains high quantity of mobile compounds that can eventually harm the environment if the containment system of the disposal sites fails. Reaching Final Storage Quality (FSQ) conditions is a hot research topic nowadays and the analysis of a long-term stabilized landfill material, in comparison with the initial one, could help to understand which compounds are expectable at the end of the aftercare and in which form, starting from the analysis of the initial raw waste.

For this purpose, this article aims to understand the evolution and the fate of the main compounds of a landfill, respect to the initial characteristics of the raw waste. Some Municipal Solid Waste (MSW) samples were taken at the beginning as well as at the end of a sustainable landfilling simulation. These samples were divided into main categories (Under-sieve < 20 mm, Kitchen residues, Green waste and wooden materials, Plastics, Textiles, Cellulosic Material) and the main species of each contaminant (carbon, nitrogen, chlorine, sulphur and Heavy Metals) were analysed. The characterization considers all the main subcategories of each chemical species, focusing especially on degradable fractions, leachable compounds, long-term persistent by-products and not mobile fraction, constituting a final sink.

Results showed that under-sieve was the most abundant fraction, especially in stabilized samples (77%), containing a significant percentage of total mobile compounds and more than 85% of final residual potential emissions. Waste mass proved to be a good sink, storing more than 55% of carbon, 53% of nitrogen 33% of sulphur and 90% of Heavy Metals (HM) initially present in the fresh waste sample. Finally, HM emissions were considered not to be relevant in landfill MSW emissions, being the most of them bond with not leachable substrates, even after a long-term aerated aftercare.

Keywords

Waste characterization; Waste compounds speciation; Landfill long-term emissions; Aftercare completion; Final Storage Quality (FSQ); Sustainable Landfilling.

3.3.1 Introduction

Modern landfilling should not overlook the application of the sustainability principle, which prescribes to guarantee environmental protection, avoid sanitary problems and ensure that the disposed waste will be chemically and biochemically stable within a reasonable amount of time. For this purpose, landfills should be designed and managed aiming to the acceleration of waste biochemical stabilization in order to reach the Final Storage Quality (FSQ) within the time span of one generation (Laner et al., 2012). Landfill aftercare completion still remain a debated issue, faced with different approaches in scientific literature and more research is required to understand which level of biochemical and chemical stabilization is effectively reachable at the Post Closure Care end. This need is related to the potential threats posed on the environment (in short and long-term) by mobile fractions in waste and to the significant role that landfills can play as sink for closing material cycles (Cossu, 2016; Pivnenko and Astrup, 2016). As consequence, the enhancement of waste stabilization through innovative landfill technology for reducing long-term emissions and the immobilization of specific compounds inside landfill bodies are hot topics nowadays and several related research projects are currently in progress worldwide (Townsend et al., 2015; Cossu et al., 2016, Christensen et al., 2011).

A landfill stores huge quantities of not mobile or harmless mobile substances, which are not an issue for environment or healthcare safety. On the other hand, carbon, nitrogen, chlorine, sulphur and Heavy Metals (HM) are compounds consistently present in a Municipal Solid Waste (MSW) landfill which can form compounds considered contaminants in case of uncontrolled emissions into the environment, especially during long-term aftercare (Christensen and Kjeldsen, 1989). LCA studies, based on literature data, estimated the magnitude of the storage potential of different technologies and substances, showing that up to 58% of carbon, 87% of nitrogen, 49% of chlorine and 99% of HM were expected to remain stored in a municipal solid waste landfill in a 100-year time simulation (Manfredi et al. 2009). Similar results were obtained by Qu et al. (2008), in terms of HM limited mobility in a full-scale bioreactor landfill. In addition to this analysis, also some refractory organic by-products and new chemicals able to produce long-term emissions are met with increasing frequency in leachate and solid waste, in particular pharmaceuticals, flame retardants, stabilizers, fillers, inks, antioxidants, personal care products and others (Bolyard and Reinhart, 2016; Pivnenko and Astrup, 2016).

This paper aims to identify the waste fractions and the contaminants most affecting the overall characteristics of young and old MSW. After that, the evolution in time and the fate of the selected contaminants is estimated through a chemical speciation of a recently collected waste in comparison with an old one coming from a long-lasting landfill simulation.

Both samples were taken from the same plant, ensuring that the fresh sample is chemically equivalent to the initial MSW loaded into the reactor. Finally, for describing the reachable chemical and biochemical conditions of the stabilized waste, the long-term residual emission potential and the storing capacity of these elements in a landfill sink are evaluated. Two MSW samples were taken, prior and after long-lasting sustainable landfilling simulation, and a chemical speciation of carbon, nitrogen, chlorine, sulphur and HM was applied. A further goal of the research project is to describe the stabilized material species, state the not-mobile fraction and quantify the residual emissions potential in comparison with local regulations and international standards.

Stored carbon can be divided into organic and inorganic fractions, the first one can be further divided in biodegradable and hardly biodegradable compounds (such as Cellulose, Hemicellulose, Lignin and Synthetic Organic Polymers), which can contribute to carbon storage. Investigations on carbon storage potential of landfilled waste (De la Cruz et al., 2013) resulted in the estimation that 35% to 95% of the biogenic carbon is likely to go into long-term storage. The lab-scale test conducted by Bolyard and Reinhart (2016), shows that 45-50% of carbon remains stored in the waste mass, while less than 5% is emitted by leaching, even after a flushing treatment reaching a Liquid-Solid ratio (L/S) of 10 L/kgTS. According to Brandstätter et al. (2015a), more than 10% of the biodegradable mobile organic carbon initially present in mobile forms in the samples is transformed into not mobile forms, probably due to the formation of humic substances. Humic and fulvic acids are refractory by-products, result of the conversion of biomass during the degradation process and they are only partially leachable, constituting a relevant contribution to long-term COD emissions in leachate.

The nitrogen mass balance shows that the majority of the initially present nitrogen remains stored into the waste mass, bounded to complex not-degradable polymers and organic matter, whatever treatment is applied (Brandstätter et al., 2015b). The lab scale test conducted by Bolyard and Reinhart, (2016), shows that 73-76 % of nitrogen remains trapped in waste mass, despite aeration and flushing reaching a L/S ratio of 10 L/kgTS. Mobile nitrogen is mainly composed by soluble ammonia ion, derived from ammonification, which is considered the most persistent contaminant in landfill leachate. The nitrification-denitrification process is the easiest method to decrease the long-term emissions of NH_4^+ (Berge et al., 2005; Ritzkowski et al., 2016), unavoidable step for reaching FSQ conditions in a sustainable time.

The chlorine emissions of landfills are mainly constituted by chloride, being persistent also in long-term emissions. Chloride solubility is generally high and partially influenced by pH; consequently, the reactor biochemical conditions only slightly affect the chloride leaching (Fellner et al., 2009; Morello et al., 2016).

The sulphur compounds chemical conditions are influenced by the environment redox properties and pH: if a reducing environment is established, sulphide prevails (in both solid samples and leachate). On the contrary, in presence of oxygen, sulphates are the most common detectable fraction.

The Heavy Metals (HM) concentration in landfilled MSW has not a great environmental interest due to their low mobility (Qu et al., 2008). However, HM presence in solid state is significant and their speciation is strictly dependent on the Redox conditions and pH: low pH increases the amount of HM in ionic mobile form, while reducing conditions enhance their precipitation. According with Kjeldsen et al. (2002), only the 0.02% of the initial Heavy Metals in the landfill is removed by leachate within 30 years of anaerobic conditions, while less than 1% considering aerobic processes. HM speciation can be a useful tool for describing their bonding state with other compounds and to understand how they could be released in the surrounding environment, as consequence. There are not standard procedures for performing this analysis because of the difficulties to identify precisely HM behaviour, dependent on several physic-chemical parameters.

3.3.2 Materials and methods

Materials

The study is based on the characterization of a fresh Municipal Solid Waste (MSW) sample taken prior to be landfilled (Fresh F sample) and a stabilized material coming from a very old lysimeter reactor at the end of its life (Stabilized S sample). Each sample was taken from the same Mechanical Biological Treatment (MBT) plant, located in Northern Italy, before the aerobic stabilization. F sample was immediately analysed immediately after collection, highlighting the initial waste conditions. S sample was constituted by material which undergone to a long-lasting sustainable landfilling simulation in a lysimeter reactor. Fresh sample was taken ensuring that its chemical characteristics are equivalent to the ones of initial MSW loaded into the reactor.

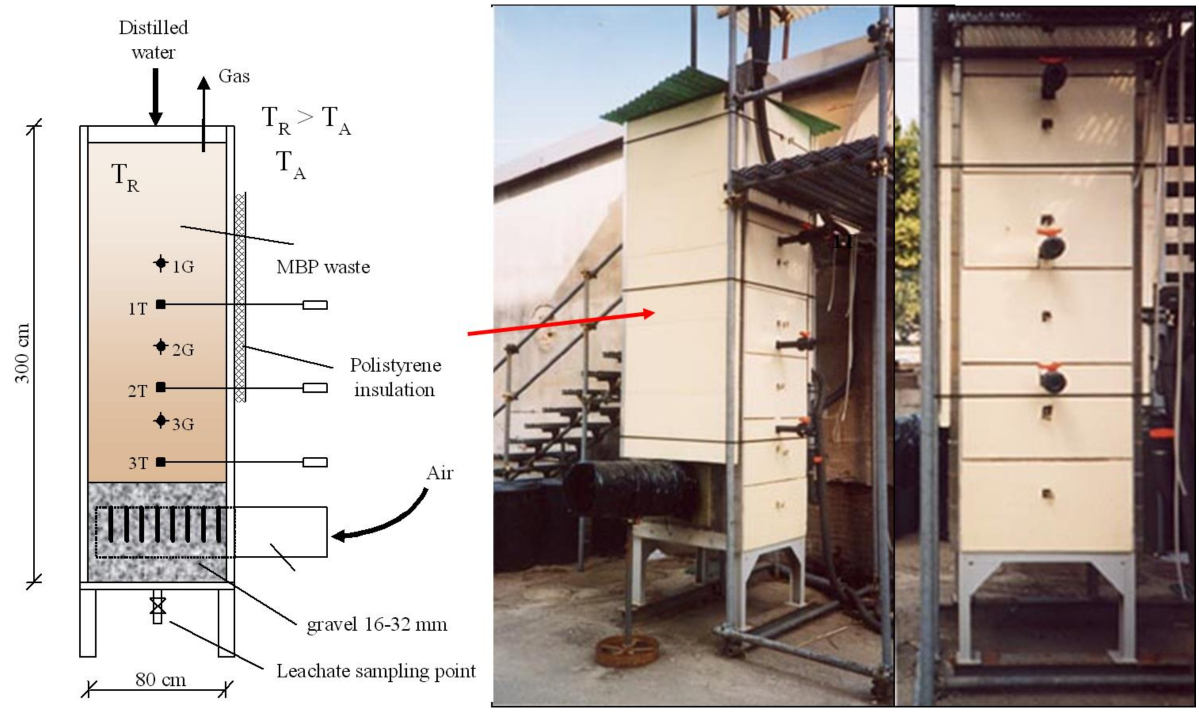

Figure 3.3.1: Sketch and picture of the lysimeter equipment with thermal insulation cover.

The lysimeter reactor was constituted by a 2 m^3 volume square based column, build for the simulation of a semi-aerobic landfill: allowing the natural air circulation driven by the temperature gradient between the waste body and the external environmental temperature (Figure 3.3.1). The reactor was equipped with a pipe (diameter 300 mm) in the bottom gravel layer for allowing the natural air flow, with a thermal insulation system and with a valve system for sampling leachate as well as monitoring gas emissions. Landfill simulation consisted in a series of treatments aimed to chemically and biochemically stabilize the waste to reach conditions in which the properties of the materials inside and the leachate emitted will ensure no harm for the environment (Final Storage Quality concept) (Vettorazzi, 2005; Piovesan, 2007; Morello, 2013). The test lasted for approximately 10 years, subdivided in a first anaerobic phase (180 days with injection of 10 litres of water per week to reach an L/S ratio of 0.82 L/kgTS) (Vettorazzi, 2005) and a long semi-aerobic aftercare period in which no water was injected. Flushing tests were performed after 1000 days (60 days with the addition of 28 liters of water per week until an L/S ratio of 1.14 L/kgTS) (Piovesan, 2007) and at the end of the whole test (180 days with a total amount of water added of 750 L to finally reach an L/S ratio of 2.76 L/kgTS) (Morello et al., 2013). The sample taken from the material at the end of the test (S sample) was estimated as biochemically stable and with low content of mobile potential polluting compounds. For certified this hypothesis, lab test results were compared with some proposed FSQ values (D.G.R. 2461/14, Laner et al., 2012).

Methodology

A fractional classification was performed as first operation on both samples. For increasing analytical precision, three sieves in series were used (100 mm, 60 mm and 20 mm), allowing to identify four different size fractions. After that, each size was divided into main fractional categories by means of a manual sorting procedure. The waste macro-categories chosen were Under-sieve < 20 mm, Kitchen residues, Green waste and wooden materials, Plastics, Textiles, Cellulosic Material, Inert, Glass, Metals, also according with the subdivision proposed by other tests (Cossu et al., 2016, Morello et al., 2016; Edjabou et al., 2015). F and S samples were prepared mixing together the same fractional categories coming from all sieve dimension: U for Under-sieve, K for Kitchen residues, G for Green waste and wooden materials, P for Plastics, T for Textiles and C for Cellulosic Material. Inert, glass and metals were not analysed because their composition is known, their emission potential is negligible and because they cannot be technically analysed with used methods. The impurities contained in separated samples are considered representative of the real subdivision which is made by the conventional mechanical sorting of a waste. Chemical analysis take into account the speciation of carbon, nitrogen, chlorine, sulphur compounds and Heavy Metals. Analysis were done on solid samples and on eluate from the leaching test, representing quantitatively the total mobile fraction of each category (Table 3.3.1).

Total Carbon content was evaluated through TC analysis, composed by Inorganic Carbon (IC) plus Total Organic Carbon (TOC). The amount of organic polymers was determined, representing the part of hardly degradable TOC that contributes to the carbon sink. Leachable fractions of carbon compounds were extracted through leaching tests and analysed (TC, TOC and IC). In addition, Volatile Fatty Acids (VFA) were measured to quantify the readily degradable compounds and humic-fulvic acids were monitored to evaluate the long-term emission potential. Finally, Respiration Index (RI_4) and BOD_5/COD ratio were useful indexes to check the biochemical stabilization of the samples (Cossu et al, 2012).

Total Nitrogen (TN) in solid samples was determined through CNH/S analysis. The speciation of TN considered Total Kjeldahl Nitrogen (TKN), including ammonia ion (NH_4^+) plus Organic Nitrogen, and oxidized forms, as nitrates (NO_3^-) and nitrites (NO_2^-). All these compounds are soluble so their quantification was done also in the eluate.

Table 3.3.1: List of parameters and analytical methods considered for each solid and eluate sample obtained from the different waste categories (U: Under-sieve, K: Kitchen residues, G: Green waste and wooden materials, P: Plastics, T: Textiles, C: Cellulosic Material). For the evaluation of organic polymers, humic acids, total chlorine and HM speciation, reference method is reported being not international standard.

Contaminants	Sample	Parameters	Analytical Method
Carbon compounds	Solid	TC, TOC, TIC	UNI-EN 13137 (TOC-VCSN Shimadzu Analyzer)
		TS, TVS	I.S.
		RI_4, RI_7	Respiration Index Standard
		Organic polymers	*Wang et al., 2013, Yang et al., 2006 and Li et al., 2004*
	Eluate	TC, TOC TIC	I.S. (TOC-VCSN Shimadzu Analyzer)
		VFA	Standard method n. 5560 C, 1989
		BOD_5	I.S.
		COD	I.S.
		Humic and fulvic acids	*Baddi et al., 2004*
Nitrogen compounds	Solid	TN	CHN/S elemental analysis
		TKN	I.S.
		NH_4^+	I.S.
	Eluate	TKN	I.S.
		NH_4^+	I.S.
		NO_2^-	I.S.
		NO_3^-	I.S.
Chlorine compounds	Solid	Total chlorine	*Okada et al., 2007*
	Eluate	Chloride	I.S.
Sulfur compounds	Solid	Total sulfur	CHN/S elemental analysis
	Eluate	Sulfate	I.S.
		Sulfide	I.S.
Heavy Metals	Solid	Total metals	EPA 1996, n. 3050 B (ICP analysis)
		Bounded metals	*Krishnamurti et al., 2002 (ICP analysis)*
	Eluate	Total meals	I.S. (ICP analysis)

Legend: TC – Total Carbon, TOC – Total Organic Carbon, TIC – Total Inorganic Carbon, RI_x – Respiration Index for x days, VFA – Volatile fatty acids, BOD_5 – Biological or Biochemical Oxygen Demand in 5 days, COD – Chemical Oxygen Demand, TN – Total Nitrogen, TKN – Total Kjeldahl Nitrogen, I.S. - International Standard: Italian Standard Methods officially derived from international certified procedures (CEN, 2002).

Total Chlorine was evaluated in the solid samples and in the related leachable fraction, which only component is chlorides.

Total Sulphur (TS) was detected through CNH/S on solid samples. In its speciation, sulphate and sulphide were considered as mobile fractions.

The total Heavy Metals (HM) (Cr, Cu, Fe, Mn, Ni, Pb, Zn) content was determined both on solid samples and on eluate to estimate the potential emissions. A deeper analysis foresaw the speciation of HM to understand the chemical form in which they were present and the compounds they were bond with.

The contaminants concentration in eluate can represent the total emission potential of the samples. Starting from this assumption, emission potential data were used to identify the fraction more influencing the total expectable residual emission of the landfill. From the comparison of the chemical speciation data, in particular observing their mutual change in time, the waste expectable characteristics after a long-term aerated and flushed Post Closure Care were estimated. Finally, the biochemical stability indexes for S sample were compared with FSQ values suggested by Lombardia Regional Government (D.G.R. 2461/14) to validate the biochemical stabilization of the material used. The situation in which threshold limit concentration for emissions in a liquid matrix (D.G.R. 2461/14) are respected by leaching test eluate, representing the total potential liquid emissions of the sample, is considered precautionary.

Sample Preparation

Fresh and Stabilized samples were both mixed, shredded (10 mm) by means of a soil mill and prepared in three different procedures according to the chemical analysis to be performed (Table 3.3.1):

- Intact solid sample were used for standard soil analysis (TOC, TC, TIC, TS, TVS, TKN RI_4, RI_7, $N\text{-}NH_4^+$,).
- Pulverized solid sample were used for some particular analysis requiring low quantities of very homogeneous materials (organic polymers, TN, total chlorine, total sulphur, HM and bounded HM). Pulverization consists in milling until obtaining a dust-mud composed by particles smaller than 1 mm size.
- Eluate form leaching tests were used for the analysis on liquid emissions (TOC, TC, TIC, VFA, BOD_5, COD, humic and fulvic acids, TKN, $N\text{-}NH_4^+$, NO_2^-, NO_3^-, Cl^-, sulphate, sulphide, HM). The leaching test performed respects the standard international procedure UNI EN 12457-2 (shredding at 4 mm, dilution with distilled water until reaching a L/S ratio equal to 10 L/kgTS, mixing for 24 h and filtering to 0.45 µm).

Analytical Methods

The chemical analysis on solid and liquid samples were always made according to the certified Italian standards, officially derived from international certified procedures (CEN, 2002), if possible (I.S. in Table 3.3.1). Solid waste analysis were always performed at least in duplicate and results are presented as the average value, ensuring that the standard deviation remains below 5% respect to the average. TOC on solid samples was measured using a TOC-VCSN Shimadzu Analyser. TC, TN and total sulphur were measured by means of a CHN/S elemental analysis equipment. HM content in solid samples and eluate were evaluated with Inductively Coupled Plasma (ICP). Respiration Index (RI_4 and RI_7 mgO_2/gTS) was determined by means of Sapromat apparatus (H+P Labortechnik, Germany). VFA were performed following the two point titration procedure (Standard n° 5560 C, 1989).

Where standard methodologies could not be applied, alternative methods available in literature were considered and results were validated comparing them with similar situations. Experimental non-standard procedures were performed for the evaluation of organic polymers (both synthetic and natural, such as cellulose, hemicellulose and lignin), humic acids, total chlorine and Heavy Metals speciation (specified in Table 3.3.1 as “bounded metals”).

The amount of polymers was determined utilizing the analytical procedures for natural polymers proposed by Wang et al., (2013), Yang et al. (2006) and Li et al. (2004). Typically, 0.5 g (dry weight) sample of every waste category had been digested in 30 mL of acetone at 90 °C for 2 h (at reflux) to extract semi-polar substances. At the end of the digestion, the sample was filtered (Whatman Glass Microfiber Filters, 1.6 μm) and dried in oven (105 °C) until constant weight. The amount of compounds extracted was calculated by difference between the dry weight of the sample before and after acetone digestion. After this determination, the sample underwent to a double-step hydrolysis with 150 mL of 72% w/v and the same amount of 3% w/v sulfuric acid solution. To enhance the reaction at each step, it was digested at 110 °C for 1 h (at reflux), after resting at 8-15 °C for 24 h. After hydrolysis, the filtered solid was washed with distilled water until sulphate ions were no more detected in the liquid phase and dried in oven at 105 °C. The amount of polymers soluble in the acid solution was calculated as difference between the dry weight of the sample before and after the double-step digestion. To determine the fraction of not hydrolysable organic polymers, the residues of the digestion processes were pyrolysed at 550 °C for 2 h in a muffle. The weight loss of the solid sample corresponded to the desired fraction, while the remaining compounds were only characterized by inorganic carbon. The amount of total hydrolysable organic polymers (including both synthetic substances, as in plastics, and natural compounds, like cellulose and hemicellulose) was calculated by difference between the TOC of eluate samples and the main results of the not hydrolysable organic polymers for each waste category.

The determination of humic and fulvic acids was performed following the procedure proposed by Baddi et al. (2004). 30 mL of each eluate sample underwent a double step centrifugation at 7000 rpm for 25 min with distilled water washing in order to remove any particulate matter in solution. The pH of the supernatant was adjusted to 2 with a sulfuric acid solution (2 M) to enhance humic acids precipitation. The samples were let setting for 24 h at 4 °C for a complete coagulation. Subsequently, a second double step centrifugation with washing was performed and the precipitate was dried under vacuum and weighted. The residue represented the amount of humic acids. The supernatant coming from centrifugation was collected and dialyzed through Spectra/Por® Dyalysis Membranes (3500 Da). The amount of eluate retained was finally dried to have the content of fulvic acids in the sample.

Total chlorine was determined according to Okada et al. (2007). The amount of solid sample considered was 0.5 g (dry weight); it underwent acid digestion with 50 mL of 10% nitric acid at 100 °C for 2 h (at reflux) and titration with silver nitrate to have the final result.

The Heavy Metals speciation was performed on solid samples through the multistep procedure proposed by Krishnamurti et al. (2002) (Table 3.3.2). This method allowed to separate eight different forms under which Heavy Metals could be found: ionic exchangeable, bounded to carbonate (adsorbed), as metal-organic complexes (associated with humic and fulvic acids), as easily reducible metal-oxides, bounded to organic matter (other than humic and fulvic acids), in amorphous mineral colloids, as crystalline iron-oxides and bounded to aluminium-silicate minerals. The sequential extraction was performed on 1 g sample with definite reagents and under controlled temperature and pH conditions as reported in Table 3.3.2. Every step required a precise mixing time for completion and was followed by double step centrifugation (at 10500 rpm for 20 min) with distilled water washing. The supernatant was collected and analysed by ICP (Inductively Coupled Plasma) under the assumption that the amount of liquid added for each extraction was enough to collect the whole analyte from the solid. Results were converted to percentages having the concentration of each metal (Cd, Cr, Pb, Cu, Ni, Zn, Fe, Mn) in the solid sample as reference. Heavy metals speciation procedure was applied only for under-sieve being it the waste category with the highest metal content.

Table 3.3.2: Heavy metals sequential extraction procedure subdivided by steps. Evaluated fraction, necessary reagents and reaction conditions are indicated for each step.

Step	Fraction	Reagent	Reaction conditions
1	Ionic exchangeable	10 mL of 1 M NH_4NO_3	pH 7, 25 °C, 4 h
2	Bound to carbonates	25 mL of 1 M CH_3COONa	pH 5, 25 °C, 6 h
3*	Humic and fulvic acid bound	30 mL of 0.1 M $Na_4P_2O_7$	pH 10, 25 °C, 20 h
4	Easily reducible metal-oxide bound	20 mL of 0.1 M NH_2OH•HCl in 0.01M HNO_3	25 °C, 30 min
5	Organic bound	5 mL of 30% H_2O_2, 3 mL of 0.02 M HNO_3 3 mL of 30% H_2O_2, 1 mL of 0.02 M HNO_3	pH 2, 85 °C, 2 h pH 2, 85 °C, 2 h
6	Amorphous mineral colloid bound	10 mL of 0.2 M $(NH_4)_2C_2O_4$/0.2 M $H_2C_2O_4$	pH 3, 25 °C, 4 h dark
7	Crystalline Fe-oxide bound	25 mL of 0.2 M $(NH_4)_2C_2O_4$/0.2 M $H_2C_2O_4$ in 0.1 M ascorbic acid	pH 3, 95 °C, 30 min

** 30 mL of 0.1 $Na_4P_2O_7$ extract was brought to pH 1 with addition of 5 M HCl and the suspension was left overnight for the coagulation of humic acids. The suspension was centrifuged at 10 500 rpm for 20 min. The amount of metals bounded with fulvic acids were determined in the supernatant. The residue was solubilized with 0.1 M $Na_4P_2O_7$ and the amount of metals attached with humic acids were calculated for the solution.*

3.3.3 Results and Discussion

Solid waste loaded into the reactor (Fresh F sample) amounted to 750 kg, which corresponds to 440 kgTS being the total solids 58% of the mass. At the end of the test, the stabilized waste (S sample) quantity was 510 kg, which corresponds to 398 kgTS being the total solids 78% of the mass. Totally, the residual waste dry mass amounted to 91%, while the remaining 9% was emitted with gas and leaching.

Results obtained from the evaluation of the fractional composition and from the main chemical analysis on solids (TOC, TKN, chloride) performed on fresh sample were strictly comparable to those obtained analysing the fresh waste loaded into the lysimeter at the start up of the test. The analytical difference was always under 6%, the collection system and the treatment plant technology were unchanged in time. For this reasons, the comparisons done between fresh and stabilized waste samples was considered coherent and substantial.

Fractional composition

The chemical and biochemical processes occurred to convert fresh waste into stabilized material promoted waste biological stabilization, emissions dropdown and size reduction of all the fractions, with consequent increase of the under-sieve from 44% to 77% by mass (Figure 3.3.2). This increase of small fractions was caused by the total reactor mass reduction, which favoured the settlement of the waste body, generating internal frictions that crumbled also non-biodegradable fractions into smaller pieces.

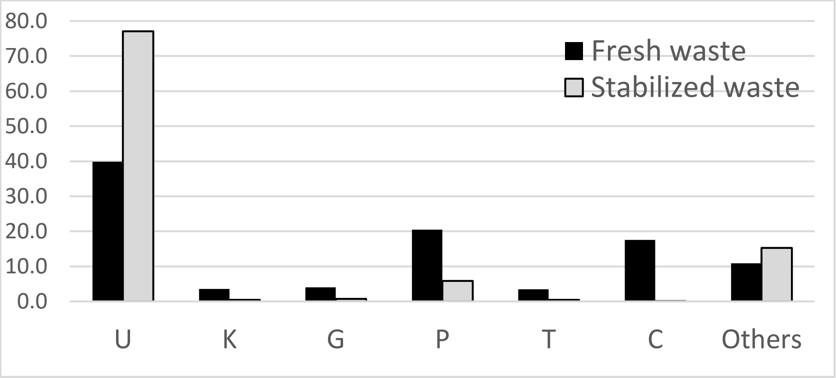

Figure 3.3.2: Fractional composition of fresh and stabilized waste.

In fresh waste, plastics amounted to 20.5%, cellulosic material totalled 17.5% and the other categories were below 8%. For stabilized material, the main residual categories were glass (8.96%), plastics (5.87%), inert (4.75%) and metals (1.62%), all the others were below 1%. This analysis showed that the under-sieve fraction was doubled in S sample, collecting materials coming from kitchen residues, green waste, plastics, textiles and cellulosic material, whose percentages drop consistently. The glass, inert and metals (others fraction) remained virtually unchanged in time (Figure 3.3.2).

The granulometric analysis showed no retention of waste in the 100 mm sieve for both fresh and stabilized samples. Textiles, plastics and metals were mainly collected in the 60 mm mesh, with traces of green and wooden materials for stabilized waste. All the other categories were found in size smaller than 60 mm for both samples. F sample material was mainly between 20-60 mm (50%), in less extent in mesh 60-100 mm (below 10%). S sample material was mainly in under-sieve fraction (77%) and in less extent in mesh 20-60 mm (20%).

Liquid emission potential

Chemical and biochemical processes happened in the reactor promoted changes in compounds subcategories and generated liquid and gaseous emissions. As mentioned before, the concentration of the main contaminants in eluates obtained with standard leaching test can estimate the liquid potential emissions of a samples. Starting from this assumption, Figure 3.3.3 shows the results of total residual emission potential for carbon, nitrogen, chloride and sulphur concentrations referred to the initial total solids presence in solid sample.

For all compounds, the highest impact on liquid emission was due to the under-sieve fraction, contributing for approximately 50% on F samples and being virtually the only residual source of emission for stabilized S sample. In fresh waste, C and P contributed to 30-40 %, while K, T and G fractions were secondary impacting categories, always totalizing less than 10% of estimated emissions.

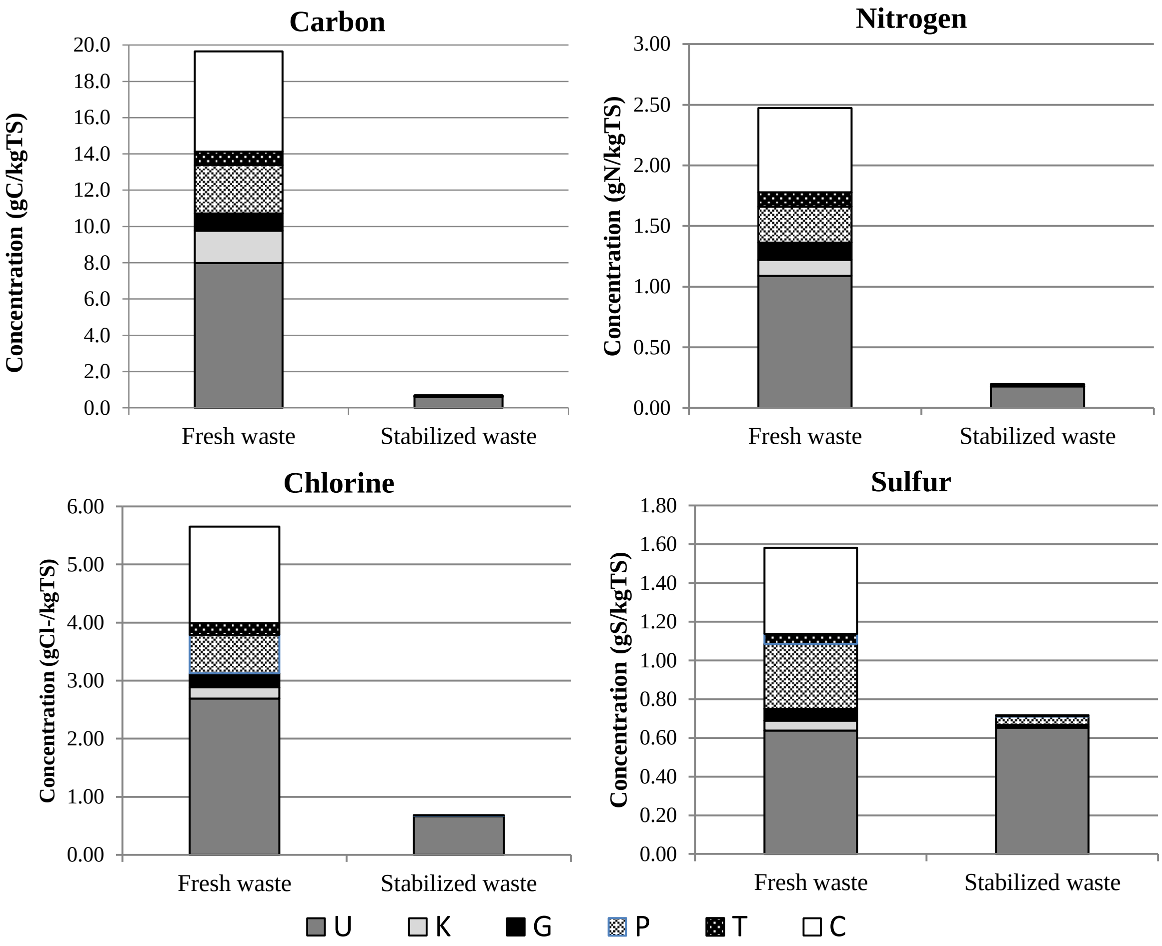

Figure 3.3.3: Carbon, nitrogen, chlorine and sulfur concentrations in eluates from leaching tests made in fresh and stabilized samples. Concentrations are subdivided considering the contribution of the main waste fractions separately (U: Under-sieve, K: Kitchen residues, G: Green waste and wooden materials, P: Plastics, T: Textiles, C: Cellulosic Material).

S sample potential emission in leachate was an order of magnitude lower respect to F sample one, except for sulphur compounds for which was halved (Figure 3.3.3). In particular, leachable carbon dropped down from 19.9 gC/kgTS to 0.7 gC/kgTS, totalizing 96% of emissions reduction.

Carbon

Total carbon in under-sieve fraction decreased from 176 gC/kgTS in F sample to 142 gC/kgTS in S one mainly due to leachable fractions reduction (IC-L, OC-L:VFA, OC-L:Humic and OC-L:Others) that became nearly undetectable (Figure 3.3.4). The most abundant subcategory of carbon was polymeric carbon (OC-NL:Polymers), which dropped from 132.6 gC/kgTS to 92.7 gC/kgTS. At the same time, the inorganic and the organic not-mobile carbon register together an increase from 20 gC/kgTS to 40 gC/kgTS, mainly due to waste S sample dilution effect and to contribution coming from other waste fractions.

Considering the whole carbon change from fresh to stabilized sample, weighted considering all fraction contribution, the total leachable fraction extracted was 8.9% with respect to initial TC, the residual extractable fraction was 0.2 % and the residual not mobile fraction was 55% (Figure 3.3.5). The great part of carbon compounds was stabilized and immobilized in a carbon sink.

Processes occurred in the reactor, enhanced by long-term aeration and flushing, caused a consistent reduction of biodegradable organic matter and leaching out of mobile substances contained in all the waste categories. As consequence, the reduction of soluble fractions can be observed with a simultaneous increase of not mobile inorganic carbon. Long-term treatments applied to S sample made also possible the reduction of organic polymers, representing the hardly degradable part of residual MSW, characterized by very slow degradation kinetics (Figure 3.3.5). The content of VFAs was smaller in stabilized material than in fresh waste, due to their fast consumption since the first stage of degradation processes (Cossu et al., 2016). The production of humic substances proceeded with waste degradation and, after reaching the peak, it underwent consequent leaching. As expected, final concentrations were smaller than input ones (Figure 3.3.4).

Table 3.3.3: Biochemical stability index (BOD_5/COD), organic compounds (COD, COD/TOC), nitrogen compounds (N-ammonia, N-Nitric) concentration for the stabilized waste sample eluate and respiration index (RI_4) for solid waste stabilized sample are reported in comparison with the FSQ values for leachates proposed by D.G.R. 2461/14. Results are reported for each waste fraction and for the stabilized sample.

Matrix	Parameter	FSQ value	U	K	G	P	T	Stabilized Waste
Eluate	COD (mgO_2/L)	1500	188	124	430	198	254	161
	BOD_5/COD	0.1	0.005	0.008	0.05	0.005	0.05	0.005
	COD/TOC	N.A.	4.71	8.38	3.29	4.44	3.69	3.97
	N-Ammonia (mgN/L)	50	2.7	7.6	7	6	4.5	2.54
	N-Nitric (mgN/L)	20	58	91	155	19	61	47.6
Solid Waste	RI_4 (mgO_2/gTS)	2	0.44	0.79	2.2	1.5	1.2	0.45

The organic compounds biodegradability in S sample can be evaluated through BOD_5/COD ratio and RI_4 which are indexes commonly used for stating biochemical stability (Cossu et al., 2012, D.G.R. 2461/14), while COD/TOC ratio can highlight the oxidation status of the organic matter (Table 3.3.3). BOD_5/COD ratio indicates the amount of biodegradable organic compounds over the total amount of oxidizable matter in liquid samples (eluate, leachate, wastewater, etc.). Ratio values comprised between 0.02 and 0.13 suggest waste biochemical stability (Sekman et al., 2011), while values between 0.4 and 0.8 mean high biodegradability (Kjeldsen et al., 2002). BOD_5/COD ratio results were always in the range suggested for biochemical stability, or even lower, in reference to the FSQ threshold limits (Table 3.3.3). Fresh waste samples showed RI_4 values ranging between 44.03 and 21.91 gO_2/kgTS, while the index in stabilized sample ranged between 2.20 and 0.44 gO_2/kgTS with a weighted average value of 0.45 gO_2/kgTS (Table 3.3.3).

As expected, the oxygen consumption in fresh waste was an order of magnitude higher respect to stabilized one, meaning consistent reduction of potential biochemical activity between the two samples. The sole value exceeding FSQ threshold limits were Respiration Indexes (RI_4) calculated for Cellulosic Material. These surpluses were tolerable considering the dilution effect among all categories: RI_4 of total S sample respected FSQ threshold limit (Table 3.3.3). COD/TOC ratio increased from fresh to stabilized waste, remaining unchanged only in green and wooden materials. Stabilized material was constituted by carbon compounds in a higher oxidized status respect to residual fresh MSW, due to the aerobic degradation occurred in the lysimeter.

Nitrogen

Total nitrogen content in under-sieve fraction decreased from 15.8 gN/kgTS in fresh waste to 10.5 gN/kgTS in S sample (Figure 3.3.4). This reduction was mainly due to organic nitrogen and ammonium ion depletion from 2.8 gN/kgTS to 0.2 gN/kgTS caused by nitrification and leaching. Moreover, nitrates were found always below 0.3 gN/kgTS in both F and S samples, being consumed by denitrification and leaching as well.

Considering the whole nitrogen change from fresh to stabilized sample, weighted considering all the fraction contribution, the total leachable fraction extracted was 13.8% with respect to initial TN, the residual extractable fraction amounted to 4.0% (mainly constituted by nitrates) and the residual not mobile fraction was 53% (Figure 3.3.5). The great part of nitrogen compounds was stabilized and immobilized in a nitrogen sink.

The organic nitrogen initially present in solid waste is progressively ammonified to $N\text{-}NH_4^+$ during the whole reactor life. Concomitantly aerobic nitrification converted ammonia ions produced into nitrite and nitrate ions, which are soluble compounds. After that, denitrification occurred in the anoxic zones of waste mass, converting nitrates into free nitrogen gas (Morello et al., 2016). As consequence of all these processes, 29.1% of nitrogen was progressively mobilized and emitted as free nitrogen gas or leachate away as organic nitrogen, ammonia ion, nitrite or nitrate (Figure 3.3.5).

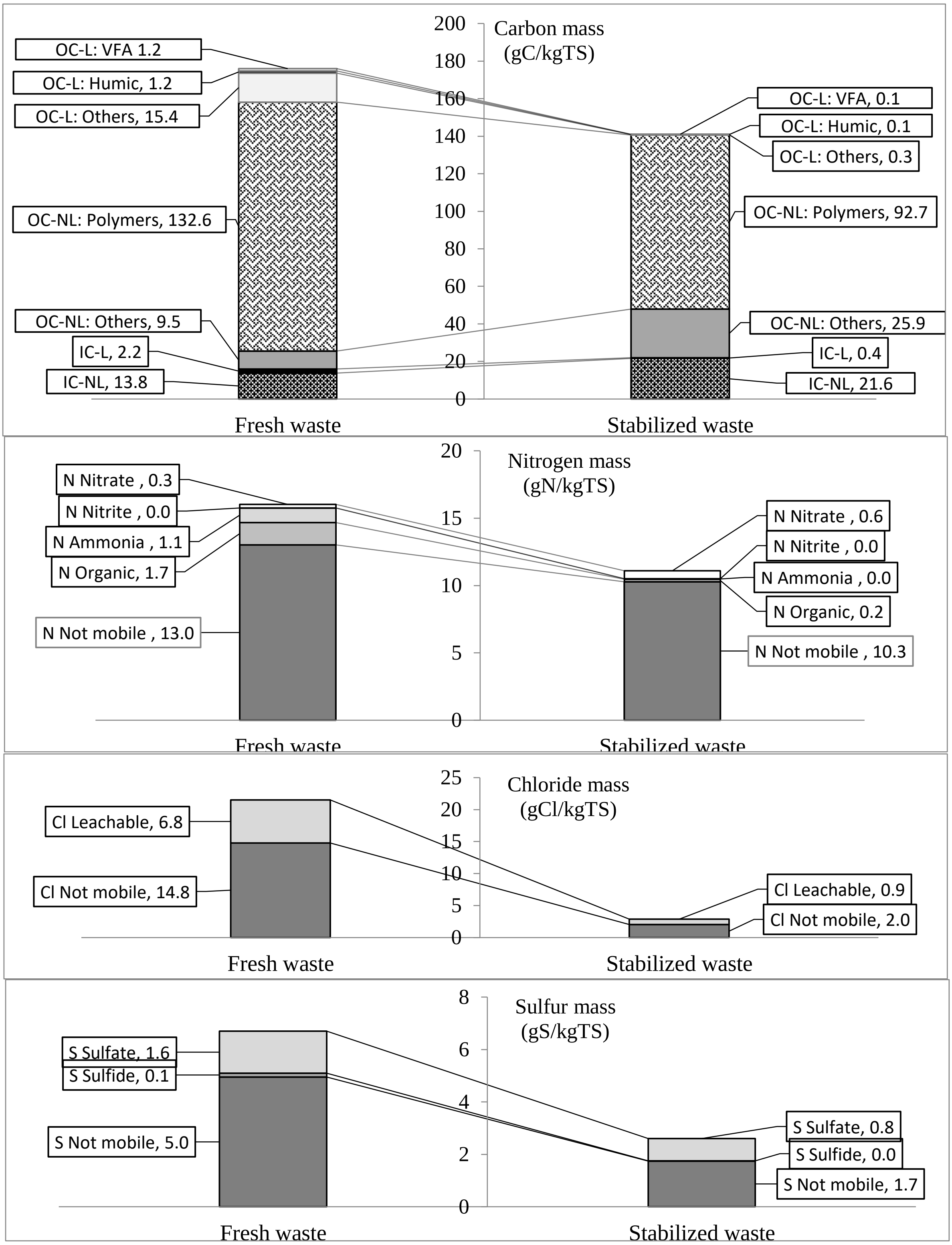

Figure 3.3.4: Carbon, nitrogen, chlorine and sulphur chemical speciation in fresh and stabilized under-sieve fraction of waste samples. Results are reported in concentration respect to the TS of each sample.

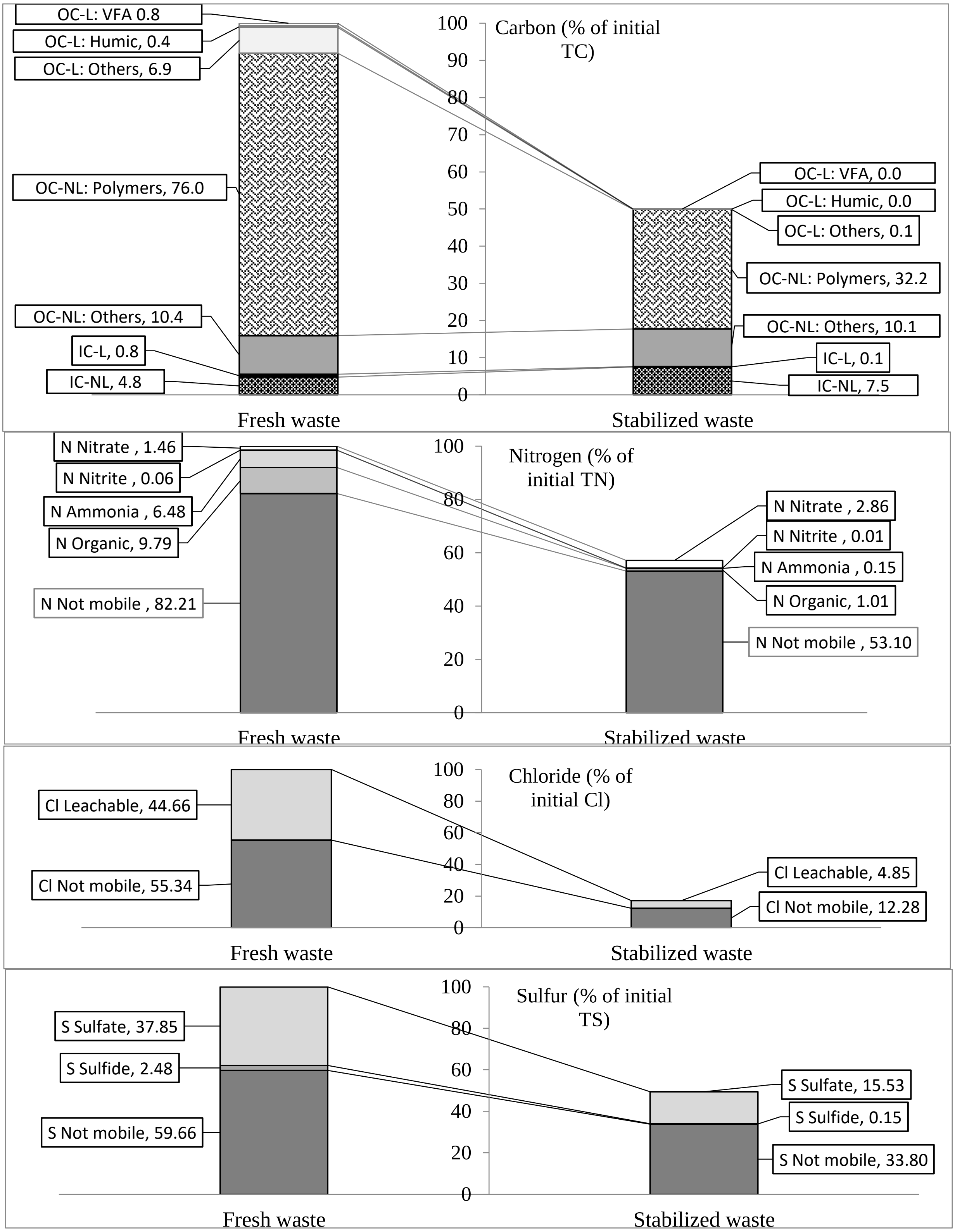

Figure 3.3.5: Carbon, nitrogen, chlorine and sulphur chemical speciation in fresh and stabilized waste samples. Results are reported in percentage (w/w) respect to initial solid waste total solids amount.

Ammonia is generally recognized as one of the most persistent leachate contaminant in long-term landfill management (Ritzkowski et al., 2016). In this case, N-NH_4^+ concentration in eluates of S samples was always below FSQ values for all the waste categories (Table 3.3.3), meaning a good nitrification efficiency. On the contrary, nitrates concentration in the same samples exceeded FSQ limits in all the cases, with the only exception for plastics.

Chlorine

Total chlorine content in under-sieve F sample was 21.7 gCl/kgTS, 87% of which was progressively leached away; remaining only 2.9 gCl/kgTS in S sample (Figure 3.3.4). Considering the whole chlorine change from fresh to stabilized sample, the final not mobile fraction amounted to 12.3%, while the still mobile one was 4.9% with respect to initial total chlorine (Figure 3.3.5). These data highlights that the greater part of chlorine was leached away and that a landfill is not a good sink for this element.

Chlorine presence in solid waste is often high and its mobile form (Chloride) is considered one of the most persistent compound in long-term landfill emissions since it can be removed only by leaching (Morello et al., 2016). The stabilized material contained mostly not mobile chlorine compounds; this means that the treatments performed in the reactor were sufficient to remove the great part of the leachable fraction.

Sulphur

Total sulphur under-sieve fraction content dropped from 6.7 gS/kgTS in F sample to 2.5 gS/kgTS in S one, totalizing 63% of reduction (Figure 3.3.4). Considering the whole sulphur change from fresh to stabilized sample, the residual not mobile fraction amounted to 33.8%, while the residual leachable fraction was 15.5% with respect to the initial total content, meaning that less than 50% of sulphur was emitted (Figure 3.3.5).

Sulphur compounds are significantly influenced by the Redox conditions of the reactor. In particular, in aerobic and semi-aerobic condition, oxidizing environments enhance sulphate production while in anaerobic conditions sulphates are used as oxygen source. Sulphide are generally only present as mobile compounds. The stabilized waste was mostly characterized by the presence of not mobile substances.

Heavy Metals

Heavy Metals presence in solid state was abundant (Table 3.3.4) while their solubility was found to be considerably lower, often negligible in stabilized waste samples (Table 3.3.5). These test results confirmed that HM emissions in leachate are generally not considered to be of environmental interest (Qu et al., 2008).

HM presence in solid state was deeply analysed to understand to which compound each metal was bonded with and how this conditions can change from F to S samples (Table 3.3.4). Compound and HM speciation results were presented for under-sieve fraction, being the most abundant in both samples and the more contributing to liquid emissions. The trend showed an immobilization of Heavy Metals in not leachable fractions over time, however these results must be carefully considered because the heterogeneity of wastes can analytically interfere even after the pulverization of the sample. HM preferred to bind with Al-Si minerals (solid state) in both fresh and stabilized waste. In general, a decrease of free metal ions (ionic exchangeable fraction) was observed from fresh to stabilized waste, while an increase of metals attached to humic and fulvic acids, other organic matter and amorphous mineral colloids was registered as consequence. Cr was mainly found together with Fe-oxides and metal-oxides in general, as done by Pb, Cu, Ni, Zn and Mn in both under-sieve samples. Pb, Cu, Ni, Zn and Mn showed a preference to be adsorbed in carbonates. HM attached to Al-Si minerals were evaluated as the fraction of each metal remained after the sequential extraction, calculated as difference between the total content found in solid samples and the sum of all the extracted contributions. Negative percentages were evaluated for Al-Si mineral bound Cu, possibly due to intrinsic errors in the extraction methods and by the difficulties in the evaluation of HM concentration near the ICP detection limits. Summarizing, the formation of not mobile compounds with Al-Si minerals, carbonates, metal-oxides and Fe-oxides prevailed and the exchangeable free metal ions decreased consistently from the fresh residual MSW to the stabilized material (Table 3.3.4). These results are interesting for understanding HM possible fate in landfills but more data on other MSW samples are required to have a solid quantification of these chemical speciation.

Table 3.3.4: Heavy metals total mass into the reactor for fresh and stabilized samples and under-sieve fraction chemical speciation results. Percentages are calculated considering the ICP values of each extraction process related to the total amount of metal in the Under-sieve solid fraction.

	Cr		**Cu**		**Fe**		**Mn**		**Ni**		**Pb**		**Zn**	
	F	S	F	S	F	S	F	S	F	S	F	S	F	S
Metals mass (kg)	0.04	0.01	1.07	0.47	16.11	15.01	0.11	1.38	0.05	0.05	0.36	0.14	0.77	3.79
Metals into Under-sieve (kg)	0.01	0.01	0.09	0.39	2.46	10.49	0.04	1.35	0.03	0.05	0.07	0.08	0.62	3.65
Chemical speciation of metals in under-sieve fraction (%)														
Ionic exchangeable	0.6	1.8	9.5	2.5	0.2	0.0	3.4	0.5	6.5	1.4	0.3	0.2	2.6	0.9
Bounded to carbonates	0.6	1.9	2.0	2.4	0.2	0.0	13.1	3.5	8.5	4.7	5.1	2.1	11.4	19.1
Bounded to fulvic acids	9.8	30.0	15.6	18.9	8.9	8.9	3.6	1.2	6.1	6.6	33.5	9.0	9.1	12.8
Bounded to humic acids	4.5	15.6	2.8	11.3	0.2	0.2	0.2	0.0	0.8	2.3	1.0	1.7	0.2	0.2
Bounded to easily reducible metal-oxide	2.0	6.4	8.2	3.3	6.7	1.1	12.1	74.6	20.3	8.0	26.0	14.2	1.9	6.9
Bounded to organic matter	8.2	23.3	90.8	11.2	4.4	7.2	5.2	4.7	16.2	19.0	10.1	43.1	2.0	1.6
Bounded to amorphous mineral colloids	11.5	22.5	5.2	3.3	27.7	54.2	7.9	1.2	2.9	20.6	1.6	7.5	0.6	0.9
Bounded to crystalline Fe-oxide	29.7	23.7	2.9	1.1	11.0	9.7	4.3	0.3	1.3	5.7	0.9	1.8	0.3	0.5
Bounded to Al-Si minerals	33.2	-25.2	-37.0	46.1	40.7	18.6	50.1	14.0	37.5	31.7	21.5	20.5	72.0	57.1

Heavy Metals presence in stabilized MSW undergone to long-lasting landfilling processes (S sample) is not matter of concern, as proven by the results comparisons with law concentration threshold FSQ Values (Table 3.3.5). In general, the residual extractable fraction of metals was less than 1% respect to the initial mass for all the HM considered, with exception for Cd and Zn. The most important contribution in total emission comes from Zn and Fe. The mobile fraction in F sample for Fe ranged between 145.8 mg/$L_{(eluate)}$ in C fraction and 20.2 mg/L$_{(eluate)}$ in G fraction, with a pondered average value of 83.5 mg/L$_{(eluate)}$. In stabilized waste, the emission potential was consistently lower and the pondered average emissions of iron were 12.9 mg/L$_{(eluate)}$ (Table 3.3.5). The residual not mobile fraction ranged between 60% and 99%, and in most of the cases it is higher than 95%. This data proved that a landfill is a good sink for HM deposited inside.

Table 3.3.5: Heavy metals content in the eluate from leaching test of fresh and stabilized waste samples. Eluate concentrations are compared with FSQ values (D.G.R. 2461/14). Results are reported in mg/L.

	Cr		Cu		Fe		Mn		Ni		Pb		Zn	
FSQ D.G.R.2461/14	2		1		2		2		2		0.2		3	
(mg/L)	F	S	F	S	F	S	F	S	F	S	F	S	F	S
U	3.19	0.04	2.84	1.52	106.8	14.0	5.27	0.80	2.37	0.14	1.30	0.25	10.86	3.65
K	2.01	0.04	0.32	0.40	36.4	1.3	1.77	0.17	1.15	0.04	0.15	0.04	5.44	0.48
G	2.77	0.13	1.92	0.71	20.2	27.7	3.32	0.19	1.57	0.14	0.77	0.25	2.94	2.38
P	1.41	0.04	1.33	2.54	56.2	31.1	3.88	0.22	1.77	0.13	0.31	0.40	1.51	3.67
T	10.93	0.04	3.10	3.47	47.7	11.0	3.16	0.37	2.33	0.19	1.11	0.18	5.91	3.83
C	6.41	0.14	4.03	6.79	145.8	43.1	5.06	0.47	2.58	0.80	2.68	0.94	8.97	9.64
Total Sample	3.26	0.03	2.31	1.35	83.5	12.9	4.09	0.64	1.95	0.12	1.13	0.22	6.73	3.07

Comparisons of HM concentration in S sample eluates with FSQ values suggested by Lombardia Regional Government (D.G.R. 2461/14) can give important information on Heavy Metals emission dangerousness (Tables 3.3.5). The law limits are given for leachates while the HM emission potential was evaluated for the eluate from leaching test so the comparison will be only general.

Despite that, FSQ threshold values for Cr, Mn and Ni were always respected in S sample, while negligible surplus were monitored for Cu, Pb and Zn. On the contrary, iron showed still high concentrations in eluate, meaning a further emission potential in leachate.

3.3.4 Conclusions

Fresh and stabilized waste characterization evidenced that under-sieve was the most abundant fraction, amounting to 44% in F sample and to 77% in S sample. Moreover, under-sieve can be considered the most environmentally relevant fraction, hosting a consistent part of initial mobile compounds (40.7% of carbon, 44.0% of nitrogen, 47.6% of chloride and 40.0% of sulphur) and the greater part of final potential emissions (88.4% of carbon, 90.9% of nitrogen, 98.4% of chloride and 91.1% of sulphur). These data highlight that the highest contribution in total potential emissions during aftercare of a MSW landfill is due to the under-sieve fraction, followed in magnitude by plastics and cellulosic material.

MSW mass proved to be a good sink, finally storing more than 55% of carbon, 53% of nitrogen 33% of sulphur and 90% of HM initially present in fresh waste samples. A general decrease in leachable fractions from fresh to stabilized waste was observed for each category.

Test showed that solid waste is not a good sink for chlorine, whose residual not mobile fraction amount only to 12.3%.

Chlorides, sulphates, nitrates and humic substances were considered as the most persistent compounds since they have the highest residual extractable capacity.

Heavy metals emissions were not of great concern. HM speciation showed that the bigger part of them is bond with not mobile Al-Si minerals, carbonates, metal-oxides and Fe-oxides, while the mobile exchangeable free metal ions and the organic bonded HM decreased consistently from fresh to the stabilized waste.

Comparisons with FSQ values, law concentration threshold limits and stabilization indexes (as COD/TOC, BOD_5/COD, RI_4) highlighted that degradation processes and mobile substances leaching occurred efficiently in the lysimeter, minimizing the residual potential emissions. Stabilized waste analysis results could be considered a useful reference for maximum long-term concentrations achievable treating a MSW in an aerated landfill.

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