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EVALUATION OF DIFFERENT BIOLOGICAL LANDFILL LEACHATE TREATMENT SYSTEMS FOR FACILITIES IN PORTUGAL

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ABSTRACT

Landfilling is the most used disposal method for solid waste in Portugal. One of the major risks associated with this technique is the pollution of ground and surface waters by leachate. Therefore, leachate needs to be treated before being discharged into the environment. Most Portuguese landfill facilities utilize biological processes prior to physico-chemical treatment, in order to reduce the leachate contents of organic matter.

The main goal of this study is to assess the extent of reduction of contaminants from leachate in biological processes applied in several landfill facilities in Portugal. It is also intended to relate the removal effectiveness with the leachate characteristics, especially since they are influenced by the age of landfill, methods of operation and waste characterization.

In order to evaluate the facilities performance, leachate samples were collected both upstream and downstream the biological units of treatments facilities. From the 35 currently operating in Portugal, 6 were selected. The treatment varied among these facilities: one that used an anaerobic lagoon, another from an aerated lagoon and the other four consisted of activated sludge units. The parameters analyzed were pH, conductivity, TOC, BOD₅; COD, TSS, VSS, TDS, NH₄⁺, NO₃⁻, NO₂⁻, Li²⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, NO₂⁻, SO₄²⁻, Br⁻, NO₃⁻ and PO₄³⁻. For the case of the influent to the treatment facility, these parameters concentrations were related to the landfill age, operation methods and waste characterization. Concerning this characterization, waste was divided into the following categories: biowastes, paper and card, composites, textile, plastics, wood, glass, metals, material smaller than 20 mm and other materials.

The landfills studied were found to be in a methanogenic phase, as it was expected, due to their advanced age. pH values support this idea. Although the landfills were methanogenic, leachates showed a high level of biodegradability and these levels may be explained by the high fraction of biowastes contained in the disposed material and the mixture with wastewater from the sanitary facilities within the landfills.

Removal efficiencies for the main components of leachate were not high. Although BOD₅ was almost totally removed, especially in activated sludge systems, the same did not happen with COD. In terms of solids content, only one of the systems appeared to be effective for their removal. High concentrations of nitrate in all the effluents suggest that denitrification did not occur at any of the treatment facilities, although in some cases there are units installed for that purpose.

In short, the biological part of the facilities studied was not considered to be effective for leachate treatment.

Keywords: leachate treatment, Portugal, activated sludge, aerated lagoon, anaerobic lagoon, waste characterization, landfill age

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TABLE OF CONTENTS

1. Introduction	1
2. Literature revision.....	5
2.1. Leachate formation.....	5
2.2. Leachate composition	5
2.2.1. Effect of waste characterization in leachate composition	7
2.2.2. Effect of landfill age on leachate composition	7
2.2.2.1. Aerobic phase	8
2.2.2.2. Anaerobic acid phase.....	8
2.2.2.3. Initial methanogenic phase.....	9
2.2.2.4. Stable methanogenic phase.....	9
2.2.2.5. Evolution of contaminants concentration with landfill age	9
2.2.2.5.1. pH.....	9
2.2.2.5.2. Dissolved organic matter.....	10
2.2.2.5.3. Inorganic macrocomponents	11
2.2.2.5.4. Heavy metals	11
2.2.2.5.5. Other parameters	12
2.3. Biological treatment of leachate	12
2.3.1. Activated sludge.....	15
2.3.1.1. Nitrification	16
2.3.1.2. Denitrification	17
2.3.1.3. Previous studies on activated sludge systems for leachate treatment.....	18
2.3.2. Aerated and anaerobic lagoons	19
2.3.2.1. Previous studies on lagooning systems for leachate treatment.....	20
3. Methodology.....	22
3.1. Selection of landfills.....	22
3.2. Samples collection and conservation	23
3.3. Parameters analyzed and methods of analysis	24
3.4. Landfill data.....	27
4. Results	29
4.1. Landfills age.....	29
4.2. Waste characterization.....	29
4.3. Influent composition	30

4.4.	Effluent composition	31
4.5.	Removal efficiencies in biological treatments	31
5.	Discussion	34
6.	Conclusions	39
6.1.	Future work	40
7.	References	41
8.	Appendices	43
8.1.	Appendix A – BOD Measurement	43
8.2.	Appendix B – COD Measurement	45
8.3.	Appendix C – Conductivity and Total Dissolved Solids Measurement	46
8.4.	Appendix D – pH Measurement	47
8.5.	Appendix F – TSS and VSS Measurement	48
8.6.	Appendix G – TOC Measurement	51
8.7.	Appendix H – Results for TF1	54
8.8.	Appendix I – Results for TF2	57
8.9.	Appendix J – Results for TF3	60
8.10.	Appendix K – Results for TF4	63
8.11.	Appendix L – Results for TF5	66
8.12.	Appendix M – Results for TF6	69
8.13.	Appendix N – Calibration curves for TC and IC	72

LIST OF TABLES

Table 1 – List of Portuguese landfills in 2011	3
Table 2 – Factors that affect leachate formation (El-Fadel et al., 2002)	5
Table 3 – Concentration ranges, in mg/L (except for pH), of leachate from new and mature landfill (Tchobanoglous et al., 1993) (Kurniawan et al., 2010)	6
Table 4 – Biological treatment systems for municipal solid waste landfills in Portugal	13
Table 5 – Major uses of the more widely used modifications of the activated sludge process (Gray, 2004)	16
Table 6 – Chronogram of the different phases of the study	22
Table 7 – Sampling points for each leachate treatment facility	23
Table 8 – Time interval between sample collection and analysis	27
Table 9 – Landfills age, identified by the number of leachate treatment facility	29
Table 10 – Waste characterization for all treatment facilities (NA means “not available”)	29
Table 11 – Age of leachate and composition of the influent for all treatment facilities	30
Table 12 – Composition of the effluent from all biological treatment systems	31
Table 13 – Removal efficiencies for all treatment facilities	32
Table 14 – Extent of formation of contaminants for all treatment facilities	32
Table 15 – VSS/TSS, BOD ₅ /COD and COD/TOC ratios for raw leachate	34
Table 16 – Charge balance for the influents	35
Table 17 – Charge balance for the effluents	38
Table 19 – Measuring range corresponding sample volume and dilution factor	43

LIST OF FIGURES

Figure 1 – MULTIMUNICIPAL and Intermunicipal Systems existing in Portugal in 2011 (APA, 2011a).....	2
Figure 2 – General trends in leachate quality over the lifetime of a landfill (Kjeldsen et al., 2002)	8
Figure 3 – PET bottles for samples collection and borosilicate bottles for samples storage	24
Figure 4 – WTW pH-Electrode SenTix 21	25
Figure 5 – WTW Tetracon® 325 conductivity meter.....	25
Figure 6 – TOC-V CSN apparatus from Shimadzu Corporation.....	25
Figure 7 – Manometric BOD Measuring Devices OxiTop® IS 12.....	26
Figure 8 – Hach COD Reactor and Hach DR/2000 Direct Reading Spectrophotometer	26
Figure 9 – Muffle furnace for the ignition of Volatile Suspended Solids, at 550°C	26

LIST OF ABBREVIATIONS

Al	Aluminium
Amagra	Association of Municipalities for the Alentejo Regional Environmental Management
Amalga	Association of Alentejo Municipalities for Environmental Management
Amcal	Association of Municipalities of the Central Alentejo
Amde	Association of Municipalities of the District of Évora
Gesamb	Environmental and Waste Management,
Ecobeirão	Association of Municipalities of the Region of Planalto Beirão
Amtres	Association of Municipalities of Cascais, Mafra, Sintra and Oeiras for the Treatment of Solid Waste
ANAMMOX	Anaerobic Ammonium Oxidation
AOP	Advanced Oxidation Processes
AOX	Adsorbable Organic Halogens
As	Arsenium
Ba	Barium
BOD₅	5-Day Biochemical Oxygen Demand
Br⁻	Bromide ion
C	Carbon
Ca²⁺	Calcium ion
CANON	Completely Autotrophic Nitrogen Removal Over Nitrite
Cd	Cadmium
CH₄	Methane
Cl	Chlorine
Cl⁻	Chloride ion
Co	Cobalt
CO₂	Carbon dioxide
COD	Chemical Oxygen Demand
Cr	Chromium
CSTR	Continuous Stirred Tank Reactor
Cu	Copper
ERSUC	Multimunicipal System for the Treatment and Recovery of Municipal Solid Waste in Litoral Centro
F⁻	Flouride ion
Fe	Iron
Fe²⁺	Ferrous ion
Fe³⁺	Ferric (III) ion
H₂CO₃	Carbonic acid
HCO₃⁻	Bicarbonate ion
Hg	Mercury
HNO₂	Nitrous acid
K⁺	Potassium ion
LEPAE-FEUP	Laboratory for Process, Environmental and Energy Engineering of the Faculty of Engineering of University Porto
Lipor	Intermunicipal Service for Waste Management of Grande Porto
MBR	Membrane Bioreactor
Mg²⁺	Magnesium ion

Mn	Manganese
N	Nitrogen
Na⁺	Sodium ion
NH₃-N	Ammonia-nitrogen
NH₄⁺	Ammonium ion
Ni	Nickel
NO₂⁻	Nitrite ion
NO₃⁻	Nitrate ion
O₂	Oxygen
OLAND	Oxygen-Limited Autotrophic Nitrification-Denitrification
ORP	Oxidation-Reduction Potential
P	Phosphorus
PAH	Polyaromatic Hydrocarbons
Pb	Lead
PCB	Polychlorinated Biphenyls
PERSU	Strategic Plan for Solid Waste
PET	Polyethylene terephthalate
PFR	Plug-Flow Reactor
PO₄³⁻	Phosphate ion
Resitejo	Association for Waste Management and Treatment of Médio Tejo
S²⁻	Sulfide ion
SBR	Sequencing Batch Reactor
Se	Selenium
SND	Simultaneous Nitrification and Denitrification
SO₄²⁻	Sulfate ion
TDS	Total Dissolved Solids
TF1	Treatment Facility 1
TF2	Treatment Facility 2
TF3	Treatment Facility 3
TF4	Treatment Facility 4
TF5	Treatment Facility 5
TF6	Treatment Facility 6
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TS	Total Solids
TSS	Total Suspended Solids
UASB	Upflow Anaerobic Sludge Blanket
USA	United States of America
VALNOR	Recovery and Treatment of Solid Waste of North Alentejo
VALORSUL	Recovery and Solid Waste Management of Lisbon and the West Region
VFA	Volatile Fatty Acid
VSS	Volatile Suspended Solids
XOC	Xenobiotic Organic Compounds
Zn	Zinc

1. INTRODUCTION

Disposal of waste is a consequence of the consumption of resources for human and animal activities, which started in primitive societies and continued through time. In the early times, waste was essentially composed of material remaining from agricultural activities and when it was thrown to the land its decomposition was natural. The amount of waste generated was small and the rate of decomposition was balanced with the rate of resources consumption. With industrial and commercial growth and a rapid urbanization and economic development in the last few decades, generation of solid waste increased significantly, with a consumption of resources faster than its decomposition and consequent regeneration by natural processes. Waste was discharged into the streets and vacant land, accumulated and was the cause for many epidemics and air and water pollution. Managing waste in the most appropriate way became a challenge for society.

Solid waste management is a discipline, related with the control of generation, storage, collection, transfer and transport, processing and disposal of wastes in a manner that is in accord with the best principles of public health, economics, engineering, conservation, aesthetics and other environmental considerations. When all these elements are matched and result in effective waste management, it can be considered that integrated solid waste management is established (Tchobanoglous et al., 1993). In other words, integrated solid waste management is a comprehensive waste prevention, recycling, composting and disposal program (EPA, 2002).

In its scope, solid waste management includes all administrative, financial, legal, planning and engineering functions involved in solutions to all problems of solid wastes. It is operated by systems involving human, logistic, equipment and infrastructure resources, called solid waste management systems (APA, 2011a). Developing and implementing solid waste management plans is essentially a local activity that involves the selection of the proper mix of alternatives and technologies to meet changing local waste management needs while meeting legislative mandates (Tchobanoglous et al., 1993).

In Portugal, the strategic guidelines for solid waste management were applied mainly from the end of the 1990s. In 1997, the Government approved a Strategic Plan for Municipal Solid Waste, PERSU, establishing the goal of closing all the dumping sites of the country and building several units for recovery and disposal of waste, as well as creating multimunicipal and intermunicipal systems for an integrated solid waste management (MAOTDR, 2007). Intermunicipal systems consist of municipalities or municipal associations that can be managed by any company, whereas multimunicipal systems are managed by companies leased mainly by public capital and administer at least two municipalities. Attending to the most recent information (from the beginning of 2011) there were 23 solid waste management systems in the Portuguese territory, 12 of them classified as multimunicipal and the remaining 11 as intermunicipal (Figure 1). This spatial organization is not

valid for the islands: in Azores the solid waste is managed by the municipal authorities, while in Madeira it is shared between the municipal authorities and the Regional Government (APA, 2011b).

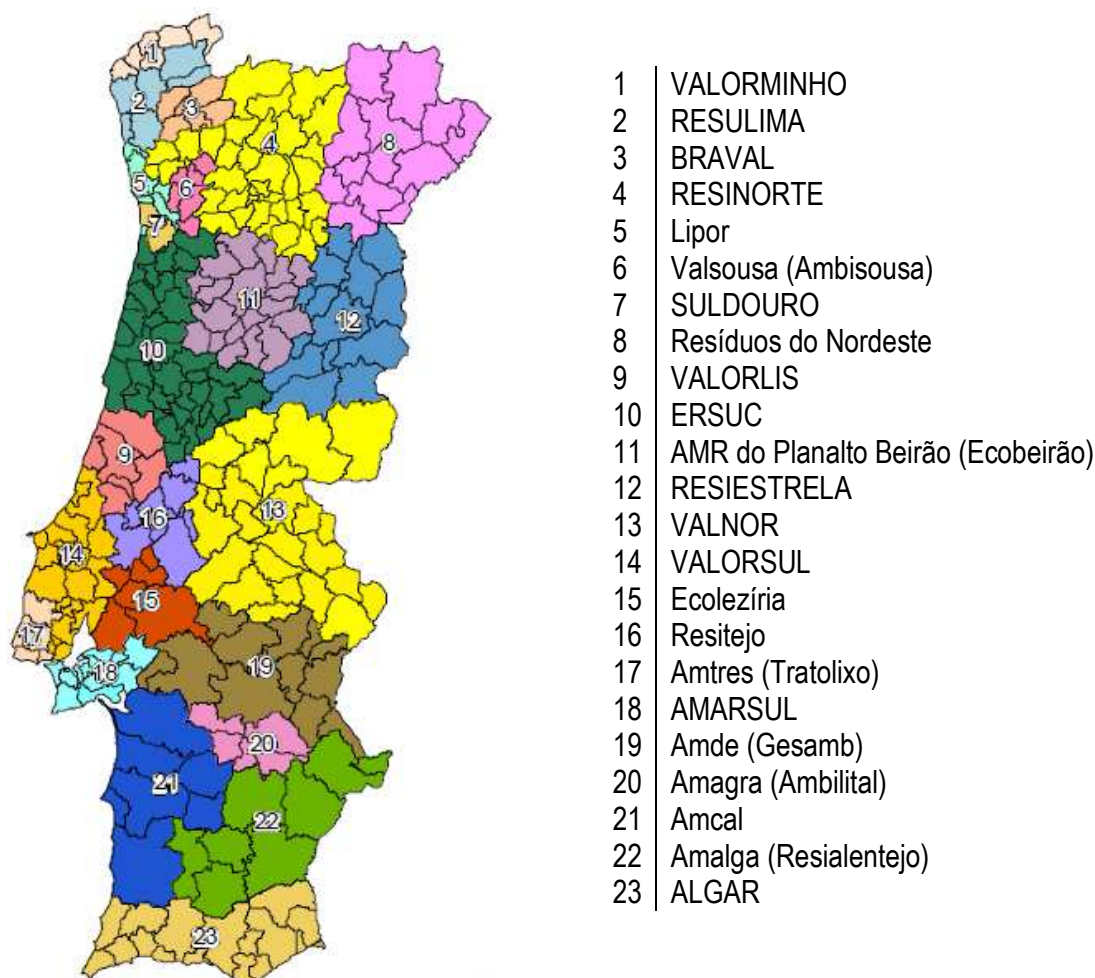


Figure 1 – MULTIMUNICIPAL and Intermunicipal Systems existing in Portugal in 2011(APA, 2011a)

Each one of the systems represented in Figure 1 owns infrastructures to ensure an appropriate destination for the solid wastes generated in their respective area, namely transfer stations, separation stations, organic recovery plants, incineration plants and sanitary landfills.

Although disposal in landfills is considered the last strategy in solid waste management, it is preferred over others, such as incineration or composting, essentially for economy reasons. In Portuguese law, a landfill is defined as the facility for the disposal of waste above or below the surface of the earth and can be classified into three different classes, according to the type of waste disposed: inert solid waste landfill, non-hazardous waste landfill and hazardous waste landfill (DL 183/09). Municipal solid waste is generally disposed into landfills for non-hazardous waste and in Portugal there are currently 35 units for this purpose, which are listed in Table 1.

Landfills can be seen as biochemical reactors, where solid waste and rainwater are the inputs and biogas and leachate are the outputs. In the past, landfills were simply places where the waste was disposed and covered at the end of each day of operation. Nowadays, sanitary landfills are engineered facilities

designed not only for the disposal of solid waste, but also to minimize impacts to public health and the environmental. Potential environmental impacts associated with landfills are the release of biogas, consisting of methane and carbon dioxide, to the atmosphere and contamination of surface and ground waters by leachate, which can lead to problems such oxygen depletion in surface waters, changes in the stream bottom fauna and ammonia toxicity (Kjeldsen et al., 2002). Therefore, leachate treatment must be considered one of the most important operations in a landfill. Given the fact that leachate has high contaminants concentration when compared to other wastewaters, its treatment remains a challenge both for technical and economic reasons and to know its composition is necessary for adequate treatment.

Table 1 – List of Portuguese landfills in 2011

Management system	Landfill
VALORMINHO	Aterro Sanitário de Valença
RESULIMA	Aterro Sanitário de Vale do Lima e Baixo Cávado
BRAVAL	Aterro Sanitário do Baixo Cávado
RESINORTE	Aterro Sanitário de Santo Tirso
	Aterro Sanitário do Baixo Tâmega
	Aterro Sanitário de Lamego
	Aterro Sanitário do Alto Tâmega
	Aterro Sanitário de Vila Real
Lipor	Aterro Sanitário da Maia
Valsousa (Ambisousa)	Aterro Sanitário de Penafiel
	Aterro Sanitário de Lustosa
SULDOURO	Aterro Sanitário de Sermonde
Resíduos do Nordeste	Aterro Sanitário de Urjais
VALORLIS	Aterro Sanitário de Leiria
ERSUC	Aterro Sanitário de Coimbra
	Aterro Sanitário de Aveiro
	Aterro Sanitário da Figueira da Foz
AMR do Planalto Beirão (Ecobeirão)	Aterro Sanitário do Planalto Beirão
RESIESTRELA	Aterro Sanitário da Cova da Beira
VALNOR	Aterro Sanitário de Castelo Branco
	Aterro Sanitário de Avis
	Aterro Sanitário de Concavada
VALORSUL	Aterro Sanitário do Oeste
	Aterro Sanitário do Mato da Cruz
Ecolezíria	Aterro Sanitário da Raposa
Resitejo	Aterro Sanitário do Arripiado
Amtres (Tratolixo)	Ecoparque da Abrunheira
AMARSUL	Aterro Sanitário de Palmela
	Aterro Sanitário do Seixal
Amde (Gesamb)	Aterro Sanitário de Évora
Amagra (Ambilital)	Aterro Sanitário do Alentejo Litoral, Aljustrel e Ferreira do Alentejo
Amcal	Aterro Sanitário de Vila Ruiva
Amalga (Resialentejo)	Aterro Sanitário de Beja
ALGAR	Aterro Sanitário do Barlavento
	Aterro Sanitário do Sotavento

Therefore, one of the main goals of this work is to understand the phenomenon of leachate formation in landfills in Portugal, especially how the composition is influenced by factors such as landfill age and operation

methods and the types of waste disposed. The other goal is to evaluate the performance of biological landfill leachate treatment systems, through the analysis of several parameters considered important for the investigation, and relate the results with the previous information on leachate characterization.

As there is little information about this specific issue published in Portugal, it is also intended with this work to create a basis of investigation that can enhance future developments and to find alternative solutions in leachate treatment, since what currently exists seems to be very narrow and does not necessarily incorporate the best technologies available.

This report is structured in six chapters. In the first chapter, the subject of this investigation is contextualized and the main goals of this work are presented.

The second chapter is dedicated to the literature revision, where the information that was collected refers to leachate formation and composition and some biological treatments. Some important factors that may cause variations in leachate composition deserved further attention, such as the different waste decomposition stages within a landfill, which may lead to changes in contaminants concentration over time, and waste characterization. These changes were analyzed in terms of each important parameter considered. Finally, regarding biological treatment methods, the focus was on systems that exist in Portugal and after a brief explanation of the principle of operation, some examples of similar systems are shown.

Third chapter focus on the methodology adopted to do the investigation. Aspects like the criteria for the selection of landfills, the methods for collection and storage of leachate and for its analysis, as well as the equipment used to perform it are here highlighted.

Fourth and fifth chapters are the results are presented and discussed. First of all, leachate is characterized in a relationship between the parameters analyzed and the age, landfill operation methods and composition of waste. Afterwards, the removal efficiencies for each parameter in different treatment systems are determined and related with data concerning the sludge production.

The sixth chapter is dedicated to the conclusions, limitations and suggestions for future work. The main results are presented.

Seventh chapter, the last, refers to the literature references that supported this report.

2. LITERATURE REVISION

2.1. LEACHATE FORMATION

In landfills, leachate is produced with water from external sources. The principal sources of water that enter the landfill include rainwater, moisture content in refuse and moisture in the cover material. If not consumed in waste decomposition reactions, or lost as water vapor or by infiltration in the soil, water is retained by holding forces in the refuse pores, against the pull of gravity. The quantity of water that can be held in a landfill against the pull of gravity is defined as field capacity (Tchobanoglous et al., 1993). Leachate is formed when landfill field capacity is exceeded (when the magnitude of gravitational forces overcomes the holding forces) and as water percolates downward the waste takes up organic and inorganic materials (El-Fadel et al., 2002). These materials can be either solid or liquid as leachate may carry insoluble liquids like oils, may become dissolved or suspended and form a solution with recognized threats to the surrounding environment.

Leachate formation is affected by several factors:

- Climatology and hydrogeology;
- Site operations and management;
- Refuse characteristics;
- Internal processes.

More detailed information about these factors is presented in Table 2.

Table 2 – Factors that affect leachate formation (El-Fadel et al., 2002)

Climatology and hydrogeology	Site operations and management	Refuse characteristics	Internal processes
• Rainfall; • Snowmelt; • Groundwater intrusion.	• Refuse pretreatment; • Compaction; • Vegetation; • Cover, sidewall and liner material; • Irrigation; • Recirculation; • Liquid waste co-disposal.	• Permeability; • Age; • Particle size; • Density; • Initial moisture content.	• Refuse settlement; • Organic material decomposition; • Gas and heat generation and transport.

2.2. LEACHATE COMPOSITION

Leachate composition is highly variable and heterogeneous. Generally, leachates are known as liquid effluents with dark color and strong odor (Levy & Cabeças, 2006). The color may vary between light yellow and dark brown, as a consequence of the ferrous ion concentration (Fe^{2+}) and the extent of oxidation from this to the ferric form Fe^{3+} . Fe^{3+} forms ferric hydroxide colloids and fulvic complexes, conferring leachate a brown color (Chu et al., 1994). For instance, Lou et al. (2009) observed for three different age leachates in Shanghai, China, that fresh leachate, from cells under operation, contained lots of black suspended particles with strong

odor and that older leachate, 11 years old, was yellowy and without odor. 5 year old semi-mature leachate maintained the odor as the fresh one, but the color was lighter.

Landfill leachate can be understood as a water based solution of four groups of compounds (Christensen et al., 2001):

- Dissolved organic matter, expressed as chemical oxygen demand (COD) or total organic carbon (TOC), which includes CH₄, volatile fatty acids and other refractory compounds, for instance fulvic-like compounds and humic-like compounds;
- Inorganic macrocomponents, like Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, Fe, Mn, Cl⁻, SO₄²⁻ and HCO₃⁻;
- Heavy metals: Cd, Cr, Cu, Pb, Ni and Zn;
- Xenobiotic organic compounds (XOC), such as aromatic hydrocarbons, phenols and chlorinated aliphatics.

Other compounds, like As, Se, Ba, Li, Hg and Co, may still be found, but in lower concentrations. A typical composition of landfill leachate is given in Table 3.

Table 3 – Concentration ranges, in mg/L (except for pH), of leachate from new and mature landfill (Tchobanoglous et al., 1993) (Kurniawan et al., 2010)

Parameter	New landfill (less than 2 years)	Mature landfill (greater than 10 years)
BOD ₅	2000-30000	20-1000
TOC	1500-20000	80-160
COD	3000-60000	5000-20000
TSS	200-2000	100-400
Organic nitrogen	10-800	80-120
Ammonia nitrogen	500-2000	400-5000
Nitrate	5-40	5-10
Total phosphorus	5-100	5-10
Ortho phosphorus	4-80	4-8
pH	4,5-6,5	7,5-9,0
Calcium	200-3000	100-400
Magnesium	50-1500	50-200
Potassium	200-1000	50-400
Sodium	200-2500	100-200
Chloride	200-3000	100-400
Sulfate	50-1000	20-50
Total iron	50-1200	20-200
Heavy metals	<2	>2

Although many of the factors presented in Table 3 affect the concentration of compounds present in leachate, it is generally accepted that refuse composition and age are the most determinant aspects to consider. Physical processes such as rainfall, rather than chemical reactions, are more important controls on the short term variation, causing great fluctuations between sampling events (Statom et al., 2004).

2.2.1. EFFECT OF WASTE CHARACTERIZATION IN LEACHATE COMPOSITION

When studying the nature of disposed solid wastes, there are important parameters to consider, such as the organic fraction, biodegradability, solubility and the material dimensions of the waste (Levy & Cabeças, 2006). These parameters vary according to the socio-economic conditions of a region, season of the year, waste collection, disposal methods and sorting procedures. For instance, in Lebanon, food wastes represent more than 60% of solid waste, whereas in USA it is only 20%. This difference makes the moisture content 2-4 times higher in Lebanon's waste, which results in a lower absorptive capacity and a higher amount of leachate generated. Moreover, if the fraction of biodegradable waste is high, its decomposition will be relatively fast. In this point, pre-sorting is aimed at reducing the leachate generation, towards the removal of organic and other bulky items that contribute to the wetness of waste. Wet waste, together with high rainfall levels, contributes to leachate formation, especially when the landfill cell is not covered (El-Fadel et al., 2002).

Ziyang and Youcai (2007) found values of 54651 mg COD/L, 3143 mg NH₄⁺/L and 54800 mg TS/L in a fresh leachate at Shanghai Laogang Refuse Landfill, the largest landfill in China in terms of refuse placement, and attributed these high concentrations to the contents of food waste, which were estimated to be between 50% and 70%.

Still regarding waste type and leachate composition, Kjeldsen et al. (2002) stated that waste composition varies within a landfill, since there are areas with different refuse ages and states of decomposition.

2.2.2. EFFECT OF LANDFILL AGE ON LEACHATE COMPOSITION

Composition of leachate over a landfill's lifetime is intimately related with the stage of decomposition of waste. Indeed, as soon as waste is disposed in a landfill, its decomposition starts immediately. This process comprises four different phases:

1. Aerobic phase;
2. Anaerobic acid phase;
3. Initial methanogenic phase;
4. Stable methanogenic phase.

The evolution of contaminants through these phases can be seen in Figure 2.

The degradation rate of the contaminants in landfill is affected by factors such as temperature, the geological condition, the local climate, living habits and operation processes (Ziyang et al., 2009). However, the factor that is considered to be the most affective to the degradation of refuse is the moisture content, and it is generally accepted that in arid regions the waste decomposes more slowly than in wet regions (Kjeldsen et al., 2002).

There are three groups of bacteria capable to degrade the waste: hydrolytic and fermentative bacteria, which hydrolyze polymers and ferment the resulting monosaccharides to carboxylic acids and alcohols; acetogenic bacteria, which convert these acids and alcohols to acetate, hydrogen and carbon dioxide; and methanogenic bacteria, that produce methane and carbon dioxide from the end products of the acetogenic phase (Kjeldsen et al., 2002).

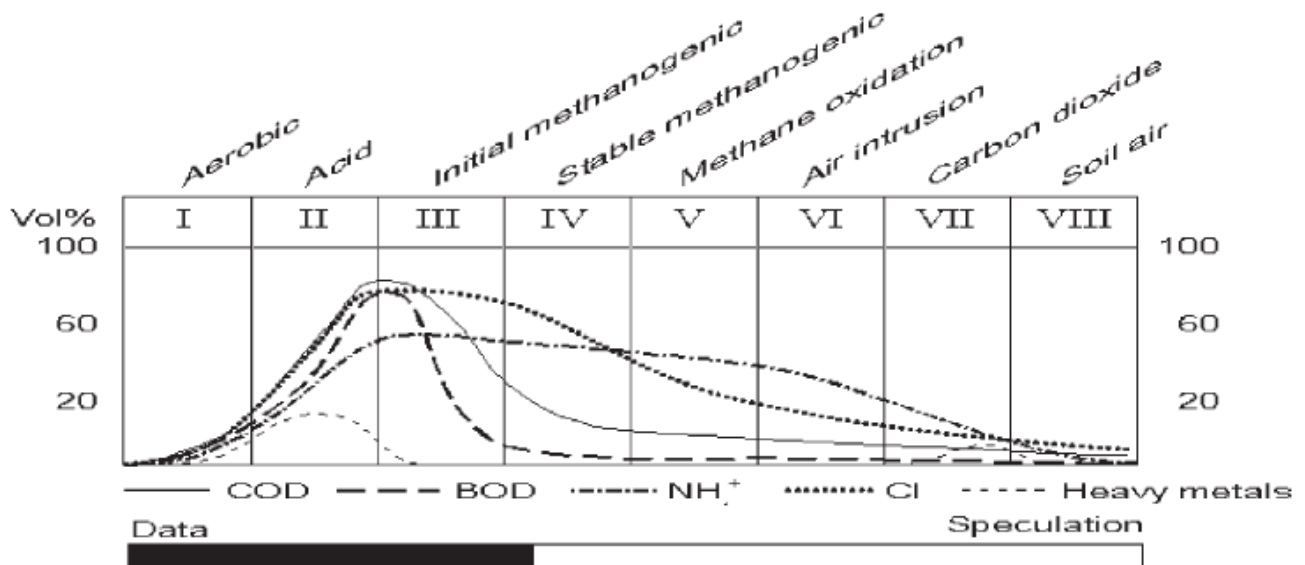


Figure 2 – General trends in leachate quality over the lifetime of a landfill (Kjeldsen et al., 2002)

2.2.2.1. AEROBIC PHASE

The oxygen present in the refuse pores is rapidly consumed in the decomposition of easily biodegradable matter, resulting in the production of CO_2 and an increase in waste temperature, which can reach 80-90°C. Most leachate resulting from this phase is from the moisture content and a small part comes from rainfall. After the consumption of oxygen, the waste becomes anaerobic, enhancing fermentation reactions (Kjeldsen et al., 2002). The aerobic phase lasts much shorter than the following anaerobic phases.

2.2.2.2. ANAEROBIC ACID PHASE

In this phase, the hydrolytic, fermentative and acetogenic bacteria dominate, resulting in the accumulation of carboxylic acids. The acidic feature of leachate enhances dissolution of many compounds, (iron, calcium and heavy metals, etc.) and decreases pH. (Kjeldsen et al., 2002). The production of ammonia-nitrogen increases significantly, due to hydrolysis and fermentation of proteins. In addition, sulfate is reduced to sulfide (Levy & Cabeças, 2006).

2.2.2.3. INITIAL METHANOGENIC PHASE

This phase starts when high concentrations of methane are verified. The pH is around 7 and it is possible for the methanogenic bacteria to grow. The acids accumulated in the acid phase are converted to methane and carbon dioxide; pH increases since the acids are consumed (Kjeldsen et al., 2002). Thus, heavy metals, iron and calcium concentrations in the leachate decrease, because they start to precipitate. Ammonia-nitrogen continues to be produced and its concentration increases because it is not metabolized under anaerobic conditions (Levy & Cabeças, 2006).

2.2.2.4. STABLE METHANOGENIC PHASE

Methane production reaches a maximum and only decreases after carboxylic acid is no longer available for consumption (Kjeldsen et al., 2002). The acids are consumed quickly and pH increases. This phase is generally long and may take between 25 and 50 years (Levy & Cabeças, 2006).

The methanogenic phase is when the landfill is most active biologically, with equilibrium between the acetogenic and the methanogenic bacteria consuming the waste.

After this whole process, it is believed that the upper layers of landfills become aerobic again, but this is only speculation, because monitored landfills have not yet reached the end of stable methanogenic phase.

2.2.2.5. EVOLUTION OF CONTAMINANTS CONCENTRATION WITH LANDFILL AGE

In general, the fundamental chemical parameters in leachate decline dramatically in the first years after the waste is disposed. The exceptions are pH, ORP, conductivity and some inorganic macrocomponents.

2.2.2.5.1. pH

pH is a measurement of leachate aggressiveness and an indicator of whether the landfill is under an anaerobic or an aerobic phase. It tends to reach a steady state as time goes on, depending not only on the concentration of acid but also on the partial pressure of CO₂ in the landfill gas that is in contact with the leachate: if CO₂ concentration increases, then H₂CO₃ will also increase, leading to an increase in pH (Lou et al., 2009).

Leachate pH increases as the concentration of volatile fatty acids (VFAs) decreases. This decrease in concentration happens in the methanogenic phase when the methanogenic bacteria consume intermediate products of waste degradation, the VFAs (Chu et al., 1994). The pH value tolerated by methanogenic bacteria is in the range 6-8, meaning that leachates from landfills in a methanogenic stage generally have neutral values (Lo, 1996). However, higher pH values, until 9, may be found in leachates from landfills undergoing that stage (Christensen et al., 2001)

2.2.2.5.2. DISSOLVED ORGANIC MATTER

Degradation of organics in nature takes between 10 and 20 years to reach stabilization. Organic matter predominates in leachates in the acid phase, especially under the form of volatile fatty acids, volatile amines and alcohols; inorganic matter predominates in leachates in the methanogenic phase (Lou et al., 2009). The decrease in organics in this phase may happen due to anaerobic methane production and leaching by rainwater. The remaining organic matter consists of high-molecular-weight hydroxyaromatic substances such as humic, fulvic, tannic and gallic acids and pyrogallol, all relatively inert to biological degradation. (Chu et al., 1994).

The presence of organic matter is studied both in terms of the individual concentration of some parameters, like BOD₅, COD and TOC.

COD fractions in leachates are often influenced by the presence of VFAs. Other important parameters accounting for COD are proteins, carbohydrates and hydroxylated aromatics. The presence of these compounds depends on the age of landfills: as the age of landfills increases, COD from VFAs decreases and COD from proteins and other refractory compounds, such as humic and fulvic acids, rises (Lema et al., 1988).

High TOC values were registered by El-Fadel et al. (2002) for the initial phase of a landfill. The explanation for this phenomenon is that organic carbon was not degraded and drained with the leachate. This non-degradation happened because the rate of carbon degradation by the methanogenic bacteria was lower than the emanation of the same carbon by the refuse mass. In general, TOC concentration decreases greatly over time, as a result of degradation of organic matter.

BOD/COD ratio is an indicator of the biodegradability of leachate, representing the proportions of easily biodegradable matter that contains a major form of carbon. The highest BOD and COD ratios happen in the anaerobic acid phase and start to decrease in the initial methanogenic phase, especially because of the consumption of carboxylic acids. In stable methanogenic phase, due to these acids are consumed in a faster rate than they are produced, the decrease in BOD concentration is even faster (Kjeldsen et al., 2002).

Salem et al. (2008) gave the value of 0,83 for the BOD/COD ratio for a landfill leachate in Algeria in the acidogenic phase and 0,05 in the methanogenic phase. In other study, BOD/COD ratios of 0,08, 0,06 and 0,05 for leachates were found for landfills in Taiwan with 17, 10 and 12 years, respectively (Fan et al., 2006). Still in Taiwan, but for more recent landfills, young leachates registered BOD/COD ratios between 0,6 and 0,8. After 5 years of operation, this value decreased to 0,2-0,4 (Chen, 1996). High values for BOD/COD ratio in younger landfills suggest that much of the organic material can be removed by biological processes. For older landfill, low BOD/COD ratios indicate that a major fraction of waste is biologically inert and biological treatment is not suitable (Lo, 1996).

COD/TOC ratio reflects the characteristics of the organic matter in the leachate: high values mean that the leachate contains a high proportion of non-oxidized organic matter. Older landfills have lower ratio values

than younger landfills. This decrease is due to the oxidation state of the products of microbial activity: as they become more oxidized, they are less available as energy sources for microbial growth (Lo, 1996). Ziyang et al. (2009) registered a decrease in TOC/COD ratio with landfill age, contradicting the previous studies (Ziyang et al., 2009).

2.2.2.5.3. INORGANIC MACROCOMPONENTS

Some inorganic macrocomponents show decreasing trends with landfill age. Compounds like Ca, Mg, Fe and Mn have lower concentrations in the methanogenic phase due to sorption and precipitation processes enhanced by a higher pH and lower concentrations of organic matter, which may complex the cations. Other contaminants, such Cl^- , Na^+ and K^+ do not show great changes, because they are not affected by these chemical and physical processes and dissolve continuously as water percolates the refuse (Christensen et al., 2001).

$\text{SO}_4^{2-}/\text{Cl}^-$ ratio may indicate the degree of stabilization of the landfill, as chloride represents the inert non-biodegradable compounds. Under anaerobic conditions, sulfate (SO_4^{2-}) is reduced to sulfide (S^{2-}), so low $\text{SO}_4^{2-}/\text{Cl}^-$ ratios can indicate the absence of oxygen in the refuse mass. The increase on sulfide concentration, together with increase of ORP, causes precipitation of insoluble metal sulfides (Lo, 1996).

Phosphorus represents a crucial condition regarding biological treatment: the optimal ratio of BOD_5 to P for aerobic treatment is 100 to 1. In many cases with old leachates, there is the need of add phosphate to accomplish the treatment, since aged refuse has a high adsorption capacity of phosphorus, decreasing its concentration in leachate over time (Chu et al., 1994).

Fresh leachate is richer in NH_4^+ than old leachate. Ammonium may be harmful to biological processes in concentrations above 1500 mg/L. Above 3000 mg/L, ammonium can even inhibit them. Concentrations between 50 and 200 mg/L are beneficial for anaerobic treatment (Lou et al., 2009).

2.2.2.5.4. HEAVY METALS

Landfill leachate is one of the major sources of discharges of heavy metals to the surrounding environment.

Average metal concentrations in leachates are low. However, it is not because they exist in low concentrations in the waste, but because sorption and precipitation are believed to be significant processes for their immobilization and consequent non-dissolution in water. Sorption to organic matter occurs in methanogenic leachate. Also in methanogenic leachate, sulfide concentrations are higher and decrease solubility of heavy metals, since both sulfides and carbonates are capable of forming precipitates with Cd, Ni, Zn, Cu and Pb. Cr is the exception and does not form any insoluble sulfide precipitate (Kjeldsen et al., 2002).

The increase in heavy metals concentration in the aqueous phase happens due to complexation to inorganic and organic ligands and sorption to colloidal matter. In fact, colloidal humic substances are suspected to play a major role concerning the speciation of heavy metals.

In spite of low concentrations for each individual metal, the total amount is high and the combined toxic effect may result in an inhibition to microbial growth in biological treatments.

Statom et al. (2004) affirmed that rather than a decreasing or increasing trend, heavy metals always showed wide fluctuations over time in terms of concentration in leachates, for a landfill in Florida. Fan et al. (2006) analyzed 13 metals in leachates in Taiwan and found that the heavy metals studied, Zn concentrations increased with age and Cu decreased over time (Fan et al., 2006).

2.2.2.5.5. OTHER PARAMETERS

Solids and conductivity are important parameters to consider when assessing leachate quality. Like the majority of contaminants present in leachate, their concentrations decrease over time, what can be explained by a higher rate of degradation of organic matter in the early stages of waste degradation. In a ten-year monitoring period, Ziyang et al. (2009) observed a decrease in conductivity from 41500 $\mu\text{S}/\text{cm}$ to 6380 $\mu\text{S}/\text{cm}$ for a leachate in China.

2.3. BIOLOGICAL TREATMENT OF LEACHATE

Landfill effluents need to be treated before their discharge into the sewer or direct disposal in surface water. Currently, for economy reasons, leachates are mainly treated by biological and physico-chemical methods. Physico-chemical methods are used to accomplish biological methods and the most used are coagulation-flocculation and reverse osmosis.

Reverse osmosis treatment is a membrane process based on the difference on the solute concentrations separated by a semi-permeable membrane. Water diffuses through the membrane, from the lower-concentration side to the higher concentration side and the concentrate gets retained in the filtering membrane. From the membrane processes range, reverse osmosis is the most able to remove smaller particles, operating typically with particles in the range 0,0001-0,001 μm . The permeate from a reverse osmosis system contains essentially water, very small molecules and ionic solutes, whereas the concentrate is composed by sulfates, nitrate, sodium and other ions (Metcalf & Eddy, 2003).

In spite of removing contaminants almost totally, especially dissolved matter, reverse osmosis is too expensive due to high energy consumption, large operational costs and membrane fouling (Ziyang & Youcai, 2007). It has been recently applied in many landfills in Portugal, as a result of several unsuccessful upgrades in leachate treatment systems.

Table 4 – Biological treatment systems for municipal solid waste landfills in Portugal

Management system	Biological treatment applied	Location
VALORMINHO	Anoxic tank + Aeration tank	Aterro Sanitário do Vale do Minho - Valença
RESULIMA	Anaerobic lagoon + Anoxic tank + Aerated lagoon	Aterro Sanitário do Vale do Lima e Baixo Cávado – Viana do Castelo
BRAVAL	Anoxic tank + Aeration tank	Aterro Sanitário do Baixo Cávado – Póvoa do Lanhoso
RESINORTE	No treatment	Aterro Sanitário de Santo Tirso
	Aerated lagoon	Aterro Sanitário de Celorico de Basto
	Aerated lagoon	Aterro Sanitário de Bigorne - Lamego
	Aerated lagoon + Aeration tank	Aterro Sanitário de Boticas
	Aerated lagoon	Aterro Sanitário de Vila Real
Lipor	Aeration tank + Anoxic tank	Aterro Sanitário da Maia
Ambisousa	Aerated lagoon	Aterro Sanitário de Penafiel
	Facultative lagoon	Aterro Sanitário de Lustosa - Lousada
SULDOURO	Aeration tank + Anoxic tank	Aterro Sanitário de Sermonde – V. N. Gaia
Resíduos do Nordeste	Aeration tank	Aterro Sanitário de Urjais - Mirandela
VALORLIS	Anaerobic lagoon + Facultative lagoon + Aeration lagoon	Aterro Sanitário da Quinta do Banco - Leiria
ERSUC	Oxidation ditch	Aterro Sanitário de Taveiro - Coimbra
	Anoxic tank + Aerobic tank	Aterro Sanitário de Aveiro
	No treatment	Aterro Sanitário da Figueira da Foz
Ecobeirão	Aeration tank + Anoxic tank	Aterro Sanitário do Borralhal - Tondela
RESIESTRELA	Anaerobic tank + Aeration tank + Anoxic tank + Aeration tank	Aterro Sanitário do Fundão
VALNOR	Anaerobic lagoon	Aterro Sanitário de Avis
	Aerated lagoon + Aeration tank	Aterro Sanitário de Castelo Branco
	No biological treatment	Aterro Sanitário de Concavada - Abrantes
VALORSUL	Aerated lagoon	Aterro Sanitário do Oeste - Cadaval
	No biological treatment	Aterro Sanitário de Mato da Cruz – V. F. Xira
Ecolezíria	No biological treatment	Aterro Sanitário da Raposa - Almeirim
Resitejo	No biological treatment	Aterro Sanitário da Carregueira - Chamusca
Tratolixo	Aerated lagoon	Ecoparque da Abrunheira
AMARSUL	No biological treatment	Aterro Sanitário do CIVTRS de Palmela
	No biological treatment	Aterro Sanitário do CIVTRS do Seixal
Gesamb	Aerated lagoon	Aterro Sanitário Intermunicipal - Évora
Ambilital	Anaerobic lagoon + Facultative lagoon + Aerated lagoon	Aterro Sanitário da AMAGRA – Santiago do Cacém
Amcal	Anaerobic lagoon + Facultative lagoon + Aerated lagoon	Aterro Sanitário de Vila Ruiva - Cuba
Resialentejo	Aerated lagoon	Parque Ambiental da Amalga - Beja
ALGAR	Aerated lagoon	Aterro Sanitário do Barlavento - Portimão
	Anoxic tank + Aeration tank	Aterro Sanitário do Sotavento

The first treatment systems implemented in the country were based on biological processes and were unable to effectively remove the contaminants. Consequently, physico-chemical processes were added, either upstream from biological treatment, to reduce the loading rates, or downstream, to improve the quality of the final effluent (Levy & Cabeças, 2006). Good quality effluents were still difficult to obtain and therefore reverse osmosis units were installed. Although this technique is effective on contaminants removal, it only transfers pollution and does not solve the environmental problem (Wiszniewski et al., 2006).

From the 35 municipal solid waste landfills existing in Portugal, three of them have no leachate treatment at all, whereas another four have no biological treatment.

Concluding, there are thirty biological treatment facilities for leachate in Portugal. The biological treatment in each landfill is identified in Table 4.

The main objective of leachate biological treatment is to remove or reduce the concentration of organic or inorganic compounds. Organics removal can achieve up to 99% and yielded effluents have COD concentrations less than 500 mg/L. The rate of $\text{NH}_3\text{-N}$ removal may be around 90%. However, good removal efficiencies are only achieved with adequate retention times (Pohland, 1987). Biological treatment also has limitations in removal of some compounds, especially toxic substances such as PAHs, polyaromatic hydrocarbons, AOXs, adsorbable organic halogens, PCBs, polychlorinated biphenyls. Thus, other treatment methods, namely advanced oxidation processes (AOPs), are being considered for an effective mineralization of recalcitrant organics in leachate (Wiszniewski et al., 2006).

The most used biological processes can be divided into aerobic and anaerobic. The most common anaerobic system is upflow anaerobic sludge blanket (UASB). Among aerobic processes, the most used are activated sludge, aerated lagoons, sequencing batch reactors and rotating biological contactors. According to Tchobanoglous et al. (1993), high COD concentrations favor anaerobic treatment, because aerobic becomes expensive, whereas high sulfate concentrations may limit it, due to production of odors from the reduction of sulfate to sulfide. One great advantage of anaerobic over aerobic treatment is the energy surplus associated with methane production, lack of aeration equipment and limited sludge production. Advantages of aerobic biological systems over anaerobic systems are low cost of construction, flexibility in use, ability to change rapidly to varying components within the leachate, quick start up times, lack of maintenance and ease in automation (Mehmood et al., 2009).

According to the information showed in Table 4, from the whole set of biological treatments, only activated sludge and aerated lagoons are applied in Portugal. Anaerobic lagoons are used as a pre-treatment, on leachate stabilization. The sections below focus on the principles of these biological processes, as well as in some studies done before about similar treatment units.

2.3.1. ACTIVATED SLUDGE

Activated sludge processes are widely employed in the treatment of wastewaters. The mode of operation relies on a mixture of microorganisms and wastewater under aerobic conditions, which enhances extremely high rates of microbial growth and respiration for the consumption of organic matter, resulting in oxidized end-products, such as CO_2 , NO_3^- , SO_4^{2-} , PO_4^{3-} , a process called mineralization, or in new microorganisms, in a process known as assimilation.

The main components of an activated sludge process are: the reactor that can be a tank, lagoon or ditch; the sludge, flocculant suspension consisting of microbial biomass, essentially bacteria; the aeration system, either surface aeration or diffused air is used; the sedimentation tank, where the separation between microbial biomass and treated effluent occurs; the returned sludge, recycled back to the reactor after settling in the sedimentation tank (Gray, 2004).

Activated sludge processes have many advantages. First of all, the systems can be adapted to any size of microbial community. Moreover, the sludge can be utilized as fertilizer in agriculture, unless it contains toxic heavy metals or organics. However, many problems may arise, such as settling difficulties. It is important that an adequate amount of sludge is present in the reactor. Although a greater amount of microorganisms enhances organic matter degradation rate, an excessive concentration will harm equilibrium between upflow and sludge settling velocities. Other weaknesses have to do with energy consumption, high production of sludge and subsequent disposal, foaming, precipitation, long periods for the stabilization of sludge and nutrient shortage (Kurniawan et al., 2010) (Wiszniewski et al., 2006).

Conventional activated sludge systems, when they started to be designed and until the late 1970s, aimed at BOD removal. However, with interest in biological nutrient removal, especially nitrogen and phosphorus, a series of complete mixed reactors have been developed, some of them including anaerobic or anoxic stages. The variety of activated sludge systems can be seen in Table 5. More recently, membrane biological reactors (MBRs) have found increasing application, for the separation of solids from treated water in biological reactors have found increasing applications, for the separation of solids from treated water in suspended growth reactors (Metcalf & Eddy, 2003).

MBRs are composed by a bioreactor where biodegradation of contaminants occurs, commonly continuous stirred tank reactor (CSTR), plug-flow reactor (PFR), SBR and UASB, and a membrane module for the separation of treated water from biosolids or microorganisms.

MBRs allow bioreactors to operate with a higher concentration of sludge than conventional activated sludge processes, where the sedimentation tanks limit sludge concentrations of 5 mg/L in the suspended growth reactor. Comparing to conventional activated sludge systems, MBRs have the advantage of providing better effluent quality, process stability, easeness in automation, smaller footprint and increased biomass retention (Ahmed & Lan, 2012).

The membrane module for the separation of solid from liquid phase is usually a microfiltration or ultrafiltration unit. These membranes operate with larger range and lower pressure than reverse osmosis (0,08-2,0 μm for microfiltration and 0,005-0,02 μm for ultrafiltration) retaining TSS, bacteria and protozoan cysts. Ultrafiltration is even capable of removing biodegradable organics and priority organic pollutants. Permeate contains essentially water and small molecules, such as salts. The membrane driving force is hydrostatic pressure difference and the typical separation mechanism is sieving.

The disadvantages related with the application of microfiltration and ultrafiltration are: intensive electricity use; need of pretreatment to prevent fouling; need for replacement of membranes every 3 or 5 years; scale formation and decline of flux over time (Metcalf & Eddy, 2003).

Table 5 – Major uses of the more widely used modifications of the activated sludge process (Gray, 2004)

Mode of operation	Major function
Conventional completely mixed systems	BOD removal
Conventional plug flow	BOD removal, nitrification
Contact stabilization	BOD removal
Extended aeration	BOD removal, nitrification
Oxidation ditch	BOD removal, nitrification, denitrification
Anoxic zone system	BOD removal, nitrification, denitrification

From Table 5, the main processes occurring in an activated sludge system can be identified as BOD removal, nitrification and denitrification. The reactions involving organics degradation in activated sludge systems are comprised in five phases (Wiszniewski et al., 2006):

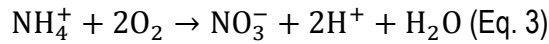
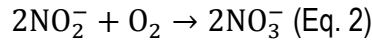
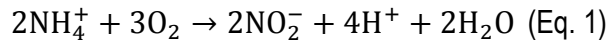
- I. Sorption of organics on the sludge flocs;
- II. Biodegradation of the organics;
- III. Ingestion of bacteria and other suspended matter by predators;
- IV. Oxidation of ammonium to nitrite and further to nitrate by the nitrifying bacteria;
- V. Oxidation of cell reserves, if insufficient energy is supplied.

General results of activated sludge treatments were reported by Kurniawan et al. (2010). 95% COD removal could be obtained for raw leachates with concentrations ranging from 1000-24000 mg/L. For $\text{NH}_3\text{-N}$ it was also effective, with 90% removal for 115-800 mg/L. These performances were obtained with a pH suitable for aerobic microorganism's activity, between 6 and 7,5 (Wiszniewski et al., 2006). Another important operational parameter is nutrient ratio: the most effective performance corresponds to the ratio 100:3,2:1,1 for $\text{BOD}_5\text{:N:P}$ (Lema et al., 1988).

2.3.1.1. NITRIFICATION

Before nitrification, organic nitrogen is converted to ammonia and thus removed from wastewaters through hydrolysis to aminoacids, which are broken down to produce ammonium or directly incorporated into microbial tissues. Nitrification itself is an irreversible process, where ammonia is sequentially oxidized to nitrate

(Eq. 3) by two groups of chemo-litotrophic bacteria. In the first step of nitrification, *Nitrosomonas* oxidize ammonium to nitrite (Eq. 1); in the second step, *Nitrobacter* oxidize nitrite to nitrate (Eq. 2).



Free ammonia and nitrous acid are toxic for nitrifiers in large concentrations. *Nitrosomonas* are inhibited at levels between 10 and 150 mg $\text{NH}_3\text{-N/L}$ and *Nitrobacter* are inhibited by concentrations of nitrous acid in the range 0,22-2,8 mg $\text{HNO}_2\text{/L}$. High heavy metals concentrations can also harm microbial growth. General requirements for nitrifiers growth are (Wiszniewski et al., 2006):

- pH between 5,5 and 9,0; the optimum pH is 7,5;
- Dissolved oxygen concentration of 1 mg $\text{O}_2\text{/L}$;
- Temperature between 5 and 40°C.

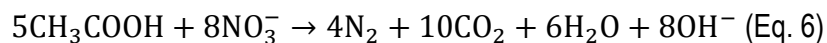
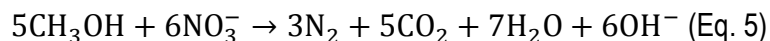
Another important parameter for the operation of nitrogen removal processes is ratio C/N. The biological process is efficient in young leachates, with high C/N ratios. For old leachates, with high levels of ammonia-nitrogen and low levels of biodegradable organics, an additional carbon source is needed.

The energy released in nitrification is used to form cell material and a small part of ammonia is fixed in new biomass. Thus, NH_4^+ needs to be removed from leachate.

In general, $\text{NH}_3\text{-N}$ removal efficiencies for nitrification can achieve 90%, with influent concentrations ranging from 270 to 535 mg/L. COD removal efficiencies of 30-55% were reported for COD concentrations in the range 1000-2116 mg/L, showing that nitrification is not suitable for organics removal from leachate, although it is for $\text{NH}_3\text{-N}$ removal (Kurniawan et al., 2010).

2.3.1.2. DENITRIFICATION

Denitrification is carried out by heterotrophic bacteria that use several organics (Eq. 4, 5 and 6) as food and energy source. Nitrate functions as an electron acceptor, producing nitrogen gas.



The most favourable conditions for denitrification to occur are (Wiszniewski et al., 2006):

- Temperature between 5 and 60°C;
- pH in the range 6-8;
- Dissolved oxygen concentrations below 0,5 mg $\text{O}_2\text{/L}$;

- Availability of an appropriate electron donor and of nitrate as electron acceptor.

The reduction of nitrite to nitrate happens with a variety of electron donors such as methanol, acetate and organic substances in wastewaters. In most countries, about 80% of wastewater treatment plants use predenitrification process for biological nitrogen removal. This typical treatment process has the advantage of shortening the aerobic phase duration by using organic carbon sources as electron donors for denitrification, which are biodegraded by denitrifying bacteria.

A disadvantage of nitrification-denitrification process is the requirement of long retention times and, consequently, large reactor volumes to accomplish complete nitrogen removal, as well as a high level of oxygen, set as 4,2 g O₂/g NH₄⁺-N. For denitrification, high concentrations of organic carbon sources are required, leading to the addition of external sources, such as methanol or acetate, when C/N ratio is low. This fact increases the operational cost of the conventional process.

The limitations of low removal efficiency, high oxygen requirement, long retention time and external carbon sources are the driving forces for developing new low-cost biological treatment processes for complete nitrogen removal, like simultaneous nitrification and denitrification (SND), shortcut nitrification and denitrification, anaerobic ammonium oxidation (ANAMMOX), aerobic deammonitrification, completely autotrophic nitrogen removal over nitrite (CANON) and oxygen-limited autotrophic nitrification-denitrification (OLAND) (Zhu et al., 2008).

2.3.1.3. PREVIOUS STUDIES ON ACTIVATED SLUDGE SYSTEMS FOR LEACHATE TREATMENT

Lo (1996) studied the ability of activated sludge process to remove contaminants from leachates in Hong Kong. For a 6 year old leachate, from an active landfill site, ammonia-nitrogen removal efficiencies of 99,80% and 99,99% were obtained for 20 d and 40 d HRTs. The rate of conversion to nitrate-nitrogen was 93% and 71%, respectively. For another leachate, with 40% of the strength, due to coming from a 12 year old closed landfill site, 20 d retention time resulted in a NH₃-N removal efficiency more than 99,8%, 80% of which was converted to nitrate-nitrogen.

Other nitrification-denitrification studies were carried out in SBRs.

Calli et al. (2005) did perform nitrification and denitrification of anaerobically treated leachate, from Komurcuoda Landfill, in Istanbul. Keeping pH at 7,5,, NH₄⁺-N efficiencies above 99% were obtained. The pH control prevented sudden pH drops and consequent free nitrous acid inhibitions. Removal efficiencies only dropped when pH increased to levels between 8,5 and 9, resulting from excess alkalinity load and heterotrophic carbon oxidation in the tank. In denitrification, sodium acetate was used as external carbon source. Denitrification efficiency reached values up to 95%.

El-Fadel et al. (2003) studied the treatability of a leachate collected from a landfill located south of Beirut, Lebanon. The biological treatment unit consisted of two SBRs operating in parallel, where after the

filling of the tank with leachate, anaerobic phase took place before aeration, so that nitrification/denitrification could occur, in order to decrease $\text{NH}_4^+\text{-N}$ concentration. COD removal efficiency was relatively stable, ranging between 76% and 99,8%. Ammonium removals varied between 31% and 99,9%. Lowest values on the efficiency were due to high temperatures, in summer, and low effluent recycling rates.

In a study with a 5 year old leachate, Kulikowska et al. (2007) found out high removal efficiencies for BOD_5 and COD in a SBR. Under anaerobic-aerobic conditions, the efficiency of BOD_5 removal ranged from 99% to 97% and COD from 83% to 76%. With only aeration, BOD_5 removal efficiency was almost identical and COD removal efficiency decreased. The conclusion is that operational conditions have no effect on BOD_5 removal, but have on COD removal. Higher COD removals are obtained with anoxic phase rather than with only aeration.

For MBRs, Ahmed and Lan (2012) reviewed that independently of leachate age, BOD removal rates can reach between 90% and 99%. On the other hand, COD removals vary a lot, from as low as 23% to as high as 90%. COD removals greater than 75% were obtained only in studies under the optimal conditions. For the treatment of both young and old leachate, MBRs can achieve over 90% on $\text{NH}_3\text{-N}$ removal efficiency. Nevertheless, high ammonia concentrations in the effluent can still inhibit nitrification. Removal efficiencies of high ammonia concentration leachates can be under 40%. MBRs are advantageous in treating old leachate: they have small footprints, better effluent quality, process stability, increased biomass retention and low sludge production.

2.3.2. AERATED AND ANAEROBIC LAGOONS

Lagoons may be an interesting treatment option. They can operate in the presence of wide fluctuations of influent concentrations and strength, have low operational and maintenance costs and are capable of removing organic compounds, nitrogen, phosphorus, suspended solids and pathogenic microorganisms. In many cases, lagoons are used as pre-treatment prior to biological treatment. They can improve removal efficiencies from 82% to 100% and from 35% to 95% for BOD and COD, respectively, as the BOD/COD ratios increase from 0,05 to 0,40. The parameters which have the most impact in lagoons performance are organic load, temperature and retention time (Frasconi et al., 2004).

Suspended growth aerated lagoons are earthen basins provided with mechanical aerators. They are classified as facultative partially mixed lagoon, aerobic flow-through partially mixed lagoon and aerobic lagoon with solids recycle (Metcalf & Eddy, 2003). As a unit process, they fall between facultative oxidation ponds and activated sludge.

The advantages of aerated lagoons are related with their ability to operate with fluctuating organics concentrations and low cost of operation and maintenance. However, there are lots of disadvantages: the energy supply for oxygenation is extremely high; there are lots of odors released; eutrophication is a very possible scenario; and long retention times are required (Kurniawan et al., 2010).

They are effective in achieving almost complete removal of $\text{NH}_3\text{-N}$ for influents with concentrations from 104 to 175 mg/L. COD can be 80% removed if initial concentration is in the range 104-175 mg $\text{O}_2\text{/L}$.

Anaerobic lagoons are generally used as a preliminary treatment, as they can considerably reduce the organic loading to secondary treatment units, thus reducing the secondary treatment capacity required. The treatment in this kind of lagoons relies on the formation of a biologically active sludge layer, which settles in the bottom. A scum layer and a supernatant layer are the other identifiable zones. Decomposition of organic matter happens both in the liquid phase that contains about 0,1% volatile solids and in the sludge blanket, which is 3-4% volatile solids. The major advantages of this system are that less sludge is produced and no aeration equipment is supplied. The limitations have to do with temperature and strength of leachate. Anaerobic activity decreases rapidly below 15°C, so treatment only happens due to physical settlement. It functions optimally in two different temperature ranges (for mesophylic and thermophylic microorganisms), so at high temperatures the rate of biogas production proceeds rapidly (Gray, 2004).

2.3.2.1. PREVIOUS STUDIES ON LAGOONING SYSTEMS FOR LEACHATE TREATMENT

Mehmood et al. (2009) studied leachate treatment by microbial oxidation in four connected on-site aerated lagoons. The overall COD removal at Bell House landfill was 75%. For each lagoon, the removals were 64% for the first one, 6% for the second, 1% for the third and 4% for the last one.

The overall removal of ammonium in the 4 lagoon system was 99% and nitrate production was approximately 71%. There was a reduction of 80% in total N concentrations. Nitrification accounted for 63% of ammonium removal. The remaining 37% could be attributed to alternative processes like volatilization by the aeration. Volatilization is important when there are long HRTs (Mehmood et al., 2009). Other ammonium removal processes include assimilation as organic N. Mehmood et al. (2009) concluded that aerated lagoons, with large HRTs are suitable for relatively weak leachates when removal of COD and nitrogen is necessary.

For a mature leachate in Taiwan, biological treatment by aeration removed 78% of BOD and 65% of COD, according to Chen (1996). $\text{NH}_4^+\text{-N}$ and TKN were removed 83% and 73%. Removal efficiency of sludge was low. Approximately 34% of total phosphorus was removed with biological treatment. Metals were retained in the sludge, which was then recirculated. This resulted in accumulation in the aeration tank and might have resulted in toxicity that inhibited microbial growth at higher concentrations. Concluding, aeration was effective on removing BOD, COD, $\text{NH}_4^+\text{-N}$ and TKN and ineffective on removing solids and phosphorus, when compared with chemical treatment. Metals removal was not effective any way.

In a wastewater treatment plant in Cyprus, anaerobic lagoons were implemented prior to facultative and aerated lagoons to improve BOD and TSS treatment performances. Türker et al. (2009) concluded that anaerobic lagoons increased water quality by 60% in terms of BOD reduction. The percentage of BOD removal achieved was 51%. In aerobic, facultative and maturation lagoons the percentages of BOD removal

were respectively 26%, 12% and 3%. Overall solids removal efficiency increased 42%. The implementation of anaerobic lagoons had a stabilizing effect on BOD removals.

Frasconi et al. (2004) determined, for a two stage anaerobic/facultative system, mean COD and BOD removal efficiencies of 40% and 64%, respectively, for a two stage anaerobic/facultative system. During 7 years, BOD removal efficiency decreased from 91% to 34%; after 9 years, it was 58%. The removal of ammonia was characterized by a decreasing trend from 95% to 60% and the average was 77%. Nitrification and sedimentation of organic N were described as the main factors for this removal, whereas volatilization was insignificant. Removal of phosphorus varied between 5% and 60%, due to adsorption on Fe, Al or Ca in the sediments or sedimentation as organic P via biological uptake. Other removals were as follows: Fe 30%, Mn 44%, Al 1%, Se 0%, Hg 0%, Zn 29%, Pb 65%, Ni 45%, As and Cd 25%, Cu 10%. Chlorinated compounds were removed on an average of 52%, mainly due to volatilization.

3. METHODOLOGY

This study was developed in five months, starting in the middle of February and ending in the beginning of July. In this period, the first phase was intended to select the landfills from which the samples would be collected, the parameters to be analyzed and the methods to do the analyses. Right after this selection period, preliminary tests were done with all the procedures and equipment. The following phase was dedicated to sample collection and analysis and the last phase was when the report was written. Literature revision occurred during all stages of the work and focused on three topics: leachate variation with waste characterization and landfill age and previous investigations on biological treatment efficiencies.

The relationship between the different phases and the corresponding months can be consulted in Table 6.

Table 6 – Chronogram of the different phases of the study

Phase	February	March	April	May	June
Literature revision					
Pre-sampling					
Samples collection and analysis					
Report writing					

3.1. SELECTION OF LANDFILLS

From the list presented in Table 4, six landfills were selected for the collection of leachate samples, according to several factors.

The first factor to consider had to do with the type of treatment. A distinction was made between activated sludge, aerated lagoon and anaerobic lagoon. From this, it was decided that at least one leachate from each type of treatment should be collected. Since there are numerous types of activated sludge processes, the number of samples related to this type of treatment systems had to be higher.

Another important reason for the selection of certain landfills was the distance to the place where the samples were analyzed. Landfills located far away, like the southern part of Portugal, was not an option, due to the costs associated with the trip and the logistics of sample preservation.

The last condition that influenced landfill selection was the willingness of the solid waste management systems to cooperate in the study. Since this study involved the publication of data associated with the performance of treatment systems, not all facilities had an interest to take part of the work. In addition, due to confidentiality agreements, information will not be disclosed concerning the treatment facilities. Therefore, the final list of treatment systems is as follows:

- Treatment Facility 1 (TF1): Anaerobic lagoon;
- Treatment Facility 2 (TF2): Activated sludge;
- Treatment Facility 3 (TF3): Aerated lagoon;

- Treatment Facility 4 (TF4): Activated sludge;
- Treatment Facility 5 (TF5): Activated sludge;
- Treatment Facility 6 (TF6): Activated sludge.

It shall be noted that in spite of Table 4 shows only one biological treatment consisting of an anaerobic lagoon, it does not mean that this corresponds to TF1. Many anaerobic lagoons exist as part of the treatment facilities, usually as stabilization ponds, so the sample may have come from any of those.

3.2. SAMPLES COLLECTION AND CONSERVATION

Leachate was collected once from each landfill and at the same times for upstream and downstream from the biological treatment. Collection conditions differed from landfill to landfill. Table 7 presents the sampling points, both for upstream and downstream collection.

Table 7 – Sampling points for each leachate treatment facility

Treatment facility	Upstream collection	Downstream collection
TF1	Pumping station	Top of lagoon
TF2	Leachate discharge pipe	Exit of sedimentation tank
TF3	Pumping station	Pumping station
TF4	Leachate discharge pipe	Tap in pipe after treatment
TF5	Leachate discharge pipe	Exit of sedimentation tank
TF6	Pumping station (1 out of 3 available)	Exit of sedimentation tank

From this table some remarks shall be mentioned. The first remark is related with the downstream collection point for TF1. In this case, the bottle was simply submerged and filled in the top of the lagoon. This procedure is believed to have significantly affected the results. The second remark has to do with the upstream point of collection of TF2, which due to a breakdown in the treatment system was inactive for one week, thus accumulating stagnant leachate for a considerable time. Regarding TF4, the leachate was collected during a week which there was some rainfall. As a consequence, leachate concentrations can be lower due to dilution by rainwater. Finally, in TF6, there were 3 pumping stations available for the collection of leachate. One of them received leachate from a closed section, other received leachate from very recent refuse, so it could have large and unpredictable variations. The chosen pumping station is thought to be the most interesting for analysis, because the leachate comes from a re-opened section, mixing old and new waste. This mixture gives the leachate stability and a smaller probability of short term variations to happen, which can affect the study, since it consists of singular sample collections.

Leachate samples were collected in 5 L PET bottles and transported by car to the laboratory where the analyses were realized. Upon arrival, small 100 mL borosilicate bottles were filled for non-immediate analyses. These bottles were then stored in a refrigerator (4°C). Both bottle types are illustrated in Figure 3.



Figure 3 – PET bottles for samples collection and borosilicate bottles for samples storage

Depending from sample to sample, variable amounts of leachate remained from the analyses. The remaining leachate was stored in the laboratory, in 5 L PET bottles, but outside the refrigerator, to save space. After distributing the leachate by the small bottles, collection bottles were washed and dried by natural aeration without a cap to eliminate the odor caused by leachate.

3.3. PARAMETERS ANALYZED AND METHODS OF ANALYSIS

To study the relationship between the characteristics of leachate and waste age and composition and the efficiency of biological treatments, the following parameters were analyzed: pH, conductivity, TOC, BOD₅; COD, TSS, VSS, TDS, NH₄⁺, Li, Na, K, Mg, Ca, F⁻, Cl⁻, NO₂⁻, SO₄²⁻, Br⁻, NO₃⁻ and PO₄³⁻. The procedures for laboratorial analysis are shown in the appendices.

Before performing the analyses, some equipment needed to be calibrated and some calibration curves needed to be made. Thus, for TOC analysis, two calibration curves were calculated, both for total carbon and inorganic carbon (Appendix 8.13).

Analyses were performed at three different places:

- pH, conductivity, TOC, BOD₅ and TDS: Department of Mining Engineering of FEUP;
- COD, TSS and VSS: Chemical Technology Laboratory of ISEP-IPP;
- Inorganic macrocomponents (NH₄⁺, Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, NO₂⁻, SO₄²⁻, Br⁻, NO₃⁻ and PO₄³⁻): LEPAE-FEUP.

The methods and equipment used for each analysis are as follows:

- pH: determined by “4500-H⁺” Method (APHA et al., 1998) with a WTW pH-Electrode SenTix 21 (Figure 4) and a WTW inoLab Level 1 pH terminal;



Figure 4 – WTW pH-Electrode SenTix 21

- Conductivity: determined by “2510 Conductivity” Method (APHA et al., 1998) with a WTW Tetracon® 325” conductivity meter (Figure 5) and a WTW inoLab Level 1 Cond terminal;



Figure 5 – WTW Tetracon® 325 conductivity meter

- TOC: determined by “5310 B. High-Temperature Combustion Method” (APHA et al., 1998), performed in a TOC-V CSN, Shimadzu Corporation apparatus (Figure 6);



Figure 6 – TOC-V CSN apparatus from Shimadzu Corporation

- BOD₅: determined by “5210 B. Respirometric Method” (APHA et al., 1998) with WTW Manometric BOD Measuring Devices OxiTop® IS 12 (Figure 7);



Figure 7 – Manometric BOD Measuring Devices OxiTop® IS 12

- COD: determined by “5220 D. Closed Reflux, Colorimetric Method” (APHA et al., 1998) with a Hach COD Reactor and a Hach DR/2000 Direct Reading Spectrophotometer (Figure 8).



Figure 8 – Hach COD Reactor and Hach DR/2000 Direct Reading Spectrophotometer

- TSS and VSS: TSS analyzed by “2540 D. Total Suspended Solids Dried at 103-105°C” and VSS analyzed by “2540 E. Fixed and Volatile Solids Ignited at 550°C” (APHA et al., 1998).



Figure 9 – Muffle furnace for the ignition of Volatile Suspended Solids, at 550°C

- TDS: determined with a WTW Tetracon® 325 conductivity meter and a WTW inoLab Level 1 Cond terminal (Figure 5);

- Inorganic macrocomponents:

- Anions: determined with ion cromatograph (Dionex ICS 2100), using Dionex Ionpac (Column: AS 11-HC 4x250 mm; supressor: ASRS®300 4 mm); the isocratic elution was done with 30 mM of NaOH, with a flow of 1,5 mL/min for 12 minutes; the samples were previously centrifuged and filtered with 0,2 µm syringe filters;

- Cations: determined with ion cromatograph (Dionex DX-120), using Dionex Ionpac (Column: CS12A 4x250 mm; supressor: CSRS®300 4 mm); the isocratic elution was done with 20 mM of methanesulfonic acid, with a flow of 1,0 mL/min for 12 minutes; the samples were previously centrifuged and filtered with 0,2 µm syringe filters.

Some of these parameters required a faster analysis than others, according to Standard Methods. Consequently, the time between sample collection and parameters analysis was monitored to make sure that all the analyses were performed within an acceptable timeframe. Table 8 indicates the time interval between collection and analysis, as well as the recommended and maximum storage time, according to the standard methods (APHA et al., 1998). For the analysis of inorganic macrocomponents, all the samples were stored and later analyzed by ion chromatography and performed after all the samples from the different facilities were collected.

Table 8 – Time interval between sample collection and analysis

Parameter	TF1	TF2	TF3	TF4	TF5	TF6	Recommended storage time	Maximum storage time
pH	5 h	3 h	4,5 h	3,5 h	5 h	2,5 h	15 min	15 min
Conductivity	5,5 h	3,5 h	5 h	3,5 h	5 h	2,5 h	48 h	48 h
TOC	2 d	1 d	6,5 h	1 d	1 d	1 d	7 d	28 d
BOD ₅	4,5 h	3 h	4,5 h	3 h	4,5 h	2 h	6 h	24 h
COD	1,5 d	2 d	6 d	4 d	2 d	6 d	7 d	28 d
TSS	2 d	2 d	6 d	4 d	2 d	6 d	24 h	7 d
VSS	2 d	2 d	6 d	4 d	2 d	6 d	24 h	7 d
TDS	5,5 h	3,5 h	5 h	4 h	5,5 h	3 h	24 h	7 d

From Table 8 can be concluded that pH analysis was not done within the recommended timeframe. However, it was not possible to carry the measuring equipment and do the analysis in-situ, so the analyses were done as quickly as possible after the arrival at the corresponding laboratory, along with BOD₅ determination.

3.4. LANDFILL DATA

Together with leachate collection, visits to the landfills were aimed at the collection of additional information concerning the landfill age, characterization of waste disposed and information about sludge fate. The intention of collecting this information was transmitted to the person responsible for leachate treatment in each landfill before the visit. However, in all cases these data were gathered by email after contact by telephone.

For waste characterization, waste was divided into the following categories:

- Biowastes, which consist of food and garden waste;
- Paper and card, which includes package paper, newspapers, magazines, flyers, office paper and cardboard;
- Composites, which consist of card and others packages and small appliances;
- Textile, such as package or non-package and sanitary textile;
- Plastics, including PE, PP, PVC and PETE;
- Wood, which consists of package or non-package wood;
- Glass, which consist of package or non-package glass;
- Metals, including ferrous packages, non-ferrous packages and other ferrous and non-ferrous materials;
- Material smaller than 20 mm;
- Other materials, consisting of unspecified combustible and non-combustible material and special domestic waste, such as batteries and accumulators, chemical products, low energy lamps and fluorescent tubes and other hazardous and special domestic wastes.

Regarding the operation methods in the landfill, the information collect in the visits was about the origin of the leachate. Thus, in TF1 and TF6 the samples collected consisted of raw leachate from the MSW landfill. For TF4, the sample collected consisted of raw leachate from two landfills: one to the disposal of MSW and the other to the disposal of ash and slag. In the case of TF3 and TF5, the samples contained both raw leachate and wastewater from the sanitary facilities within the landfill. For TF2, besides these two types of wastewater, the sample contained even water from the washing operations in the landfill and leachate from a nearby closed dump.

4. RESULTS

4.1. LANDFILLS AGE

Portuguese landfills are quite old and the majority started operating few years after the implementation of PERSU, in 1997. For instance, from Table 9, which summarizes the age of the landfills studied in this work, it is suggested that the landfill from TF5 started operating right after the implementation of this strategic plan.

Table 9 – Landfills age, identified by the number of leachate treatment facility

Landfill	Age
TF1	5
TF2	13,5
TF3	10,5
TF4	11
TF5	14
TF6	4

The youngest landfills from the table are TF1 and TF6. As stated in the methodology chapter, the section studied from TF6 was closed and reopened. It started receiving waste 4 years ago and was closed two and a half years later. Recently, it was reopened.

4.2. WASTE CHARACTERIZATION

Waste fractions, listed in Table 10, are very similar for all the landfills, reflecting the same conditions and social behaviors in the regions from where the samples were taken.

Table 10 – Waste characterization for all treatment facilities (NA means “not available”)

Waste fraction	TF1	TF2	TF3	TF4	TF5	TF6
Biowastes	45,99%	46,55%	42,12%	44,34%	NA	NA
Paper and card	10,04%	10,95%	12,10%	7,35%	NA	NA
Composites	3,30%	2,91%	3,27%	4,68%	NA	NA
Textile	9,07%	9,73%	10,92%	16,93%	NA	NA
Plastics	9,68%	9,38%	9,49%	10,98%	NA	NA
Wood	0,53%	0,46%	0,71%	0,06%	NA	NA
Glass	2,48%	3,57%	7,73%	4,29%	NA	NA
Metals	1,80%	1,52%	1,75%	2,14%	NA	NA
< 20 mm	14,06%	11,71%	9,24%	8,72%	NA	NA
Others	3,05%	3,22%	2,67%	0,51%	NA	NA

Biowastes represent the major fraction of waste disposed, consisting of almost half of its composition. The other representative fractions are paper and cardboard, textiles and material smaller than 20 mm, with percentages around 10%. Wood present in the refuse is insignificant, with less than 1% of the composition. The landfill of TF4 shows the most significant variations compared to the others, more precisely in the paper and cardboard fraction, which is smaller, and in the textile fraction, in which the sanitary textile has a great influence, with 11,20% out of 16,93% for TF4 and values below 6% for the others.

It shall be noted that for TF3, the waste characterization is related to more than one landfill. It is managed by a solid waste management system which is responsible for more than one landfill and the waste characterization is made for all those landfills together. However, it appears not to have a large influence on the results, since the landfills are close to the one in this study.

4.3. INFLUENT COMPOSITION

The term influent is meant to represent the waste stream that enters the leachate treatment facility. Actually, it cannot be considered raw leachate in all of the cases, because of the mixture with wastewater from sanitary facilities within the landfill in some of them. Thus, raw leachate is the influent for TF1, TF6 and TF4. For TF4, the leachate from the landfill is mixed with wastewater from a septic tank. However, the mixture ratios do not influence leachate concentration. Mixed leachate is the influent in TF2, TF3 and TF5. The results of the influents analyses are showed in Table 11.

Table 11 – Age of leachate and composition of the influent for all treatment facilities

Parameter	TF1	TF2	TF3	TF4	TF5	TF6
pH	8,4	8,1	7,3	7,4	7,5	7,8
Conductivity (mS/cm)	24,87	34,50	18,86	84,17	18,52	36,03
TOC (mg C/L)	1678	1494	2157	960	674	894
BOD ₅ (mg O ₂ /L)	1630	3233	5067	600	567	1567
COD (mg O ₂ /L)	4620	5060	6600	1860	1133	5953
TDS (mg/L)	14067	20867	10900	47400	11400	19200
TSS (mg/L)	870	1460	1130	3950	570	590
VSS (mg/L)	485	810	680	410	270	320
NH ₄ ⁺ (mg/L)	1321	6918	1915	1072	2222	12161
NO ₂ ⁻ (mg/L)	165,0	270,0	76,3	76,1	158,0	343,0
NO ₃ ⁻ (mg/L)	<2	11,00	3,43	<2	<2	<2
Li ⁺ (mg/L)	0,56	0,64	0,52	3,56	0,44	0,50
Na ⁺ (mg/L)	2736	3094	1572	11510	1314	3069
K ⁺ (mg/L)	2776	2320	1169	11942	916	2278
Mg ²⁺ (mg/L)	391,0	295,0	165,0	65,1	257,0	133,0
Ca ²⁺ (mg/L)	462	208,	774	1278	410	135
F ⁻ (mg/L)	328	258	205	177	<2	174
Cl ⁻ (mg/L)	3770	3406	1802	28782	1660	3554
SO ₄ ²⁻ (mg/L)	<10	<10	<10	<10	<10	<10
Br (mg/L)	8,00	11,10	241,00	13,80	6,44	23,20
PO ₄ ³⁻ (mg/L)	<10	<10	<10	<10	<10	<10

Some parameters are out of the detection range of the equipment used. The ammonium concentration for TF6 is estimated to be 12161 mg/L, but the upper detection limit of the ion chromatograph is 10000 mg/L. Nitrate was only detected for TF2 and TF3, since the concentration for the other leachates was lower than the 2 mg/L lower detection limit. The same happens for fluoride in TF5. The contents of sulfate and phosphate are also small, less than 10 mg/L. In TF4, chloride concentration is above the upper detection limit, as well as sodium and potassium.

4.4. EFFLUENT COMPOSITION

The concentrations of the effluent from the biological treatment are showed in Table 12. Here, chloride concentrations are again above detection limit for TF4. Sulfate and phosphate again have values below the lower detection limit of 10 mg/L.

Table 12 – Composition of the effluent from all biological treatment systems

Parameter	TF1	TF2	TF3	TF4	TF5	TF6
pH	8,7	6,9	8,3	7,9	4,9	7,3
Conductivity (mS/cm)	29,67	18,20	21,73	66,77	4,16	21,53
TOC (mg C/L)	1647	1246	904	346	102	1101
BOD ₅ (mg O ₂ /L)	405	84	217	44	9	687
COD (mg O ₂ /L)	3267	2393	1413	570	206	2247
TDS (mg/L)	15100	9800	13000	37400	1797	11233
TSS (mg/L)	940	343	860	396	155	490
VSS (mg/L)	440	188	460	46	105	310
NH ₄ ⁺ (mg/L)	551,0	558,0	1873,0	50,8	65,5	1735,0
NO ₂ ⁻ (mg/L)	140,00	3508,00	170,00	2640,00	6,64	192,00
NO ₃ ⁻ (mg/L)	455,00	81,70	9,10	87,90	1098,00	4,24
Li ⁺ (mg/L)	0,59	0,61	0,53	2,73	0,44	0,52
Na ⁺ (mg/L)	4095	1917	2121	9959	413	1935
K ⁺ (mg/L)	3503	1364	1548	8846	240	1712
Mg ²⁺ (mg/L)	487,0	92,2	360,0	51,5	42,4	193,0
Ca ²⁺ (mg/L)	266	197	191	815	172	627
F ⁻ (mg/L)	162,00	4,75	208,00	65,30	54,90	164,00
Cl ⁻ (mg/L)	5868	2176	2425	22023	521	2374
SO ₄ ²⁻ (mg/L)	<10	<10	<10	<10	<10	<10
Br (mg/L)	681,0	69,2	912,0	87,5	20,6	79,9
PO ₄ ³⁻ (mg/L)	<10	<10	<10	<10	<10	<10

4.5. REMOVAL EFFICIENCIES IN BIOLOGICAL TREATMENTS

The parameters concentrations had several variations along the treatments applied. In some cases, such as BOD or COD, there was always a reduction in concentration, whereas in others, such as nitrate or some salts, the concentration increased. For sulfate and phosphate, it was not possible to do calculations due to the lack of obtained concentration values; for nitrates, when the concentration in the effluent was <2 mg/L, this value was adopted in order to determine either reduction or formation.

Table 13 presents the removal rates for the parameters which values could be determined using the criteria mentioned above.

The results show that there are high removal rates of BOD₅ for all the facilities and of NH₄⁺, for the treatment facilities TF2, TF4, TF5 and TF6, which correspond to activated sludge treatments. Activated sludge treatments also showed the removal of some salts, such as Na⁺, K⁺ and Cl⁻, and removal rates higher than aerated and the anaerobic lagoon in terms of suspended and volatile solids.

Table 13 – Removal efficiencies for all treatment facilities

Parameter	TF1	TF2	TF3	TF4	TF5	TF6
Conductivity (mS/cm)	-	47,2%	-	20,7%	77,5%	40,2%
TOC (mg C/L)	1,9%	16,6%	58,1%	64,0%	84,9%	-
BOD ₅ (mg O ₂ /L)	75,2%	97,4%	95,7%	92,7%	98,4%	56,2%
COD (mg O ₂ /L)	29,3%	52,7%	78,6%	15,1%	81,9%	62,3%
TDS (mg/L)	-	53,0%	-	21,1%	84,2%	41,5%
TSS (mg/L)	-	76,5%	23,9%	90,0%	72,8%	16,9%
VSS (mg/L)	9,3%	76,9%	32,4%	88,7%	61,1%	3,1%
NH ₄ ⁺ (mg N/L)	58,3%	91,9%	2,2%	95,3%	97,1%	85,7%
NO ₂ ⁻ (mg N/L)	15,2%	-	-	-	95,8%	44,0%
NO ₃ ⁻ (mg N/L)	-	-	-	-	-	-
Li ⁺ (mg/L)	-	4,7%	-	23,3%	0,0%*	-
Na ⁺ (mg/L)	-	38,0%	-	13,5%	68,6%	37,0%
K ⁺ (mg/L)	-	41,2%	-	25,9%	73,8%	24,8%
Mg ²⁺ (mg/L)	-	68,7%	-	20,9%	83,5%	-
Ca ²⁺ (mg/L)	42,4%	5,3%	75,3%	36,2%	58,0%	-
F ⁻ (mg/L)	50,6%	98,2%	-	63,1%	-	5,7%
Cl ⁻ (mg/L)	-	36,1%	-	23,5%	68,6%	33,2%
SO ₄ ²⁻ (mg/L)	-	-	-	-	-	-
Br (mg/L)	-	-	-	-	-	-
PO ₄ ³⁻ (mg/L)	-	-	-	-	-	-

*Neither formed or removed

The extent of formation for the parameters that were not removed is presented in Table 14.

Table 14 – Extent of formation of contaminants for all treatment facilities

Parameter	TF1	TF2	TF3	TF4	TF5	TF6
Conductivity (mS/cm)	19,3%	-	15,2%	-	-	-
TOC (mg C/L)	-	-	-	-	-	23,2%
BOD ₅ (mg O ₂ /L)	-	-	-	-	-	-
COD (mg O ₂ /L)	-	-	-	-	-	-
TDS (mg/L)	7,3%	-	19,3%	-	-	-
TSS (mg/L)	8,0%	-	-	-	-	-
VSS (mg/L)	-	-	-	-	-	-
NH ₄ ⁺ (mg/L)	-	-	-	-	-	-
NO ₂ ⁻ (mg/L)	-	1199,3%	122,8%	3369,1%	-	-
NO ₃ ⁻ (mg/L)	22650,0%	642,7%	165,3%	4295,0%	54800,0%	112,0%
Li ⁺ (mg/L)	5,4%	-	1,9%	-	0,0%*	4,0%
Na ⁺ (mg/L)	49,7%	-	34,9%	-	-	-
K ⁺ (mg/L)	26,2%	-	32,4%	-	-	-
Mg ²⁺ (mg/L)	24,6%	-	118,2%	-	-	45,1%
Ca ²⁺ (mg/L)	-	-	-	-	-	364,4%
F ⁻ (mg/L)	-	-	1,5%	-	2645,0%	-
Cl ⁻ (mg/L)	55,6%	-	34,6%	-	-	-
SO ₄ ²⁻ (mg/L)	-	-	-	-	-	-
Br (mg/L)	8412,5%	523,4%	278,4%	534,1%	219,9%	244,4%
PO ₄ ³⁻ (mg/L)	-	-	-	-	-	-

*Neither formed or removed

Nitrate formation occurred in a very large extent in all the treatment facilities. Also bromide increased in concentration. Nitrite removal did not occur in TF2, TF3 and TF4.

5. DISCUSSION

The age of the landfills suggests that they are in a methanogenic phase. Although TF1 is only 5 years old and TF6 is 4, this age is long enough to establish methanogenic conditions, since the aerobic phase is generally much faster than 4 years. The difference between these two landfills and TF2, TF3, TF4 and TF5 landfills may be that TF1 and TF6 are undergoing the initial methanogenic phase while the others are undergoing the stable methanogenic phase. However, this is impossible to predict since the leachate is mixed with other types of wastewater in some facilities and consequently the concentration of some contaminants that could confirm this idea is affected by this mixture rather than by the age of the landfill. It is believed that this combination of leachate with wastewater increases significantly the concentration of organic and suspended matter and salinity. If a comparison is made between the data obtained and the data presented in Table 3, leachate composition is much closer to a fresh leachate than to a mature leachate. The only data that may suggest that methanogenic conditions are present is pH, with values between 7,3 and 8,4 (in literature, general pH values for methanogenic leachates are in the range 6-8, although values until 9 were also determined). Sulfate concentration could confirm it, but since the total sulfur concentration is not known, it is impossible to determine to what extent the anaerobic reduction to sulfide did occur. By the sum of all these factors, it is possible to conclude that in this study the leachate composition is not closely related to the age of the landfill.

On the other hand, waste characterization can be related to the influent composition. Actually, the high content of organics may have some relationship with the large fraction of biowastes disposed in the landfill. Almost half of the refuse is composed of rotten matter, which when decomposed increases BOD₅ contents of leachate. BOD₅ values from Table 11 are relatively high and BOD₅/COD ratios presented in Table 15 also attest the high biodegradability or the organic matter present in leachate. In addition, the variations verified between different influent compositions do not seem to be affected by the waste characterization, which is similar from facility to facility.

Table 15 – VSS/TSS, BOD₅/COD and COD/TOC ratios for raw leachate

Facility	TF1	TF2	TF3	TF4	TF5	TF6
VSS/TSS	0,56	0,55	0,60	0,10	0,47	0,54
BOD ₅ /COD	0,35	0,64	0,77	0,32	0,50	0,26
COD/TOC	2,75	3,39	3,06	1,94	1,68	6,66

Indeed, the factor that was determined to affect the influent characteristics the most is the mixture of raw leachate with the wastewater from sanitary facilities within the landfill. As indicated in Table 15, in TF2, TF3 and TF5 this mixture increases the BOD₅/COD ratio to values from 0,5 to values much higher than the ones presented in section 2.2 for methanogenic leachates. TF3 appears to have large contents of organic matter,

not only because of BOD₅/COD ratio but also because of VSS/TSS and COD/TOC ratios, apparently resulting from the combination of wastewater with raw leachate.

COD/TOC ratios are high for all the influents, when compared to other mature leachates, especially in the case of TF6. This value is much higher than the other facilities. This can be explained by the fact that the landfill section that corresponds to that influent was reopened for waste disposal. Not all the new organic matter may have been converted, and therefore increased COD concentration and consequently, the ratio value.

In terms of solids, the influent of TF4 presents high concentrations, but not for VSS. This is reflected by the VSS/TSS ratio value of 0,1, which is much smaller when compared to the other facilities (Table 15). The explanation of such a low ratio is the existence of an ash and slag landfill, in which leachate is piped to the same treatment facility as the MSW landfill. Most of the material disposed in this landfill is inert ashes, so at the end, the VSS fraction is only from the MSW landfill, whereas the TSS content is the sum of particulate matter from both of the referred landfills. The other facilities have high VSS/TSS ratios, suggesting high biomass content in the influent.

TDS and some salts concentration as well as conductivity were determined to have higher values for treatment facility TF4. The reason for such is the same as for TSS. The trends of TDS and conductivity are similar and depend on the salt concentration. For all leachates, the most representative salts are Cl⁻, K⁺ and Na⁺. Ca²⁺, Mg²⁺, F⁻ and Br⁻ and are present in smaller concentrations. However, these appear not to be the only salts present in the solutions. A charge balance, where the concentration of each contaminant is calculated back to mole and then multiplied by the ion charge, can give a better impression on this and is summarized in Table 16.

Table 16 – Charge balance for the influents

Facility	Balance
TF1	+192,2
TF2	+497,8
TF3	+190,8
TF4	+112,6
TF5	+196,0
TF6	+768,4

The positive results for the balances in all facilities suggest that more salts are present in the solution and they also are negatively charged. According to the leachate composition given in section 2.2, one of the inorganic macrocomponents which concentration was not determined is HCO₃⁻. Bicarbonate is an intermediate product of the dissociation of carbonic acid to carbonate. In an aqueous solution the three species, H₂CO₃^{*}, HCO₃⁻ and CO₃²⁻ exist in equilibrium and bicarbonate prevails with pH values around 8. This is the case of these influents, so it is very possible that one other salt present there is bicarbonate. Carbonate may also exist, but in lower concentrations. Another possibility is the presence of sulfide and hydrogen sulfide. The

sulfide resulting from the methanogenic consumption of organic matter in the landfill dissolves in water and may react with protons to form hydrogen sulfide, HS^- , and hydrogen sulfide gas, H_2S . At $\text{pH}=7$ and 30°C , the percentage of H_2S is around 60% and the percentage of HS^- is around 40%. As pH increases and temperature rises, the percentage of hydrogen sulfide increases over the percentage of hydrogen sulfide gas.

Before discussing the effluent concentrations and respective removal rates, it is important to mention that the methodology adopted for sample collection can affect the results in an extent that cannot be defined. More precisely, as the samples were collected in the same day both for upstream and downstream from the treatment facility, there is a time lag between influent and effluent. Indeed, the effluent analyzed corresponds to an influent that entered the treatment facility before the studied influent. This time interval corresponds to the hydraulic retention time and, attending to it, the leachate composition can change due to climate conditions or other factors that were already presented and discussed.

On the effluents, BOD_5 concentrations (Table 12) were much lower compared to the influents. This was expected since these were from biological treatment facilities and the removal efficiencies, listed in Table 13, for this parameter are high. The only exception happens to be TF6, because the raw leachate analyzed is assumed as the influent to the treatment facility but in fact was not the case, as explained in section 3.2. The mixture one of an older leachate with more recent one, just prior to the treatment facility, alters the contents of the real influent in a way that may increase the organics concentrations, due to the age of the most recent section operating. Thus, biological treatment removes an initial organic matter concentration higher than the determined for raw leachate in TF6 and, consequently, the effluent concentration is higher than if the treatment was only applied to the raw leachate studied. On the calculations, the difference between the effluent concentration and the influent concentration is smaller than in reality, so removal efficiency is smaller too.

For TF1, BOD_5 removal is not so efficient because the lagoon is not aerated. However, a removal of 75,2% is high when compared to previous studies presented in section 2.3.2.1. This suggests that the fact that the lagoon was not covered induced some oxygen transfer in the top of the lagoon.

Although BOD_5 removal rates are high, the same does not happen with COD. This suggests that many of the organic compounds are not biodegradable. BOD_5/COD ratios in Table 15 confirm this, with the exception for TF1 and TF6. In fact, the data suggests that there is COD in the influents that were not accessible for microorganisms or biodegradable, because it may consist of organic compounds too complex for biodegradation. One way to overcome would be to apply advanced oxidation processes (AOPs) prior to nitrification/denitrification processes or in the recycle line. Assuming that conventional biological treatment is worthwhile only for influents with values higher than 0,5 for BOD_5/COD ratio, then it can be concluded that this kind of treatment is not suitable for these leachates.

For ammonium removal, activated sludge efficiencies were above 90%. Aeration appears to be an effective way to reduce NH_4^+ content, in spite of the fact that removal efficiency from the aerated lagoon of TF3 was insignificant. In fact, it is believed that the high concentration of ammonium in the effluent from this lagoon

is due to the death of nitrifying bacteria, as a consequence of being retained under anaerobic conditions, for one week, after the aeration stage. For TF1, it is contradictory that the treatment is anaerobic and the ammonium removal rate reaches 58,3%. This suggests that the presence of some oxygen to enhance nitrification and that oxygen appears to transfer from air to the leachate through the uncovered lagoon surface.

One of the major shortcomings in leachate treatment found in this work has to do with denitrification. As presented in Table 14, nitrate concentrations in the effluents were determined to have a large increase relative to the influents. The only facility where this was expected was TF3, since it does not have an anoxic stage for nitrate removal. Also in TF1, ammonium removal was observed, which was not expected since it was from anaerobic treatment. Focusing on activated sludge systems, low denitrification efficiencies can be explained by the lack of substrate available for denitrifying bacteria, suggesting that the addition of biodegradable substrate to increase biodegradable COD appears to be insignificant or not enough. Other possible reasons for such low removal efficiencies may be the presence of inhibitory substances in the solution, such as heavy metals. An analysis to heavy metals concentration could help on understanding these results.

The high nitrification rate on TF5, with an ammonium removal of 97,1% and a nitrite removal of 95,8% (nitrite is removed in the intermediate step of nitrification, as written in Eq. 2) results in a great decrease on pH and a high nitrate formation rate. Eq. 4 can explain this trend, since the release of H^+ ions in the ammonium dissociation step gives the leachate an acidic feature. The final pH values for the activated sludge processes are influenced by the monitoring carried out to make sure that the conditions for microbial activity are established.

Solids removal is better in the activated sludge processes, as shown in Table 13 for TF2, TF4 and TF5. Liquid/solid separation appears to have a significant effect in the separation of the sludge from the treated effluent. In TF1, there is no liquid-solid separation in the anaerobic lagoon and both sludge and supernatant are separated after the lagoon. Consequently, there is an increase in solids content, but it is not very sharp. In fact, this was expectable since sludge formation in anaerobic processes is smaller than in aerobic processes. However, the value of 940 mg TSS/L, in Table 12, may be affected by the sampling conditions. As stated in Table 7, the leachate sample was collected by simply submerging the bottle in the upper part of the lagoon. The bottle was not submerged very deep, so the sample may contain a less concentrated solution due to particle settling in the lagoon, since concentrations near the surface are less than very deep there.

Conductivity and salts evolution along the treatments is widely variable. From Table 13 and Table 14, Na^+ , K^+ and Cl^- were removed in activated sludge processes. For Mg^{2+} and Li^+ , similar characteristics were observed, but in TF6 they were formed rather than have been removed. The removal rates of these ions suggest that they were removed from leachate through co-precipitation as a salt. The charge balance presented in Table 17 may help to understand these trends.

Table 17 – Charge balance for the effluents

Facility	Balance
TF1	+157,0
TF2	+45,9
TF3	+181,2
TF4	+37,4
TF5	-1,9
TF6	+191,6

Comparing with the data from Table 16, all the charge balances reduce their values. Nitrate formation and ammonium removal have a great influence on these trends, especially nitrate due to its high molecular weight. TF5 charge balance has a small negative value, which suggests that there is a small presence of other metals dissolved that were not analyzed. The pH value of 4,9 reinforces this idea, in the sense that in acid solutions metals solubility increases.

One last remark goes to the formation of bromide. It is still not known how this ion significantly increases in concentration and further research is needed to understand the process and its impacts.

In spite of the ion reduction percentages obtained, the salinity of the treated effluents remains high. The conductivity and TDS contents require additional treatment and the reverse osmosis units applied in many landfills can be useful to this end. However, if to the energy consumption of reverse osmosis is added the energy consumption of aerated systems in biological treatments, the final energy requirements for the whole leachate treatment facility would become very expensive and may not be economically viable. Therefore, with the presence of reverse osmosis units, it is important to determine how useful are biological treatments and what their contribution is to the overall treatment performance.

6. CONCLUSIONS

The main goal of this was to evaluate the performance of the biological treatment systems applied for landfill leachates in Portugal. To better understand this performance, leachate was characterized and related with the age of the landfills, waste characterization and methods of operation in the landfill, especially what kind of wastewaters are added to the treatment facilities.

Leachate characterization was highly affected by the operating conditions in the landfill. From the six facilities studied, leachate was mixed with wastewater from the sanitary facilities within the landfill for three plants, whereas in another one the leachate corresponded not only to a MSW landfill, but also to an ash and slag landfill. For the facilities where the influent was a mixture of raw leachate with wastewater, this mixture appeared to increase the contents of the organic matter in leachate and its biodegradability, with BOD₅/COD ratios above 0,5 for COD concentrations on the order of 5 g/L. For the leachate from two kinds of landfills, the ash and slag landfill was shown to have a large influence on inorganic matter contents. On the one hand, VSS/TSS ratio was 0,1, suggesting that most of the particulate matter present in leachate was inorganic. On the other hand, conductivity, TDS and inorganic macrocomponents had concentrations much higher when compared with the influents of all the other treatment facilities.

Waste characterization also appeared to have some influence on the biodegradability of leachates' organic matter. With almost half of the waste disposed in the landfill consisting of biowastes, the high values of BOD₅/COD ratio can also be attributed to the high content of rotten material in the refuse, besides the mixtures mentioned above.

Contrary to many previous studies, age did not seem to be a relevant factor determining leachate composition. The leachate composition did not seem to indicate that the landfills are methanogenic due to their age.

Regarding the treatment facilities performance, the collection of samples both for influent and effluent analysis at the same time may have affected the results. Different systems were studied: four activated sludge, one aerated lagoon and one anaerobic lagoon. BOD₅ removal rates were determined to be 90%, except for two facilities. The case was different for COD, with removal rates varying from 52,7% and 81,9% for systems with aeration and around 30% for a system without aeration. The effluents' COD concentrations were still high, suggesting that the biological treatments applied are not suitable for leachate treatment. Activated sludge systems appeared to be the most effective on solids removal, with removal rates between 70% and 90%. Denitrification did not occur at any of the facilities studied, suggesting either a lack of substrate or biodegradable material for denitrifying bacteria to consume the nitrate, in spite of the addition of some nutrients, or the presence of inhibitory compounds for the growth of these microorganisms. Many ions appeared to be removed by coprecipitation with other ions as salts, except bromide, which increased in all the biological treatment systems studied, by reasons that could not be explained.

6.1. FUTURE WORK

The data collected in this work constitutes a basis for leachate treatment studies. Consequently, some aspects shall deserve attention in future similar works, or in the continuation of this:

- To know the ratios of the mixture of leachate with other wastewaters which may be helpful to determine what extent this mixture has on the composition of the influents to the treatment facilities;
- Heavy metals analyses can help to understand whether they are present in low or high concentrations and, in this last case, how their presence affects biological treatment;
- Energy balances to the biological treatment units may be useful in understanding how much energy is applied and whether this energy use is efficient relative to the removal rates of the contaminants;
- Bromide formation in biological processes may help to understand why there is an increase in concentration in the treatment facilities;
- The analysis of anions and cations that were above the detection limit of the cromatograph may be repeated to determine more precisely their concentration and removal rates.

7. REFERENCES

- Ahmed, F. N., & Lan, C. Q. (2012). Treatment of landfill leachate using membrane bioreactors: A review. *Desalination*, 287(0), 41-54.
- APA. (2011a). Caracterização da situação actual 2010/2011 - Sistemas de Gestão de RU - Infra-estruturas e equipamentos.
- APA. (2011b). Resíduos Urbanos em 2010.
- APHA, AWWA, & WEF. (1998). *Standard Methods for the Examination of Water and Wastewater* (Vol. 20th). Baltimore, Maryland: American Public Health Association.
- Calli, B., Mertoglu, B., & Inanc, B. (2005). Landfill leachate management in Istanbul: applications and alternatives. *Chemosphere*, 59(6), 819-829.
- Chen, P. H. (1996). Assessment of leachates from sanitary landfills: Impact of age, rainfall, and treatment. *Environment International*, 22(2), 225-237.
- Christensen, T. H., Kjeldsen, P., Bjerg, P. L., Jensen, D. L., Christensen, J. B., Baun, A., . . . Heron, G. (2001). Biogeochemistry of landfill leachate plumes. *Applied Geochemistry*, 16(7-8), 659-718.
- Chu, L., Cheung, K., & Wong, M. (1994). Variations in the chemical properties of landfill leachate. *Environmental Management*, 18(1), 105-117.
- Eddy, M. (2003). *Wastewater Engineering: Treatment and Reuse* (International ed.). Boston: McGraw Hill.
- El-Fadel, M., Bou-Zeid, E., & Chahine, W. (2003). Landfill evolution and treatability assessment of high-strength leachate from msw with high organic and moisture content. *International Journal of Environmental Studies*, 60, 603-615.
- El-Fadel, M., Bou-Zeid, E., Chahine, W., & Alayli, B. (2002). Temporal variation of leachate quality from pre-sorted and baled municipal solid waste with high organic and moisture content. *Waste Management*, 22(3), 269-282.
- EPA. (2002). What is Integrated Solid Waste Management?
- Fan, H.-j., Shu, H.-Y., Yang, H.-S., & Chen, W.-C. (2006). Characteristics of landfill leachates in central Taiwan. *Science of The Total Environment*, 361(1-3), 25-37.
- Fascari, D., Bronzini, F., Giordano, G., Tedioli, G., & Nocentini, M. (2004). Long-term characterization, lagoon treatment and migration potential of landfill leachate: a case study in an active Italian landfill. *Chemosphere*, 54(3), 335-343.
- Gray, N. F. (2004). *Biology of Wastewater treatment* (2nd ed. Vol. IV). London: Imperial College Press.
- Kjeldsen, P., Barlaz, M. A., Rooker, A. P., Baun, A., Ledin, A., & Christensen, T. H. (2002). Present and Long-Term Composition of MSW Landfill Leachate: A Review. *Critical Reviews in Environmental Science and Technology*, 32(4), 297-336.
- Kulikowska, D., Klimiuk, E., & Drzewicki, A. (2007). BOD5 and COD removal and sludge production in SBR working with or without anoxic phase. *Bioresource Technology*, 98(7), 1426-1432.

- Kurniawan, T. A., Lo, W., Chan, G., & Sillanpaa, M. E. T. (2010). Biological processes for treatment of landfill leachate. *Journal of Environmental Monitoring*, 12(11), 2032-2047.
- Lema, J. M., Mendez, R., & Blazquez, R. (1988). Characteristics of landfill leachates and alternatives for their treatment: A review. *Water, Air, & Soil Pollution*, 40(3), 223-250.
- Levy, J. d. Q., & Cabeças, A. J. (2006). *Resíduos Sólidos Urbanos - Princípios e Processos* (1st ed.). Lisboa: AEPSA - Associação das Empresas Portuguesas para o Sector do Ambiente.
- Lo, I. M. C. (1996). Characteristics and treatment of leachates from domestic landfills. *Environment International*, 22(4), 433-442.
- Lou, Z., Dong, B., Chai, X., Song, Y., Zhao, Y., & Zhu, N. (2009). Characterization of refuse landfill leachates of three different stages in landfill stabilization process. *Journal of Environmental Sciences*, 21(9), 1309-1314.
- MAOTDR. (2007). PERSU II - Plano Estratégico para os Resíduos Sólidos Urbanos 2007-2016 (1st ed., pp. 196).
- Decreto-Lei nº 183/2009 (2009).
- Mehmood, M. K., Adetutu, E., Nedwell, D. B., & Ball, A. S. (2009). In situ microbial treatment of landfill leachate using aerated lagoons. *Bioresource Technology*, 100(10), 2741-2744.
- Pohland, F. G. (1987). Critical review and summary of leachate and gas production from landfills. 7.
- Salem, Z., Hamouri, K., Djemaa, R., & Allia, K. (2008). Evaluation of landfill leachate pollution and treatment. *Desalination*, 220(1-3), 108-114.
- Statom, R. A., Thyne, G. D., & McCray, J. E. (2004). Temporal changes in leachate chemistry of a municipal solid waste landfill cell in Florida, USA. *Environmental Geology*, 45(7), 982-991.
- Tchobanoglous, G., Theisen, H., & Vigil, S. (1993). *Intergrated Solid Waste Management: Engineering Principles and Management Issues* (International ed.). New York: McGraw Hill.
- Türker, U., Okaygün, M., & Almaqadma, S. J. (2009). Impact of anaerobic lagoons on the performance of BOD and TSS removals at the Haspolat (Mia Milia) Wastewater Treatment Plant. *Desalination*, 249(1), 403-410.
- Wiszniewski, J., Robert, D., Surmacz-Gorska, J., Miksch, K., & Weber, J. (2006). Landfill leachate treatment methods: A review. *Environmental Chemistry Letters*, 4(1), 51-61.
- Zhu, G., Peng, Y., Li, B., Guo, J., Yang, Q., & Wang, S. (2008). Biological Removal of Nitrogen from Wastewater
- Reviews of Environmental Contamination and Toxicology. In D. M. Whitacre (Ed.), (Vol. 192, pp. 159-195): Springer New York.
- Ziyang, L., & Youcai, Z. (2007). Size-fractionation and characterization of refuse landfill leachate by sequential filtration using membranes with varied porosity. *Journal of Hazardous Materials*, 147(1-2), 257-264.
- Ziyang, L., Youcai, Z., Tao, Y., Yu, S., Huili, C., Nanwen, Z., & Renhua, H. (2009). Natural attenuation and characterization of contaminants composition in landfill leachate under different disposing ages. *Science of The Total Environment*, 407(10), 3385-3391.

8. APPENDICES

8.1. APPENDIX A – BOD MEASUREMENT

Principle

“The biochemical oxygen demand (BOD) test is used to determine the relative oxygen requirements of wastewaters, effluents and polluted waters. (...) This test measures the molecular oxygen utilized for the biochemical degradation of organic material and the oxygen used to oxidized inorganic material such as sulfides and ferrous ion.(...) It also may measure the amount of oxygen used to oxidize reduced forms of nitrogen unless their oxidation is prevented by an inhibitor. (...) Respirometric methods provide direct measurements of the oxygen consumed from an air or oxygen-enriched environment in a closed vessel under conditions of constant temperature and agitation.”

Material

- OxiTop® measuring system;
- Inductive stirring system;
- Incubator thermostatic box (temperature $20^{\circ}\text{C} \pm 1\text{K}$);
- Sample bottles brown (nominal volume 510 mL);
- Stirring rods;
- Stirring rod remover;
- Suitable overflow measuring beakers;
- Rubber quivers;
- Sodium hydroxide tablets.

Sample volume determination

1. Estimate the BOD_5 value to be expected for the wastewater sample (80% of the COD value);
2. Look for corresponding measuring range in Table 1 and gather correct values for sample and volume factor.

Table 18 – Measuring range corresponding sample volume and dilution factor

Sample volume (mL)	Measuring range (mg/L)	Factor
432	0-40	1
365	0-80	2
250	0-200	5
164	0-400	10
97	0-800	20
43,5	0-2000	50
22,7	0-4000	100

Measurement

1. Rinse measuring bottle with sample;
2. Empty thoroughly;
3. Exactly measure the required oxygen-saturated (thoroughly homogenized) quantity of the sample according to information (dilute if necessary);
4. Put the magnetic stirring rod into the bottle;
5. Insert a rubber quiver in the neck of the bottle;
6. Put 2 sodium hydroxide tablets into the rubber quiver with a tweezers (The tablets must never come into the sample!);
7. Screw OxiTop® directly on sample bottle (tightly close);
8. Start measurement:
 - a. Press S and M simultaneously, 2 seconds, until the display shows 00 (meaning stored values are deleted);
 - b. Keep the measuring bottle with the OxiTop® put on for 5 days at 20°C (e.g. in an incubator);
 - c. During the 5 days the sample is continuously stirred (to have the current value shown press the M key);
 - d. Readout of the stored values after the 5 days have passed:
 - i. Press S until measured value is displayed (1 second);
 - ii. Scroll to next day by repressing the S key while the measured value is displayed (5 seconds);
 - iii. Fast scrolling by repeatedly pressing the S key.

To clean, remove gross contaminations mechanically (e.g. with a brush) and rinse the bottles with clear water or with water of the next sample (do not use disinfectants, alcohol or acetone).

Calculations

$$BOD_5(mg\ O_2/L) = \text{Measured value} \times \text{Factor} \times \text{Dilution factor}$$

References

APHA, AWWA, & WEF. (1998). *Standard Methods for the Examination of Water and Wastewater* (Vol. 20th). Baltimore, Maryland: American Public Health Association.

8.2. APPENDIX B – COD MEASUREMENT

Principle

“Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with a sample under controlled conditions.(...) Both organic and inorganic components of the sample are subject to oxidation, but in most cases the organic component predominates and is of the greater interest.(...) Most types of organic matter are oxidized by boiling a mixture of chromic and sulfuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate.”

Material

- Digestion tubes;
- Heating block;
- Test-tube rack;
- Spectrophotometer;
- Micropipette and respective tips
- Volumetric flasks and glass (for possible dilutions)

Reagents

- Digestion solution (already prepared)
- Sulfuric acid reagent (already prepared);
- Distilled water.

Procedure

1. Measure 2,5 mL of sample into a tube (dilute if necessary);
2. Add 3,5 mL of digestion solution and 1,5 mL of sulfuric acid reagent;
3. Prepare a blank solution with 2,5 mL of distilled water
4. Digest samples in heating blocks for 2h at 150°C;
5. Cool samples to room temperature, slowly to avoid precipitate formation;
6. With spectrophotometer at 600 nm, read the blank sample as reference solution;
7. Measure samples COD.

Calculations

$$COD(mg/L) = COD_{measured} \times Dilution\ factor$$

References

APHA, AWWA, & WEF. (1998). *Standard Methods for the Examination of Water and Wastewater* (Vol. 20th). Baltimore, Maryland: American Public Health Association.

8.3. APPENDIX C – CONDUCTIVITY AND TOTAL DISSOLVED SOLIDS MEASUREMENT

Principle

“Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement.” ‘Total dissolved solids’ is a measure of the content of organic and inorganic matter in a solution under the form of molecular, ionized and colloidal particles. Electrical conductivity is related to the concentration of ionized solids, so both can be measured using a conductivity meter.

Material

- Conductivity meter;
- Glass.

Procedure

1. Turn sample into a glass;
2. Turn on conductivity meter
3. Press M button successively to select the unit $\mu\text{S}/\text{cm}$, for conductivity measurement;
4. Dip the electrode in the sample;
5. Press AR button to enable Auto-Read measurement;
6. Start the measurement by pressing Run-Enter button;
7. Wait until AR indication stops blinking in the screen;
8. Register temperature and conductivity.
9. Press M button successively to select the unit mg/L ;
10. Dilute sample if necessary;
11. Register TDS concentration.

References

APHA, AWWA, & WEF. (1998). *Standard Methods for the Examination of Water and Wastewater* (Vol. 20th). Baltimore, Maryland: American Public Health Association.

8.4. APPENDIX D – pH MEASUREMENT

Principle

“Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water treatment is pH-dependent. Electrometric pH measurement is a determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode”

Material

- pH meter;
- Glass.

Procedure

1. Turn sample into a glass;
2. Stir sample to ensure homogeneity (stir gently to minimize carbon dioxide entrainment);
3. Equilibrate electrodes by immersing in three or four successive portions of sample;

Take a fresh sample to measure pH.

References

APHA, AWWA, & WEF. (1998). *Standard Methods for the Examination of Water and Wastewater* (Vol. 20th). Baltimore, Maryland: American Public Health Association.

8.5. APPENDIX F – TSS AND VSS MEASUREMENT

Principle

“Solids refer to matter suspended or dissolved in water or wastewater. (...) ‘Total solids’ is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids include ‘total suspended solids’, the portion of total solids retained by a filter.” After heating total solids to dryness, the weight loss on ignition is called ‘volatile solids’.

When a sample is evaporated in a weighed dish and dried to constant weight in an oven at 103 to 105°C, the increase in weight represents the total solids. When this residue is ignited to constant weight at 550°C, the weight lost represents the volatile solids.

Material

- Glass-fiber filter;
- Pipet;
- Glass;
- Vacuum filtration apparatus;
- Oven;
- Muffle furnace;
- Desiccator;
- Scale;
- Magnetic stirrer;
- Aluminum weighing dish;
- Evaporating dish;
- Tweezers.

Reagents

- Distilled water

TOTAL SUSPENDED SOLIDS (TSS)

Selection of filter and sample sizes

9. Choose sample volume to yield between 2,5 and 200 mg dried residue;
 - a. If volume filtered fails to meet minimum yield, increase sample volume up to 1 L;
 - b. If complete filtration takes more than 10 min, increase filter diameter or decrease sample volume.

Preparation of glass-fiber filter disk

1. Insert disk with wrinkled side up in filtration apparatus;
2. Apply vacuum and wash disk with three successive 20 mL portions of distilled water;
3. Remove all traces of water, turn vacuum off and discard washings;;
4. Ignite filter at 550°C for 15 minutes in a muffle furnace (for VSS measurement);
5. Cool in desiccator;
6. Repeat cycle until weight change is less than 4% of the previous weighing or 0,5 mg;
7. Store in desiccator.

Sample analysis

1. Wet filter with a small volume of distilled water to seat it;
2. Stir sample with a magnetic stirrer to obtain a more uniform particle size;
3. While stirring, pipet a measured volume onto the seated filter;
4. Pipet from a point middepth and midway between wall and vortex;
5. Wash filter with three successive 10 mL volumes of distilled water (may require additional washings);
6. Continue suction for about 3 min after filtration is complete;
7. Transfer filter to an aluminum weighing dish as support;
8. Dry for at least 1 h at 103 to 105°C in an oven and cool in a desiccator;
9. Repeat cycle until weight change is less than 4% of the previous weighing or 0,5 mg;
10. Analyze at least 10% of all samples in duplicate;
11. Duplicate determinations should agree within 5% of their average weight.

Sample analysis

1. Transfer total filtrate from TSS measurement to a weighed evaporating dish;
2. Dry evaporated sample for at least 1 h in an oven at $180 \pm 2^\circ\text{C}$ and cool in a dessicator;
3. Repeat cycle until weight change is less than 4% of the previous weighing or 0,5 mg;
4. Analyze at least 10% of all samples in duplicate;
5. Duplicate determinations should agree within 5% of their average weight.

VOLATILE SUSPENDED SOLIDS (VSS)

1. Ignite residue in the filter to constant weight in a previously warmed (15 to 20 min) muffle furnace at a temperature of 550°C;
2. Ignite a blank glass fiber filter along with samples;

3. Cool partially in air until most of the heat has been dissipated;
4. Transfer to a desiccator for final cooling in a dry atmosphere;
5. Weigh dish or disk as soon as it has cooled;
6. Repeat cycle until weight change is less than 4% of the previous weighing or 0,5 mg;
7. Analyze at least 10% of all samples in duplicate;
8. Duplicate determinations should agree within 5% of their average weight.

Calculations

$$m_{TSS} = \frac{(m_{dried\ residue+filter} - m_{filter})}{V_{sample}}$$
$$m_{VSS} = \frac{(m_{residue+filter\ before\ ignition} - m_{residue+filter\ after\ ignition})}{V_{sample}}$$

References

APHA, AWWA, & WEF. (1998). *Standard Methods for the Examination of Water and Wastewater* (Vol. 20th). Baltimore, Maryland: American Public Health Association.

8.6. APPENDIX G – TOC MEASUREMENT

Principle

“Total Organic Carbon (TOC) is an expression of total organic content in water or wastewater, (...) independent of the state of oxidation of the organic matter and does not measure organically bound elements and inorganics that can contribute to the oxygen demand measured by BOD or COD. (...) High temperature combustion method has been used for a variety of samples. The samples are injected into a heated reaction chamber packed with an oxidative catalyst. The water is vaporized and the organic carbon is oxidized to carbon dioxide and water. The carbon dioxide from oxidation of organic and inorganic carbon is transported in the carrier-gas streams and measured by means of a nondispersive infrared analyzer.”

Material

- Scale;
- Weighing dish;
- Spatula;
- Oven;
- Desiccator;
- Volumetric flask;
- TOC apparatus;
- Magnetic stirrer.

Reagents

- Potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{KO}_4$);
- Distilled water;
- H_3PO_4 or H_2SO_4 ;
- Sodium hydrogen carbonate (NaHCO_3);
- Sodium carbonate (Na_2CO_3).

Preparation of TC Standard Solution

1. Accurately weigh 2,125 g of reagent grade potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{KO}_4$) previously dried at 105-120°C for about 1 h and cooled in a desiccator;
2. Transfer to a 1L volumetric flask and dissolve in zero water;
3. Store at 4°C.

Preparation of IC Standard Solution

1. Accurately weigh 3,50 g of reagent grade sodium hydrogen carbonate (NaHCO_3) previously dried for 2 hours in a silica gel desiccator and 4,41 g of sodium carbonate (Na_2CO_3) previously dried for 1 h at 280-290°C and cooled in a desiccator;
2. Transfer the weighed materials to a 1 L volumetric flask;
3. Add zero water to the 1 L mark;
4. Stir well to mix.

Preparation of standard curve

1. Prepare standard organic and inorganic carbon series by diluting standard solutions to cover the expected range in samples within the linear range of the instrument;
2. Set the parameters for the 1st point of the calibration curve;
3. Set parameters for the 2nd and subsequent points of the calibration curve;
4. Set the standard solution;
5. Analyze.

Sample treatment

1. If the sample contains gross solids or insoluble matter, homogenize until satisfactory replication is obtained;
2. Analyze a homogenizing blank consisting of reagent water carried through the homogenizing treatment.

Sample injection

1. Select sample according to manufacturer's direction;
2. Stir sample containing particles with a magnetic stirrer;
3. Select needle size consistent with sample with sample particulate size;
4. Dilute sample in a ratio 1:10;
5. Inject sample and standards into the analyzer according to manufacturer's directions and record response;
6. Repeat injection until consecutive measurements obtained are reproducible within 10%.

Sample analysis

1. Set the parameters for the first analysis mode;
2. Set the parameters for the second and subsequent analysis modes;
3. Set the sample;

4. Analyze.

8.7. APPENDIX H – RESULTS FOR TF1

Table H.1 – TF1 upstream results

SAMPLING DATE 16-04-2012
SAMPLING TIME 15:30
SAMPLING POINT Upstream

pH			
Date	16-04-2012		
Time	20:30		
Assay	pH	Temperature (°C)	
1	8,364	19,8	
2	8,432	19,7	
3	8,388	19,7	
			pH 8,395
Conductivity			
Date	16-04-2012		
Time	21:00		
Assay	Conductivity (mS/cm)	Temperature (°C)	
1	24,8	19,60	
2	24,9	19,50	
3	24,9	19,50	
			Conductivity (mS/cm) 24,87
TOC			
Date	18-04-2012		
Time	16:00		
Assay	TC (mg C/L)	IC (mg C/L)	
1	3535	1870	
2	3572	1870	
3	3530	1862	
		TC (mg C/L) 3546	
		IC (mg C/L) 1867	TOC (mg C/L) 1678
BOD ₅			
Date	16-04-2012		
Time	20:00		
Assay	Digits	BOD ₅ (mg O ₂ /L)	
1	34	1700	
2	34	1700	
3	34	1700	
		Dillution (1:x) 1	
		Factor 50	BOD₅ (mg O₂/L) 1700,0
Date	16-04-2012		
Time	20:00		
Assay	Digits	BOD ₅ (mg O ₂ /L)	
1	13	1560	
2	15	1800	
3	11	1320	
		Dillution (1:x) 6	
		Factor 20	BOD₅ (mg O₂/L) 1560,0
COD			
Date	18-04-2012		
Time	11:00		
Assay	Dillution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)
1	20	233	4660
2	20	233	4660
3	20	227	4540
			COD (mg O₂/L) 4620
TDS			
Date	16-04-2012		
Time	21:00		
Assay	TDS (mg/L)		
1	14500		

2	14000				TDS (mg/L)
3	13700				14067
TSS					
Date	19-04-2012				
Time	10:30		Sample volume	10	mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)	
1	0,0872	0,0960	0,0088	880,0	TSS (mg/L)
1	0,0867	0,0953	0,0086	860,0	870,0
VSS					
Date	19-04-2012				
Time	12:00		Sample volume	10	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,0960	0,0914	0,0046	460,0	VSS (mg/L)
2	0,0953	0,0902	0,0051	510,0	485,0

Table H.2 – TF1 downstream results

pH					
Date		16-04-2012			
Time		20:30			
Assay	pH	Temperature (°C)			
1	8,713	19,4			
2	8,708	19,4			
3	8,706	19,5			
Conductivity					
Date		16-04-2012			
Time		21:00			
Assay	Conductivity (mS/cm)		Temperature (°C)		
1	29,6		19,9		
2	29,7		20,0		
3	29,7		19,9		
			Conductivity (mS/cm)		
			29,67		
TOC					
Date		18-04-2012			
Time		17:00			
Assay	TC (mg C/L)	IC (mg C/L)		TC (mg C/L)	
1	3185	1569		3216	
2	3234	1565		IC (mg C/L)	
3	3228	1573		TOC (mg C/L)	
			1569		1647
BOD ₅					
Date		17-04-2012			
Time		15:30			
Assay	Digits	BOD ₅ (mg O ₂ /L)		Dillution (1:x)	
1	8	400		1	
2	8	400		Factor	
3	9	450		50	
			BOD ₅ (mg O ₂ /L)		
			416,7		
Date		17-04-2012			
Time		15:30			
Assay	Digits	BOD ₅ (mg O ₂ /L)		Dillution (1:x)	
1	20	400		1	
2	19	380		Factor	
3	20	400		20	
			BOD ₅ (mg O ₂ /L)		
			393,3		
COD					

Date	18-04-2012			
Time	11:00			
Assay	Dilution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)	
1	20	169	3380	
2	20	162	3240	
3	20	159	3180	
				COD (mg O ₂ /L)
				3267
TDS				
Date	16-04-2012			
Time	21:30			
Assay	TDS (mg/L)			
1	14500			
2	15800			
3	15000			
				TDS (mg/L)
				15100
TSS				
Date	19-04-2012			
Time	10:30			
		Sample volume	10	mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)
1	0,0917	0,1015	0,0098	980,0
2	0,0879	0,0969	0,0090	900,0
				TSS (mg/L)
				940,0
VSS				
Date	19-04-2012			
Time	12:00			
		Sample volume	10	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)
1	0,1015	0,0970	0,0045	450,0
2	0,0969	0,0926	0,0043	430,0
				VSS (mg/L)
				440,0

8.8. APPENDIX I – RESULTS FOR TF2

Table I.1 – TF2 upstream results

SAMPLING DATE 17-05-2012
SAMPLING TIME 15:30
SAMPLING POINT Upstream

pH				
Date		17-05-2012		
Time		18:30		
Assay	pH	Temperature (°C)		
1	8,063	23,7		
2	8,076	23,6		
3	8,052	23,6		
Conductivity				
Date		17-05-2012		
Time		19:00		
Assay	Conductivity (mS/cm)		Temperature (°C)	
1	34,4		24,30	
2	34,5		24,10	
3	34,6		23,90	
TOC				
Date		18-05-2012		
Time		16:30		
Assay	TC (mg C/L)	IC (mg C/L)		TC (mg C/L)
1	4283	2853		4314
2	4300	2803		IC (mg C/L)
3	4358	2803		2820
BOD ₅				
Date		17-05-2012		
Time		18:30		
Assay	Digits	BOD ₅ (mg O ₂ /L)		Dilution (1:x)
1	34	3400		2
2	30	3000		Factor
3	33	3300		50
COD				
Date		19-05-2012		
Time		11:00		
Assay	Dilution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)	
1	20	270	5400	
2	20	251	5020	
3	20	238	4760	
TDS				
Date		17-05-2012		
Time		19:00		
Assay	TDS (mg/L)			
1	21100			
2	20900			
3	20600			
TSS				
Date		19-05-2012		
Time		12:00		
Sample volume				5 mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)
1	0,0912	0,0987	0,0075	1500,0
2	0,0924	0,0995	0,0071	1420,0
TSS (mg/L)				
1460,0				

VSS					
Date	19-05-2012				
Time	12:00				
			Sample volume	5	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,0987	0,0944	0,0043	860,0	VSS (mg/L)
2	0,0995	0,0957	0,0038	760,0	810,0

Table I.2 – TF2 downstream results

SAMPLING DATE 24-04-2012
 SAMPLING TIME 11:30
 SAMPLING POINT Downstream

pH			
Date	24-04-2012		
Time	16:30		
Assay	pH	Temperature (°C)	
1	6,677	18,9	
2	6,914	18,8	
3	6,969	18,8	
			pH
			6,853

Conductivity			
Date	24-04-2012		
Time	16:40		
Assay	Conductivity (mS/cm)	Temperature (°C)	
1	18,21	19,1	
2	18,20	19,2	
3	18,20	19,2	
			Conductivity (mS/cm)
			18,20

TOC			
Date	27-04-2012		
Time	9:00		
Assay	TC (mg C/L)	IC (mg C/L)	TOC (mg C/L)
1	1293	46,26	1247
2	1291	44,87	1246
3	1290	44,84	1245
			TC (mg C/L)
			1291
			IC (mg C/L)
			45,32
			TOC (mg C/L)
			1246

BOD ₅					
Date	24-04-2012				
Time	16:00				
Assay	Digits	BOD ₅ (mg O ₂ /L)	Dillution (1:x)		
1	42	84	1		
2	44	88	Factor		BOD ₅ (mg O ₂ /L)
3	40	80		2	84,0
Assay	BOD ₁ (mg O ₂ /L)	BOD ₂ (mg O ₂ /L)	BOD ₃ (mg O ₂ /L)	BOD ₄ (mg O ₂ /L)	
1	8	14	21	31	
2	9	15	23	33	
3	8	14	21	30	

COD			
Date	26-04-2012		
Time	10:30		
Assay	Dillution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)
1	20	128	2560
2	20	114	2280
3	20	117	2340
			COD (mg O ₂ /L)
			2393

TDS	
Date	24-04-2012

Time		17:00			
Assay	TDS (mg/L)				
1	9700				
2	9800				
3	9900				
TDS (mg/L)					
9800					
TSS					
Date		26-04-2012			
Time		12:00		Sample volume	20 mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)	
1	0,0890	0,0955	0,0065	325,0	
2	0,0915	0,0987	0,0072	360,0	
TSS (mg/L)					
342,5					
VSS					
Date		26-04-2012			
Time		12:00		Sample volume	20 mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,0955	0,0918	0,0037	185,0	
2	0,0987	0,0949	0,0038	190,0	
VSS (mg/L)					
187,5					

8.9. APPENDIX J – RESULTS FOR TF3

Table J.1 – TF3 upstream results

SAMPLING DATE 27-04-2012

SAMPLING TIME 15:30

SAMPLING POINT Upstream

pH				
Date	27-04-2012			
Time	20:00			
Assay	pH	Temperature (°C)		
1	7,267	17,4		
2	7,262	17,4		
3	7,263	17,5		
pH				
7,264				
Conductivity				
Date	27-04-2012			
Time	20:30			
Assay	Conductivity (mS/cm)		Temperature (°C)	
1	18,82		18,4	
2	18,87		18,3	
3	18,90		18,2	
Conductivity (mS/cm)				
18,86				
TOC				
Date	27-04-2012			
Time	22:00			
Assay	TC (mg C/L)	IC (mg C/L)	TC (mg C/L)	
1	3508	1362	3510	
2	3521	1353	IC (mg C/L)	
3	3501	1344	1353	
			TOC (mg C/L)	
			2157	
BOD ₅				
Date	27-04-2012			
Time	20:00			
Assay	Digits	BOD ₅ (mg O ₂ /L)	Dillution (1:x)	
1	28	5600	2	
2	23	4600	Factor	
3	25	5000	100	
BOD ₅ (mg O ₂ /L)				
5066,7				
COD				
Date	03-05-2012			
Time	11:00			
Assay	Dillution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)	
1	50	134	6700	
2	50	-	-	
3	50	130	6500	
COD (mg O ₂ /L)				
6600				
TDS				
Date	27-04-2012			
Time	20:45			
Assay	TDS (mg/L)			
1	10600			
2	10900			
3	11200			
TDS (mg/L)				
10900				
TSS				
Date	03-05-2012			
Time	12:30			
Sample volume				5 mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)
1	0,0873	0,0930	0,0057	1140,0
2	0,0876	0,0932	0,0056	1120,0
TSS (mg/L)				
1130,0				

VSS					
Date	03-05-2012				
Time	12:30				
	Sample volume			5	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,0930	0,0898	0,0032	640,0	VSS (mg/L)
2	0,0932	0,0896	0,0036	720,0	680,0

Table J.2 – TF3 downstream results

SAMPLING DATE 27-04-2012
 SAMPLING TIME 15:30
 SAMPLING POINT Downstream

pH			
Date	27-04-2012		
Time	20:15		
Assay	pH	Temperature (°C)	
1	8,305	17,9	
2	8,299	17,9	
3	8,305	17,9	
			pH
			8,303

Conductivity			
Date	27-04-2012		
Time	20:30		
Assay	Conductivity (mS/cm)	Temperature (°C)	
1	21,7	18,9	
2	21,7	18,5	
3	21,8	18,4	
			Conductivity (mS/cm)
			21,73

TOC			
Date	27-04-2012		
Time	23:00		
Assay	TC (mg C/L)	IC (mg C/L)	
1	2699	1790	
2	2686	1779	
3	2681	1785	
			TC (mg C/L)
			2689
			IC (mg C/L)
			1785
			TOC (mg C/L)
			904

BOD ₅			
Date	27-04-2012		
Time	20:00		
Assay	Digits	BOD ₅ (mg O ₂ /L)	
1	6	300	
2	3	150	
3	4	200	
			Dillution (1:x)
			1
			Factor
			50
			BOD ₅ (mg O ₂ /L)
			216,7

COD			
Date	03-05-2012		
Time	11:00		
Assay	Dillution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)
1	20	71	1420
2	20	71	1420
3	20	70	1400
			COD (mg O ₂ /L)
			1413

TDS			
Date	27-04-2012		
Time	20:45		
Assay	TDS (mg/L)		
1	12500		
2	12700		
3	13800		
			TDS (mg/L)
			13000

TSS					
Date	03-05-2012				
Time	12:30				
	Sample volume			5	mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)	
1	0,0865	0,0910	0,0045	900,0	TSS (mg/L)
2	0,0862	0,0903	0,0041	820,0	860,0
VSS					
Date	03-05-2012				
Time	12:30				
	Sample volume			5	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,0910	0,0886	0,0024	480,0	VSS (mg/L)
2	0,0903	0,0881	0,0022	440,0	460,0

8.10. APPENDIX K – RESULTS FOR TF4

Table K.1 – TF4 upstream results

SAMPLING DATE 14-06-2012
SAMPLING TIME 11:00
SAMPLING POINT Upstream

pH					
Date		14-06-2012			
Time		14:30			
Assay	pH	Temperature (°C)			
1	7,426	22,4			
2	7,386	22,4			
3	7,396	22,4			
					pH
					7,403
Conductivity					
Date		14-06-2012			
Time		14:45			
Assay	Conductivity (mS/cm)		Temperature (°C)		
1	84,1		22,7		
2	84,2		22,7		
3	84,2		22,7		
					Conductivity (mS/cm)
					84,17
TOC					
Date		15-06-2012			
Time		14:00			
Assay	TC (mg C/L)	IC (mg C/L)			
1	2058	1104			
2	2048	1091			
3	2053	1084			
			TC (mg C/L)		
			2053		
			IC (mg C/L)	TOC (mg C/L)	
			1093	960	
BOD ₅					
Date		14-06-2012			
Time		14:00			
Assay	Digits	BOD ₅ (mg O ₂ /L)			
1	5	500			
2	6	600			
3	7	700			
			Dilution (1:x)		
			2		
			Factor	BOD ₅ (mg O ₂ /L)	
			50	600,0	
COD					
Date		18-06-2012			
Time		12:00			
Assay	Dilution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)		
1	20	94	1880		
2	20	93	1860		
3	20	92	1840		
					COD (mg O ₂ /L)
					1860
TDS					
Date		14-06-2012			
Time		15:00			
Assay	TDS (mg/L)				
1	45900				
2	48000				
3	48300				
					TDS (mg/L)
					47400
TSS					
Date		18-06-2012			
Time		12:00			
				Sample volume	5 mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)	
1	0,0885	0,1083	0,0198	3960,0	
2	0,0882	0,1079	0,0197	3940,0	
					TSS (mg/L)
					3950,0

VSS					
Date	18-06-2012				
Time	12:00				
	Sample volume			5	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,1083	0,1064	0,0019	380,0	VSS (mg/L)
2	0,1079	0,1057	0,0022	440,0	410,0

Table K.2 – TF4 downstream results

SAMPLING DATE 14-06-2012
 SAMPLING TIME 11:00
 SAMPLING POINT Downstream

pH			
Date	14-06-2012		
Time	14:45		
Assay	pH	Temperature (°C)	
1	7,877	24,5	
2	7,877	24,4	
3	7,876	24,4	
			pH
			7,877

Conductivity			
Date	14-06-2012		
Time	14:30		
Assay	Conductivity (mS/cm)	Temperature (°C)	
1	66,7	24,8	
2	66,8	24,7	
3	66,8	24,7	
			Conductivity (mS/cm)
			66,77

TOC				
Date	15-06-2012			
Time	14:00			
Assay	TC (mg C/L)	IC (mg C/L)	TC (mg C/L)	
1	417,8	69,86	416	
2	415,5	69,63	IC (mg C/L)	TOC (mg C/L)
3	413,2	69,67	70	346

BOD ₅				
Date	14-06-2012			
Time	14:00			
Assay	Digits	BOD ₅ (mg O ₂ /L)	Dillution (1:x)	
1	19	38	1	
2	24	48	Factor	BOD ₅ (mg O ₂ /L)
3	23	46	2	44,0

COD				
Date	18-06-2012			
Time	12:00			
Assay	Dillution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)	
1	10	47	470	
2	10	67	670	
3	-	-	-	COD (mg O ₂ /L)
				570

TDS			
Date	14-06-2012		
Time	15:00		
Assay	TDS (mg/L)		
1	37600		
2	37500		
3	37100		
			TDS (mg/L)
			37400

TSS					
Date	18-06-2012				
Time	12:00				
	Sample volume			40	mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)	
1	0,0863	0,1015	0,0152	380,0	TSS (mg/L)
2	0,0889	0,1054	0,0165	412,5	396,3
VSS					
Date	18-06-2012				
Time	12:00				
	Sample volume			40	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,1015	0,0996	0,0019	47,5	VSS (mg/L)
2	0,1054	0,1036	0,0018	45,0	46,3

8.11. APPENDIX L – RESULTS FOR TF5

Table L.1 – TF5 upstream results

SAMPLING DATE 22-05-2012
SAMPLING TIME 11:30
SAMPLING POINT Upstream

pH			
Date	22-05-2012		
Time	16:30		
Assay	pH	Temperature (°C)	
1	7,464	21,7	
2	7,477	21,9	
3	7,577	21,8	
			pH 7,506
Conductivity			
Date	22-05-2012		
Time	16:15		
Assay	Conductivity (mS/cm)	Temperature (°C)	
1	18,46	22,0	
2	18,55	21,7	
3	18,56	21,8	
			Conductivity (mS/cm) 18,52
TOC			
Date	23-05-2012		
Time	16:00		
Assay	TC (mg C/L)	IC (mg C/L)	
1	2644	2009	
2	2679	1979	
3	2657	1971	
		TC (mg C/L) 2660	
		IC (mg C/L) 1986	TOC (mg C/L) 674
BOD ₅			
Date	22-05-2012		
Time	16:00		
Assay	Digits	BOD ₅ (mg O ₂ /L)	
1	12	600	
2	11	550	
3	11	550	
		Dilution (1:x) 1	
		Factor 50	BOD ₅ (mg O ₂ /L) 566,7
COD			
Date	24-05-2012		
Time	12:00		
Assay	Dilution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)
1	20	59	1180
2	20	56	1120
3	20	55	1100
			COD (mg O ₂ /L) 1133
TDS			
Date	22-05-2012		
Time	16:45		
Assay	TDS (mg/L)		
1	11000		
2	11600		
3	11600		
			TDS (mg/L) 11400
TSS			
Date	24-05-2012		
Time	14:00		
		Sample volume	5 mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)
			TSS (mg/L)

1	0,0923	0,0951	0,0028	560,0	TSS (mg/L)
2	0,0882	0,0911	0,0029	580,0	570,0
VSS					
Date	24-05-2012				
Time	14:00				
	Sample volume			5	mL
Assay	m_{before heating} (g)	m_{after heating} (g)	m_{solids} (g)	VSS (mg/L)	
1	0,0951	0,0936	0,0015	300,0	VSS (mg/L)
2	0,0911	0,0899	0,0012	240,0	270,0

Table L.2 – TF5 downstream results

SAMPLING DATE 22-05-2012
SAMPLING TIME 11:30
SAMPLING POINT Downstream

pH					
Date	22-05-2012				
Time	16:30				
Assay	pH	Temperature (°C)			
1	4,952	21,7			
2	4,830	21,8			
3	4,834	21,9			
					pH
					4,872

Conductivity					
Date	22-05-2012				
Time	16:30				
Assay	Conductivity (mS/cm)	Temperature (°C)			
1	4,16	21,9			
2	4,16	21,6			
3	4,17	21,8			
					Conductivity (mS/cm)
					4,16

TOC					
Date	23-05-2012				
Time	17:00				
Assay	TC (mg C/L)	IC (mg C/L)			
1	111,7	10,37			
2	111,9	10,58			
3	112,9	10,40			
			TC (mg C/L)		
			112,2		
			IC (mg C/L)	TOC (mg C/L)	
			10	102	

BOD₅					
Date	22-05-2012				
Time	16:00				
Assay	Digits	BOD₅ (mg O₂/L)			
1	5	10			
2	4	8			
3	5	10			
			Dilution (1:x)		
			1		
			Factor		
			2		
					BOD₅ (mg O₂/L)
					9,3

COD					
Date	24-05-2012				
Time	12:00				
Assay	Dilution (1:x)	COD_{measured} (mg O₂/L)	COD (mg O₂/L)		
1	1	208	208		
2	1	206	206		
3	1	203	203		
					COD (mg O₂/L)
					206

TDS					
Date	22-05-2012				
Time	16:30				
Assay	TDS (mg/L)				
1	1797				

2	1797				TDS (mg/L)
3	1797				1797
TSS					
Date	24-05-2012				
Time	14:00		Sample volume	10	mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)	
1	0,0910	0,0925	0,0015	150,0	TSS (mg/L)
2	0,0914	0,0930	0,0016	160,0	155,0
VSS					
Date	24-05-2012				
Time	14:00		Sample volume	10	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,0925	0,0914	0,0011	110,0	VSS (mg/L)
2	0,0930	0,0920	0,0010	100,0	105,0

8.12. APPENDIX M – RESULTS FOR TF6

Table M.1 – TF6 upstream results

SAMPLING DATE 31-05-2012
SAMPLING TIME 16:00
SAMPLING POINT Downstream

pH		
Date	31-05-2012	
Time	18:45	
Assay	pH	Temperature (°C)
1	7,798	24,2
2	7,784	24,3
3	7,781	24,3

pH
7,788

Conductivity		
Date	31-05-2012	
Time	18:30	
Assay	Conductivity (mS/cm)	Temperature (°C)
1	35,9	24,5
2	36,1	24,3
3	36,1	24,4

Conductivity (mS/cm)
36,03

TOC			
Date	01-06-2012		
Time	14:00		
Assay	TC (mg C/L)	IC (mg C/L)	TC (mg C/L)
1	4505	3655	4537
2	4551	3643	IC (mg C/L)
3	4554	3631	3643

TOC (mg C/L)
894

BOD ₅			
Date	31-05-2012		
Time	18:00		
Assay	Digits	BOD ₅ (mg O ₂ /L)	Dilution (1:x)
1	16	1600	2
2	16	1600	Factor
3	15	1500	

BOD₅ (mg O₂/L)
1566,7

COD			
Date	06-06-2012		
Time	12:00		
Assay	Dilution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)
1	20	301	6020
2	20	321	6420
3	20	271	5420

COD (mg O₂/L)
5953

TDS	
Date	31-05-2012
Time	19:00
Assay	TDS (mg/L)
1	19200
2	19100
3	19300

TDS (mg/L)
19200

TSS				
Date	06-06-2012			
Time	11:00			
	Sample volume		10,00	mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)

1	0,0873	0,0927	0,0054	540,0	TSS (mg/L)
2	0,0873	0,0937	0,0064	640,0	590,0
VSS					
Date 06-06-2012					
Time 11:00					
Sample volume				10	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,0927	0,0898	0,0029	290,0	VSS (mg/L)
2	0,0937	0,0902	0,0035	350,0	320,0

Table M.2 – TF6 downstream results

SAMPLING DATE 31-05-2012
SAMPLING TIME 16:00
SAMPLING POINT Upstream

pH					
Date 31-05-2012					
Time 18:30					
Assay	pH	Temperature (°C)			
1	7,339	24,0			
2	7,350	24,1			
3	7,347	24,1			
					pH
					7,345

Conductivity					
Date 31-05-2012					
Time 18:45					
Assay	Conductivity (mS/cm)	Temperature (°C)			
1	21,5	24,3			
2	21,6	24,4			
3	21,5	24,4			
					Conductivity (mS/cm)
					21,53

TOC					
Date 01-06-2012					
Time 15:00					
Assay	TC (mg C/L)	IC (mg C/L)			
1	3188	2085			
2	3142	2055			
3	3165	2051			
			TC (mg C/L)		
			3165		
			IC (mg C/L)	TOC (mg C/L)	
			2064	1101	

BOD₅					
Date 31-05-2012					
Time 18:00					
Assay	Digits	BOD ₅ (mg O ₂ /L)			
1	35	700			
2	31	620			
3	37	740			
			Dilution (1:x)		
			1		
			Factor		
			20		
					BOD₅ (mg O₂/L)
					686,7

COD					
Date 06-06-2012					
Time 12:00					
Assay	Dilution (1:x)	COD _{measured} (mg O ₂ /L)	COD (mg O ₂ /L)		
1	20	110	2200		
2	20	117	2340		
3	20	110	2200		
					COD (mg O₂/L)
					2247

TDS		
Date	31-05-2012	
Time	19:00	
Assay	TDS (mg/L)	
1	11000	11400

2	11300				TDS (mg/L)
3	11400				11233
TSS					
Date	06-06-2012				
Time	11:00		Sample volume	10	mL
Assay	m _{filter} (g)	m _{filter+solids} (g)	m _{solids} (g)	TSS (mg/L)	
1	0,0876	0,0927	0,0051	510,0	TSS (mg/L)
2	0,0885	0,0932	0,0047	470,0	490,0
VSS					
Date	06-06-2012				
Time	11:00		Sample volume	10	mL
Assay	m _{before heating} (g)	m _{after heating} (g)	m _{solids} (g)	VSS (mg/L)	
1	0,0927	0,0895	0,0032	320,0	VSS (mg/L)
2	0,0932	0,0902	0,0030	300,0	310,0

8.13.APPENDIX N – CALIBRATION CURVES FOR TC AND IC

STD	(ORG / DL)	AREA	SD	CV %
0.001mg/L	(0.001/1.00)	1.364	0.11	8.43
50.00mg/L	(50.00/1.00)	56.65	0.47	0.84
200.0mg/L	(200.0/1.00)	215.5	0.75	0.35
500.0mg/L	(500.0/1.00)	550.9	1.47	0.27
1000mg/L	(1000/1.00)	1102	1.53	0.14

Linear regression for TC

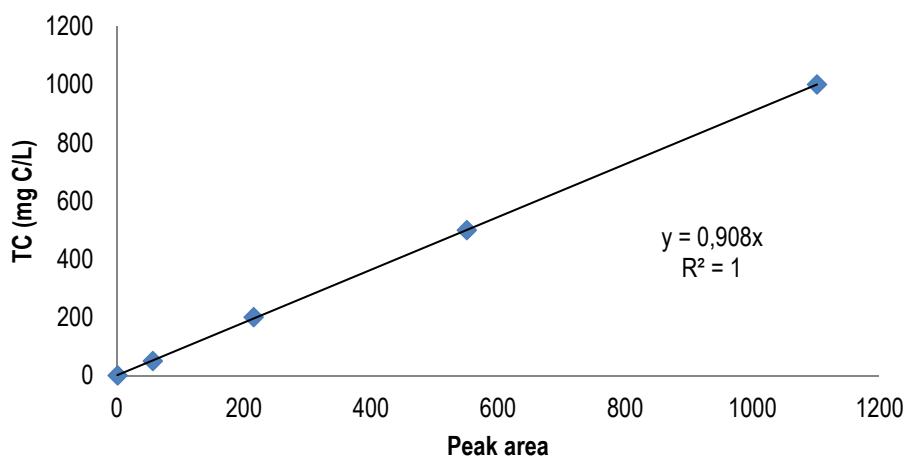


Figure N.1 – Calibration data for TC and respective linear regression

STD	AREA	SD	CV %
0.001mg/L	15.99	0.04	0.24
50.00mg/L	92.38	0.68	0.73
200.0mg/L	297.6	1.87	0.63
500.0mg/L	728.3	1.70	0.23
1000mg/L	1404	2.00	0.14

Linear regression for IC

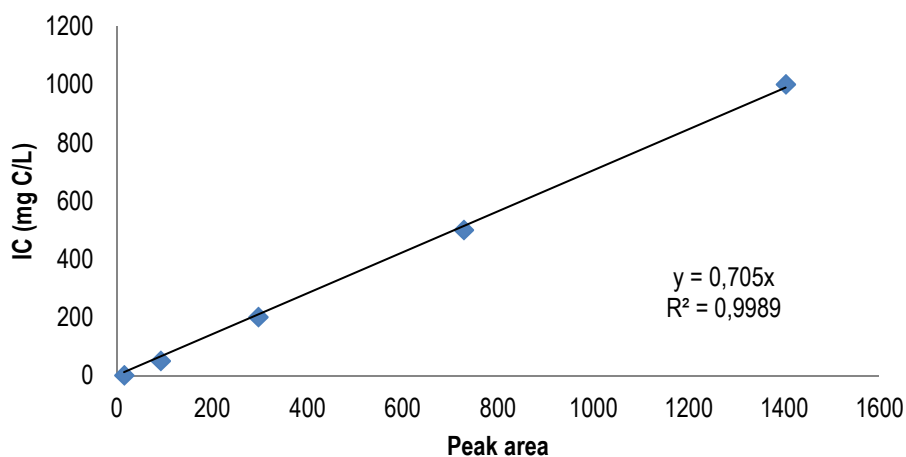


Figure N.2 – Calibration data for IC and respective linear regression