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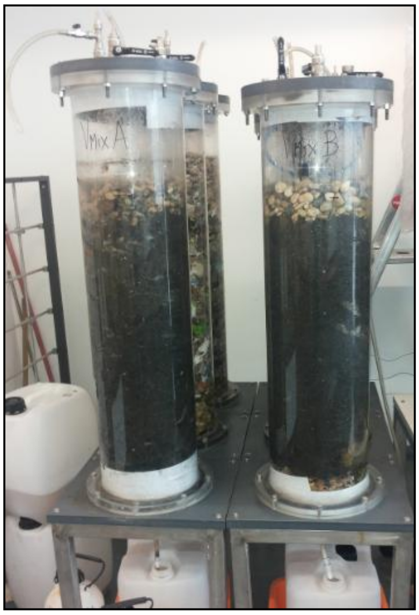

Master Thesis
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USE OF LEACHING TESTS TO CHARACTERIZE LANDFILL LEACHATES IN THE LONG-TERM PERIOD. APPLICATION IN RISK ANALYSIS.

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THESIS INDEX

PART ONE – GENERAL ASPECTS

1 Introduction and thesis objectives

Landfill is the most common solid waste disposal method in the world, because it is the simplest, the cheapest and the most cost-effective way of disposing waste. Uncontrolled landfilling, also known as open dumping, was very common during the past, and it was not subjected to regulations governing modern landfills. In the last years the sustainable concept became the base criterion to design all waste management systems, which include sustainable landfills with pre-treatment of waste before disposal, proper bottom liner which prevent the escape of leachate into the surrounding environment, cover system, leachate and gas collection systems, in order to prevent uncontrolled emissions into the environment, and enhance the quantities of controlled and collected ones, ensuring their treatment.

Generation of contaminated leachate remains an inevitable consequence of the practice of waste disposal. Leaching is the process of dissolution of harmful chemicals or compounds from landfills. There is therefore an obvious risk that leachate from landfills may directly affect and contaminate the groundwater and or downstream surface water (Rosqvist and Destouni, 2000), problem of great concern mainly in urban areas, being the groundwater a major resource of water in many of these areas. In absence of evidence to the contrary, most regulatory agencies prefer to assume that any leachate produced will contaminate either ground or surface waters.

Groundwater contamination from landfills typically forms a "plume" that moves outward and downward into surrounding and underlying aquifers, with the potential to contaminate and damage them. Landfills should be designed to prevent any waste or leachate from ever moving into adjacent areas.

Municipal solid waste (MSW) landfills are potential long-term sources of emissions, in particular leachate and biogas. For this reason, they need to be managed after closure until they do not pose a threat to human health or to ecosystem (Laner et al., 2011). Aftercare management of closed landfills typically includes monitoring of emissions and receiving systems (e.g. groundwater, surface water, soil, and air) and maintenance of the cover, leachate and gas collection systems, if present in the landfill site (Laner et al., 2012).

The long-term hazard potential for landfills is an aspect not well quantified (Bozkurt et al., 2000). An understanding of leachate composition and an integrated strategy for risk assessment are crucial and necessary to correctly face this problem and for making projections on the long-term impacts of a landfill, in particular for old and uncontrolled landfills (Baderna et al., 2011).

In order to assess the evolution of landfills over long times and predict leachate concentration levels, many different types of data are required. Looking at landfills, the sources of information are field studies, laboratory experiments and theoretical modeling (Bozkurt et al., 2000).

The objectives of the following study are performing dynamic leaching tests with columns full of waste, coming from an old uncontrolled landfill, simulating anaerobic and aerobic landfill conditions, in order to:

- reach high values of Liquid/Solid ratio (L/S) and verify if it is necessary and indicative, or if the behavior of some contaminants stabilize before the value of L/S=10 l/kg; this could be an interesting and useful result because of the practical difficulties in reaching so high values of L/S ratio in laboratory experiments;
- use the laboratory data in a risk analysis to predict leachate concentration in the long-term, period in which data on leachate are not present, and confront these data with the ones resulted in several experimental studies;
- make a comparison between anaerobic and aerobic conditions, with particular consideration on metals.

2 Leachate from landfill: quantity and quality

Landfill leachate is generated by the infiltration and percolation of rainfall, groundwater, runoff or floodwater into and through the layers of waste, deposited in an existing or closed landfill site (Baderna et al., 2011). A combination of physical, chemical and microbial processes in the waste transfers pollutants from the waste material to the percolating water, creating a water-based solution that may be harmful to a class of organisms, including human, but also to environmental receptors (Baderna et al., 2011). The health effects from leachate are not limited to drinking water but may also occur through the food chain due to the ingestion of other organisms as fish and aquatic plants, which habitate an environment contaminated by leachate.

In the development of more sustainable landfill concepts high detailed characterization methods are needed in order to identify the release controlling processes (solubility limitations, sorption, degradation, particulate and dissolved organic matter interaction) and mechanisms (percolation, diffusion and preferential flow), the mutual interaction between wastes and the effect of external stresses causing changes in leaching behavior in the long term (oxidation, carbonation) (Van Der Sloot et al., 2005).

Leachate is highly variable and heterogeneous, and it is very difficult to characterize (Kulikowska et al., 2008). Results from many leaching tests and monitoring wells in several landfills, showed high horizontal and vertical variability in leachate quality, indicating that age, volume and properties of waste, local conditions inside the body landfill, degradation and dilution processes, climatic and meteorological conditions of the site, and the amount of water infiltrated have a marked effect on local leachate quality and quantity (Sormunen et al., 2008).

For the latter aspect, as a first approximation, the quantity of leachate produced may be regarded as proportional to the volume of water percolating through the waste (Lema et al., 1988).

There are several numerical models that can be applied to estimate the amount of water infiltrating the landfill body and contributing to leachate production. Examples of these models are: DMLRM (Deterministic Multiple Linear Reservoir Model), SMLRM (Stochastic Multiple Linear Reservoir Model), and the HELP model (Hydrologic Evaluation of Landfill Performance), created by the United States EPA, Environmental Protection Agency, which is the most used and accredited hydrologic numerical model. All these models are very useful tools even in the project phase, because they allow the comparison between several landfill designs alternatives as judged by their water balances.

All these models are based on the hydrologic balance inside the landfill, shown in the following figure. This balance can be reduced, in the simplest way, to:

$$L = P - R - ET - \Delta U_w \tag{1}$$

where:

L is the leachate produced (mm/d);

R is the runoff from the landfill to the surrounding (mm/d);

ET is the term which takes into account the evaporation or the evapo-transpiration, if plants and grass are present on the top cover (mm/d);

ΔU_w is the variation of water quantity inside the landfill due to the biological activity or to the moisture variation of waste (mm/d).

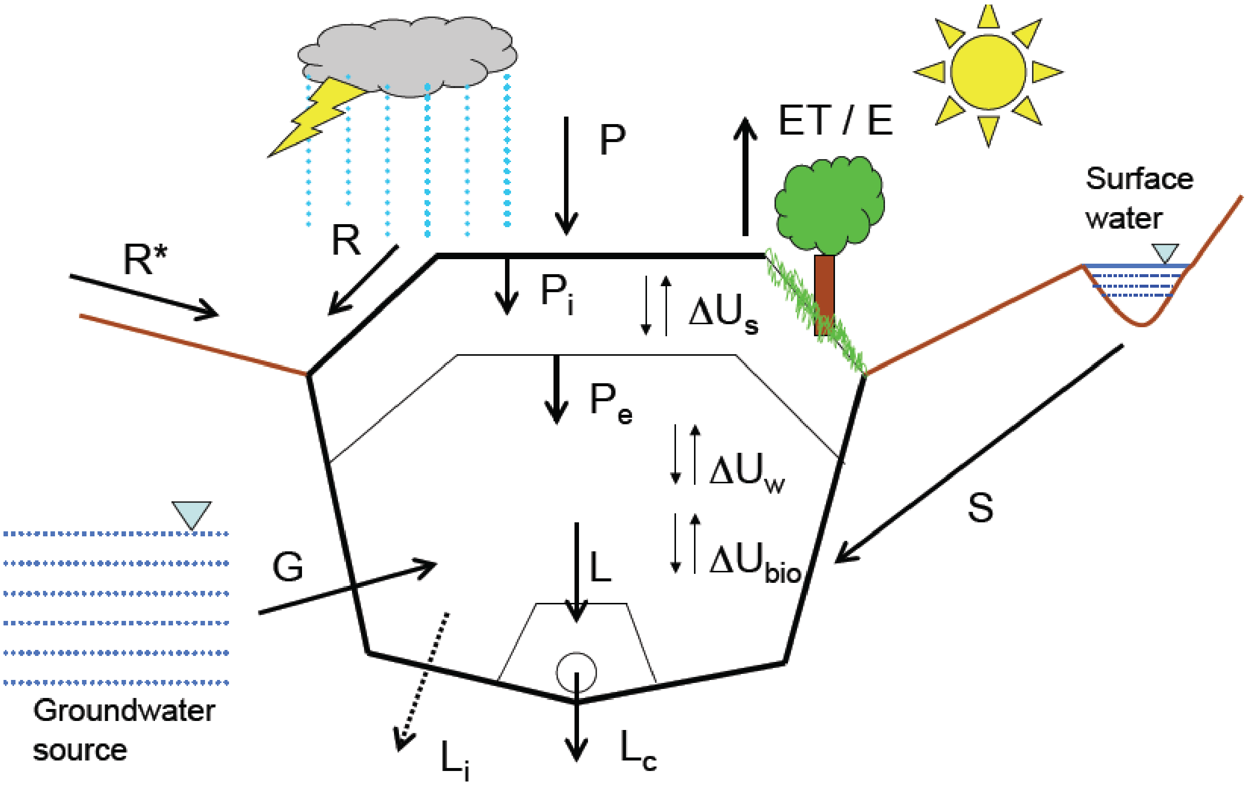

Figure 1.1. Water balance inside a landfill.

Seasonal rainfall data, geometric and operational characteristics of the landfill site are required to estimate the amount of leachate produced by a landfill.

As regard the quality, in general terms, landfill leachate from municipal, commercial, and mixed industrial waste, may be characterized as a water-based solution of four groups of contaminants; dissolved organic matter (alcohols, acids, aldehydes, short chain sugars etc.), inorganic macro components (common cations and anions including sulfate, chloride, iron, aluminum, zinc and ammonia), heavy metals (Pb, Ni, Cu, Hg), and xenobiotic organic compounds such as halogenated organics, (PCBs, dioxins, etc.) (Kjeldstein et al., 2002). The main quantity of leachate is produced in the second anaerobic phase of the degradation of waste happening in the landfills. In fact, the first aerobic phase, due to the presence of air still inside the waste, interests a minimum part of the total leachate production, and it is characterized by an high content of COD. The anaerobic phase can be subdivided into two stages: the first acidogenic step, is responsible of a leachate with pH between 5,5 and 6,5, characterized by high values of BOD, NH_3, Cl, SO_4^{2-} and increasing values of metals concentrations. In this phase biodegradable material begins to be converted into VFAs. In the second methanogenic stage, VFAs are transformed into methane, and leachate becomes neutral or slightly alkaline, even up to value of 8,5, developing lower concentrations of BOD due to biological processes, of SO_4^{2-} due to its transformation into S^{2-}, and of Cl^- because of the washout.

In addition to organics, ammonia results to be the principal pollutant in leachate. Ammonia nitrogen is present in leachate from young landfills owing to the deamination of amino acids during destruction of organic compounds, while leachate from older landfills is rich in ammonia nitrogen due to hydrolysis and fermentation of the nitrogenous fractions of biodegradable substrates (Kulikowska and Klimiuk, 2008).

Results from several leaching tests and monitoring wells show and confirm that in the short-term, the emissions of main interest are organic compounds, for the reasons here above explained. Instead, the release of metals is low during the initial anaerobic phases. This implies that metals accumulate in the deposits and thus have a high future contamination potential (Bozkurt et al., 2000).

Many ranges of typical values for leachate characterization, distinguishing the age of the landfill, are available in literature. Some examples are reported in the table below.

Table 1.1. Ranges of typycal values for landfill leachate (Tchobanoglous et al., 1993; Stegmann and Ehrig, 1989).

	(Tchobanoglous et al., 1993)			(Stegmann and Ehrig, 1989)	
	young landfill		*old landfill (>10 years)*	*acidogenic phase*	*methanogenic phase*
	range (mg/l)	most probable (mg/l)	range (mg/l)	range (mg/l)	range (mg/l)
pH	4,5-7,5	6	6,6-7,5	4,5-7,5	7,5-9
BOD_5	2000-30000	10000	100-200	4000-40000	20-550
TOC	1500-20000	6000	80-160		
COD	3000-60000	18000	100-500	6000-60000	500-4500
BOD/COD				0,58	0,06
TSS	200-2000	500	100-400		
Norg	10-800	200	80-120		
Ptot	5-100	30	5-10		
Ma	50-1500	250	50-200		
NO_3	5-40	25	5-10		
K	200-1000	300	50-400		
Na	200-2500	500	100-200		
SO_4^{2-}	50-1000	300	20-50	70-1750	10-420
Ca				10-2500	20-600
Mg				50-1150	40-350
Fe				20-2100	3-280
Mn				0,3-65	0,03-45
Zn				0,1-120	0,03-0,4

The IWWG, International Waste Working Group, has also created a database, “LEACH 2000”, in which can be found leaching data from laboratory testing for wastes and related materials, data from lysimeter studies, composition data and landfill leachate information (www.iwwg.eu), representing data from over 200 landfills.

2.1 Factors influencing leaching quality

There are many factors influencing leaching; among these the main important are: L/S ratio, water exchange, biological degradation, recirculation of leachate, size of particles, temperature (Kylefors et al., 2003). Among these factors could be search the cause of the disagreement between results in leachate characterization obtained from laboratory studies and from monitoring wells.

2.1.1 L/S ratio

As already said, the landfill Liquid/Solid ratio is the parameter that best describes the amount of water that flow through a small former waste disposal site. This value set the water infiltration in a landfill into relationship to the dry mass of the waste body.

This parameter, being directly related to the climatic conditions of the site, the surface cover system and the height of the landfill, and to the several landfill phases, can be mathematically calculated through the following equation (Allgaier and Sregmann, 2006):

$$\frac{L}{S}\left(\frac{l}{kg}\right) = \frac{[I_0 * (a_0 - f_i)] + [I_r * (a_r + f_i)]}{m_{DM}} * f_g \tag{2}$$

where:

I_0 is the infiltration into the uncovered landfill during the operation, expressed as l/(y*m^2);

I_r is the infiltration into the closed and or recultivated landfill during, expressed as l/(y*m^2);

a_0 is the number of years of waste disposal;

a_r is the number of years in which the landfill is closed;

f_i is a factor considering the presence of intermediate coverage during landfill operations ($f_i = \frac{a_0}{2}$), or the absence of this ($f_i = 0$);

f_g is a factor considering the influence of groundwater level on the disposal site ($f_g = 1{,}5$), or the absence of this ($f_g = 0$);

m_{DM} is the weight expressed in kg of the dry matter of the landfill section of 1 m^2 multiplied with the estimated average height of the landfill body; this is well explained in the figure below:

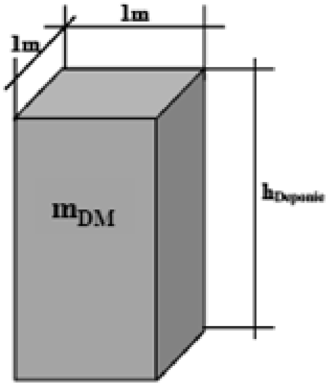

Figure 1.2. Weight of dry matter considered in the calculation of the L/S ratio (Allgaier and Stegmann, 2006).

Several lysimeter investigations performed in the laboratory shown good correlations between the determined Liquid/Solid ratio in the body and the corresponding leachate concentrations in the Landfill Simulation Reactors (LSR) (Baderna et al, 2011).

In leaching tests, this L/S ratio can be calculated, in a progressive way, dividing the total amount of fresh water entering the waste body to the total dry mass of waste considered in the test. It is the water inserted in the system that is related to the time.

In landfills, the real L/S ratio is obtained knowing the temporal variation of rainfall in the disposal site, and dividing it to total amount of waste disposed, calculated from the density of the waste and the geometrical characteristics of the site, which give the volume of it. In this way it is possible the correlation between leachate from laboratory experiments and leachate produced in a real landfill.

Performing leaching tests in an enhanced way would make it possible to generate results of leaching tests that cover a wide L/S interval and also consider biological activity. Such information is lacking today, as simulator tests only cover a short L/S interval. The predictions of today are based on prolonged (mathematically extrapolated) trends of simulator leaching. Actual data that covers a broad L/S interval would make the predictions more reliable (Kylefors et al., 2003), making possible the determination of the remaining pollution potential of waste disposed in landfills (Fellner et al, 2009).

2.1.2 Biological activity

Biological degradation is another important factor influencing leachate quality. The degradation processes inside the landfill are the key aspects to understand and control the environmental impacts. Physical, chemical and microbial processes are taking place in the waste and result in the release of gaseous and dissolved compounds, in terms of landfill gas and leachate (Christensen and Kjeldsen).

Degradation processes in landfills take place over a very long period of time. Until now, considerable work has been done on the early phases, the initial aerobic phase, and the following anaerobic one. The subsequent phase, which is reached after perhaps one century is called ‘the humic phase’; its duration is expected to be very long, up to probably many thousands of years. The humic phase is not well described in the literature and quantitative descriptions of processes during this phase are scarce (Bozkurt et al., 1999).

It is not just the presence or absence of biological activity that influences leaching. The aspect that particularly affects leachate quality is the kind of biological activity (Kylefors et al., 2003).

At anaerobic degradation, two major degradation phases exist, the acidogenic and the methanogenic. The acidogenic phase, the first one, is characterized by high organic content; instead the methanogenic leachate, has a much lower organic content (Kylefors et al., 2003).

2.1.3 Recirculation

Water enhances biological processes, and thus leachate recirculation is a basic method derived from bioreactor practices, which aims to control and enhance stabilization of the landfill. In fact recirculation of leachate promotes biological activity, increasing and equalizing the moisture content, permitting a good contact between microbes, substrate and nutrients, and carrying away degradation products. The advantages of leachate recirculation include distribution of nutrient and enzymes, pH buffering, dilution of inhibitory compounds, recycling and distribution of methanogens, liquid storage and evaporation opportunities. The effectiveness of leachate recirculation has been well documented in many studies performed on lysimeter, test cells and full-scale experiments (Bilgili et al., 2007).

Many studies have reported the positive effects of leachate recirculation: not only the acceleration of the biodegradation of organic compounds, but also the reduction of the time required for stabilization from several decades to 2–3 years (Huang et al., 2008).

The rate of recirculation is an important factor responsible for the enhancement of degradation (Kylefors et al., 2003).

In fact, recirculation of leachate into fresh waste also can lead to the inhibition of methanogenesis due to accumulation of volatile fatty acids (VFAs) and low pH and/or to accumulation of ammonia nitrogen in effluent leachate (Jiang et al., 2007).

2.1.4 Preferential pathways

Preferential pathways of leachate in landfill is another important aspect which influences the variation of leachate quality. The highly heterogeneous physical structure of the solid waste material that composes a landfill, facilitates water flow in restricted channels and voids. The existence of rapid flow through favored flow paths in solid waste media has been reported in several field studies, as well as in studies on laboratory scale (Rosqvist and Destouni, 2000; Oxarango et al., 2011; Sormunen et al., 2008).

Prediction models based on the representation of the solid waste as a homogenous porous medium, the commonly used approach for modeling water flow and solute transport in solid waste, are not appropriate. In order to improve long-term predictions of leachate quality, the consequences of fast water flow in preferential flow paths need to be considered and quantified (Rosqvist and Destouni, 2000).

The presence of these preferential pathways could give non uniformity between results from flow of water in field-scale landfills and from laboratory reactors. For instance, it has been found that in laboratory-scale experiments around 40% of pore water participates in advective solute transport, whereas in the investigated full-scale landfill this fraction amounts to less than 0.2%, leading to differences in moisture distribution and water flow (Fellner et al., 2009).

The promoted biological activity can affect the flow paths of the water (Kylefors et al., 2003). As degradation proceeds, it weakens the structure of the waste, channels within the waste will collapse, and thus the water finds new pathways. Waste that was not initially involved in the leaching can be then incorporated into the process.

Also plastic bags containing waste, present in the landfill body, are efficient barriers for the water flow in the waste body: they may be able to force the water flow and to prevent water from coming in contact with waste (Kylefors et al., 2003).

2.1.5 Aeration

As already said the sustainable landfill is a fundamental goal in waste management worldwide. Connected to this, landfill aeration contributes towards an accelerated, controlled and sustainable conversion of conventional anaerobic landfills into a biological stabilized state, associated with a minimized emission potential (Ritzkowski and Stegmann, 2012). The aeration of MSW landfills has an impact on the accordant leachate composition. According to the overall aim of landfill aeration the emission behavior should be remarkably enhanced, i.e. compounds such as dissolved organic carbon and ammonium-nitrogen should be significantly reduced in concentration, because of an efficient conversion of the biodegradable organic compounds as regard the first aspect, and processes of nitrification and simultaneous de-nitrification as regard the second one. The previous results are obtained in several studies (Ritzkowski, 2011). Nowadays landfill aeration methods are not yet well established, and use different pressures, systems for injecting air and systems for disposing of off-gases (www.ec.europa.eu).While high pressure aeration is usually intended to minimize explosion danger and odor annoyance during landfill excavation or landfill mining projects, low pressure aeration as well as the semi aerobic method has been recognized for its potential towards landfill remediation aimed at accelerated biological waste stabilization (Ritzkowski and Stegmann, 2012; Matsufuji and Tachifuji, 2007).

The effectiveness of landfill in situ aeration depends on proper control of oxygen distribution, waste temperature and moisture content; proper management of air flow and water inlet in the landfill body is required, based on the results of lab scale and full scale preliminary tests (Raga and Cossu, 2013). Manu results are available in the literature. Local climatic conditions must be taken into account when selecting an aeration method for a particular disposing site.

Many studies, through Landfill Simulation Reactors (LSRs), were conducted on waste samples taken from the landfill site prior to the full scale aeration in order to determine the potential emission reduction of the landfilled waste and its long-term emission behavior after aeration completion (Hrad M. et al., 2013) and state the positive effects of aeration on leachate quality (Raga and Cossu, 2013).

2.2 Leaching tests

The word leaching means the extraction of elements under the effect of a solvent, which in general is water. In the field of waste management, the waste body deposited in landfills, is subjected to percolation of water, coming from rainfall, groundwater or surface runoff. This cause the passage of pollutants from the waste to the water, which could come in contact with the environment. The leaching behavior of a waste corresponds to the way this waste is going to release or not its constituents under the influence of the conditions of exposure. This behavior can be experimentally expected through leaching tests. In this way it is possible to characterize leachate in the long-term period. These tests consist on liquid loaded with chemical and bacteriological elements by the degradation of the waste during the circulation of water in the waste.

In the field of leaching test methods there is the need to distinguish between characterization and compliance testing. The firsts give understanding of processes controlling release from specific stabilized waste but also the basis for development of criteria for acceptance in a suitable release scenario, the seconds are used for regular verification of waste with specific reference thresholds (Aarnink et al., 2007).

There are different leaching tests, which can be classified as (www.tice.insa-lyon.fr; www.iwwg.eu):

- static tests, which aim at reaching the equilibrium for some parameters, as for instance pH in the pH dependence leaching test. Two European tests aiming at studying the influence of the pH on the elements solubilisation are: the standardized test XP CEN / TS 14429 of May, 2006 (Characterization of waste - Leaching behavior tests - Influence of pH on leaching with initial acid/base addition) and the standardized test XP CEN / TS 14997 of December, 2006 (Characterization of waste - Leaching behavior tests - Influence of pH on leaching with continuous pH-control). These pH dependence leaching tests could give a measure of the chemical speciation and a measure of the acid/base neutralization capacity of the material of interest (Van Der Sloot et al., 2005).

- dynamic tests, which objective is the release dynamics of the material in standard conditions. In these tests leachant passes through the body waste in a continuous way. They could be percolation tests or column leaching tests for granular material, or monolith leach tests, also called tank tests, for monolithic material. The latter kind of test can be performed in batch, if liquid is periodically renewed, or continuously, if liquid is continuously renewed. Granular and monolithic materials are performed in different testing, being the release mechanisms for both types of materials fundamentally different (Van Der Sloot et al., 2005).

The leaching tests provide the basic characterization against which results from simpler tests can be judged and confronted.

In this study the leaching tests performed in the waste are column leaching tests, in order to obtain information on characteristic properties of the waste and on their short and long-term behaviors in the conditions specified by the considered scenario: anaerobic and aerobic conditions. A certain amount of fresh water flows through the column full of waste. Laboratory analyses are performed on the eluate periodically retiring from the columns. The concentrations of the compounds analyzed can be plotted with the Liquid/Solid ratios calculated. The cumulated L/S ratio represents at the moment t, the total volume of liquid passed through the waste divided by the dry mass of waste, supposing that the total dry mass of the waste remains unchanged during the experiment.

2.3 Heavy metals in leachate

The quantity of discarded consumer electronics devices has greatly increased in recent years in MSW, raising questions about the fate of these devices in the landfill environment. They typically contain lead, cadmium, mercury, arsenic, copper, zinc and other heavy metals and rare earth metals (Aucott, 2006). This is the reason why, one of the main groups present in the leachate coming from landfill used as deposit of municipal, commercial, and mixed industrial waste are heavy metals, as cadmium (Cd), nickel (Ni), zinc (Zn), copper (Cu), lead (Pb), mercury (Hg), chromium (Cr) arsenic (As), but also iron (Fe) and manganese (Mn) as well, even if some authors consider them inorganic macro-components (Christensen et al, 2001).

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or dangerous even at low concentrations (www.lenntech.com). One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnifications causing heavier exposure for some organisms in the environment, when these compounds are taken up and stored faster than they are metabolized or extracted. Some of these heavy metals could have also negative effects to the environment. For these reasons, their concentrations in landfill leachate must be monitored and confronted with regulation limits. The mobility and toxicity of heavy metals present in landfills, depend on the chemical form of the metals (Esakku et al.). It has been reported that the great part of the total metal content in MSW is present in an inert form, not undergoing chemical reactions in landfills but leaching from the waste bed. Moreover, metals may be bound within a matrix or encased within a structure that can be expected to remain stable or intact for long periods of time in a landfill environment (Aucott M., 2006). The knowledge of the heavy metal content, their species and the leachability at various environmental conditions is a prerequisite for the assessment of reclamation and hazardous potential of the waste landfilled. In literature are available a lot data concerning concentration of heavy metals in several waste types, calculated from many experimental studies through leaching tests, even simulating several landfill operations, as aeration and leachate recirculation (Bilgili et al, 2007; Christensen et al, 2001; El-Fadel et al., 2002; Hrad et al., 2013; Oman et al, 2008; Oygard et al, 2004 and 2005; Thomsen et al., 2012; Wang et al, 2012).

In the table below are reported some measured concentrations of heavy metals in leachate, obtained from the “LEACH 2000” database (www.iwwg.eu); they are the mean concentrations of many values available. In the table are also reported the EPA drinking water standards for the same heavy metals.

Table 1.2. Concentrations of heavy metals in landfill leachate (www.iwwg.eu; Aucott, 2006).

Metal	**Mean concentration (mg/l)**	**EPA (mg/l)**
Arsenic	0,441	0,01
Barium	0,866	2
Cadmium	0,283	0,005
Chromium	0,235	0,1
Lead	0,133	0,015
Mercury	0,00715	0,002
Selenium	0,585	0,05
Silver	0,0537	NA

The main processes for the low metal concentrations in landfill leachate are sorption and precipitation, the significant mechanisms for metals immobilization and the subsequent low leachate concentrations. Heavy metal balances for landfills performed in several studies, have shown that less than 0.02% of heavy metals received at landfills are leached out after 30 years (Kjeldsen et al., 2002). Other studies confirmed that the removal of metals as Cd, Cr, Hg, Pb is less than 1% (Manfredi and Christensen, 2009). Moreover, solid wastes contain soils and organic matter, which have a significant sorptive capacity, especially at high pH values, property of methonegenic leachate. Metal precipitation in landfill body resulted in an increase in heavy metal content of solid waste samples (Bilgili et al., 2007).

The most significant parameter considered to greatly affect metal concentrations in landfill leachate is pH. Metals and heavy metals have minimum solubility when pH is in the range 7-10: metal dissolution is enhanced at low pH, in the earlier phase of landfill life. The concentrations of metals are expected to reduce as the leachate changes from acidogenic to methanogenic phase, concurrent with a decrease in redox potential and an increase in pH. Also carbonates influence metals concentrations. When carbonate species increase, heavy metals concentrations decrease, because heavy metals precipitate with carbonates and sulfides increasing metal content of solid waste samples. Occasionally, phosphates and hydroxides can also precipitate metals (Bilgili et al., 2007). In fact Cr tends to form insoluble precipitates with hydroxide rather than with sulfides.

2.3.1 Effects of heavy metals to humans and to the environment

The heavy metals considered to be the most pollutant are lead, chromium, cadmium and mercury. Cadmium is bio-persistent: once it is absorbed by an organism, it remains resident for many years although excreted. The risks associated with long-term and high exposure of cadmium are renal disfunction, lung diseases as cancer, and bone defects. In animals it has been found that cadmium can be linked to increased blood pressure. The effects caused by exposure to lead vary depending on the level and duration of exposure. The damages can interest kidneys, gastrointestinal tract, joints, reproductive and nervous system. As regard mercury, its inorganic poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformation. Low-level exposure of chromium can irritate the skin and cause ulceration, while long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissues. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium. Copper and nickel are essential substances to human life, but in high doses can cause negative health problems as anemia, liver and kidney damages, intestinal irritation in one case and heart, liver damage and skin irritation in the other.

3 Risk analysis

The main problem related to long-term emissions of leachate is the temporal variation in the concentration of pollutants present in the leachate emitted by the landfill, and how it is possible to characterize these concentration from laboratory analyses. In the last decade leaching tests and associated modelling tools have been developed to address long-term release characteristics of contaminants from wastes for use in risk assessments (Van Der Sloot et al., 2005).

Risk assessment is an effective management tool for protecting the environment against landfills' hazards. To achieve maximum protection of the environment against the hazards associated with landfill sites, all potential hazards must be identified and risks associated with them assessed (Butt et al., 2008). The problem is that an integrated risk assessment methodology does not exist, even because it faces large uncertainties and requires a high level of expertise. The same for a holistic knowledge-based computer model, which could perform the process of risk assessment for landfills up to the calculation of risk quantification and hazard indices (Butt and Oduyemi, 2003).

The actual methods applied for a proper risk analysis on landfills are described by the National agency APAT (Agenzia per la Protezione dell'Ambiente e per i servizi Tecnici) in the document "Criteri metodologici per l'applicazione dell'analisi assoluta di rischio alle discariche" of 2005. The goal is to help public administrations, researchers and practitioners, in making environmental and health risk assessments for contaminated sites (see document "Criteri metodologici per l'applicazione dell'analisi assoluta di rischio ai siti contaminati" of 2008), but in particular, with the previous cited document, risk analysis in the case of landfills.

Risk is not just a matter of existence of hazard and its nature, pathway, and target. The degree of risk is significantly dependent on the concentration of a given hazard that reaches a given target, enters the target's boundaries, and the safe and acceptable levels of hazard concentration for the given target (Butt and Oduyemi, 2003).

Risk analysis can be classified as direct, if the risk is calculated from available data on concentrations, inverse if acceptable limits of risk are decided at priori, and from these values, concentrations respecting these limits are obtained.

The steps for a risk analysis are:

- characterization of the source of contamination, which in the case of a landfill is the landfill itself and its emissions, mainly leachate and biogas;

- characterization of the exposure routes, in the case of a landfill mainly through the atmosphere, the surface water and the groundwater;
- characterization of the target location, which can be the environment or humans;
- calculation of the exposure, considering several exposure paths and scenarios, between them can be considered ingestion, dermal contact, indoor and outdoor inhalation, contact and or ingestion with surface water or groundwater;
- characterization of the risk: threshold concentrations are compared with hazards' concentrations.

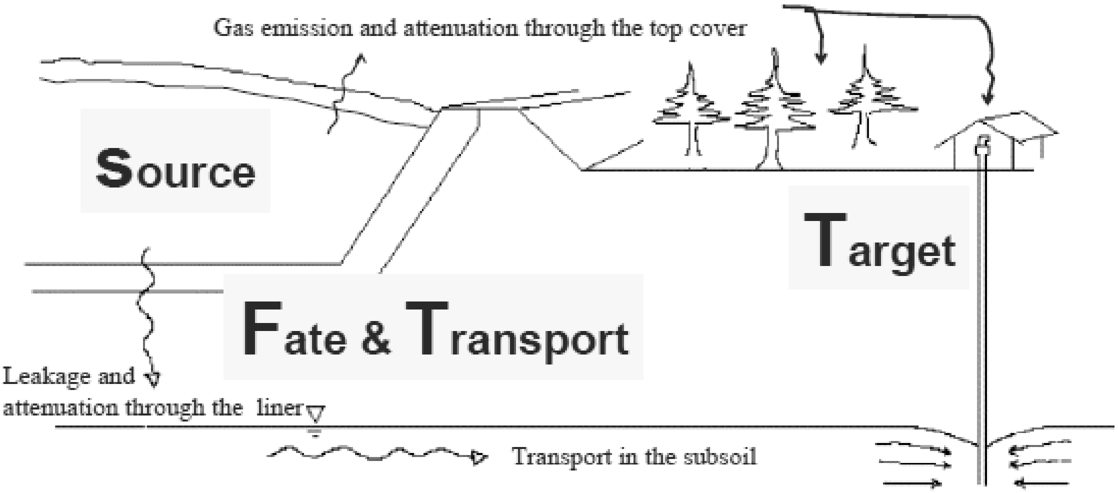

Figure 1.3. Scheme of the procedure of risk assessment.

The APAT document describes in detail all the parameters and the information needed to face each steps of the procedure, highlighting also the difficulties and criticism in performing a proper risk analysis.

In particular, in the case of a landfill, the characterization of leachate is a difficult aspect, mainly for the old and uncontrolled landfills, for which sufficient information is lacking.

3.1 Leachate characterization: dependence with time or with L/S ratio

As already stated, range of values for concentration of contaminants in the landfill are available in literature, depending on the age and on the type of the landfill. A characterization of leachate, if no other experimental and laboratory data are available in the case of interest, could be based on these ranges.

In a more detailed and site-specific analysis, the decline in concentration with time can be empirically approximated to be a first-order rate equation, describing quite always an exponential curve, as:

$$C = C_0 * e^{-(k*t)} \tag{3}$$

Sometimes others kinds of curves may be used (Kylefors, 2002), as the following:

$$C = C_0 * A * t \tag{4}$$

Others authors instead use the liquid to solid ratio as an alternative of time in the first equation, because this L/S ratio is a more objective tool, since it considers both the amount of solid waste as well as the amount of water added to the waste and it can be related to time, being the amount of infiltrated water time-dependent. The use of L/S has proven to be useful in the comparisons made between different leaching tests (Kylefors et al., 2003).

The variation of concentration, or mass for a compound, with respect to the L/S, obtained from leaching tests, is an information required to predict leaching characterization from a landfill in a long-term period.

For a landfill the information required to calculate the L/S ratio are:

- geometrical characteristics of the landfill body;
- properties of waste, in particular density;
- climatic and meteorological data in the site of interest;
- operational conditions of the landfill site.

The ratio is obtained dividing the amount of water infiltrating the waste body by the mass of the waste, known from the density and the volume of the waste.

If leaching tests could be performed, APAT proposed the following equation describing the temporal variation of the concentration of a non volatile contaminant in the landfill:

$$C^L(t) = C_0^L * e^{-\left(K*\frac{L}{S}\right)} \tag{5}$$

where:

C_0^L is the concentration of the contaminant in the leachate at time t=0;

$C^L(t)$ is the concentration of the contaminant in the leachate at time t;

K is the value obtained from laboratory results of leaching tests;

L/S is the liquid solid ratio expressed as l/kg, in which L is the amount of water entering the system and S the quantity of waste.

A contaminant species with a high value of K is leached more rapidly than a species with a low value of K, and its concentration in leachate will decrease more rapidly.

For a volatile compound, having an higher tendency to dissociate into the gaseous phase rather than into the liquid phase, its concentration variation can be calculated through the following exponential equation:

$$C^L(t) = {C_0}^L * e^{-x*t} \tag{7}$$

where:

C_0^L is the concentration of the contaminant in the leachate at time t=0;

$C^L(t)$ is the concentration of the contaminant in the leachate at time t;

x is the half-life time of the volatile compound, expressed as y^{-1}; the most conservative value used is 0,1 y^{-1} (APAT, 2005), being the half-life constant for the initial concentration of a volatile species in the leachate equal to 10 years.

In both cases, if no values of C_0^L are available in the site of interest, some representative values are reported in the table (APAT, 2005, Appendix 2).

Table 1.3. Minimum, maximum and typical values of landfill leachate (APAT, 2005).

	range (mg/l)	most probable (mg/l)
cadmium (Cd)	0,0019- 0,105	0,0101
chrome (Cr)	0,0231-0,416	0,0981
copper (Cu)	0,0129-0,191	0,0509
nickel (Ni)	0,0345-0,627	0,126
lead (Pb)	0,0337-0,34	0,111
zinc (Zn)	0,0296-9	0,362
chlorides (Cl)	227-2650	997
manganese (Mn)	0,0771-324	0,78
ammonia (NH_3)	32,1-1100	267
iron (Fe)	0,29-5530	9,93
Arsenic	0,00371-0,0107	0,00485
calcium (Ca)	12,2-6650	119
magnesium (Ma)	7,93-828	183
mercury	0,000039-0,00195	0,0000891
nitrates (NO_3)	0,06-32,8	1,4
nitrites (NO_2)	0,01-6,01	0,27
phosphates	0,01-22,6	2,54
potassium (K)	40,8-1140	321
sodium (Na)	13,8-5410	1760
SO_4^{2-}	1,6-2800	231

3.1.1 *Experimental procedure to obtain the value of* ***K***

The procedure to obtained the value of K is explained in the appendix 3 of the same document. It needs to perform leaching tests with columns full of waste. A flux of water enters the column, and sample of leachate are collected when the L/S ratio reaches the values of 0.1, 0.2, 0.5, 1, 2, 5 and 10 l/kg. From these samples the concentration of contaminants are calculated.

For each contaminant of interest, in a graph are reported the values of the natural logarithm of the concentrations (mg/l) with respect to the value of L/S (l/kg), calculated as the mean value between an interval. An example is reported in the figure below.

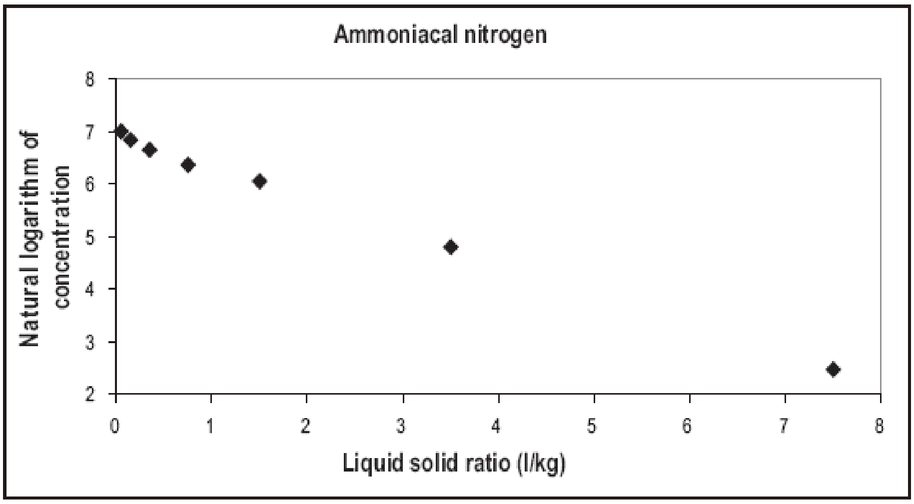

Figure 1.4. Example of curve obtained with results from the leaching tests (APAT, 2005).

The value of the slope of the line which best approximates the points in the graph is the value of K for each contaminants.

The rate of change in concentration is determined by this species specific K value. Over two thousand K values for different species in different waste types were collated. Analysis of the data has found that a single K range cannot be established for each species, which would adequately represent all types of waste. A strong correlation was identified between the initial concentration of a species in leachate (C_0^L) and the value of K (Golder Associates, 2003).

This relation can be expressed by the following equation:

$$K = m * \ln(C_0^L) + c \tag{8}$$

where

m, c are two empirical constants, expressed as kg/l;

$({C_0}^L)$ is the initial concentration expressed as μg/l.

Values of m and c which describes this best correlation are reported in the following table.

Table 1.4. Values of m and c for several compounds obtained in an empirical way (Golder Associates, 2003).

Compound	**m (kg/l)**	**c (kg/l)**
arsenic (As)	0,0415	-0,0862
barium (Ba)	0,0806	-0,2754
cadmium (Cd)	0,0823	0,1589
chrome (Cr)	0,0514	0,045
copper (Cu)	0,0664	-0,0488
silver (Hg)	0,0767	0,1643
molybdenum (Mo)	0,0646	-0,0152
nickel (Ni)	0,0987	-0,1479
lead (Pb)	0,0443	0,0171
antimony (Sb)	0,0763	-0,1303
selenium (S)	0,1063	-0,062
pond (Sn)	0,0544	-0,0483
vanadium (V)	0,0542	-0,1619
zinc (Zn)	0,0403	0,0561
bromine (Br)	0,0383	0,2613
chlorides (Cl^-)	0,0298	0,2919
total cyanides (CN tot)	0,1038	-0,1836
cyanide-free (CN free)	0,1001	-0,0099
fluorine(F)	0,0217	0,1077
ammonia (NH_3)	0	0,59
sulphates (SO_4^{2-})	0,0166	0,1209

From this procedure, values of L/S ratio up to 10 in the leaching tests are needed. Such information is lacking today, as simulator tests only cover a short L/S interval (Kylefors et al., 2003).

Another objective of the study is to verify if this correlation is representative for the examined situation, or if other relations can be found.

4 Experimental study

4.1 Materials and Methods

4.1.1 Waste samples

The waste was collected in two old uncontrolled landfills, the Servizi Costieri S.r.l. and the Noè-Tebaldi, in Comune di San Bonifacio (VR), Italy. The landfills were used to deposit urban waste and industrial waste since the 1970's and were closed without an emission controlled system, either for leachate either for biogas. A sketch of the area, Cà Lioncello, in which the two uncontrolled landfills are present is shown in the figure below.

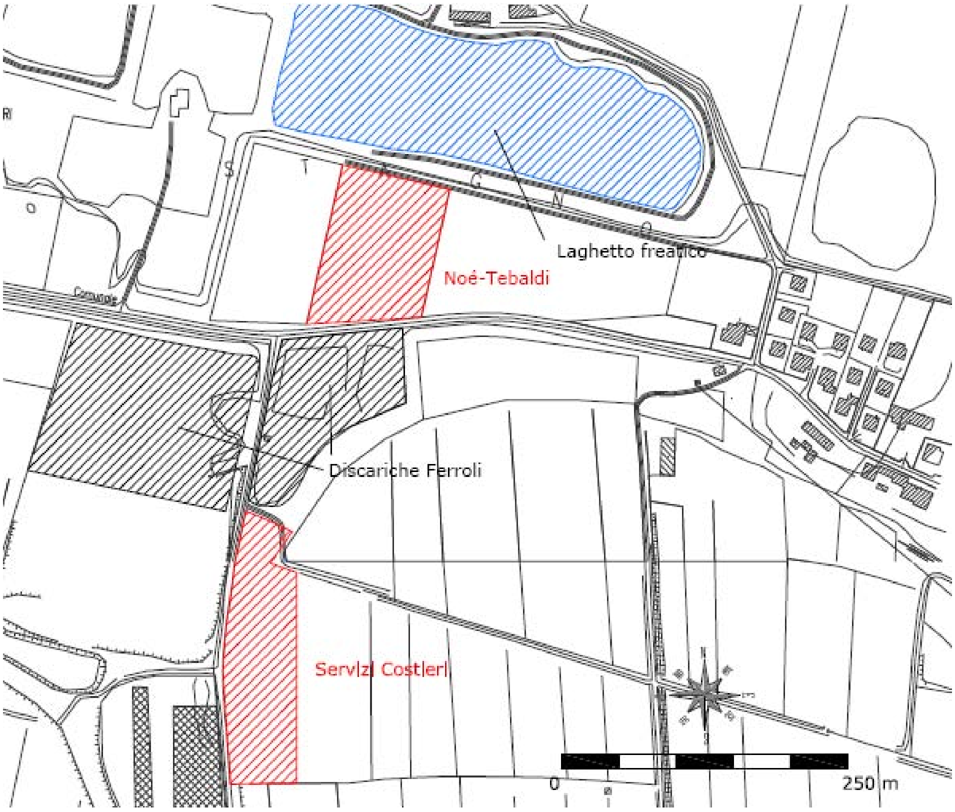

Figure 1.5. View of the Cà Lioncello area.

The waste conferred at the Servizi Costieri landfill were mainly foundry sand, but also branches and waste from road sweeping. This conferment of waste lasted 5 years, from 1988 to 1992. As regard the other landfill, the Noé-Tebaldi, in operation during the 70s', the information regarding the site, and the waste conferred at it, is very little.

Five samples were extracted from each landfill. The samples from the landfill Noè-Tebaldi were called V1, V2, V3, V4, V5, and those from the Servizi Costieri landfill, SC1, SC2, SC3, SC4, SC5.

The position of the sampling has been decided in order to obtain the maximum variability of the waste contained in each landfill. Each sample was taken with a probing from the ground level up to the depth of 10-15 meters. It was observed in situ that the sample V2 reached the groundwater level, and that the sample SC5 showed the presence of unidentified material aggregated in yellow little blocks.

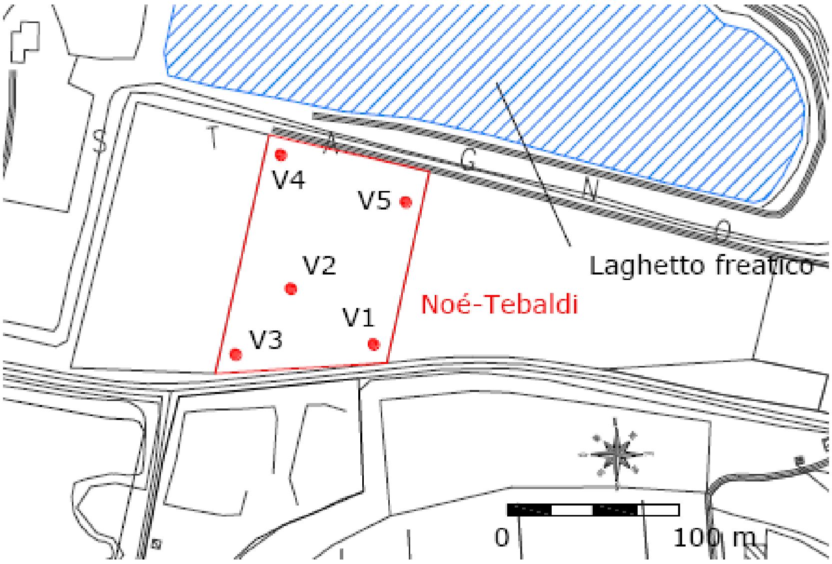

Figure 1.6. Sampling points for the Noé-Tebaldi landfill.

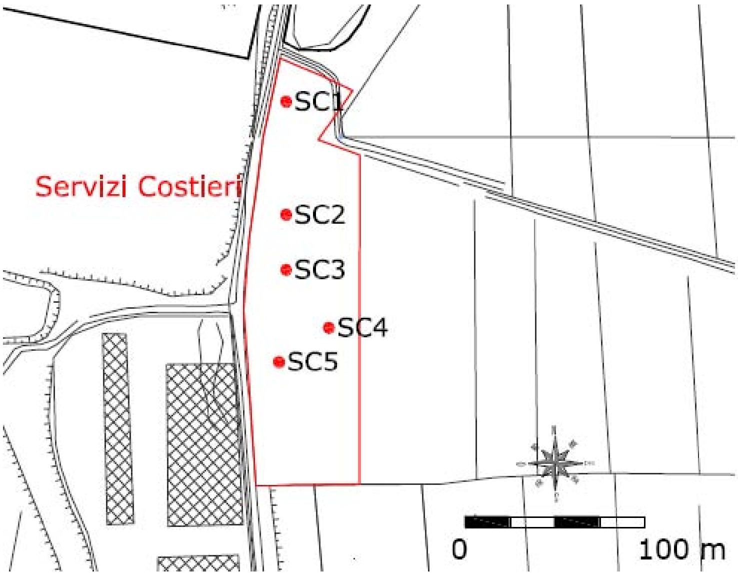

Figure 7. Sampling points for the Servizi Costieri landfill.

In a following phase, the samples from each landfill have been completely mixed up and sieved (20 mm) in order to extract a sample of two kilograms of weight, for solid analysis. Every sample contained only the 2-3 % of inherts that was discharged to obtain a more representative sample.

In the soil analysis, the following parameters were analyzed: total solids (%), TOC, TKN, $N\text{-}NH_4^+$, respiration index (IR_4). Some metals and heavy metals were been analysed as well; the compounds were: Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As and Hg.

4.1.2 Columns and other equipments

For the experiment were set up seven bioreactors, called VmixA, VmixB, V2A, V2B, SC5, SCmixA and SCmixB. V2 and SC5 were filled with waste deriving from samples V2 and SC5, respectively. These two samples were chosen for the experimental work, since they have different characteristics from the others samples. The other bioreactors, Vmix and SCmix derive from the mixing of V1, V3, V4 and V5 and SC1, SC2, SC3 and SC4, respectively. In each column the waste is composed both of under sieve and coarse material. Each column was used to simulate a different landfill concept, and the A and B in the name of the reactor means respectively anaerobic and aerobic conditions.

The reactors were columns made of plexiglas. The reactors were sealed on the top and on the bottom. The upper end has two valves (with certification of operation); one of them permits the extraction of air and the other allows the introduction of water and leachate, if necessary. To improve a better distribution of the liquids, fresh water or leachate, a perforated tubular ring was put at the top of the column. The lower end is equipped with tap allowing leachate extraction and the introduction of air into the reactor.

The columns VmixA and VmixB have an internal diameter of 250 mm and a height of 1000 mm.

Figure 1.8. Image of reactors VmixA and VmixB.

The columns SCmixA, SC5, V2A, SCmix and V2B, smaller than the others, have an internal diameter of 100 mm and an effective height of 800 mm.

Figure1. 9. Image of reactors SCmixA, SC5, V2A, SCmixB, V2B.

In all columns, a 100 mm thick gravel layer (gravel particle size 10-15 mm) was placed at the bottom and at the top of each bioreactor for leachate drainage, to better distribute the liquids.

The reactors were operated under anaerobic and/or aerobic conditions for reactors VmixB, SCmixB, V2B. When they were operated under aerobic conditions, air was introduced into reactor VmixB by RESON® Air-pump AC-9601, and BOYU® S-9901 for reactors SCmixB and V2B. The gaseous emissions from columns under aerobic conditions were sent out of the operating room through a PVC pipe. This pipe was connected to the air outlet valve installed on the top of the column.

Characteristics and operational conditions in which the seven reactors were performed are listed in the table below.

Table 1.6. Properties and operational conditions performed in the reactors.

Bioreactor	*Samples*	*Refuse weight (kg)*	*Mass of dry matter (kg_{DM})*	*Operating conditions*	*Airflow (l/min)*
VmixA	V1, V3, V4, V5	52,5	42,914	anaerobic	-
VmixB	V1, V3, V4, V5	52,5	43,258	aerobic	1,8
V2A	V2	7,5	5,822	anaerobic	-
V2B	V2	7,5	5,822	aerobic	2
SC5	SC5	7,5	6,160	anaerobic	-
SCmixA	SC1, SC2, SC3, SC4	7,5	6,390	anaerobic	-
SCmixB	SC1, SC2, SC3, SC4	7,5	6,390	aerobic	2

4.1.3 Experimental procedure

Until the field capacity was reached, the reactors were filled with distilled water and its recirculation was made in order to avoid losses of contaminants from the waste. In that phase, all the reactors were run under anaerobic conditions.

After the field capacity was reached, the columns VmixA, VmixB, SCmixA, SC5, V2A were completely saturated, in order to simulate the worst case. This happens when the groundwater levels grows up and saturate the waste in the landfill. The water was maintained in the reactor for two weeks. The controlled samples of the reactors were collected after these two weeks.

Before being saturated, the reactors V2B and SCmixB were aerated two weeks, ten work days, 8 hours per days. The flow pump was about 2 l/min. After these two weeks of aeration, reactors were saturated as the others. The controlled samples of these two reactors were collected after the two weeks for saturation. The analyses were done for the following compounds: pH, conductivity, TOC, COD, BOD_5, TKN, $N\text{-}NH_4^+$, NO_3^-, SO_4, Cl^-, P_{tot}, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As and Hg.

Then, reactors VmixA, SCmixA, SC5 and V2A were maintained in anaerobic conditions and used as controls, to comparing the results with the reactors VmixB, SCmixB and V2B working in aerobic conditions. The procedure is shown in the following scheme.

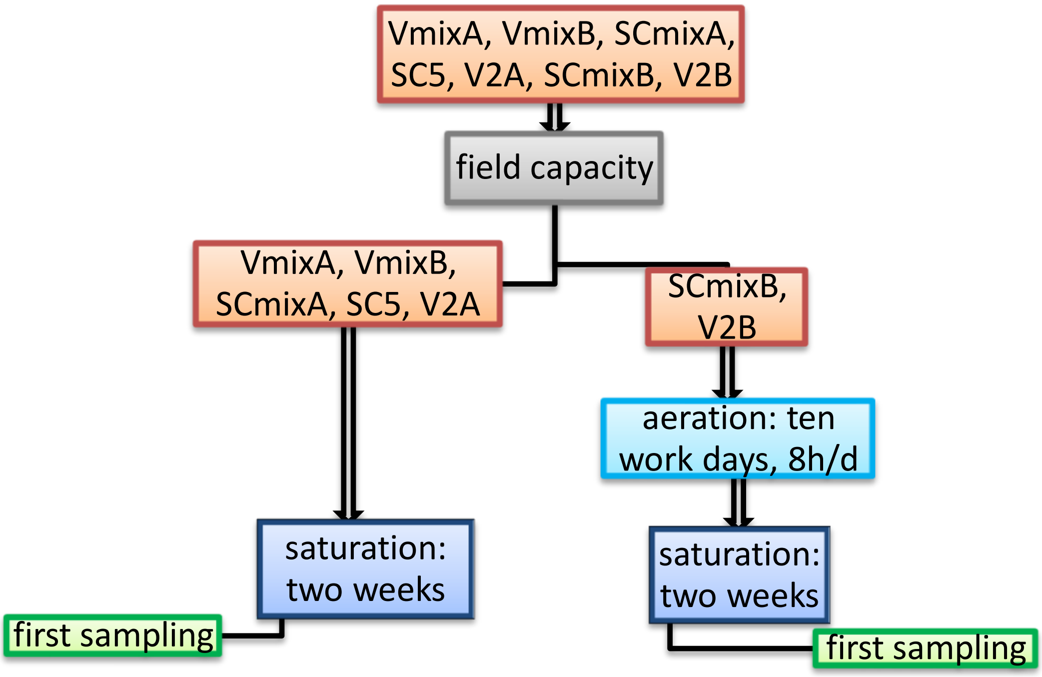

Figure 1.10. Steps of the experimental procedure of the first phase for all the reactors.

To perform the aeration of the tree columns, the air pumps were installed on the bottom of the reactor, with the same exit for the leachate sample. The pump and the reactor were connected with an aeration pipe.

The aeration of the reactor VmixB was made with a pump flow of 1,8 l/min about 8 hours per day. For reactors SCmixB and V2B the flow pump was the same as before, 2 l/min about 8 hours per day. After the aeration of aerobic reactors, was put into all reactors a certain decided amount of fresh water per week; the injection of this fresh water was subdivided into the five days of a week, in order to ensure a best contact of all the water with the waste, because fresh water percolated the waste, washing it and accelerated the metabolic processes (Fellner et al, 2009). Every day the eluate resulting from the leaching process was collected, in sealed bottles, placed under the columns. The amount of leachate collected corresponded almost always at the amount of fresh water addicted the day before. The leachate collected in one day were transferred to the accumulated samples' plastic bottles, placed in the fridge at a temperature between 4-5ºC for further analysis.

Figure 1.11. Image of plastic bottles and samples used for the collection of leachate from the reactors.

In all experiment, the reactors had been working at room temperature.

In the table is summarized the procedure of this second phase of the study.

Table 1.7. Steps for the experimental procedure of the second phase for all the reactors.

		1st day	**2nd day**	**3rd day**	**4th day**	**5th day**	
VmixB, SCmixB, V2B	*morning*	collection of L (l/d)	collection of L (l/d)	collection of L (l/d)	collection of L (l/d)	collection of L (l/d)	Total L collected during the 5 days (l/w)
						*sample for analysis**	
	afternoon	aeration (8h)	aeration (8h)	aeration (8h)	aeration (8h)	aeration (8h)	
		input of FW (l/d)	input of FW (l/d)	input of FW (l/d)	input of FW (l/d)	input of FW (l/d)	Total FW input during the 5 days (l/w)
VmixA, SCmixA, SC5, V2A	*morning*	collection of L (l/d)	collection of L (l/d)	collection of L (l/d)	collection of L (l/d)	collection of L (l/d)	Total L collected during the 5 days (l/w)
						*sample for analysis**	
	afternoon	/	/	/	/	/	
		input of FW (l/d)	input of FW (l/d)	input of FW (l/d)	input of FW (l/d)	input of FW (l/d)	Total FW input during the 5 days (l/w)

**sample of leachate from the 5 days for the analysis (0,5l)*

The amount of fresh water addicted weekly into the reactors have been changed during the experimental study, and during the last weeks has been greatly increased in order to reach an high value of L/S, equal to 10 l/kg for all the reactors. The amount of water injected every week into each reactor is summarized in the following table.

Table 1.8. Weekly amount of fresh water (FW) injected in each reactors during all the experimental study.

	VmixA	**VmixB**	**SCmixA**	**SC5**	**V2A**	**SCmixB**	**V2B**
	Aeration:NO	Aeration:8h/d	Aeration:NO	Aeration:NO	Aeration:NO	Aeration:8h/d	Aeration:8h/d
1st week	4 l/w	4 l/w	1 l/w	1 l/w	1 l/w	1 l/w	1 l/w
2nd week	4 l/w	4 l/w	1 l/w	1 l/w	1 l/w	1 l/w	1 l/w
3rd week	4 l/w	4 l/w	1 l/w	1 l/w	1 l/w	1 l/w	1 l/w
4th week	4 l/w	4 l/w	1 l/w	1 l/w	1 l/w	1 l/w	1 l/w
5th week	4 l/w	4 l/w	2 l/w	1 l/w	1,5 l/w	1 l/w	1 l/w
6th week	4 l/w	4 l/w	3 l/w	3 l/w	3 l/w	3 l/w	3 l/w
7th week	4 l/w	4 l/w	3 l/w	3 l/w	3 l/w	3 l/w	3 l/w
8th week	4 l/w	4 l/w	7,5 l/w	7,5 l/w	5 l/w	7,5 l/w	5 l/w
9th week	5 l/w	5 l/w	10 l/w	10 l/w	10 l/w	10 l/w	10 l/w
10th week	50 l/w	50 l/w	10 l/w	10 l/w	10 l/w	10 l/w	10 l/w
11th week	50 l/w	50 l/w	10 l/w	10 l/w	9 l/w	10 l/w	9 l/w
12th week	50 l/w	50 l/w	10 l/w	9 l/w	9 l/w	9 l/w	9 l/w
13th week	52 l/w	52 l/w	/	/	/	/	/
14th week	54 l/w	54 l/w	/	/	/	/	/
15th week	50 l/w	50 l/w	/	/	/	/	/
16th week	62 l/w	62 l/w	/	/	/	/	/

All the previous quantities, as already said, were subdivided into 5 work days and injected into each reactor day after day.

Each week is possible to determine an L/S ratio, because of the continuous process of water injection. All the values of L/S ratio reached by all seven reactors during the experiment, week after week is shown in the table. Not all the leachate collected every week were analyzed. The number of sample to be analyzed was chosen on the basis of the criteria proposed by APAT for the realization of a risk assessment for a landfill site. The predicting temporal variation of leachate can be based on values of concentration obtained from leaching tests analyzed corresponding to L/S = 0.1, 0.2, 0.5, 1, 2, 5, 10 l/kg.

From this set of data, the choice of the number of sample, indicated by the colored cells in the table, was performed in order to correspond as more as possible at the values proposed by APAT.

Table 1.9. Progressive values of L/S ratio in all seven reactors during the experiment.

	VmixA	*VmixB*	*V2A*	*SC5*	*SCmixA*	*V2B*	*SCmixB*
	L/S (l/kg)	*L/S (l/kg)*	*L/S (l/kg)*	*L/S (l/kg)*	*L/S (l/kg)*	*L/S (l/kg)*	*L/S (l/kg)*
first sampling	0,117	0,125	0,567	0,666	0,5634	0,773	0,923
1st week	0,228	0,236	0,739	0,828	0,720	0,945	1,080
2nd week	0,322	0,328	0,910	0,990	0,876	1,116	1,236
3rd week	0,415	0,421	1,082	1,153	1,033	1,288	1,393
4th week	0,508	0,513	1,254	1,315	1,189	1,460	1,549
5th week	0,601	0,606	1,512	1,477	1,502	1,632	1,706
6th week	0,694	0,698	2,027	1,964	1,972	2,147	2,175
7th week	0,788	0,791	2,542	2,451	2,441	2,662	2,645
8th week	0,881	0,883	3,401	3,669	3,615	3,521	3,818
9th week	0,997	0,999	5,119	5,292	5,180	5,239	5,383
10th week	2,162	2,155	6,836	6,916	6,745	6,956	6,948
11th week	3,328	3,310	8,382	8,539	8,310	8,502	8,513
12th week	4,493	4,466	9,928	10,000	9,875	9,997	9,922
13th week	5,704	5,668					
14th week	6,963	6,917					
15th week	8,128	8,072					
16th week	9,573	9,506					

Then the accumulated samples of one week for all reactors were analysed. The analyses, performed in the accumulated samples of the weeks, decided at the beginning, were done considering the following compounds: pH, conductivity, TOC, TKN, $N\text{-}NH_4^+$, just for the big reactors, and Cl^-, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn.

In this way it is possible to present the leachate concentration as a function of L/S ratio. This model allows estimating the evolution of leachate quality within the emission projections under different conditions (Laner et al, 2011).

The experimental study has lasted 16 weeks for reactors VmixA and VmixB, and 12 weeks for the other five reactors, with the realization of 10 and 7 analyses respectively.

The concentrations were analyzed corresponding to values of L/S ≈ 0.1, 0.2, 0.3, 0.5, 0.6, 0.8, 1, 2, 5, 10 l/kg, for reactors VmixA and VmixB, and corresponding to L/S ≈ 0.5, 1, 1.2, 2, 5, 7, 10 l/kg for the others, as close as possible to the values proposed by APAT (APAT, 2005).

4.2 Data elaboration

In all the reactors the water balance was taken under consideration. The quantities of water entering (FW_{in}), exiting (V_{out}) in the every systems were constantly monitored. The water remaining in the columns was calculated as:

$$WHC\ (l) = FW_{in}(l) - V_{out}(l) \tag{9}$$

The elaboration of the data started from the results of the analyses performed in the laboratory, on the collected samples from the reactors: concentration of TOC, TKN and NH_4^+ just for reactors VmixA and VmixB, and concentration of Cl^-, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn for all the seven reactors. Also pH was a parameter analyzed in laboratory.

The values of the concentration can be plotted in a graph with respect to the value of the L/S ratio. This value is calculated dividing the progressive total amount of fresh water coming in contact with the waste ($Total\, FW_{in}$) to the weight of the dry matter of the waste inside the reactor. The equations used are the following:

$$\frac{L}{S}\left(\frac{l_{H_2O}}{kg_{DM}}\right) = \frac{Total\, FW_{in}(l)}{M_{DM}\ (kg_{DM})} \tag{10}$$

$$Total\, FW_{in}(l)_{(i)_{th}\, week} = Total\, FW_{in}(l)_{(i-1)_{th}\, week} + FW_{in}(l)_{(i)_{th} week} \tag{11}$$

where $Total\, FW_{in}(l)_{(i)_{th}\, week}$ is the total amount of distilled water injected in the system from the beginning of the experimental study, until the considered i_{th} week, calculated as the sum of $Total\, FW_{in}(l)_{(i-1)_{th}\, week}$, the quantity of water inserted until the week before, the $(i-1)_{th}$, and $FW_{in}(l)_{(i)_{th} week}$, the water inserted the i_{th} week.

The values of concentrations resulted from the analyses of the first samples, were used as the values representing the initial concentrations, $C_L{}^0$.

The results of the parameter pH is reported in Annex I.

All the results and the elaboration of the results of the samples analyzed from all seven reactors, are shown in Annex II.

The mass of the contaminant extracted in every sample was calculated multiplying its concentration with the volume of the leachate extracted with the collection during the week, through the equation:

$$M_i(mg) = C_i\left(\frac{mg}{l}\right) * V_{out}(l) \tag{12}$$

The mass was then calculated with respect to the dry matter of the waste present in the columns (M_{DM}), in the following way:

$$Mass_{DM} = \left(\frac{mg_i}{kg_{DM}}\right) = \frac{M_i(mg)}{M_{DM}(kg)} \tag{13}$$

In this way it was possible to calculate the total mass of the compound of interest removed with the leachate from all the process, and calculate the percentages of removal of them with respect to the first analyses on the solid sample.

*4.2.1 Experimental calculation of the constant **K***

For all the seven reactors, in which were performed landfill simulating operations, it was calculated the value of the constant K present in the equation used to characterize leachate in the long-term period, from the results of the analyses performed in the laboratory.

So it has been possible to compare the obtained values with the ones proposed by APAT (APAT, 2005). The calculations can be obtained following the procedure already explained and available in the document (APAT, 2005), but with the same results and in a more rapid way, in this study the values of K were obtained experimentally from the exponential interpolation of the points representing leachate concentrations, obtained from analyses results, plotted versus L/S ratio. It was decided to use an exponential interpolation, even if it is not sure that it is the best equation approximating all the results, in order to compare the results to the ones proposed by APAT, calculated through the equation (8), with m and c experimental constants available in literature and already reported in a table. For the values C_0, where they were not under the detection limits of the instrument, have been used the first values obtained from the sample analyses, corresponding to an L/S ratio of almost 0,1 l/kg. If this value were not available because under the detectable limits, have been used values from the literature (Golder Associates, 2003).

The calculations to define the behavior of concentrations described by equation (5) are reported in Annex III.

In the table below are summarized all the data used to obtained the K values for anaerobic reactors.

Table 1.10. Values of initial concentration for several compounds in landfill leachate, those modeled in risk analysis and those obtained in this experimental study.

	Golder Associates, 2003		VmixA	V2A	SCmix A	SC5	Golder Associates, 2003	
	C_0 (mg/l)		**C_0 (mg/l)**	**C_0 (mg/l)**	**C_0 (mg/l)**	**C_0 (mg/l)**	**m (kg/l)**	**c (kg/l)**
	range	most probable value						
cadmium (Cd)	0,002-0,105	0,010	< 0,01	< 0,01	< 0,01	< 0,01	0,082	0,159
chrome (Cr)	0,023-0,416	0,098	0,0256	< 0,02	< 0,02	< 0,02	0,051	0,045
copper (Cu)	0,013-0,191	0,051	0,0714	< 0,02	< 0,02	< 0,02	0,066	-0,049
nickel (Ni)	0,035-0,126	0,126	0,0812	0,804	0,11	0,129	0,099	-0,148
lead (Pb)	0,034-0,34	0,111	< 0,03	< 0,03	< 0,03	< 0,03	0,044	0,017
zinc (Zn)	0,030-9	0,362	0,114	0,0546	0,167	0,094	0,040	0,056
chlorides (Cl)	227-2650	997	333	518	49,6	35,4	0,030	0,292
manganese (Mn)	0,077-324	0,780	0,382	0,492	0,27	1,068	/	/
ammonia (NH_4^+)	32,10-1100	267	143	/	/	/	0,000	0,590
iron (Fe)	0,290-5530	9,93	4,82	3,12	0,112	0,24	/	/

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PART TWO – SCIENTIFIC ARTICLE

Abstract

The characterization of landfill leachate is a problem, which still nowadays is full of uncertainties and related to many problematic aspects. In this experimental work leaching tests on waste coming from two old uncontrolled landfill, simulating aerobic and anaerobic landfill operations. The results allowed a comparison between the two operating conditions, confirming the positive effects of aeration on leachate quality, the not well defined behavior of metals and enhancing the importance of leaching tests, through which base the prediction of concentration of compound in landfill leachate.

1 Introduction

Landfill is the most common solid waste disposal method in the world, because it is the simplest, the cheapest and the most cost-effective way of disposing waste. Generation of contaminated leachate, a potential long-term source of emissions, remains an inevitable consequence of the practice of waste disposal. There is therefore an obvious risk that leachate from landfills may directly affect and contaminate the groundwater and or downstream surface water (Rosqvist and Destouni, 2000). The long-term hazard potential for landfills is an aspect nowadays, not well quantified (Bozkurt et al., 2000) because of the many problematic and critical aspects which are present, when addressing this problem. An understanding of leachate composition and an integrated strategy for risk assessment are crucial and necessary to correctly face this problem and for making projections on the long-term impacts of landfills, in particular for old and uncontrolled ones, for which information available is scarce (Baderna et al., 2011). The problem is that an integrated risk assessment methodology does not exist, even because it faces large uncertainties and requires a high level of expertise (Butt and Oduyemi, 2003).

The characterization of leachate from landfills in the long-term period, are based on data coming from field studies, concerning monitoring wells or field research on leachate generation rate, laboratory experiments as leaching tests, landfill simulator reactors and theoretical modeling based on experimental data. The main problem related to long-term emissions of leachate is the temporal variation in the concentration of pollutants present in the leachate emitted by the landfill, and how it is possible to characterize these concentration from laboratory analyses.

Leaching tests are experimental tools used to understand processes controlling release from waste. They can be used for characterization or, as compliance testing, for regular verification with reference threshold. The prediction of leachate concentration nowadays is mainly based on time or on the ratio Liquid/Solid (L/S). In laboratory experiments it represents at the moment t, the total cumulate volume of liquid passed through the waste divided by the dry mass of waste. L/S ratio is, until now, the best parameter found to be correlated with real landfill, more than time parameter. In landfills the L/S ratio is calculated from data concerning temporal variation of rainfall in a disposal site and its geometrical characteristics. Performing leaching tests in an enhanced way would make it possible to generate results of leaching tests that cover a wide L/S interval and also consider biological activity. Such information is lacking today, as simulator tests only cover a short L/S interval, due to practical difficulties in reaching so high values of L/S ratio in laboratory experiments: long time required to reach L/S=10 l/kg, or high quantities of water to be mobilized. The predictions of today are based on prolonged (mathematically extrapolated) trends of simulator leaching. Actual data that covers a broad L/S interval would make the predictions more reliable (Kylefors et al., 2003).

The use of results coming from laboratory experiments must be used in a very careful and critical way. In fact many studies have reported differences in the results coming from laboratory studies and from real scale landfill or monitoring wells.

The objectives of the following study are performing leaching tests through columns full of waste, coming from two old uncontrolled landfills, simulating anaerobic and aerobic conditions, in order to:

- Define L/S values for which the eluate concentrations stabilize and reach low values;
- use the laboratory data in a risk analysis to predict leachate concentration in the long-term period, in which data on leachate are not present;
- compare the results with data available in literature and coming from other similar studies;
- make a comparison between anaerobic and aerobic conditions, with particular consideration on metals;
- increase the amount of data and knowledge related to the problem of landfill leachate characterization in the long term period, and decrease the amount of uncertainties present when performing risk analysis.

2 Problems and critical aspects in leachate characterization

Landfill leachate is generated by the infiltration and percolation of rainfall, groundwater, runoff or floodwater into and through the layers of waste placed in an existing or closed landfill site. A combination of physical, chemical and microbial processes in the waste transfers pollutants present into the waste material to the percolating water, creating a water-based solution that may be harmful to a class of organisms, including human, but also to environmental receptors (Baderna et al., 2011). Leachate is highly variable and heterogeneous, and it is very difficult to characterize (Kulikowska et al., 2008). Results from many leaching tests and monitoring wells in several landfills, showed high horizontal and vertical variability in leachate quality, indicating that many aspects, including age, volume and properties of waste, degradation and dilution processes, climatic and meteorological conditions of the site, have a marked effect on local leachate quality and quantity (Sormunen et al., 2008).

There are many factors influencing leaching, and among these could be search the cause of the disagreement between results in leachate characterization obtained from laboratory studies and from monitoring wells. The main important are: waste typology, L/S ratio, biological degradation, recirculation of leachate, preferential pathways in the landfill body and aeration. While recirculation and aeration are optional operations which can be monitored, biological activity and preferential water flow are aspects normally occurring, but difficult to control, both at laboratory scale, both in real landfill.

The landfill Liquid/Solid ratio is the parameter that best describes the amount of water that flows through a waste disposal site. This parameter set the water infiltration in a landfill into relationship to the dry mass of the waste body (Allgaier and Stegmann, 2006).

Biological degradation is another important factor influencing leachate quality. Degradation processes in landfills take place over a very long period of time, but it is not just the presence or absence of biological activity that influences leaching. The aspect that particularly affects leachate quality is the kind of biological activity (Kylefors et al., 2003).

Water enhances biological processes, and thus leachate recirculation is a basic method which aims to control and reduce the time required for stabilization of the landfill, accelerating the biodegradation of organic compounds. In fact recirculation of leachate promotes biological activity, increasing and equalizing the moisture content, permitting a good contact between microbes, substrate and nutrients, and carrying away degradation products. Many studies reported the positive effects of leachate recirculation (Huang et al., 2008; Bilgili et al., 2007).

Also preferential pathway of leachate in landfill influences the variation of leachate quality. The highly heterogeneous physical structure of the solid waste material that composes a landfill, facilitates water flow in restricted channels and voids, aspect reported in several field studies, as well as in studies on laboratory scale (Rosqvist and Destouni, 2000). The flow paths of the water can also be affected by biological activity (Kylefors et al., 2003). As degradation proceeds, it weakens the structure of the waste, channels within the waste collapse, and thus the water finds new pathways. Also plastic bags containing waste, present in the landfill body, are efficient barriers for the water flow in the waste body (Kylefors et al., 2003). The presence of these preferential pathways could give non uniformity between results from flow of water in field-scale landfills and from laboratory reactors. For this reason the consequences of fast water flow in preferential flow paths need to be considered and quantified (Rosqvist and Destouni, 2000).

Aeration of landfill is an aspect strictly connected to the concept of sustainable landfill. Landfill aeration contributes towards an accelerated, controlled and sustainable conversion of conventional anaerobic landfills into a biological stabilized state, associated with a minimized emission potential (Ritzkowski and Stegmann, 2012).

3 State of the art

As already said, the prediction of future landfill leachate characterization is mainly based on leaching tests, simulating the real conditions of the landfill, or on studies based on results coming from monitoring wells of landfills. Many studies have faced this problem and many values of concentrations of compounds present in landfill leachate are available in literature.

There could be situations in which neither experimental and laboratory data, neither monitoring studies, are not available; the leachate characterization could be based on studies and researches, performed on leachate coming from landfills operating in similar conditions as the ones of the cases of interest.

3.1 Experimental references

The experimental studies on landfill leachate characterization, report the variation of concentration as a function of time or as a function of L/S ratio. Van Der Sloot is the main researcher in the field of leaching tests; he is responsible of the creation of a database in which are collected many leaching data from laboratory testing from wastes and related materials, data from lysimeter studies, composition data and landfill leachate information (Van Der Sloot et al., 2005; Van Der Sloot et al., 2011). Bilgili studied metal concentrations in leachate from pilot scale landfill reactors, simulating aerobic and anaerobic operating conditions (Bilgili et al., 2007). The effects of leachate recirculation was also studied. Variations of metals concentrations in leachate are expressed as function of operational time of the studied reactors. Kulikowska and Klimiuk evaluated leachate composition from a municipal landfill, from leachate sampling (Kulikowska and Klimiuk, 2008). In this study the results are reported as a statistical analysis of all the samples analyzed. Similarly Oman and Junestedt, characterize leachate from 12 landfills (Oman and Junestedt, 2008). The same work, from pre-sorted and baled municipal solid waste, was done by El-Fadel and others (El-Fadel et al., 2002), with the representation of the results with respect to time. Other studies concern the behavior of heavy metals and the several complex processes related to this, in different scenario (Bozkurt et al., 2000; Flyhammar and Hakansson, 1999; Christensen et al., 2001). The variation of metal concentration was reported also a function of depth of collecting sample (Ostman et al., 2006). Some researchers studied the differences between lab-scale investigations and field-scale monitoring in old landfills, and others stated the positive effects of aeration on leachate quality (Hrad et al., 2013; Raga and Cossu, 2013).

3.2 Modelling approach

The actual methods applied for risk analysis on landfills are described by the National agency APAT (Agenzia per la Protezione dell’Ambiente e per i servizi Tecnici) in the document “Criteri metodologici per l’applicazione dell’analisi assoluta di rischio alle discariche” of 2005 (APAT, 2005). The document describes in detail the parameters and the information needed to face each steps of the procedure, with the goal of helping public administrations, researchers and practitioners, in making environmental and health risk assessments. As already said, prediction of leaching characterization from a landfill in a long-term period can be empirically calculate through laboratory analyses on leaching tests.

The decline of concentration in landfill leachate can be related to time, but typically it is used the liquid to solid ratio instead of time, because this L/S ratio is a more objective tool, since it considers both the amount of solid waste as well as the amount of water added to the waste, which can be related to time (Kylefors et al., 2003). The ratio is obtained dividing the amount of water infiltrating the waste body by the dry mass of the waste, known from the density and the volume of the waste. Moreover L/S ratio is the parameter which best set correlation between laboratory data and data coming from monitoring wells. The equation which describes the temporal variation of the concentration of a non volatile contaminant in the landfill, related to L/S ratio, and which is used for future leachate characterization is reported here below (APAT, 2005):

$$C^L(t) = C_0^L * e^{-\left(K * \frac{L}{S}\right)} \tag{1}$$

where:

C_0^L is the concentration of the contaminant in the leachate at time t=0;

$C^L(t)$ is the concentration of the contaminant in the leachate at time t;

K is the value obtained from laboratory results of leaching tests.

A contaminant species with a high value of K is leached more rapidly than a species with a low value of K, and its concentration in leachate will decrease more rapidly. These values of K can be obtained from the exponential interpolation of the data representing concentrations, plotted versus L/S ratio. The procedure is explained in the appendix 3 of the same document (APAT, 2005).

If leaching tests could not be performed, over two thousand K values for different species in different waste types, disposed in anaerobic conditions, were collected. Analysis of the data has found that a single K range cannot be established for each species, but many empirical values of K are available in literature (Golder Associates, 2003).

The equation used is an exponential one, but it is not sure that it is the best way to represent the decline in concentrations of all the compounds present in landfill leachate.

With this present study it wants to compare the behavior of same waste performed in aerobic and anaerobic conditions, as some studies have already done, but it wants to study this behavior with respect to L/S ratio in order to compare the results with the modeled ones and use them to understand the best way to predict leachate characterization.

4 Experimental study

4.1 Materials and Methods

4.1.1 Waste samples

The wastes were collected in two old uncontrolled landfills, the Noè-Tebaldi and the Servizi Costieri S.r.l., both sited in Comune di San Bonifacio (VR), Italy. They were used to deposit urban and industrial waste, and also foundry sand in the second one, since the 1970's and were closed without an emission controlled system, either for leachate either for biogas. The information regarding the site, and the waste conferred at it, is very little.

Five samples were extracted from the landfills, in positions aiming at obtaining the maximum variability of the waste landfilled. The samples from the landfill Noè-Tebaldi were called V1, V2, V3, V4, V5; those from the Servizi Costieri landfill SC1, SC2, SC3, SC4 and SC5. Each sample was taken with a probing from the ground level up to the depth of 10-15 meters. It was observed in situ that the sample V2 reached the groundwater level and that the sample SC5 showed the presence of unidentified material aggregated in yellow little blocks..

In a following phase, the samples have been completely mixed up and sieved in order to extract a sample of two kilograms of weight, for solid analysis.

4.1.2 Columns and other equipments

For the experiment were set up seven bioreactors, called VmixA, VmixB, V2A, V2B, SC5, SCmixA and SCmixB. V2 and SC5 were filled with waste deriving from samples V2 and SC5, respectively, chosen for the experimental work, since they have different characteristics from the others samples. The other bioreactors, Vmix and SCmix derived from the mixing of all the others samples. Each column was used to simulate a different landfill concept, and the “A” and “B” in the name of the reactor means respectively anaerobic and aerobic conditions.

The reactors VmixA and VmixB were columns made of plexiglass, with an internal diameter of 250 mm and a height of 1000 mm. The others, smaller had an internal diameter of 100 mm and an effective height of 800 mm.

They were sealed on the top and on the bottom. The upper end had two valves, one permitting the extraction of air and the other allowing the introduction of water and leachate. A 100 mm thick gravel layer (gravel particle size 10-15 mm) was placed at the bottom and at the top of the bioreactors for leachate drainage, to better distribute the liquids. The lower end was equipped with tap allowing leachate extraction and the introduction of air into the reactor. A sketch of the reactors is represented in figure 1.

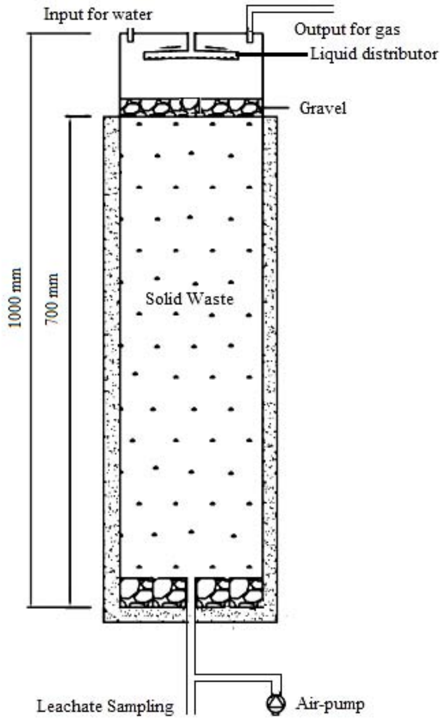


Figure 2.1. Landfill simulator reactor.

All reactors were operated in anaerobic conditions in a first phase, then reactors VmixB, SCmixB, V2B started to work in aerobic condition, 8h/d. When they were operated under aerobic conditions, air was introduced into reactor VmixB by RESON® Air-pump AC-9601, and by BOYU® S-9901 for reactors SCmixB and V2B.

Characteristics and operational conditions in which the reactors were performed are listed in table 1.

Table 2.1. Properties and operational conditions performed in the reactors.

Bioreactor	*Samples*	*Refuse weight (kg)*	*Mass of dry matter* (*kg*$_{DM}$)	*Operating conditions*	*Airflow (l/min)*
VmixA	V1, V3, V4, V5	52,5	42,914	Anaerobic	-
VmixB	V1, V3, V4, V5	52,5	43,258	Aerobic	1,8
V2A	V2	7,5	5,822	Anaerobic	-
V2B	V2	7,5	5,822	Aerobic	2
SC5	SC5	7,5	6,160	Anaerobic	-
SCmixA	SC1, SC2, SC3, SC4	7,5	6,390	Anaerobic	-
SCmixB	SC1, SC2, SC3, SC4	7,5	6,390	Aerobic	2

4.1.3 Experimental procedure

Until the field capacity was reached, the reactors were filled with distilled water and its recirculation was made in order to avoid losses of contaminants from the waste. Then the columns were completely saturated, in order to simulate the worst case. This happens when the groundwater level grows up and saturates the waste in the landfill. Before being saturated, the reactors V2B and SCmixB were aerated two weeks, ten work days, 8 hours per days. The flow pump was about 2 l/min. After these two weeks of aeration, reactors were saturated as the others. The water was maintained in the reactor for two weeks and a first leachate sample from the reactors was collected after these two weeks. This procedure is explained in table 2.

Table 2.2. Procedure of the first part of the experimental study.

VmixA	field capacity	-	saturation: 2 weeks	1st sampling
VmixB	field capacity	-	saturation: 2 weeks	1st sampling
SCmixA	field capacity	-	saturation: 2 weeks	1st sampling
SCmixB	field capacity	aeration: 10 days, 8h/d	saturation: 2 weeks	1st sampling
SC5	field capacity	-	saturation: 2 weeks	1st sampling
V2A	field capacity	-	saturation: 2 weeks	1st sampling
V2B	field capacity	aeration: 10 days, 8h/d	saturation: 2 weeks	1st sampling

In a second phase, the reactors VmixB, SCmixB and V2B started to work in aerobic conditions, 8 hours per day. The others were maintained in anaerobic conditions and used as control, to compare the results coming from aerobic reactors, and evaluate in this way the effects of the aeration. A certain decided amount of distilled water per week was injected in all the columns. The amount of fresh water addicted weekly have been changed during the experimental study, and greatly increased in the final phase, in order to reach an high value of L/S, equal to 10 l/kg. The injection of this fresh water every week, was subdivided into the five days of the week, in order to ensure a best contact of all the water with the waste, because fresh water percolated the waste, washing it and accelerated the metabolic processes (Fellner et al, 2009). Every day the eluate resulting from the leaching process was collected into sealed bottles, placed under the columns. The amount of leachate collected every day corresponded almost always at the amount of fresh water addicted the day before. The leachate of the day were transferred to accumulated samples' plastic bottles, placed in the fridge at a temperature between 4-5ºC for further analysis.

The experimental study lasted 16 weeks for reactors VmixA and VmixB, and 12 weeks for the other five reactors, with the realization of 10 and 7 analyses, respectively. The number of samples analyzed was chosen on the basis of the criteria proposed by APAT for the experimental procedure to characterize landfill leachate in the long-term period (APAT, 2005).

4.1.4 Data elaboration

Each week, in all reactors, it is possible to determine an L/S ratio. This value is calculated dividing the progressive total amount of fresh water coming in contact with the waste with the weight of the dry matter of the waste inside the reactor. The equations used are the following:

$$\frac{L}{S}\left(\frac{l_{H_2O}}{kg_{DM}}\right)=\frac{Total\,FW_{in}(l)}{M_{DM}\,(kg_{DM})} \tag{2}$$

$$Total\,FW_{in}(l)_{(i)_{th}\,week}=Total\,FW_{in}(l)_{(i-1)_{th}\,week}+FW_{in}(l)_{(i)_{th}week} \tag{3}$$

where $Total\,FW_{in}(l)_{(i)_{th}\,week}$ is the total amount of distilled water injected in the system, from the beginning of the experimental study until the considered i_{th} week, calculated as the sum of $Total\,FW_{in}(l)_{(i-1)_{th}\,week}$, the quantity of water inserted until the week before, the $(i-1)_{th}$, and $FW_{in}(l)_{(i)_{th}week}$, the water inserted the i_{th} week.

From the values of concentration, knowing the volumes leached out, it was calculated the mass of the compound extracted from each sample of leachate analyzed, and this mass was expressed as function of the dry matter of waste present in each columns. The sum of all the masses extracted in each sample gave the total mass of each compound removed from the waste and transferred in the leachate. From these values were calculated, moreover, the percentages of removal for all the compounds in each reactors, with respect to the values of the first solid analyses, present in table 4.

For the samples not analyzed it was supposed that the concentrations were the ones obtained from the exponential interpolation of the experimental results.

From the results of the laboratory analyses, it is possible to present the leachate concentration of the compounds, as a function of L/S ratio. The behaviours of anaerobic and aerobic reactors were compared, in order to evaluate the effects of aeration. The results of this raw data, were compared also with other experimental studies available in literature.

In a graphical way, for each compound was considered the exponential interpolation line, which describe the behaviour of the results of the laboratory analyses, which could be used to estimate the long-term emissions of a landfill. This dependence with L/S ratio can be used to predict landfill leachate characterization in the long term. The L/S ratio in a landfill is calculated from data about temporal variation of rainfall in the disposal site, and its geometrical characteristics. It was decided to consider an exponential interpolation of the results, even if it is not sure that that is the best interpolation line, in order to make a comparison with equation (1), the method used nowadays to model risk analysis.

To model equation (1), as values ${C_L}^0$, were used the first values obtained from the sample analyses, corresponding to an L/S ratio of almost 0,1 l/kg. If these initial values were not available, because under the detection limits of the laboratory instrument, were used values from the literature (Golder Associates, 2003). The distribution of these values were obtained by the mean of several samples of spot measurements coming from several existing sites. For K values were used the ones proposed by APAT calculated as:

$$K = m * \ln(C_0^L) + c \qquad (4)$$

with m and c constants available in literature (Golder Associates, 2003). The K value for any species is strongly influenced by the partitioning of the species between solid waste and leachate. The correlation between K and ${C_L}^0$, were found plotting all the specific values of K collected for all types of waste, against the initial leachate concentration of the contaminant of interest, derived from column tests (Golder Associates, 2003).
All the values used are listed in table 3:

Table 2.3. Typical values of initial concentrations (Golder Associates, 2003), values of initial concentrations obtained from the study and values of m and c present in equation (4) (Golder Associates, 2003).

	MODELLED VALUES				*EXPERIMENTAL VALUES*			
	Golder Associates, 2003				VmixA	V2A	SCmixA	SC5
	C_0^L (mg/l)		**m (kg/l)**	**c (kg/l)**	C_0^L (mg/l)			
	range	most probable value						
Cd	0,002-0,105	0,0101	0,0823	0,1589	< 0,01	< 0,01	< 0,01	< 0,01
Cr	0,023-0,416	0,0981	0,0514	0,045	0,0256	< 0,02	< 0,02	< 0,02
Cu	0,013-0,191	0,0509	0,0664	-0,0488	0,0714	< 0,02	< 0,02	< 0,02
Ni	0,035-0,126	0,126	0,0987	-0,1479	0,0812	0,804	0,11	0,129
Pb	0,034-0,34	0,111	0,0443	0,0171	< 0,03	< 0,03	< 0,03	< 0,03
Zn	0,030-9	0,362	0,0403	0,0561	0,114	0,0546	0,167	0,094
Cl^-	227-2650	997	0,0298	0,2919	333	518	49,6	35,4
Mn	0,077-324	0,78	/	/	0,382	0,492	0,27	1,068
NH_4^+	32,10-1100	267	0	0,59	143	/	/	/
Fe	0,290-5530	9,93	/	/	4,82	3,12	0,112	0,24

4.2 Results and discussion: raw data

In the first solid analysis, the following parameters were analyzed: total solids (%), TOC, TKN, N-NH_4^+, Cl, respiration index (IR_4). Some metals and heavy metals were been analysed as well; the compounds were: Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As and Hg.

The results from the first solid analysis performed on the under sieve of each sample, are reported in table 4.

Table 2.4. Characterization of solid waste from the under sieve (20 mm) of the sample.

Parameters	**V2**	**Vmix**	**SC5**	**Scmix**
TS (%)	82	86	88	90
TOC (mgTOC/kgDM)	18200	17300	17500	11100
TKN (mgN/kgDM)	1469	2095	664	921
N-NH_4 (mgN/kgDM)	530	313	664	921
IR4 (mgO_2/gDM)	0,72	0,74	-	-
Cd (mgCd/kgDM)	1,67	2,02	0,54	1,39
Cr (mgCr/kgDM)	131	284	145	38,7
Cu (mgCu/kgDM)	102	471	157	67,5
Fe (mgFe/kgDM)	40905	39405	91867	24167
Mn (mgMn/kgDM)	410	316	1308	558
Ni (mgNi/kgDM)	64,4	48,3	64,2	25,2
Pb (mgPb/kgDM)	155	233	122	562
Zn (mgZn/kgDM)	467	350	126	450
As (mgAS/kgDM)	0,80	0,32	0,36	0,63
Hg (mgHg/kgDM)	0,62	7,31	35,20	0,26
Cl (mgCl/kg_{DM})	418,44	138,98	12,1	12,4

In the leachate sample analyses, performed during the study, were considered the following compounds: pH, conductivity, TOC, TKN, NH_4^+, Cl^- just for reactor VmixA and VmixB, and Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn for all the reactors.

In the following graphs are reported the results of the analyses. All values are plotted with L/S ratio, allowing a projection of leachate characterization in the long-term period. Each graph contains the results coming from both anaerobic and aerobic conditions of the same waste, coming from the same landfill, ensuring a better comparison of the two.

The graphs in figure 2 shown the behavior of pH.

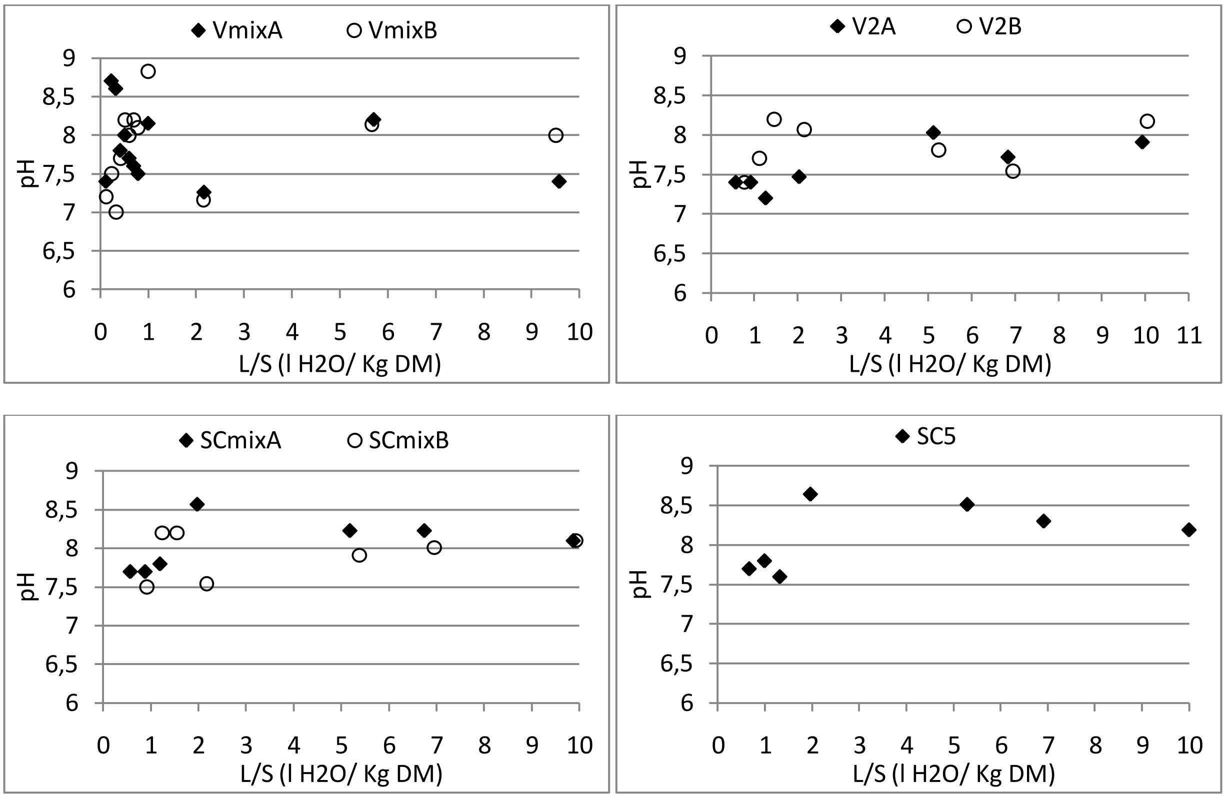


Figure2. 2. Evolution of pH in all reactors; “A” in the name means anaerobic conditions, “B” aerobic ones.

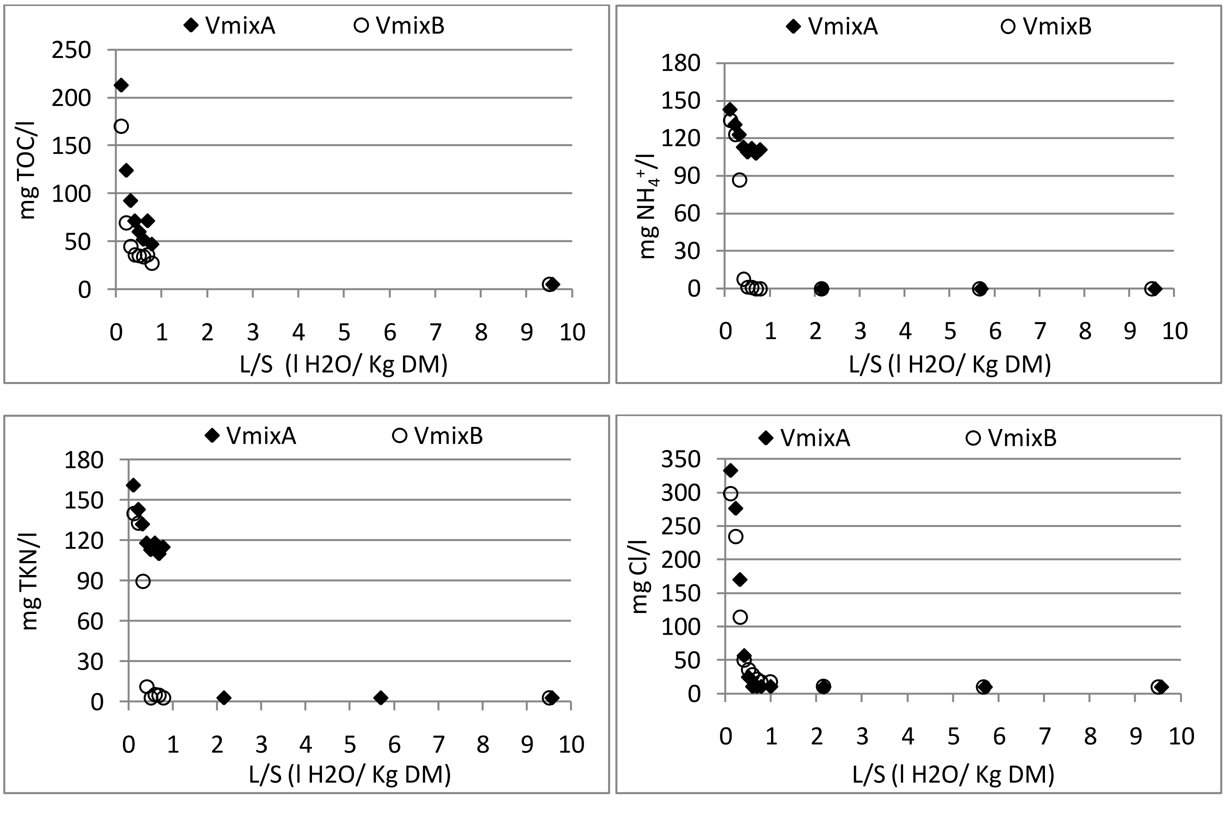
In both reactors VmixA and VmixB, pH is in the range 7-9, with some various tendency of increasing and decreasing not well defined. In these smaller columns, the range of variation of pH is narrower, between 7 and 8,5. In anaerobic reactors V2A, SCmixA and SC5 is well visible the tendency of increasing of pH, followed by a constant decrease, while the behavior in aerobic reactors V2B and SCmixB is somehow inverse: a first decrease followed by a slightly increase.

One of the most common group of contaminants in landfill leachate is heavy metals such as chromium (Cr), nickel (Ni), zinc (Zn), copper (Cu), cadmium (Cd), lead (Pb), and iron (Fe). Landfill leachate might contain heavy metals in considerable concentrations among many other constituents. The concentrations of metals are expected to reduce as the leachate changes from acidogenic to methanogenic, concurrent with a decrease in redox potential and an increase in pH.

For the concentrations resulting in some analysis, lower than the detectable limit of the instrument, in the graphs, it was decided to consider the worst case, in which the concentration is the highest, equal to this limiting value.

4.2.1 Reactors Vmix

From the graphs in figure 3 it can be observed, at first sight, the positive effect of aeration in the waste. TOC concentration decreased in both reactors, but while at the beginning of the process there was a greatly reduction in VmixB with respect to VmixA, in the longer term, concentrations in anaerobic reactor decreased more rapidly, suggesting that the influence of aeration decreases (Ritzkowski, 2011), and resulted lower than 5 mg/l in both case at L/S=9,5 l/kg. Again, TKN and NH_4^+ decreased more rapidly in reactor VmixB with respect to reactor VmixA. In fact the concentration of TKN and NH_4^+ reached values lower 3 mg/l soon at L/S of 0,5 l/kg in aerobic reactor, while stabilized at value 110 mg/l at L/S=0,5 l/kg in reactor VmixA and decreased under 3 mg/l at the end of the experiment. As regard Cl concentration instead, aeration has no effects. The behavior of Cl was very similar in VmixA and VmixB, decreasing very rapidly, in both cases, below 10 mg/l at L/S of 0,8 l/kg, and remaining below this value, the limit detectable by the instrument, up to L/S=10 l/kg.



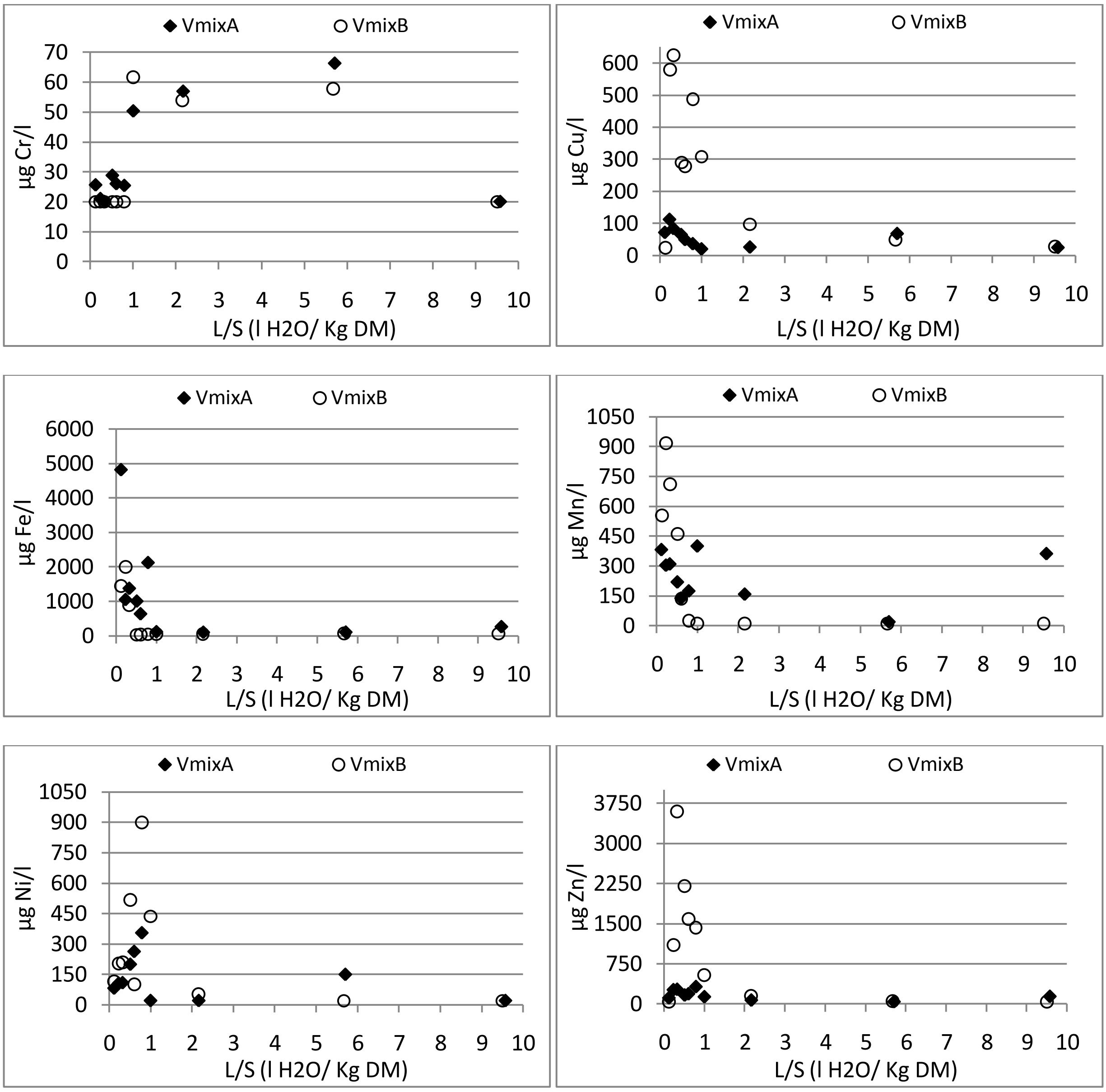


Figure 2.3. Concentrations of TOC, TKN, NH_4^+, Cl, Cr, Cu, Fe, Mn, Ni, Zn in leachate samples from anaerobic reactor VmixA and aerobic reactor VmixB.

Cd and Pb concentrations were always below 10 μg/l and 30 μg/l respectively, the detection limits of the instrument, in both reactors, anaerobic and aerobic. This complies with many studies, reporting very low concentrations of Cd and Pb in anaerobic and aerobic reactors (Bilgili et. al. 2007; Christensen et al., 2001).

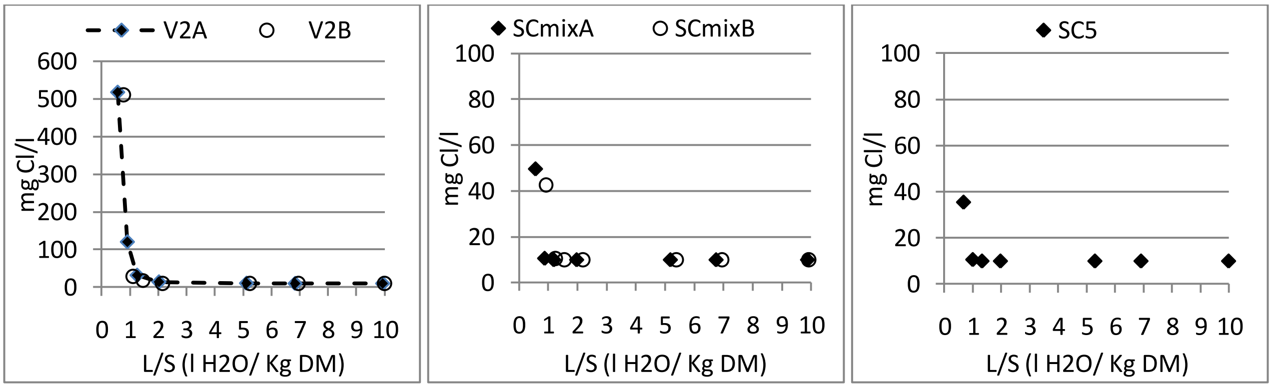
In reactor VmixA Cr concentrations were very low, between 20 and 30 μg/l at the beginning of the operation, and then increased up to value of 66.4 μg/l and decreased under 20 μg/l at L/S=9,5 l/kg.

In aerobic reactor VmixB, Cr concentration resulted higher than the 20 μg/l, limit detectable by the instrument, only in three sample analyzed.

In anaerobic reactor VmixA, Mn concentration had some variations until L/S reached value of 1 l/kg, then decreased constantly to the value of 20 μg/l at L/S=5,5 l/kg, followed by a further increase up to values of 362 μg/l. The same for Fe concentrations, resulted very high at the beginning, and decreased to values lower than 100 μg/l from L/S=1 l/kg. Zn concentrations were always under 350 μg/l, decreasing and reaching even lower values, from L/S=1 l/kg. the same for Ni concentrations, always in the range 350-20 μg/l; three concentrations analyzed for Ni concentration resulted lower than 20 μg/l, the limit detectable by the instrument. As regard concentrations of Cu, Ni and Zn performed in aerobic conditions, it was observed very variable values up to an L/S ratio of 2 l/kg; these concentrations reached the maximum values of 630 μg/l, 900 μg/l and 3600 μg/l respectively. Then the concentrations started to decreased constantly reaching very low values at L/S=2 l/kg. Mn and Fe concentration in aerobic reactor VmixB, started the decreasing tendency already from L/S=1 l/kg. The initial concentrations of Fe and Mn were very high, reaching maximum values of 1500 μg/l and 920 μg/l respectively. From the graphs it is possible to see, at first sight, the effects of aeration on leachate quality. Until a liquid/solid ratio equals to 2 l/kg, metals concentrations reach very high value, then decrease constantly, some compounds even from value L/S= 1 l/kg.

4.2.2 Reactors V2, SCmix and SC5

A similar work done before, was done also for the smaller columns, just for metals and chlorides. The results are shown in the following graphs, in figure 4.



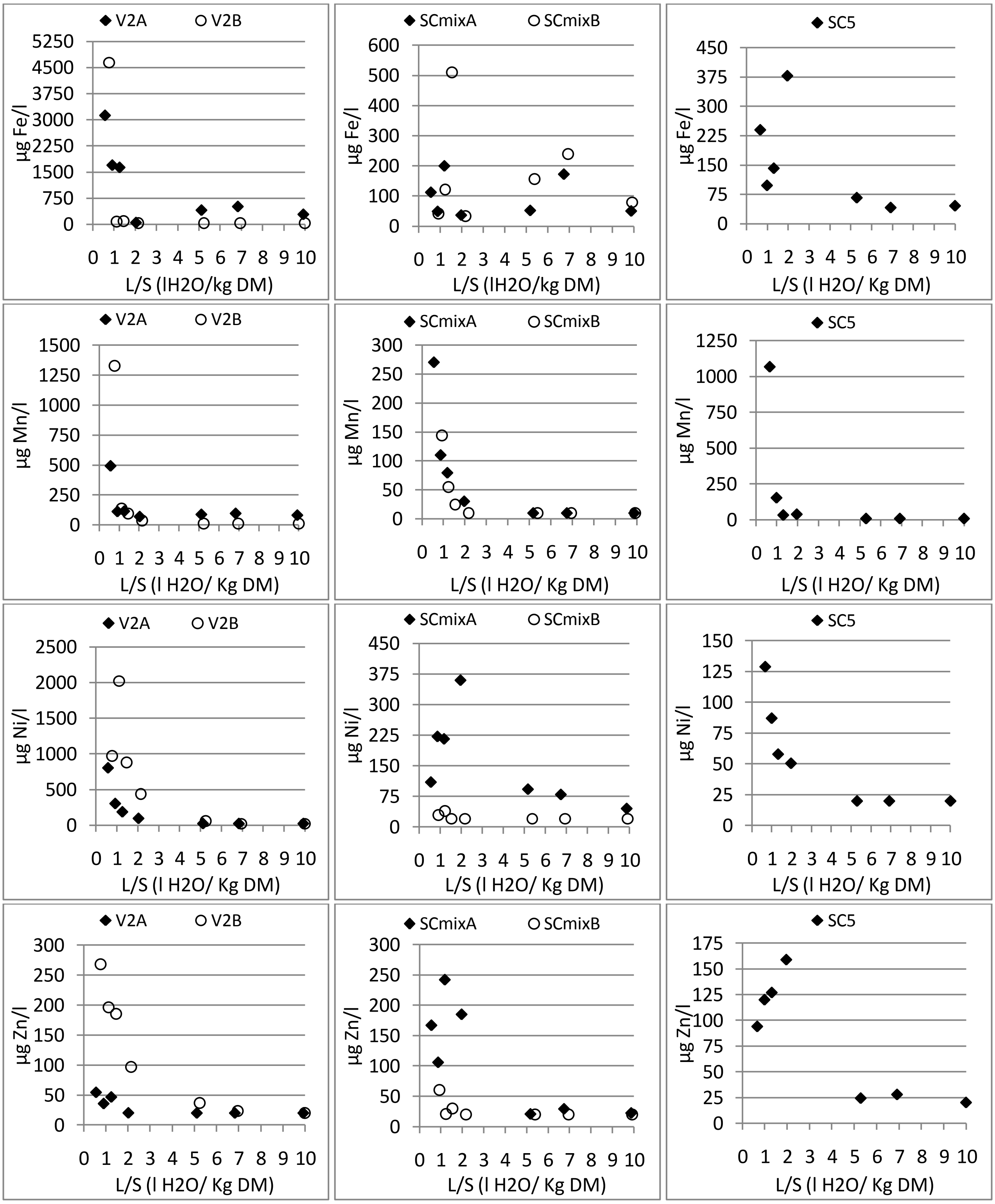


Figure 2.4. Concentrations of Cl, Fe, Mn, Ni, Zn in leachate samples from anaerobic reactors V2A, SCmixA and SC5, and from aerobic reactors SCmixB and VmixB.

The behavior of Cl concentrations reflects what already said for reactors VmixA and VmixB; the aeration had no effects on them and their concentrations constantly decreased, reaching values under 10 μg/l at L/S=1 l/kg, in all reactors. The concentrations of Cd, Cr and Pb in all five reactors resulted to be lower than the limits detectable by the laboratory instruments, as happened in reactors VmixA and VmixB, with only one value of Cr concentration higher than the limit one, but never higher than 50 μg/l. Cu concentrations, only in reactor V2B, at the beginning of the experiments were in the range 110-40 μg/l; then they decreased and remained under 20 μg/l, the limit detectable by the instruments, until the end. In all other reactors Cu concentrations were always under the limits detectable by the instrument, 20 μg/l, except for one value in SCmixA and SC5, which however were never higher 72 μg/l. Mn concentrations decreased to values lower than 10 μg/l at L/S=2 l/kg, in all reactors, excepted in V2A, in which concentrations stabilized at value 80 μg/l from L/S=2 l/kg until the end. The behavior of Mn concentration was similar in all reactors: a constant decrease until the stabilization. Ni and Zn concentrations resulted to be similar in all reactors; variations until L/S=5 l/kg, followed by a constant decrease under the limits detectable by the instrument, 20 μg/l, in all reactors. Fe concentration is very high at the beginning in reactor V2A and V2B, 3620 μg/l and 4640 μg/l respectively, and started to decrease immediately, reaching values of 286 μg/l and 37 μg/l at L/S=10 l/kg. In the other reactors its concentration had some variation in the range 30-500 μg/l, reaching values lower than 100 μg/l in the last samples analyzed.
Even in these smaller reactors, the effect of aeration are immediately visible. In some case metals concentration at the beginning is higher in aerobic conditions with respect to anaerobic ones, but then at L/S=2 l/kg decreased constantly and resulted to be lower in aerobic reactors.

4.2.3 *Percentages of removal*

In table 5 are reported the values of percentages of removal for each compound, calculated in each reactors. As already said these values were obtained dividing the total mass extracted from the waste with the leachate, by the mass of each compound obtained from the analyses, reported in table 4, of the first solid samples, the starting point of all the experimental procedure.

Table 2.5. Ranges of percentages of removal obtained from this experimental study.

Compound	**V2A**	**V2B**	**VmixA**	**VmixB**	**SC5**	**SCmixA**	**SCmixB**
TOC			1,57-1,53	1,13-1,08			
TKN			5,71-8,60	2,48-4,46			
N-NH4			35,96-36,19	15,44-16,50			
Cd	0-5,94	0-5,78	4,78	4,84	0-18,35	0-7,16	0-6,82
Cl	99,17-100	60,55-75,53	83,55-100	91,42-100	93,72-100	93,17-100	86,32-100
Cr	0,006-0,15	0,006-0,15	0,13-0,12	0,12-0,11	0,005-0,14	0,02-0,52	0,10-0,50
Cu	0-0,19	0,17-0,28	0,08-0,08	0,18	0,008-0,13	0,07-0,34	0-0,28
Fe	0,015	0,005	0,009	0,03	0,001	0,03	0,005
Mn	0,28	0,17-0,19	0,55	0,16-0,11	0,06-0,06	0,05-0,06	0,03-0,04
Ni	1,33-1,49	3,13-3,28	1,28-1,17	1,37-1,25	0,36-0,55	4,34	0,12-0,81
Pb	0,19	0-0,19	0,12	0,13	0-0,24	0-0,05	0-0,05
Zn	0,05-0,19	0,12-0,13	0,30	0,59	0,36-0,39	0,13	0,01-0,05

In some cases the percentages are reported as ranges, because in many analyses the concentrations resulted lower than the limits detectable by the laboratory instruments. In these cases it was considered both the worst case, in which the concentrations were supposed to be equal to the limit values, giving the maximum percentages of removal, both the case in which these concentrations were supposed to be zero, situations in which the removal percentages are the minimum. As it can see, the percentages of removal for metals are always very low, and in general never exceed the value of 1%, confirming what already said by other authors (Manfredi and Christensen, 2009; Kjeldsen et al., 2002). The percentages resulted higher than 5% corresponds to the cases in which laboratory analyses gave values not detectable by the instrument; for this the removal percentages calculated are the highest possible. This means that the great amount of metals present in the waste, generally remains inside it,, even at high L/S ratio, without leaching out. Instead the great amount of Cl inside the waste was resulted to be washout with the leachate; removal percentages of Cl resulted quite always near 100%.

4.3 Modeling of the results

One of the objective of the study is to compare prediction of leachate characterization in anaerobic conditions, which could be obtained from the experimental results with the one proposed nowadays and expressed by the exponential equation (1). For this reason the results of the analyses performed in anaerobic reactors were interpolated with an exponential curve. The comparison can be done only for the anaerobic reactors, being the modeled values of K, present in the same equation, related to landfills working in anaerobic conditions.

In figures 5 and 6 are reported the graphs with the experimental points coming from the laboratory analyses, the exponential interpolation lines which best approximate the experimental results, and the behavior of concentrations calculated from equation (1).

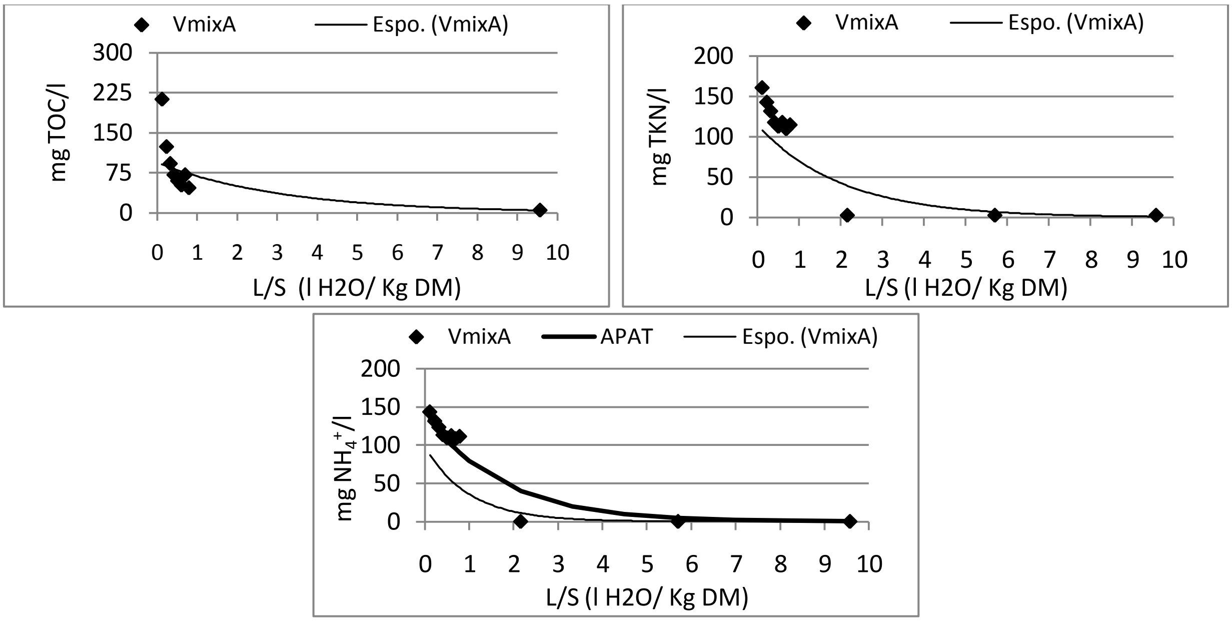
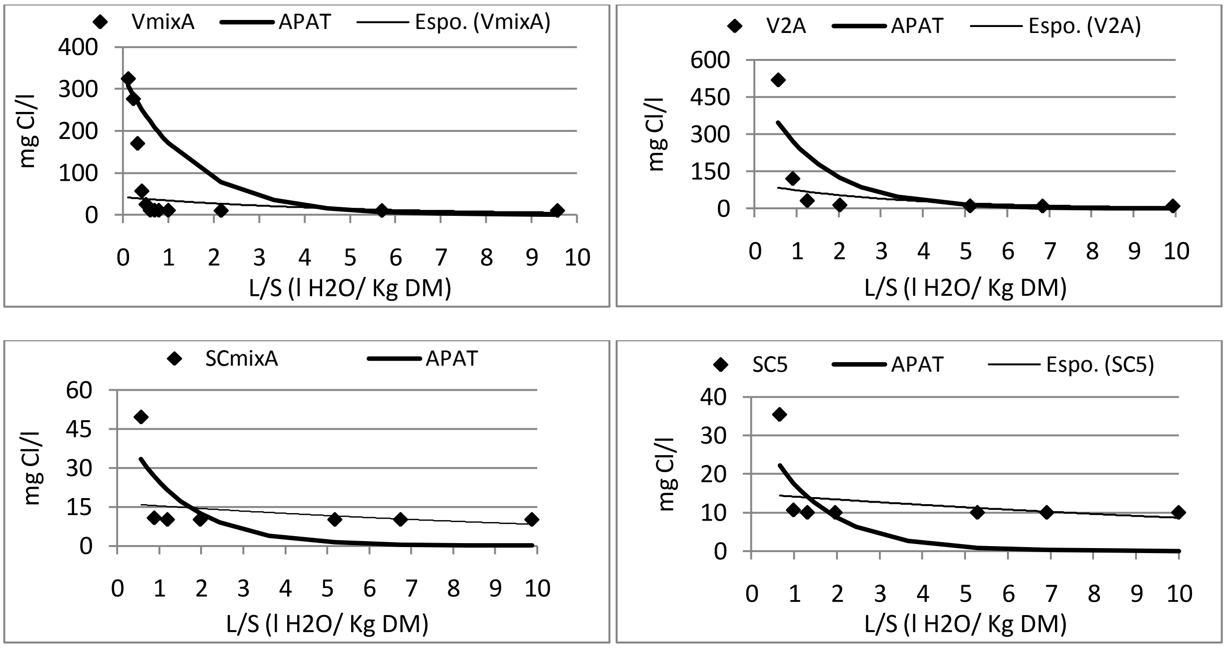
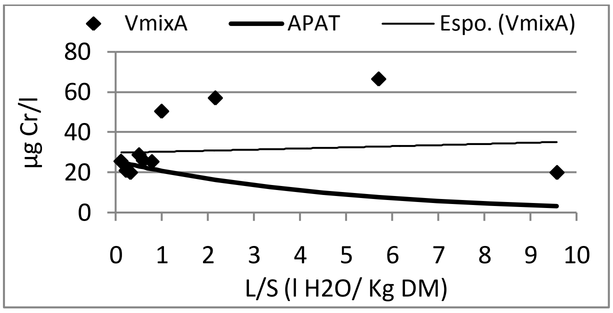
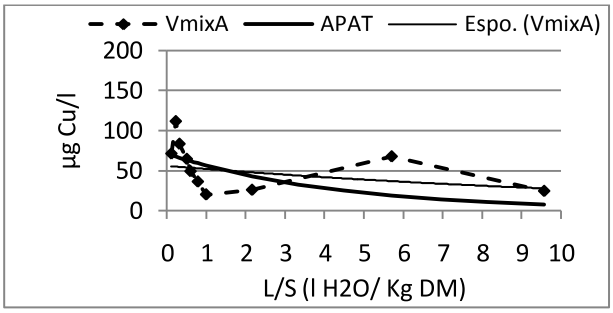
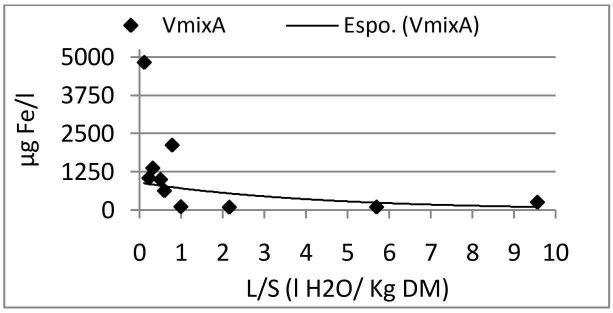


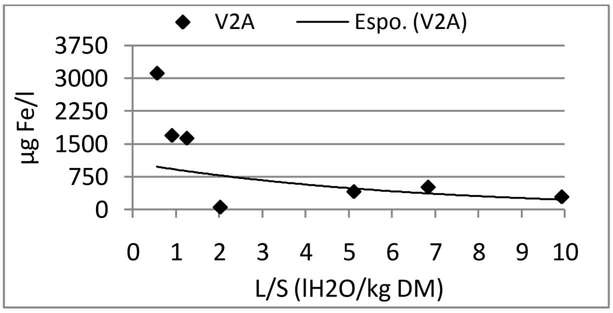
Figure 2.5. Experimental results, exponential interpolation lines and modeled behavior of TOC, TKN and NH_4^+ for anaerobic reactor VmixA.

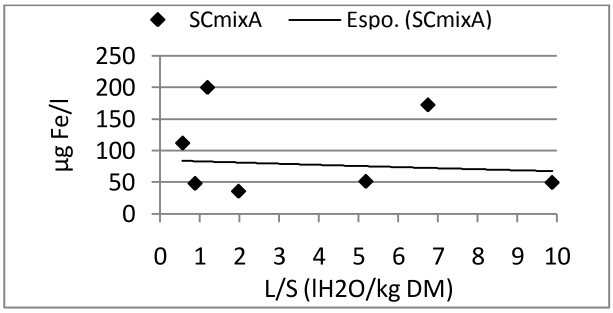


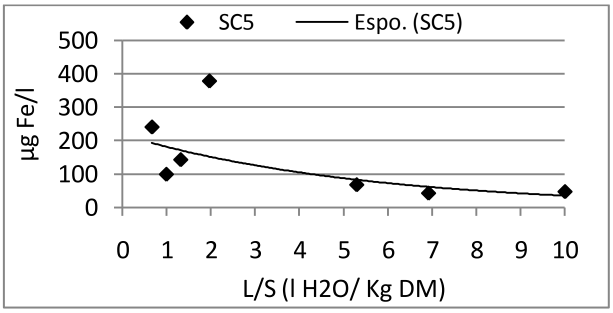

VmixA
APAT
Espo. (VmixA)
µg Cr/l
80
60
40
20
0
0 1 2 3 4 5 6 7 8 9 10
L/S (l H2O/ Kg DM)

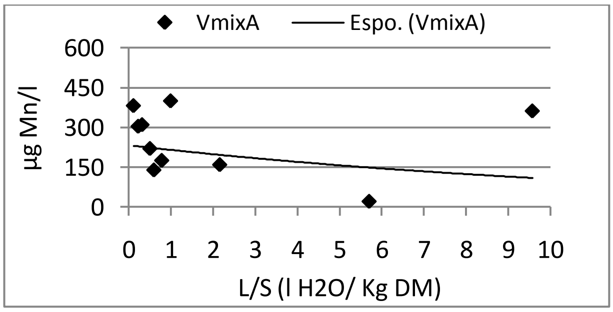

VmixA
APAT
Espo. (VmixA)
µg Cu/l
200
150
100
50
0
0 1 2 3 4 5 6 7 8 9 10
L/S (l H2O/ Kg DM)

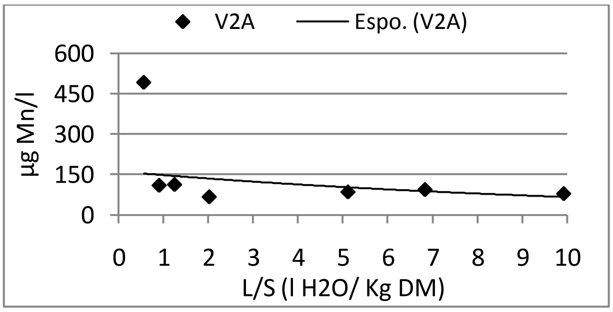

VmixA
Espo. (VmixA)
µg Fe/l
5000
3750
2500
1250
0
0 1 2 3 4 5 6 7 8 9 10
L/S (l H2O/ Kg DM)

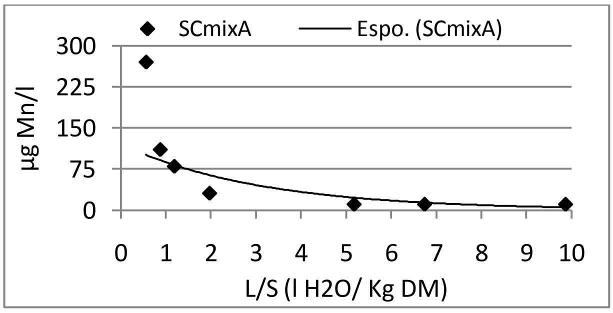

V2A
Espo. (V2A)
µg Fe/l
3750
3000
2250
1500
750
0
0 1 2 3 4 5 6 7 8 9 10
L/S (lH2O/kg DM)

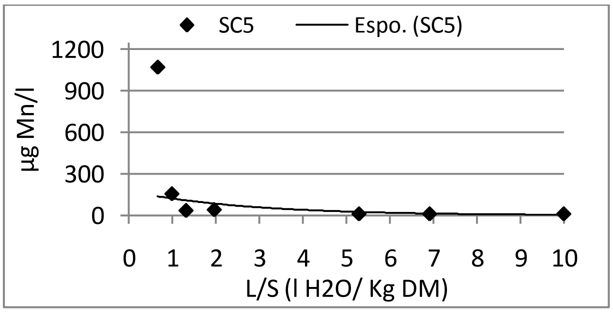

SCmixA
Espo. (SCmixA)
µg Fe/l
250
200
150
100
50
0
0 1 2 3 4 5 6 7 8 9 10
L/S (lH2O/kg DM)


SC5
Espo. (SC5)
µg Fe/l
500
400
300
200
100
0
0 1 2 3 4 5 6 7 8 9 10
L/S (l H2O/ Kg DM)


VmixA
Espo. (VmixA)
µg Mn/l
600
450
300
150
0
0 1 2 3 4 5 6 7 8 9 10
L/S (l H2O/ Kg DM)


V2A
Espo. (V2A)
µg Mn/l
600
450
300
150
0
0 1 2 3 4 5 6 7 8 9 10
L/S (l H2O/ Kg DM)


SCmixA
Espo. (SCmixA)
µg Mn/l
300
225
150
75
0
0 1 2 3 4 5 6 7 8 9 10
L/S (l H2O/ Kg DM)


SC5
Espo. (SC5)
µg Mn/l
1200
900
600
300
0
0 1 2 3 4 5 6 7 8 9 10
L/S (l H2O/ Kg DM)

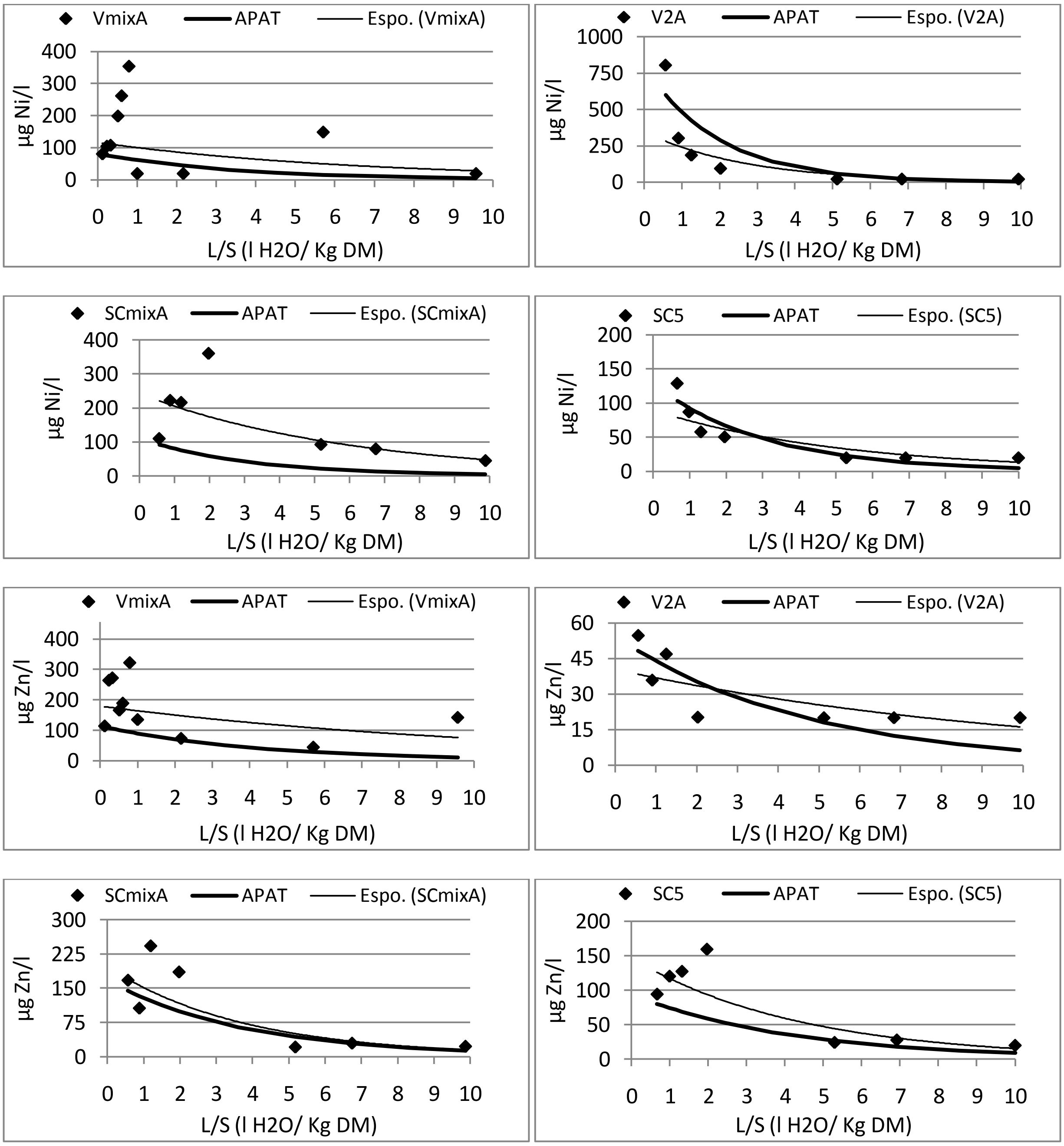


Figure 2.6. Experimental results, exponential interpolation lines and modeled behaviour of Cl, Cd, Cr, Cu, Fe, Mn, Ni and Zn for anaerobic reactor VmixA, V2A, SCmixA and SC5.

In table 6 are reported the values of *K* calculated from the values proposed by APAT and the ones obtained from the present study, together with the correlation coefficient. For Fe and Mn values of *K* are not available, because not modeled in the APAT document. The number of experimental points from which were obtained the interpolation curves were 10 for reactors VmixA and VmixB, and 7 for the others.

Table 2.6. Comparison between the modeled values of kappa proposed by APAT, and the values of K obtained from the experimental analyses performed in anaerobic reactors: 10 in VmixA, 7 in reactors V2A, SCmixA and SC5.

	VmixA			**V2A**			**SCmixA**			**SC5**		
	Golder Associates, 2003	this study (10 experimental points)		Golder Associates, 2003	this study (7 experimental points)		Golder Associates, 2003	this study (7 experimental points)		Golder Associates, 2003	this study (7 experimental points)	
	K	*K*	R^2	*K*	*K*	R^2	*K*	*K*	R^2	*K*	*K*	R^2
TOC	-	0,314	0,8451	-	-	-	-	-	-	-	-	-
TKN	-	0,493	0,6952	-	-	-	-	-	-	-	-	-
Cd	0,349	-	-	0,349	-	-	0,349	-	-	0,349	-	-
Cr	0,212	-0,017	0,0141	0,281	-	-	0,281	-	-	0,281	-	-
Cu	0,235	0,073	0,1518	0,212	-	-	0,212	-	-	0,212	-	-
Ni	0,286	0,148	0,1788	0,512	0,367	0,765	0,316	0,164	0,6659	0,332	0,19	0,7823
Pb	0,226	-	-	0,226	-	-	0,226	-	-	0,226	-	-
Zn	0,247	0,09	0,2052	0,217	0,093	0,5431	0,262	0,262	0,7675	0,239	0,227	0,8267
Cl^-	0,671	0,215	0,1924	0,684	0,305	0,5092	0,614	0,069	0,1697	0,604	0,055	0,1714
Mn	-	0,079	0,0765	-	0,089	0,2293	-	0,324	0,7404	-	0,37	0,5784
NH_4^+	0,590	1,005	0,6938	0,590	-	-	0,590	-	-	0,590	-	-
Fe	-	0,232	0,2716	-	0,156	0,1591	-	0,023	0,0146	-	0,183	0,6227

From the table, but already from the graphs, it is possible to notice that the behavior of Mn, Cl, Zn, Ni concentration is similar in reactors VmixA and V2A, and in reactors SCmixA and SC5, being the first reactors full of waste coming from one landfill, and the second reactors full of other waste. Also Fe concentration resulted to have a similar trend. The values of *K* resulted for reactors VmixA and V2A are 0,148 and 0,367 for Ni, 0,09 and 0,093 for Zn, 0,215 and 0,305 for Cl, 0,079 and 0,089 for Mn, 0,232 and 0,156 for Fe. For the same compounds resulted in reactors SCmixA and SC5 the values of *K* resulted 0,164 and 0,19, 0,262 and 0,227, 0,069 and 0,055, 0,324 and 0,37 and 0,023 and 0,183 respectively for the previous compounds. The predictive behaviors resulted in this experimental study are similar to the ones proposed by APAT, in particular for Zn and Ni, even if it is possible to notice that the exponential interpolation is not always the best approximation of the experimental results. In particular the results for Cr and Cu concentration, available only for reactor VmixA, being these concentrations in the other reactors lower the limit detectable by the instrument, are very different from the concentrations calculate by equation (1), and moreover the experimental exponential interpolation does not represent well the results. The same for Mn and Fe concentrations, even if the results are similar in all reactors. For the prediction of Cd and Pb concentration it cannot say anything, being the concentrations in all samples analyzed lower than 10 μg/l.

In all reactors, and in particular in anaerobic ones, it is possible to notice the variability with respect to L/S ratio of metals concentration; this fact is due to all the complex processes concerning the release and the retention of metals in landfill leachate, which could be present and different in each situation. For these reasons the prediction of compounds concentration, such as heavy metals, could give uncertainties and differences from the real behavior, which, however, could be reduce by the performance of proper leaching tests.

4.4 Conclusions

Leaching tests, through columns full of waste, coming from two old and uncontrolled landfills were performed. The experimental procedure of this study, was based on the daily injection of distilled water into seven different columns, until each column reached values of L/S ratio of 10 l/kg. The leachate produced were collected and analyzed for compounds as TOC, TKN, NH3, Cl and for some metals, as Cd, Cr, Cu, Fe, Mn, Pb, Ni and Zn. In each column, landfill aerobic or anaerobic conditions were simulated, allowing a comparison between the two performances. The values of concentration obtained from the analyses were plotted versus L/S ratio.

The effects of aeration resulted immediately from the results of the laboratory analyses. In reactors performed with aerobic conditions the concentration of metals released in the leachate collected and analyzed is generally higher, with respect to the ones in anaerobic conditions, until L/S=1 l/kg, meaning that the aeration enhances the release of metals content from the waste, then their concentration starts to decrease constantly, even reaching in many cases values too low to be detectable by the instruments. For this reason the L/S resulted necessary to reach the stability of the concentration in landfill leachate is L/S=2 l/kg. The low total quantities of metals transferred from the waste to the leachate, confirmed what previous studies had already said, that is that only a small percentage of metal content is released with the leachate. All the remaining part remains inside the landfill body, even after high levels of dilution, corresponding to L/S=10 l/kg.

Concentrations of each compound, plotted against L/S ratio could be used to predict leachate characterization in the long-term period. The predictions were performed with exponential interpolation lines of the experimental points, obtained from the analyses. It resulted that this exponential interpolation, is not always the best way to approximate the experimental results. In particular for metals it is difficult the prediction in the future of their concentration in the landfill leachate, because the results could give errors, being the process of releasing metals very complex and difficult to foresee and calculate. The results show also the importance of performing leaching tests in the leachate characterization, in order to obtain results site-specific of the case and more coherent with the situation, in particular in the case of metals. The heterogeneity of the waste material, which could be disposed in landfills, is another reason for which performing leaching tests. Being the modern landfills performed in operating conditions always more different from the past, new leaching tests, simulating these new operating conditions, such as leachate recirculation, different methodologies of aeration, should be performed. Further studies could be make in order to enhance the information concerning the leachate characterization, and to improve the equation used to predict leachate characterization.

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PART THREE - ANNEXES

Annex 1: Measures of pH in the reactors

In the table below are reported the values of pH measured in the leachate samples analyzed from all seven reactors. In the table are reported also the value of L/S reached by each column every week of the experimental procedure.

Table 3.1. Values of pH measured during the experimental study in all seven reactors.

	VmixA		**VmixB**		**V2A**		**V2B**		**SCmixA**		**SCmixB**		**SC5**	
	L/S	*pH*	*L/S*	*pH*	*L/S*	*pH*	*L/S*	*pH*	*L/S*	*pH*	*L/S*	*pH*	*L/S*	*pH*
1st week	0,117	7,40	0,125	7,2	0,567	7,40	0,773	7,40	0,563	7,70	0,923	7,50	0,666	7,70
2nd week	0,228	8,70	0,236	7,5	0,739	-	0,945	-	0,720	-	1,080	-	0,828	-
3rd week	0,322	8,60	0,328	7	0,910	7,40	1,116	7,70	0,876	7,70	1,236	8,20	0,990	7,80
4th week	0,415	7,80	0,421	7,7	1,082	-	1,288	-	1,033	-	1,393	-	1,153	-
5th week	0,508	8,00	0,513	8,2	1,254	7,20	1,460	8,20	1,189	7,80	1,549	8,20	1,315	7,60
6th week	0,601	7,70	0,606	8	1,512	-	1,632	-	1,502	-	1,706	-	1,477	-
7th week	0,694	7,60	0,698	8,2	2,027	7,47	2,147	8,07	1,972	8,57	2,175	7,54	1,964	8,64
8th week	0,788	7,50	0,791	8,1	2,542	-	2,662	-	2,441	-	2,645	-	2,451	-
9th week	0,881	-	0,883	-	3,401	-	3,521	-	3,615	-	3,818	-	3,669	-
10th week	0,997	8,15	0,999	8,83	5,119	8,03	5,239	7,81	5,180	8,23	5,383	7,91	5,292	8,51
11th week	2,162	7,26	2,155	7,16	6,836	7,72	6,956	7,54	6,745	8,23	6,948	8,01	6,916	8,30
12th week	3,328	-	3,310	-	8,382	-	8,502	-	8,310	-	8,513	-	8,539	-
13th week	4,493	-	4,466	-	9,928	7,91	9,997	8,17	9,875	8,10	9,922	8,10	10,000	8,19
14th week	5,704	8,20	5,668	8,14										
15th week	6,963	-	6,917	-										
16th week	8,128	-	8,072	-										
17th week	9,573	7,40	9,506	8										

Annex II: Results of laboratory analyses and their elaboration

Here below are reported all the water balance in all reactors, the values of concentration derived from the samples of leachate analyzed. The compounds analyzed are TOC, TKN, NH_4^+ just for reactors VmixA and VmixB, and Cl, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn for all seven reactors. In the cases in which the concentration analyzed resulted lower than the limit detectable by the laboratory instrument, it was decided to consider the worst situation, in which the concentration is equal to the limit one.

Table 3.1a. Water balance, L/S ratio and elaboration of laboratory results for TOC, TKN and NH_4^+ of leachate samples from anaerobic reactor VmixA.

	WATER BALANCE					***L/S***	***TOC***			***TKN***			***NH_3***		
	V_{inside} (l)	FW_{in} (l)	V_{out} (l)	WHC (l)	Total FW_{in} (l)	L/S (l/kg)	C (mg/l)	Mass (mg)	$Mass_{DM}$	C (mg/l)	Mass (mg)	$Mass_{DM}$	C (mg/l)	Mass (mg)	$Mass_{DM}$
1st sample	12,9	5	8,3	0	5	0,12	213,00	1773,23	41,32	161,00	1340,33	31,23	143,00	1190,48	27,74
1st week	9,6	4,8	3,8	1	9,8	0,23	124,00	471,20	10,98	143,00	543,40	12,66	131,00	497,80	11,60
2nd week	10,6	4	3,6	0,4	13,8	0,32	92,40	332,64	7,75	132,00	475,20	11,07	123,00	442,80	10,32
3rd week	11,0	4	4,0	0	17,8	0,41	71,30	285,20	6,65	118,00	472,00	11,00	113,00	452,00	10,53
4th week	11,0	4	3,7	0,3	21,8	0,51	60,00	222,00	5,17	113,00	418,10	9,74	109,00	403,30	9,40
5th week	11,3	4	3,6	0,4	25,8	0,60	51,90	186,84	4,35	118,00	424,80	9,90	112,00	403,20	9,40
6th week	11,7	4	3,9	0,1	29,8	0,69	71,30	278,07	6,48	110,00	429,00	10,00	108,00	421,20	9,81
7th week	11,8	4	3,7	0,3	33,8	0,79	46,90	173,53	4,04	115,00	425,50	9,92	111,00	410,70	9,57
8th week	12,1	4	3,6	0,4	37,8	0,88	-	-	-	-	-	-	-	-	-
9th week	12,5	5	4,9	0,1	42,8	1,00	-	-	-	-	-	-	-	-	-
10th week	12,6	50	50,3	-0,3	92,8	2,16	-	-	-	2,80	140,84	3,29	0,5	25,15	0,57
11th week	12,3	50	50,8	-0,8	142,8	3,33	-	-	-	-	-	-	-	-	-
12th week	11,5	50	50,7	-0,7	192,8	4,49	-	-	-	-	-	-	-	-	-
13th week	10,8	52	52,7	-0,7	244,8	5,70	-	-	-	2,80	147,56	3,44	0,5	26,35	0,61
14th week	10,1	54	54,4	-0,4	298,8	6,96	-	-	-	-	-	-	-	-	-
15th week	9,7	50	50,6	-0,6	348,8	8,13	-	-	-	-	-	-	-	-	-
16th week	9,1	62	62,2	-0,2	410,8	9,57	5,00	311,00	7,25	2,80	174,16	4,06	0,5	31,10	0,72

Table 3.1b. Elaboration of laboratory results for Cl, Cd, Cr, Cu and Fe of leachate samples from anaerobic reactor VmixA.

	L/S	***Cl***			***Cd***			***Cr***			***Cu***			***Fe***		
	L/S (l/kg)	C (mg/l)	Mass (mg)	Mass_{DM}	C (μg/l)	Mass (μg)	Mass_{DM}	C (μg/l)	Mass (μg)	Mass_{DM}	C (μg/l)	Mass (μg)	Mass_{DM}	C (μg/l)	Mass (μg)	Mass_{DM}
1st sample	0,12	324,76	2703,64	63,00	10,00	83,25	1,94	25,60	213,12	4,97	71,40	594,41	13,85	4820,00	40126,50	935,04
1st week	0,23	276,56	1050,95	24,49	10,00	38,00	0,89	21,00	79,80	1,86	112,00	425,60	9,92	1046,00	3974,80	92,62
2nd week	0,32	170,19	612,70	14,28	10,00	36,00	0,84	20,00	72,00	1,68	83,60	300,96	7,01	1372,00	4939,20	115,10
3rd week	0,41	56,73	226,92	5,29	-	-	-	-	-	-	-	-	-	-	-	-
4th week	0,51	24,82	91,83	2,14	10,00	37,00	0,86	28,80	106,56	2,48	64,60	239,02	5,57	1000,00	3700,00	86,22
5th week	0,60	10,64	38,29	0,89	10,00	36,00	0,84	26,00	93,60	2,18	49,20	177,12	4,13	632,00	2275,20	53,02
6th week	0,69	10,64	41,48	0,97	-	-	-	-	-	-	-	-	-	-	-	-
7th week	0,79	10,64	39,36	0,92	10,00	37,00	0,86	25,40	93,98	2,19	36,20	133,94	3,12	2120,00	7844,00	182,78
8th week	0,88	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9th week	1,00	10,64	52,14	1,21	10,00	49,00	1,14	50,40	246,96	5,75	20,00	98,00	2,28	111,00	543,90	12,67
10th week	2,16	10,00	503,00	11,72	10,00	503,00	11,72	57,00	2867,10	66,81	25,80	1297,74	30,24	95,60	4808,68	112,05
11th week	3,33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12th week	4,49	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
13th week	5,70	10,00	527,00	12,28	10,00	527,00	12,28	66,40	3499,28	81,54	67,80	3573,06	83,26	99,80	5259,46	122,56
14th week	6,96	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
15th week	8,13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
16th week	9,57	10,00	622,00	14,49	10,00	622,00	14,49	20,00	1244,00	28,99	24,40	1517,68	35,37	258,00	16047,60	373,95

Table 3.1c. Elaboration of laboratory results for Mn, Ni, CPb and Zn of leachate samples from anaerobic reactor VmixA.

	L/S	Mn			Ni			Pb			Zn		
	L/S (l/kg)	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$
1st sample	0,12	382,00	3180,15	74,11	81,20	675,99	15,75	30,00	249,75	5,82	114,00	949,05	22,12
1st week	0,23	304,00	1155,20	26,92	105,00	399,00	9,30	30,00	114,00	2,66	264,00	1003,20	23,38
2nd week	0,32	310,00	1116,00	26,01	108,00	388,80	9,06	30,00	108,00	2,52	272,00	979,20	22,82
3rd week	0,41	-	-	-	-	-	-	-	-	-	-	-	-
4th week	0,51	220,00	814,00	18,97	199,00	736,30	17,16	30,00	111,00	2,59	166,00	614,20	14,31
5th week	0,60	139,00	500,40	11,66	262,00	943,20	21,98	30,00	108,00	2,52	189,00	680,40	15,85
6th week	0,69	-	-	-	-	-	-	-	-	-	-	-	-
7th week	0,79	175,00	647,50	15,09	354,00	1309,80	30,52	30,00	111,00	2,59	322,00	1191,40	27,76
8th week	0,88	-	-	-	-	-	-	-	-	-	-	-	-
9th week	1,00	400,00	1960,00	45,67	20,00	98,00	2,28	30,00	147,00	3,43	135,00	661,50	15,41
10th week	2,16	159,00	7997,70	186,37	20,00	1006,00	23,44	30,00	1509,00	35,16	73,00	3671,90	85,56
11th week	3,33	-	-	-	-	-	-	-	-	-	-	-	-
12th week	4,49	-	-	-	-	-	-	-	-	-	-	-	-
13th week	5,70	20,40	1075,08	25,05	149,00	7852,30	182,98	30,00	1581,00	36,84	44,40	2339,88	54,52
14th week	6,96	-	-	-	-	-	-	-	-	-	-	-	-
15th week	8,13	-	-	-	-	-	-	-	-	-	-	-	-
16th week	9,57	362,00	22516,40	524,69	20,00	1244,00	28,99	30,00	1866,00	43,48	142,00	8832,40	205,82

Table 3.2a. Water balance, L/S ratio and elaboration of laboratory results for TOC, TKN and NH_4^+ of leachate samples from aerobic reactor VmixB.

	WATER BALANCE					**L/S**	**TOC**			**TKN**			**NH_4^+**		
	V_{inside} (l)	FW_{in} (l)	V_{out} (l)	WHC (l)	Total FW_{in} (l)	L/S (l/kg)	C (mg/l)	Mass (mg)	$Mass_{DM}$	C (mg/l)	Mass (mg)	$Mass_{DM}$	C (mg/l)	Mass (mg)	$Mass_{DM}$
1st sample	13,14	5,40	9,30	0,00	5,40	0,12	170,00	1581,00	36,55	140,00	1302,00	30,10	134,00	1246,20	28,81
1st week	9,24	4,80	3,80	1,00	10,20	0,24	69,40	263,72	6,10	133,00	505,40	11,68	123,00	467,40	10,80
2nd week	10,24	4,00	3,90	0,10	14,20	0,33	44,30	172,77	3,99	89,60	349,44	8,08	86,80	338,52	7,83
3rd week	10,34	4,00	4,00	0,00	18,20	0,42	36,10	144,40	3,34	11,20	44,80	1,04	7,56	30,24	0,70
4th week	10,34	4,00	3,80	0,20	22,20	0,51	34,80	132,24	3,06	2,80	10,64	0,25	1,12	4,26	0,10
5th week	10,54	4,00	3,80	0,20	26,20	0,61	33,60	127,68	2,95	5,32	20,22	0,47	0,84	3,19	0,07
6th week	10,74	4,00	3,90	0,10	30,20	0,70	36,10	140,79	3,25	4,76	18,56	0,43	0,05	0,20	0,00
7th week	10,84	4,00	3,70	0,30	34,20	0,79	27,40	101,38	2,34	2,80	10,36	0,24	0,50	1,85	0,04
8th week	11,14	4,00	3,90	0,10	38,20	0,88	-	-	-	-	-	-	-	-	-
9th week	11,24	5,00	5,00	0,00	43,20	1,00	-	-	-	-	-	-	-	-	-
10th week	11,24	50,00	51,10	-1,10	93,20	2,15	-	-	-	2,80	143,08	3,31	0,50	25,55	0,59
11th week	10,14	50,00	50,60	-0,60	143,20	3,31	-	-	-	-	-	-	-	-	-
12th week	9,54	50,00	51,10	-1,10	193,20	4,47	-	-	-	-	-	-	-	-	-
13th week	8,44	52,00	53,70	-1,70	245,20	5,67	-	-	-	2,80	150,36	3,48	0,50	26,85	0,62
14th week	6,74	54,00	55,00	-1,00	299,20	6,92	-	-	-	-	-	-	-	-	-
15th week	5,74	50,00	51,60	-1,60	349,20	8,07	-	-	-	-	-	-	-	-	-
16th week	4,14	62,00	64,50	-2,50	411,20	9,51	5,00	322,50	7,46	2,80	180,60	4,17	0,50	32,25	0,75

Table 3.2b. Elaboration of laboratory results for Cl, Cd, Cr, Cu and Fe of leachate samples from aerobic reactor VmixB.

	L/S	***Cl***			***Cd***			***Cr***			***Cu***			***Fe***		
	L/S (l/kg)	C (mg/l)	Mass (mg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$
1st sample	0,12	298,00	2771,40	64,07	10,00	93,00	2,15	20,00	186,00	4,30	24,20	225,06	5,20	1442,00	13410,60	310,01
1st week	0,24	234,02	889,26	20,56	10,00	38,00	0,88	20,00	76,00	1,76	580,00	2204,00	50,95	1996,00	7584,80	175,34
2nd week	0,33	113,46	442,50	10,23	10,00	39,00	0,90	20,00	78,00	1,80	624,00	2433,60	56,26	886,00	3455,40	79,88
3rd week	0,42	49,64	198,56	4,59	-	-	-	-	-	-	-	-	-	-	-	-
4th week	0,51	35,46	134,74	3,11	10,00	38,00	0,88	20,00	76,00	1,76	290,00	1102,00	25,48	28,40	107,92	2,49
5th week	0,61	28,37	107,79	2,49	10,00	38,00	0,88	20,00	76,00	1,76	278,00	1056,40	24,42	34,80	132,24	3,06
6th week	0,70	21,27	82,97	1,92	-	-	-	-	-	-	-	-	-	-	-	-
7th week	0,79	17,73	65,60	1,52	10,00	37,00	0,86	20,00	74,00	1,71	488,00	1805,60	41,74	43,60	161,32	3,73
8th week	0,88	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9th week	1,00	17,73	88,65	2,05	10,00	50,00	1,16	61,60	308,00	7,12	308,00	1540,00	35,60	59,20	296,00	6,84
10th week	2,15	10,64	543,70	12,57	10,00	511,00	11,81	54,00	2759,40	63,79	96,80	4946,48	114,35	47,20	2411,92	55,76
11th week	3,31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12th week	4,47	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
13th week	5,67	10,00	537,00	12,41	10,00	537,00	12,41	57,80	3103,86	71,75	49,20	2642,04	61,08	64,20	3447,54	79,70
14th week	6,92	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
15th week	8,07	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
16th week	9,51	10,00	645,00	14,91	10,00	645,00	14,91	20,00	1290,00	29,82	27,40	1767,30	40,85	62,00	3999,00	92,45

Table 3.2c. Elaboration of laboratory results for Mn, Ni, Pb and Zn of leachate samples from aerobic reactor VmixB.

	L/S	***Mn***			***Ni***			***Pb***			***Zn***		
	L/S (l/kg)	C (μg/l)	Mass (μg)	Mass_{DM}	C (μg/l)	Mass (μg)	Mass_{DM}	C (μg/l)	Mass (μg)	Mass_{DM}	C (μg/l)	Mass (μg)	Mass_{DM}
1st sample	0,12	554,00	5152,20	119,10	115,00	1069,50	24,72	30,00	279,00	6,45	44,00	409,20	9,46
1st week	0,24	918,00	3488,40	80,64	204,00	775,20	17,92	30,00	114,00	2,64	1106,00	4202,80	97,16
2nd week	0,33	712,00	2776,80	64,19	210,00	819,00	18,93	30,00	117,00	2,70	3600,00	14040,00	324,56
3rd week	0,42	-	-	-	-	-	-	-	-	-	-	-	-
4th week	0,51	460,00	1748,00	40,41	518,00	1968,40	45,50	30,00	114,00	2,64	2200,00	8360,00	193,26
5th week	0,61	136,00	516,80	11,95	102,00	387,60	8,96	30,00	114,00	2,64	1586,00	6026,80	139,32
6th week	0,70	-	-	-	-	-	-	-	-	-	-	-	-
7th week	0,79	24,80	91,76	2,12	900,00	3330,00	76,98	30,00	111,00	2,57	1424,00	5268,80	121,80
8th week	0,88	-	-	-	-	-	-	-	-	-	-	-	-
9th week	1,00	10,00	50,00	1,16	436,00	2180,00	50,40	30,00	150,00	3,47	542,00	2710,00	62,65
10th week	2,15	10,00	511,00	11,81	52,60	2687,86	62,14	30,00	1533,00	35,44	147,00	7511,70	173,65
11th week	3,31	-	-	-	-	-	-	-	-	-	-	-	-
12th week	4,47	-	-	-	-	-	-	-	-	-	-	-	-
13th week	5,67	10,00	537,00	12,41	20,00	1074,00	24,83	30,00	1611,00	37,24	53,20	2856,84	66,04
14th week	6,92	-	-	-	-	-	-	-	-	-	-	-	-
15th week	8,07	-	-	-	-	-	-	-	-	-	-	-	-
16th week	9,51	10,00	645,00	14,91	20,00	1290,00	29,82	30,00	1935,00	44,73	38,40	2476,80	57,26

Table 3.3a. Water balance, L/S ratio and elaboration of laboratory results for Cl, Cd, Cr, and Cu of leachate samples from anaerobic reactor SCmixA.

	WATER BALANCE					***L/S***	***Cl***			***Cd***			***Cr***			***Cu***		
	V_{inside} (l)	FW_{in} (l)	V_{out} (l)	WHC (l)	Total FW_{in} (l)	L/S (l/kg)	C (mg/l)	Mass (mg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$
1st sample	2,79	1,60	3,28	0,00	3,60	0,56	49,60	162,44	25,42	10,00	32,75	5,13	20,00	65,50	10,25	20,00	65,50	10,25
1st week	1,11	1,00	0,90	0,10	4,60	0,72	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	1,21	1,00	1,00	0,00	5,60	0,88	10,64	10,64	1,66	10,00	10,00	1,56	20,00	20,00	3,13	20,00	20,00	3,13
3rd week	1,21	1,00	1,00	0,00	6,60	1,03	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,21	1,00	1,00	0,00	7,60	1,19	10,00	10,00	1,56	10,00	10,00	1,56	42,20	42,20	6,60	71,60	71,60	11,21
5th week	1,21	2,00	2,10	-0,10	9,60	1,50	-	-	-	-	-	-	-	-	-	-	-	-
6th week	1,11	3,00	3,00	0,00	12,60	1,97	10,00	30,00	4,69	10,00	30,00	4,69	20,00	60,00	9,39	66,20	198,60	31,08
7th week	1,11	3,00	3,00	0,00	15,60	2,44	-	-	-	-	-	-	-	-	-	-	-	-
8th week	1,11	7,50	7,20	0,30	23,10	3,62	-	-	-	-	-	-	-	-	-	-	-	-
9th week	1,41	10,00	10,70	-0,70	33,10	5,18	10,00	107,00	16,74	10,00	107,00	16,74	20,00	214,00	33,49	20,00	214,00	33,49
10th week	0,71	10,00	10,10	-0,10	43,10	6,74	10,00	101,00	15,81	10,00	101,00	15,81	20,00	202,00	31,61	20,00	202,00	31,61
11th week	0,61	10,00	10,20	-0,20	53,10	8,31	-	-	-	-	-	-	-	-	-	-	-	-
12th week	0,41	10,00	10,10	-0,10	63,10	9,87	10,00	101,00	15,81	10,00	101,00	15,81	20,00	202,00	31,61	20,00	202,00	31,61

Table 3.3b. Elaboration of laboratory results for Fe, Mn, Ni, Pb and Zn of leachate samples from anaerobic reactor SCmixA.

	L/S	***Fe***			***Mn***			***Ni***			***Pb***			***Zn***		
	L/S (l/kg)	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$
1st sample	0,56	112,00	366,80	57,40	270,00	884,25	138,38	110,00	360,25	56,38	30,00	98,25	15,38	167,00	546,93	85,59
1st week	0,72	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	0,88	48,20	48,20	7,54	110,00	110,00	17,21	222,00	222,00	34,74	30,00	30,00	4,69	106,00	106,00	16,59
3rd week	1,03	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,19	200,00	200,00	31,30	79,40	79,40	12,43	216,00	216,00	33,80	30,00	30,00	4,69	242,00	242,00	37,87
5th week	1,50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6th week	1,97	35,80	107,40	16,81	30,20	90,60	14,18	360,00	1080,00	169,01	30,00	90,00	14,08	185,00	555,00	86,85
7th week	2,44	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8th week	3,62	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9th week	5,18	51,40	549,98	86,07	10,00	107,00	16,74	92,60	990,82	155,06	30,00	321,00	50,23	21,00	224,70	35,16
10th week	6,74	172,40	1741,24	272,49	10,00	101,00	15,81	79,60	803,96	125,82	30,00	303,00	47,42	29,40	296,94	46,47
11th week	8,31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12th week	9,87	49,60	500,96	78,40	10,00	101,00	15,81	45,20	456,52	71,44	30,00	303,00	47,42	22,60	228,26	35,72

Table 3.4a. Water balance, L/S ratio and elaboration of laboratory results for Cl, Cd, Cr, and Cu of leachate samples from anaerobic reactor SC5.

	WATER BALANCE					***L/S***	***Cl***			***Cd***			***Cr***			***Cu***		
	V_{inside} (l)	FW_{in} (l)	V_{out} (l)	WHC (l)	Total FW_{in} (l)	L/S (l/kg)	C (mg/l)	Mass (mg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$
1st sample	2,37	2,10	3,13	0,00	4,10	0,67	35,40	110,80	17,99	10,00	31,30	5,08	20,00	62,60	10,16	20,00	62,60	10,16
1st week	1,34	1,00	0,90	0,10	5,10	0,83	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	1,44	1,00	1,00	0,00	6,10	0,99	10,64	10,64	1,73	10,00	10,00	1,62	20,00	20,00	3,25	20,00	20,00	3,25
3rd week	1,44	1,00	1,00	0,00	7,10	1,15	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,44	1,00	1,00	0,00	8,10	1,31	10,00	10,00	1,62	10,00	10,00	1,62	41,60	41,60	6,75	20,00	20,00	3,25
5th week	1,44	1,00	1,00	0,00	9,10	1,48	-	-	-	-	-	-	-	-	-	-	-	-
6th week	1,44	3,00	3,00	0,00	12,10	1,96	10,00	30,00	4,87	10,00	30,00	4,87	20,00	60,00	9,74	25,00	75,00	12,18
7th week	1,44	3,00	3,10	-0,10	15,10	2,45	-	-	-	-	-	-	-	-	-	-	-	-
8th week	1,34	7,50	7,60	-0,10	22,60	3,67	-	-	-	-	-	-	-	-	-	-	-	-
9th week	1,24	10,00	10,00	0,00	32,60	5,29	10,00	100,00	16,23	10,00	100,00	16,23	20,00	200,00	32,47	20,00	200,00	32,47
10th week	1,24	10,00	10,10	-0,10	42,60	6,92	10,00	101,00	16,40	10,00	101,00	16,40	20,00	202,00	32,79	20,00	202,00	32,79
11th week	1,14	10,00	10,20	-0,20	52,60	8,54	-	-	-	-	-	-	-	-	-	-	-	-
12th week	0,94	9,00	9,00	0,00	61,60	10,00	10,00	90,00	14,61	10,00	90,00	14,61	20,00	180,00	29,22	20,00	180,00	29,22

Table 3.4b. Elaboration of laboratory results for Fe, Mn, Ni, Pb and Zn of leachate samples from anaerobic reactor SC5.

	L/S	***Fe***			***Mn***			***Ni***			***Pb***			***Zn***		
	L/S (l/kg)	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$
1st sample	0,67	240,00	751,20	121,95	1068,00	3342,84	542,67	129,00	403,77	65,55	30,00	93,90	15,24	94,00	294,22	47,76
1st week	0,83	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	0,99	98,20	98,20	15,94	155,00	155,00	25,16	87,20	87,20	14,16	30,00	30,00	4,87	120,00	120,00	19,48
3rd week	1,15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,31	142,00	142,00	23,05	34,40	34,40	5,58	58,00	58,00	9,42	30,00	30,00	4,87	127,00	127,00	20,62
5th week	1,48	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6th week	1,96	378,00	1134,00	184,09	40,00	120,00	19,48	50,60	151,80	24,64	30,00	90,00	14,61	159,00	477,00	77,44
7th week	2,45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8th week	3,67	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9th week	5,29	66,80	668,00	108,44	10,00	100,00	16,23	20,00	200,00	32,47	30,00	300,00	48,70	24,20	242,00	39,29
10th week	6,92	41,60	420,16	68,21	10,00	101,00	16,40	20,00	202,00	32,79	30,00	303,00	49,19	27,80	280,78	45,58
11th week	8,54	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12th week	10,00	46,20	415,80	67,50	10,00	90,00	14,61	20,00	180,00	29,22	30,00	270,00	43,83	20,00	180,00	29,22

Table 3.5a. Water balance, L/S ratio and elaboration of laboratory results for Cl, Cd, Cr, and Cu of leachate samples from anaerobic reactor V2A.

	WATER BALANCE					***L/S***	***Cl***			***Cd***			***Cr***			***Cu***		
	V_{inside} (l)	FW_{in} (l)	V_{out} (l)	WHC (l)	Total FW_{in} (l)	L/S (l/kg)	C (mg/l)	Mass (mg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$
1st sample	3,40	1,30	3,03	0,00	3,30	0,57	518,00	1566,95	269,14	10,00	30,25	5,20	20,00	60,50	10,39	20,00	60,50	10,39
1st week	1,68	1,00	0,90	0,10	4,30	0,74	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	1,78	1,00	1,00	0,00	5,30	0,91	120,55	120,55	20,71	10,00	10,00	1,72	20,00	20,00	3,44	20,00	20,00	3,44
3rd week	1,78	1,00	1,00	0,00	6,30	1,08	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,78	1,00	1,00	0,00	7,30	1,25	31,91	31,91	5,48	10,00	10,00	1,72	44,20	44,20	7,59	20,00	20,00	3,44
5th week	1,78	1,50	1,30	0,20	8,80	1,51	-	-	-	-	-	-	-	-	-	-	-	-
6th week	1,98	3,00	3,10	-0,10	11,80	2,03	14,18	43,96	7,55	10,00	31,00	5,32	20,00	62,00	10,65	20,00	62,00	10,65
7th week	1,88	3,00	3,10	-0,10	14,80	2,54	-	-	-	-	-	-	-	-	-	-	-	-
8th week	1,78	5,00	4,90	0,10	19,80	3,40	-	-	-	-	-	-	-	-	-	-	-	-
9th week	1,88	10,00	10,20	-0,20	29,80	5,12	10,64	108,53	18,64	10,00	102,00	17,52	20,00	204,00	35,04	20,00	204,00	35,04
10th week	1,68	10,00	10,10	-0,10	39,80	6,84	10,00	101,00	17,35	10,00	101,00	17,35	20,00	202,00	34,70	20,00	202,00	34,70
11th week	1,58	9,00	9,10	-0,10	48,80	8,38	-	-	-	-	-	-	-	-	-	-	-	-
12th week	1,48	9,00	9,00	0,00	57,80	9,93	10,00	90,00	15,46	10,00	90,00	15,46	20,00	180,00	30,92	20,00	180,00	30,92

Table 3.5b. Elaboration of laboratory results for Fe, Mn, Ni, Pb and Zn of leachate samples from anaerobic reactor V2A.

	L/S	***Fe***			***Mn***			***Ni***			***Pb***			***Zn***		
	L/S (l/kg)	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$
1st sample	0,57	3120,00	9438,00	1621,09	492,00	1488,30	255,63	804,00	2432,10	417,74	30,00	90,75	15,59	54,60	165,17	28,37
1st week	0,74	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	0,91	1694,00	1694,00	290,97	110,00	110,00	18,89	302,00	302,00	51,87	30,00	30,00	5,15	35,80	35,80	6,15
3rd week	1,08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,25	1630,00	1630,00	279,97	113,00	113,00	19,41	185,00	185,00	31,78	30,00	30,00	5,15	46,80	46,80	8,04
5th week	1,51	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6th week	2,03	49,40	153,14	26,30	67,40	208,94	35,89	93,20	288,92	49,63	30,00	93,00	15,97	20,20	62,62	10,76
7th week	2,54	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8th week	3,40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9th week	5,12	406,00	4141,20	711,30	85,60	873,12	149,97	20,00	204,00	35,04	30,00	306,00	52,56	20,00	204,00	35,04
10th week	6,84	510,00	5151,00	884,75	94,20	951,42	163,42	20,00	202,00	34,70	30,00	303,00	52,04	20,00	202,00	34,70
11th week	8,38	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12th week	9,93	286,00	2574,00	442,12	79,20	712,80	122,43	20,00	180,00	30,92	30,00	270,00	46,38	20,00	180,00	30,92

Table 3.6a. Water balance, L/S ratio and elaboration of laboratory results for Cl, Cd, Cr, and Cu of leachate samples from aerobic reactor SCmixB.

	WATER BALANCE					**L/S**	**Cl**			**Cd**			**Cr**			**Cu**		
	V_{inside} (l)	FW_{in} (l)	V_{out} (l)	WHC (l)	Total FW_{in} (l)	L/S (l/kg)	C (mg/l)	Mass (mg)	$Mass_{DM}$	C (μg/l)	Mass (μg)	$Mass_{DM}$	C (μg/l)	Mass (μg)	$Mass_{DM}$	C (μg/l)	Mass (μg)	$Mass_{DM}$
1st sample	4,61	3,90	3,50	0,40	5,90	0,92	42,55	148,92	23,31	10,00	35,00	5,48	20,00	70,00	10,95	20,00	70,00	10,95
1st week	1,11	1,00	0,90	0,10	6,90	1,08	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	1,21	1,00	1,00	0,00	7,90	1,24	10,64	10,64	1,66	10,00	10,00	1,56	20,00	20,00	3,13	20,00	20,00	3,13
3rd week	1,21	1,00	1,00	0,00	8,90	1,39	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,21	1,00	1,00	0,00	9,90	1,55	10,00	10,00	1,56	10,00	10,00	1,56	49,00	49,00	7,67	20,00	20,00	3,13
5th week	1,21	1,00	0,90	0,10	10,90	1,71	-	-	-	-	-	-	-	-	-	-	-	-
6th week	1,31	3,00	3,00	0,00	13,90	2,18	10,00	30,00	4,69	10,00	30,00	4,69	20,00	60,00	9,39	20,00	60,00	9,39
7th week	1,31	3,00	2,90	0,10	16,90	2,64	-	-	-	-	-	-	-	-	-	-	-	-
8th week	1,41	7,50	7,60	-0,10	24,40	3,82	-	-	-	-	-	-	-	-	-	-	-	-
9th week	1,31	10,00	10,00	0,00	34,40	5,38	10,00	100,00	15,65	10,00	100,00	15,65	20,20	202,00	31,61	20,00	200,00	31,30
10th week	1,31	10,00	9,90	0,10	44,40	6,95	10,00	99,00	15,49	10,00	99,00	15,49	20,00	198,00	30,99	20,00	198,00	30,99
11th week	1,41	10,00	9,90	0,10	54,40	8,51	-	-	-	-	-	-	-	-	-	-	-	-
12th week	1,51	9,00	9,00	0,00	63,40	9,92	10,00	90,00	14,08	10,00	90,00	14,08	20,00	180,00	28,17	20,00	180,00	28,17

Table 3.6b. Elaboration of laboratory results for Fe, Mn, Ni, Pb and Zn of leachate samples from anaerobic reactor SCmixB.

	L/S	Fe			Mn			Ni			Pb			Zn		
	L/S (l/kg)	C (µg/l)	Mass (µg)	Mass$_{DM}$	C (µg/l)	Mass (µg)	Mass$_{DM}$	C (µg/l)	Mass (µg)	Mass$_{DM}$	C (µg/l)	Mass (µg)	Mass$_{DM}$	C (µg/l)	Mass (µg)	Mass$_{DM}$
1st sample	0,92	41,20	144,20	22,57	144,00	504,00	78,87	29,40	102,90	16,10	30,00	105,00	16,43	60,40	211,40	33,08
1st week	1,08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	1,24	121,00	121,00	18,94	55,20	55,20	8,64	38,60	38,60	6,04	30,00	30,00	4,69	21,00	21,00	3,29
3rd week	1,39	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,55	510,00	510,00	79,81	24,40	24,40	3,82	20,00	20,00	3,13	30,00	30,00	4,69	30,00	30,00	4,69
5th week	1,71	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6th week	2,18	32,80	98,40	15,40	10,00	30,00	4,69	20,00	60,00	9,39	30,00	90,00	14,08	20,00	60,00	9,39
7th week	2,64	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8th week	3,82	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9th week	5,38	156,00	1560,00	244,13	10,00	100,00	15,65	20,00	200,00	31,30	30,00	300,00	46,95	20,00	200,00	31,30
10th week	6,95	240,00	2376,00	371,83	10,00	99,00	15,49	20,00	198,00	30,99	30,00	297,00	46,48	20,00	198,00	30,99
11th week	8,51	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12th week	9,92	79,20	712,80	111,55	10,00	90,00	14,08	20,00	180,00	28,17	30,00	270,00	42,25	20,00	180,00	28,17

Table 3.7a. Water balance, L/S ratio and elaboration of laboratory results for Cl, Cd, Cr, and Cu of leachate samples from aerobic reactor V2B.

	WATER BALANCE					***L/S***	***Cl***			***Cd***			***Cr***			***Cu***		
	V_{inside} (l)	FW_{in} (l)	V_{out} (l)	WHC (l)	Total FW_{in} (l)	L/S (l/kg)	C (mg/l)	Mass (mg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$	C (µg/l)	Mass (µg)	$Mass_{DM}$
1st sample	3,78	2,50	2,10	0,40	4,50	0,77	510,58	1072,22	184,17	10,00	21,00	3,61	20,00	42,00	7,21	106,00	222,60	38,23
1st week	1,68	1,00	0,90	0,10	5,50	0,94	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	1,78	1,00	1,00	0,00	6,50	1,12	28,37	28,37	4,87	10,00	10,00	1,72	20,00	20,00	3,44	44,00	44,00	7,56
3rd week	1,78	1,00	1,00	0,00	7,50	1,29	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,78	1,00	1,00	0,00	8,50	1,46	17,73	17,73	3,05	10,00	10,00	1,72	46,80	46,80	8,04	103,00	103,00	17,69
5th week	1,78	1,00	0,90	0,10	9,50	1,63	-	-	-	-	-	-	-	-	-	-	-	-
6th week	1,88	3,00	3,00	0,00	12,50	2,15	10,64	31,92	5,48	10,00	30,00	5,15	20,00	60,00	10,31	20,00	60,00	10,31
7th week	1,88	3,00	2,90	0,10	15,50	2,66	-	-	-	-	-	-	-	-	-	-	-	-
8th week	1,98	5,00	5,00	0,00	20,50	3,52	-	-	-	-	-	-	-	-	-	-	-	-
9th week	1,98	10,00	10,00	0,00	30,50	5,24	10,00	100,00	17,18	10,00	100,00	17,18	20,00	200,00	34,35	20,00	200,00	34,35
10th week	1,98	10,00	10,10	-0,10	40,50	6,96	10,00	101,00	17,35	10,00	101,00	17,35	20,00	202,00	34,70	20,00	202,00	34,70
11th week	1,88	9,00	9,30	-0,30	49,50	8,50	-	-	-	-	-	-	-	-	-	-	-	-
12th week	1,58	8,70	9,00	-0,30	58,20	10,00	10,00	90,00	15,46	10,00	90,00	15,46	20,00	180,00	30,92	20,00	180,00	30,92

Table 3.7b. Elaboration of laboratory results for Fe, Mn, Ni, Pb and Zn of leachate samples from anaerobic reactor V2B.

	L/S	***Fe***			***Mn***			***Ni***			***Pb***			***Zn***		
	L/S (l/kg)	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$	C (μg/l)	Mass (μg)	Mass$_{DM}$
1st sample	0,92	4640,00	9744,00	1673,65	1328,00	2788,80	479,01	972,00	2041,20	350,60	30,00	63,00	10,82	268,00	562,80	96,67
1st week	1,08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2nd week	1,24	83,00	83,00	14,26	137,00	137,00	23,53	2020,00	2020,00	346,96	30,00	30,00	5,15	196,00	196,00	33,67
3rd week	1,39	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4th week	1,55	92,60	92,60	15,91	95,40	95,40	16,39	882,00	882,00	151,49	30,00	30,00	5,15	185,00	185,00	31,78
5th week	1,71	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6th week	2,18	34,00	102,00	17,52	37,80	113,40	19,48	436,00	1308,00	224,67	30,00	90,00	15,46	97,00	291,00	49,98
7th week	2,64	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8th week	3,82	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9th week	5,38	37,20	372,00	63,90	10,00	100,00	17,18	58,00	580,00	99,62	30,00	300,00	51,53	36,80	368,00	63,21
10th week	6,95	38,00	383,80	65,92	10,00	101,00	17,35	20,00	202,00	34,70	30,00	303,00	52,04	23,60	238,36	40,94
11th week	8,51	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12th week	9,92	36,60	329,40	56,58	10,00	90,00	15,46	20,00	180,00	30,92	30,00	270,00	46,38	20,00	180,00	30,92

Annex III: Equation used to model leachate characterization

In the following tables are reported all the calculations performed in order to obtain the modeled behavior of compound concentration in landfill leachate, proposed in the APAT document (APAT, 2005). The experimental behaviors obtained in the present study were confronted with these values. The equations used to obtain the following tables are equation (5) for the variation of concentrations with respect to L/S ratio, and equation (8) for the value of $kappa$. The experimental values of $C_0{}^L$, when were under the limits detectable by the laboratory instruments, were substituted with typical values of initial concentration (Environment Agency, 2003). The reactors considered for the confront are only the anaerobic ones, VmixA, V2A, SCmixA and SC5, being all the values available in literature referring to anaerobic conditions.

Table 3.1. Variation of concentration with respect to L/S ratio, modeled by APAT, for anaerobic reactor VmixA.

	Cd	Cr	Cu	Ni	Pb	Zn	Cl	NH_3
$C_{0\ (experim.)}$	< 0,01	0,0256	0,0714	0,0812	< 0,03	0,114	333	143
$C_{0\ (APAT)}$	0,0101	0,0981	0,0509	0,126	0,111	0,362	997	267
c	0,1589	0,045	-0,0488	-0,1479	0,0171	0,0561	0,2919	0,59
m	0,0823	0,0514	0,0664	0,0987	0,0443	0,0403	0,0298	0
kappa	0,349	0,212	0,235	0,286	0,226	0,247	0,671	0,59
L/S	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (mg/l)*	*C (mg/l)*
0,12	9,70	24,98	69,47	78,54	29,22	110,77	307,96	133,50
0,23	9,33	24,39	67,68	76,06	28,49	107,75	285,70	124,97
0,32	9,03	23,92	66,21	74,06	27,90	105,30	268,38	118,29
0,41	8,74	23,45	64,78	72,11	27,32	102,90	252,12	111,96
0,51	8,46	22,99	63,38	70,22	26,75	100,56	236,84	105,97
0,60	8,19	22,54	62,01	68,37	26,19	98,27	222,48	100,30
0,69	7,93	22,10	60,67	66,57	25,65	96,03	208,99	94,93
0,79	7,67	21,67	59,35	64,82	25,11	93,85	196,33	89,85
0,88	7,43	21,25	58,07	63,11	24,59	91,71	184,43	85,04
1,00	7,13	20,73	56,50	61,04	23,95	89,11	170,56	79,39
2,16	4,75	16,20	42,99	43,74	18,41	66,83	78,06	39,92
3,33	3,16	12,66	32,71	31,34	14,15	50,12	35,73	20,08
4,49	2,10	9,89	24,88	22,46	10,88	37,59	16,35	10,10
5,70	1,38	7,65	18,73	15,88	8,28	27,87	7,25	4,94
6,96	0,89	5,86	13,94	11,08	6,23	20,42	3,12	2,35
8,13	0,59	4,58	10,61	7,94	4,79	15,32	1,43	1,18
9,57	0,36	3,37	7,56	5,25	3,46	10,72	0,54	0,50

Table 3.2. Variation of concentration with respect to L/S ratio, modeled by APAT, for anaerobic reactor V2A.

	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cl**
$C_{0\ (experim.)}$	< 0,01	< 0,01	< 0,01	0,804	< 0,03	0,05446	518
$C_{0\ (APAT)}$	0,0101	0,0981	0,0509	0,126	0,111	0,362	997
c	0,1589	0,045	-0,0488	-0,1479	0,0171	0,0561	0,2919
m	0,0823	0,0514	0,0664	0,0987	0,0443	0,0403	0,0298
kappa	0,349	0,281	0,212	0,512	0,226	0,217	0,684
L/S	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (mg/l)*
0,57	8,29	83,67	45,13	601,35	26,40	48,27	347,66
0,74	7,80	79,73	43,52	550,69	25,39	46,50	308,09
0,91	7,35	75,98	41,96	504,30	24,43	44,80	273,02
1,08	6,92	72,40	40,46	461,82	23,50	43,16	241,94
1,25	6,52	68,99	39,01	422,91	22,60	41,58	214,40
1,51	5,96	64,18	36,94	370,61	21,33	39,31	178,86
2,03	4,98	55,54	33,11	284,62	18,99	35,15	124,47
2,54	4,16	48,06	29,68	218,58	16,90	31,43	86,63
3,40	3,08	37,76	24,74	140,77	13,92	26,08	47,34
5,12	1,69	23,32	17,18	58,38	9,45	17,95	14,14
6,84	0,93	14,40	11,94	24,22	6,41	12,36	4,22
8,38	0,54	9,33	8,60	10,97	4,52	8,83	1,42
9,93	0,32	6,04	6,19	4,97	3,19	6,31	0,48

Table 3.3. Variation of concentration with respect to L/S ratio, modeled by APAT, for anaerobic reactor SCmixA.

	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cl**
$C_{0\ (experim.)}$	< 0,01	< 0,01	< 0,02	0,11	< 0,03	0,167	49,6
$C_{0\ (APAT)}$	0,0101	0,0981	0,0509	0,126	0,111	0,362	997
c	0,1589	0,045	-0,0488	-0,1479	0,0171	0,0561	0,2919
m	0,0823	0,0514	0,0664	0,0987	0,0443	0,0403	0,0298
kappa	0,349	0,281	0,212	0,316	0,226	0,262	0,614
L/S	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (mg/l)*
0,56	8,30	83,75	45,17	92,06	26,42	144,05	33,37
0,72	7,85	80,15	43,69	87,62	25,50	138,26	29,89
0,88	7,44	76,71	42,26	83,39	24,62	132,70	26,77
1,03	7,04	73,41	40,88	79,36	23,76	127,36	23,98
1,19	6,67	70,25	39,55	75,54	22,94	122,24	21,48
1,50	5,98	64,34	37,01	68,42	21,37	112,60	17,24
1,97	5,07	56,40	33,50	58,99	19,22	99,55	12,39
2,44	4,31	49,44	30,32	50,85	17,29	88,01	8,90
3,62	2,86	35,56	23,64	35,09	13,27	64,69	3,90
5,18	1,65	22,92	16,96	21,40	9,32	42,91	1,30
6,74	0,96	14,77	12,17	13,05	6,54	28,46	0,43
8,31	0,55	9,52	8,73	7,96	4,60	18,88	0,14
9,87	0,32	6,13	6,27	4,85	3,23	12,52	0,05

Table 3.4. Variation of concentration with respect to L/S ratio, modeled by APAT, for anaerobic reactor SC5.

	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cl**
$C_{0\,(experim.)}$	< 0,01	< 0,01	< 0,02	0,129	< 0,03	0,094	35,4
$C_{0\,(APAT)}$	0,0101	0,0981	0,0509	0,126	0,111	0,362	997
c	0,1589	0,045	-0,0488	-0,1479	0,0171	0,0561	0,2919
m	0,0823	0,0514	0,0664	0,0987	0,0443	0,0403	0,0298
kappa	0,349	0,281	0,212	0,332	0,226	0,239	0,604
L/S	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (µg/l)*	*C (mg/l)*
0,67	8,01	81,38	44,20	103,44	25,81	80,17	22,16
0,83	7,56	77,76	42,70	98,02	24,89	77,11	19,77
0,99	7,15	74,29	41,26	92,88	23,99	74,18	17,64
1,15	6,75	70,98	39,86	88,01	23,13	71,35	15,73
1,31	6,38	67,82	38,51	83,39	22,30	68,63	14,04
1,48	6,03	64,80	37,21	79,02	21,49	66,02	12,52
1,96	5,09	56,52	33,55	67,23	19,26	58,76	8,89
2,45	4,29	49,30	30,26	57,20	17,25	52,30	6,31
3,67	2,80	35,03	23,37	38,19	13,11	39,08	2,68
5,29	1,59	22,21	16,56	22,29	9,08	26,51	0,86
6,92	0,90	14,08	11,74	13,01	6,30	17,98	0,27
8,54	0,51	8,93	8,32	7,59	4,37	12,19	0,09
10,00	0,31	5,92	6,10	4,67	3,14	8,60	0,03