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Analysis and modelling of leachate and gas generation at landfill sites focused on mechanically-biologically treated waste

Ph.D DISSERTATION

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ABSTRACT

Despite significant efforts have been directed toward reducing waste generation and encouraging alternative waste management strategies, landfills still remain the main option for Municipal Solid Waste (MSW) disposal in many countries. Hence, landfills and related impacts on the surroundings are still current issues throughout the world. Actually, the major concerns are related to the potential emissions of leachate and landfill gas into the environment, that pose a threat to public health, surface and groundwater pollution, soil contamination and global warming effects. To ensure environmental protection and enhance landfill sustainability, modern sanitary landfills are equipped with several engineered systems with different functions. For instance, the installation of containment systems, such as bottom liner and multi-layers capping systems, is aimed at reducing leachate seepage and water infiltration into the landfill body as well as gas migration, while eventually mitigating methane emissions through the placement of active oxidation layers (*biocovers*). Leachate collection and removal systems are designed to minimize water head forming on the bottom section of the landfill and consequent seepages through the liner system. Finally, gas extraction and utilization systems, allow to recover energy from landfill gas while reducing explosion and fire risks associated with methane accumulation, even though much depends on gas collection efficiency achieved in the field (range: 60-90% Spokas et al., 2006; Huitric and Kong, 2006). Hence, impacts on the surrounding environment caused by the polluting substances released from the deposited waste through liquid and gas emissions can be potentially mitigated by a proper design of technical barriers and collection/extraction systems at the landfill site. Nevertheless, the long-term performance of containment systems to limit the landfill emissions is highly uncertain and is strongly dependent on site-specific conditions such as climate, vegetative covers, containment systems, leachate quality and applied stress. Furthermore, the design and operation of leachate collection and treatment systems, of landfill gas extraction and utilization projects, as well as the assessment of appropriate methane reduction

strategies (*biocovers*), require reliable emission forecasts for the assessment of system feasibility and to ensure environmental compliance. To this end, landfill simulation models can represent an useful supporting tool for a better design of leachate/gas collection and treatment systems and can provide valuable information for the evaluation of best options for containment systems depending on their performances under the site-specific conditions. The capability in predicting future emissions levels at a landfill site can also be improved by combining simulation models with field observations at full-scale landfills and/or with experimental studies resembling landfill conditions. Indeed, this kind of data may allow to identify the main parameters and processes governing leachate and gas generation and can provide useful information for model refinement.

In view of such need, the present research study was initially addressed to develop a new landfill screening model that, based on simplified mathematical and empirical equations, provides quantitative estimation of leachate and gas production over time, taking into account for site-specific conditions, waste properties and main landfill characteristics and processes. In order to evaluate the applicability of the developed model and the accuracy of emissions forecast, several simulations on four full-scale landfills, currently in operative management stage, were carried out. The results of these case studies showed a good correspondence of leachate estimations with monthly trend observed in the field and revealed that the reliability of model predictions is strongly influenced by the quality of input data. In particular, the initial waste moisture content and the waste compression index, which are usually data not available from a standard characterisation, were identified as the key unknown parameters affecting leachate production. Furthermore, the applicability of the model to closed landfills was evaluated by simulating different alternative capping systems and by comparing the results with those returned by the Hydrological Evaluation of Landfill Performance (HELP), which is the most worldwide used model for comparative analysis of composite liner systems. Despite the simplified approach of the developed model, simulated values of infiltration and leakage rates through the analysed cover systems were in line with those of HELP.

However, it should be highlighted that the developed model provides an assessment of leachate and biogas production only from a quantitative point of view. The leachate and biogas composition was indeed not included in the forecast model, as strongly linked to

the type of waste that makes the prediction in a screening phase poorly representative of what could be expected in the field. Hence, for a qualitative analysis of leachate and gas emissions over time, a laboratory methodology including different type of lab-scale tests was applied to a particular waste material. Specifically, the research was focused on mechanically biologically treated (MBT) wastes which, after the introduction of the European Landfill Directive 1999/31/EC (European Commission, 1999) that imposes member states to dispose of in landfills only wastes that have been preliminary subjected to treatment, are becoming the main flow waste landfilled in new Italian facilities. However, due to the relatively recent introduction of the MBT plants within the waste management system, very few data on leachate and gas emissions from MBT waste in landfills are available and, hence, the current knowledge mainly results from laboratory studies. Nevertheless, the assessment of the leaching characteristics of MBT materials and the evaluation of how the environmental conditions may affect the heavy metals mobility are still poorly investigated in literature. To gain deeper insight on the fundamental mechanisms governing the constituents release from MBT wastes, several leaching experiments were performed on MBT samples collected from an Italian MBT plant and the experimental results were modelled to obtain information on the long-term leachate emissions. Namely, a combination of experimental leaching tests were performed on fully-characterized MBT waste samples and the effect of different parameters, mainly pH and liquid to solid ratio (L/S,) on the compounds release was investigated by combining pH static-batch test, pH dependent tests and dynamic up-flow column percolation experiments. The obtained results showed that, even though MBT wastes were characterized by relatively high heavy metals content, only a limited amount was actually soluble and thus bioavailable. Furthermore, the information provided by the different tests highlighted the existence of a strong linear correlation between the release pattern of dissolved organic carbon (DOC) and several metals (Co, Cr, Cu, Ni, V, Zn), suggesting that complexation to DOC is the leaching controlling mechanism of these elements. Thus, combining the results of batch and up-flow column percolation tests, partition coefficients between DOC and metals concentration were derived. These data, coupled with a simplified screening model for DOC release, allowed to get a very good prediction of metal release during the experiments and may

provide useful indications for the evaluation of long-term emissions from this type of waste in a landfill disposal scenario.

In order to complete the study on the MBT waste environmental behaviour, gas emissions from MBT waste were examined by performing different anaerobic tests. The main purpose of this study was to evaluate the potential gas generation capacity of wastes and to assess possible implications on gas generation resulting from the different environmental conditions expected in the field. To this end, anaerobic batch tests were performed at a wide range of water contents (26-43 %w/w up to 75 %w/w on wet weight) and temperatures (from 20-25 °C up to 55 °C) in order to simulate different landfill management options (dry tomb or bioreactor landfills). In nearly all test conditions, a quite long lag-phase was observed (several months) due to the inhibition effects resulting from high concentrations of volatile fatty acids (VFAs) and ammonia that highlighted a poor stability degree of the analysed material. Furthermore, experimental results showed that the initial waste water content is the key factor limiting the anaerobic biological process. Indeed, when the waste moisture was lower than 32 %w/w the methanogenic microbial activity was completely inhibited. Overall, the obtained results indicated that the operative conditions drastically affect the gas generation from MBT waste, in terms of both gas yield and generation rate. This suggests that particular caution should be paid when using the results of lab-scale tests for the evaluation of long-term behaviour expected in the field, where the boundary conditions change continuously and vary significantly depending on the climate, the landfill operative management strategies in place (e.g. leachate recirculation, waste disposal methods), the hydraulic characteristics of buried waste, the presence and type of temporary and final cover systems.

SOMMARIO

Nonostante le recenti politiche ambientali volte a ridurre la produzione di rifiuti urbani ed a promuovere strategie di gestione alternative, le discariche continuano a rappresentare l'opzione principale per lo smaltimento dei Rifiuti Solidi Urbani (RSU) nel contesto europeo e mondiale. Per tale ragione, le questioni legate alle discariche ed ai loro potenziali impatti ambientali costituiscono ancora temi di forte attualità ed interesse scientifico. In effetti, i principali rischi derivanti dall'esistenza e dall'esercizio delle discariche sono legati alla potenziale fuoriuscita del percolato e del gas di discarica nell'ambiente esterno, con conseguenti effetti di inquinamento delle acque superficiali e sotterranee, di riscaldamento globale, di contaminazione del suolo nonché di pericolo per la salute pubblica. Al fine di garantire un elevato grado di tutela ambientale e migliorare la sostenibilità delle discariche, i moderni impianti di smaltimento sono dotati di sistemi ingegneristici con specifiche funzioni atte a limitare la diffusione incontrollata delle emissioni nell'ambiente circostante. Ad esempio, i sistemi artificiali di contenimento, come il rivestimento impermeabile del fondo e delle sponde ed il sistema di copertura multistrato (*capping*), mirano a ridurre le perdite di percolato dal fondo discarica e le infiltrazioni di acqua piovana nell'ammasso di rifiuti, nonché a limitare la migrazione di gas serra in atmosfera favorendo, eventualmente, l'ossidazione del metano mediante l'installazione di coperture biologicamente attive (*biocovers*). I sistemi di raccolta e rimozione del percolato sono progettati per minimizzare il battente di acqua che si instaura sulla sezione inferiore del corpo discarica e, di conseguenza, l'entità delle fuoriuscite di percolato attraverso la barriera di contenimento. Infine, i sistemi di captazione, trattamento ed utilizzo del gas da discarica consentono il recupero energetico garantendo, contemporaneamente, una riduzione dei rischi di esplosione e di incendio legati al possibile accumulo di metano. Dunque, l'impatto ambientale derivante dalla mobilizzazione di sostanze rilasciate o prodotte dai rifiuti attraverso le emissioni liquide e gassose può essere potenzialmente

mitigato attraverso una adeguata progettazione delle barriere tecniche e dei sistemi di raccolta ed estrazione. Tuttavia, l'efficienza a lungo termine di tali sistemi nel limitare le emissioni da discarica risulta estremamente incerta e strettamente dipendente dalle condizioni specifiche del sito in esame quali, ad esempio, il regime climatico, il tipo di copertura vegetale, le caratteristiche del percolato prodotto (aggressività chimica) e l'entità degli sforzi agenti. Oltretutto, la progettazione ed il corretto funzionamento dei sistemi di raccolta e trattamento del percolato, delle reti di estrazione del gas di discarica e il dimensionamento dei sistemi di utilizzo o recupero energetico del biogas, così come la valutazione di adeguate strategie di riduzione del metano (*biocovers*), richiedono previsioni affidabili delle emissioni nel tempo per analizzare la fattibilità del progetto e garantire il pieno rispetto delle prescrizioni ambientali. A tal fine, i modelli di simulazione delle discariche possono rappresentare uno strumento utile di supporto sia alla fase di progettazione e gestione dei sistemi di raccolta/estrazione del gas e del percolato sia alla fase di valutazione preliminare delle migliori configurazioni dei sistemi di contenimento, sulla base delle prestazioni ambientali ottenibili nelle specifiche condizioni del sito. L'utilizzo di modelli di simulazione combinato con campagne di monitoraggio presso reali impianti discariche e/o con studi sperimentali volti a riprodurre su piccola o vasta scala le condizioni in discarica, consente di migliorare la capacità previsionale dei livelli di emissioni in uno specifico sito discarica. Infatti, i dati ottenuti da tali indagini possono consentire di identificare i principali parametri e processi che governano la produzione di percolato e gas in discarica e, quindi, possono fornire informazioni utili per il miglioramento o la taratura del modello stesso.

In tale contesto, il presente studio è stato inizialmente indirizzato a sviluppare un modello di screening della discarica che, sulla base di equazioni semplificate di tipo analitico ed empirico, consenta di ottenere una stima quantitativa del percolato e del gas producibili nel tempo, tenendo conto delle particolari condizioni sito-specifiche, delle proprietà dei rifiuti, delle principali caratteristiche della discarica e dei processi fondamentali che interessano l'ammasso dei rifiuti. Il modello sviluppato è stato quindi utilizzato per l'analisi di quattro impianti discarica, situati in diverse zone d'Italia ed attualmente in fase di gestione operativa, al fine di individuarne i parametri significativi e valutarne l'applicabilità ai diversi contesti sito-specifici. I risultati di tali simulazioni

hanno mostrato una buona corrispondenza tra la produzione simulata di percolato ed il trend reale misurato in campo, rivelando inoltre che l'affidabilità delle previsioni modellistiche dipende fortemente dalla qualità dei dati di input utilizzati nelle simulazioni. In particolare, i casi studio analizzati hanno evidenziato che l'umidità iniziale dei rifiuti ed il coefficiente di compressione degli stessi sono parametri chiave per la valutazione dei volumi di percolato producibile.

La capacità predittiva del modello nell'analisi di discariche in fase di post-gestione è stata invece valutata prendendo in considerazione diversi scenari di copertura finale e confrontando i risultati delle simulazioni con quelli restituiti dal modello idrologico HELP (*Hydrological Evaluation of Landfill Performance*), che rappresenta lo strumento più utilizzato nel panorama mondiale per l'analisi comparativa di sistemi di impermeabilizzazione compositi. In questo caso, i risultati hanno evidenziato che, nonostante il modello sviluppato adotti un approccio semplificato, risulta in grado di fornire stime attendibili dei tassi di infiltrazione e percolazione in discariche chiuse, mostrando previsioni in linea con il modello HELP. Tuttavia, è importante sottolineare che il modello presentato fornisce una valutazione della produzione di percolato e di biogas solo da un punto di vista quantitativo. In effetti, la stima della composizione qualitativa delle emissioni non è stata inclusa nella modellazione in quanto, essendo fortemente dipendente dal tipo di rifiuto abbancato e dalle sue caratteristiche chimico-fisiche, renderebbe la previsione in un fase di screening poco rappresentativa di quello che si potrebbe realmente verificare in campo.

Quindi, per l'analisi qualitativa delle emissioni di percolato, è stata adottata un metodologia sperimentale, comprendente diversi tipi di prove su scala di laboratorio, prendendo in esame una particolare tipologia di rifiuti. Nello specifico, la ricerca è stata focalizzata sui rifiuti prodotti dal trattamento meccanico biologico (TMB) in quanto, in seguito all'attuazione della direttiva comunitaria in materia di discariche 1999/31/CE che impone agli stati membri di smaltire in discarica esclusivamente i rifiuti che siano stati sottoposti ad un trattamento preliminare o ad incenerimento, tali materiali, attualmente, costituiscono il flusso principale di rifiuti in ingresso ai nuovi impianti di smaltimento in Italia. Tuttavia, a causa della relativamente recente introduzione della tecnologia TMB all'interno del sistema di gestione integrata dei rifiuti urbani, ad oggi, pochissimi dati sono disponibili sul comportamento ambientale di questo materiale una

volta smaltito in discarica e, dunque, la conoscenza attuale deriva essenzialmente da studi condotti su scala di laboratorio.

In particolare, la valutazione del comportamento a lisciviazione e dell'influenza delle condizioni ambientali sulla mobilizzazione dei contaminanti dai rifiuti TMB rappresenta un ambito ancora poco studiato in letteratura. Per avere una visione più approfondita sul meccanismo di lisciviazione e sulla modellazione del rilascio di inquinanti dai rifiuti TMB, sono stati quindi eseguiti diversi esperimenti di lisciviazione su alcuni campioni di rifiuti prelevati da un impianto italiano di trattamento meccanico biologico che riceve rifiuti urbani indifferenziati. Nello specifico, il rifiuto TMB è stato dapprima caratterizzato mediante analisi chimo-fisiche e successivamente sottoposto a test statici di eluizione, test a pH variabile e test di percolazione in colonna, al fine di valutare l'effetto di diversi parametri, in particolare il pH ed il rapporto liquido/solido, sul rilascio di contaminanti dalla matrice in esame. I risultati ottenuti hanno mostrato che, nonostante i rifiuti TMB siano contraddistinti da un elevato contenuto di metalli pesanti, solo una ridotta percentuale degli stessi appare realmente solubile e quindi biodisponibile. Inoltre, le informazioni derivate dai diversi test hanno evidenziato l'esistenza di una stretta correlazione tra le concentrazioni in soluzione del carbonio organico disciolto (DOC) e di alcuni metalli (Co, Cr, Cu, Ni, V, Zn), suggerendo che il loro rilascio sia essenzialmente governato da reazioni di complessazione al DOC. I risultati dei diversi test di lisciviazione sono stati quindi interpolati al fine di determinare, per ciascuno metallo, i valori dei coefficienti di ripartizione DOC-Me. Questi dati, insieme ad un modello semplificato che descrive il rilascio del DOC, hanno consentito di ottenere un buon accordo tra le concentrazioni simulate e quelle misurate durante gli esperimenti in colonna, fornendo inoltre alcune informazioni utili per la valutazione delle emissioni a lungo termine da questo tipo di rifiuto in uno scenario di smaltimento in discarica.

Al fine di completare lo studio relativo al comportamento ambientale dei rifiuti TMB in riferimento al processo di generazione del biogas, il campione di rifiuto è stato sottoposto ad alcuni test batch anaerobici. L'obiettivo è stato quello di valutare sia la biodegradabilità dei rifiuti TMB, in termini di capacità massima di gas producibile, che gli effetti sul processo di metanizzazione derivanti da differenti condizioni ambientali. Nello specifico, le prove sono state condotte variando il contenuto di acqua nei rifiuti e

la temperatura operativa, assumendo per tali parametri un range di valori rappresentativo di differenti opzioni di gestione della discarica ("*dry tomb*" o bioreattori). In quasi tutte le condizioni di prova è stato osservato un periodo di latenza piuttosto lungo (diversi mesi) a causa degli effetti di inibizione derivanti dalle elevate concentrazioni di acidi grassi volatili (VFA) e ammoniaca misurate nel sistema, che hanno rivelato una scarsa stabilità biologica del rifiuto in esame. Inoltre, i risultati sperimentali hanno dimostrato che il contenuto d'acqua nei rifiuti rappresenta il fattore chiave che può limitare lo sviluppo del processo biologico anaerobico. Infatti, per valori del contenuto iniziale di acqua nei rifiuti inferiori al 32%w/w, l'attività metanogenica è apparsa del tutto inibita. In generale, le evidenze di questo studio sperimentale hanno indicato che le condizioni operative influenzano drasticamente la generazione del biogas dai rifiuti TMB, sia in termini di produzione specifica di gas che di velocità della cinetica di formazione. Ciò suggerisce che si deve prestare particolare attenzione quando i risultati dei test condotti su scala di laboratorio vengono impiegati per le valutazioni del comportamento a lungo termine di tali rifiuti in discarica, dove oltremodo le condizioni al contorno cambiano in continuazione e variano notevolmente a seconda del clima, delle strategie di gestione operativa applicate (es. ricircolo del percolato, metodo di abbancamento/compattazione dei rifiuti, co-smaltimento), delle caratteristiche idrauliche di rifiuti abbancati, della presenza e della tipologia dei sistemi di copertura temporanee e finali posti in essere.

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CHAPTER 1

INTRODUCTION AND AIMS OF THE RESEARCH

1.1 LANDFILL EMISSIONS AND IMPACTS

Waste landfill issues and related impacts on the surroundings are current topics throughout the world. In fact, while efforts have been directed toward reducing waste generation and encouraging recycling/recovery of waste, landfill still remains the dominant option for Municipal Solid Waste (MSW) disposal in many countries and an integral part of most solid waste management plans (Adhikari et al., 2014; Laner et al., 2012; Levis and Barlaz, 2011). For instance, even though during the last decade Italy has continuously decreased the amounts of landfilled waste, currently, about 42 % of MSW produced (corresponding to 13.2 Mt during 2011, ISPRA, 2013) is still disposed of in landfills after preliminary treatments. Despite of their widespread use, landfills can represent a source of main environmental impacts and risks for human health that may last for decades to centuries (Bozkurt et al., 1999; Cossu et al., 2001). These risks are closely linked to the potential emission of landfill gas and strongly polluted leachate, which may cause groundwater pollution, soil contamination and global warming effects. Leachate escaping from the bottom liner system is considered as one of the major threats to surface and groundwater resources (Adhikari et al., 2014; Nagarajan et al., 2012). Moreover, landfill has been recognized as one of the main sources of anthropogenic methane emission and a significant contributor to global warming (Mou et al., 2015; Scaglia and Adani, 2008; Scheutz et al., 2011; Thompson et al., 2009). Since the pollutant load on the environment is directly related to the qualitative and quantitative characteristics of leachate and gas emitted, understanding and predicting landfill emissions over the entire lifetime of a landfill is a key issue in order to reduce its potential risks (Fellner and Brunner, 2010; Laner et al., 2011; Rodriguez et al., 2009; Sivakumar, 2013).

1.2 LEACHATE GENERATION PROCESS

Leachate is defined as the contaminated liquid which forms from the precipitation entering the landfill body and the moisture content of the emplaced waste. Due to the contact with buried waste, leachate may contain high concentrations of organic and inorganic contaminants. Indeed, landfill leachate shows significant temporal variability, in terms of quantity and composition, and varies substantially from site to another due to the synergetic interaction of several processes and parameters (El-Fadel et al., 2002; Koda, 2012; São Mateus et al., 2012). Namely, the amount of leachate generated in landfills depends on several factors that can be classified as:

- *Meteorological factors*: rainfall is the main parameter since it affects the water infiltration within a landfill and, hence, contributes directly to leachate formation. Furthermore, mean, minimum and maximum air temperature and humidity, as well as wind velocity, are also important parameters that determine the rate of evaporation (active cells)/ evapotranspiration (vegetative capping) losses and thereby the change in water storage of the exposed layers. This implies that an aliquot of precipitation may be stored within the upper layer without percolating towards the bottom section.
- *Waste factors*: initial water content of waste, as well as its hydraulic conductivity, has a huge influence on water transport through the waste mass. Furthermore, waste composition, organic content, particle size, emplacement density and waste age contribute in different way to determine leachate generation rate.
- *Landfill aspects*. Landfill geometry (surface area, height, slopes), landfill design (leachate and gas removal systems, intermediate and final cover systems) and landfill operation (duration of landfilling activity, waste disposal/co-disposal practice, compaction degree, leachate recirculation, recultivation of closed landfills) can directly and indirectly influence leachate generation rates.

Leachate is also affected by physical, chemical and biological processes occurring in landfills, such as generation and migration of gas and fluid, biological and chemical

degradation of waste, materials aging and waste compression (Oni and Okunade, 2009; São Mateus et al., 2012) that modify waste characteristics over time. For instance, waste field capacity, porosity and hydraulic conductivity of the refuse decrease due to the applied overburden pressure, which increases with the progressive landfilling, and to the degradation of waste organic matter (Di Bella et al., 2012; Machado et al., 2010; Powrie et al., 2000; Reddy et al., 2011; Staub et al., 2009; Stoltz et al,. 2010; Wu et al., 2012). Hence, the lower/older waste layers becomes less permeable than upper layers, leading to different flow pattern and water distribution into the landfill body (Demirekler et al., 1999). Moreover, progressive compression of emplaced waste due to the applied pressure stress may lead to a water release, due to water escaping from pores, and thus contributes to leachate formation.

1.2.1 LEACHATE COMPOSITION

The long-term chemical composition of leachate results from a complex interaction of hydrological and biochemical processes occurring within the landfill (Johnson et al., 1999; Kylefors et al., 2003). The former mainly determine the extent of leaching whereas the latter directly affect the major environmental parameters, such as redox potential and pH, which in turn influence the solubility and mobility of heavy metals and organic compounds contained in the waste solid matrix (Johnson et al., 1999; Poulsen et al., 2002). In particular, biodegradation of waste organic matter is among the most important processes determining leachate quality in sanitary landfill (Adhikari et al., 2014; El-Fadel et al., 2002; Modin et al., 2009; Kjeldsen et al., 2002). In fact, the temporal trend of leachate composition is usually related with theoretical phases of the anaerobic process, as shown in Figure 1.1. Specifically, during the aerobic stage (I), which is quite short owing to high oxygen demand of waste relative to the limited amount of oxygen contained in the waste layer, no substantial leachate generation takes place (Heyer and Stegmann, 2001). The following stage (II) is characterised by a drop in leachate pH due to the fast production of volatile fatty acids and high partial pressure of CO_2. As a consequence, high concentrations of BOD_5 and COD (>10000 mg/l and >18000 mg/l, respectively), high BOD_5/COD ratio (>0.5-0.7), relevant concentrations of ammonia (500-1000 mg/l) and inorganic ions (Cl^-, SO_4^{2-},Ca^{2+}, Mg^{2+}, Na^{2+}) are

usually observed in leachates from this phase. Thereafter, leachate pH slowly increases due to the progressive degradation of VFAs (stage III) until reaching a neutral value that allows the stable methanogenic phase to start (stage IV). The increase in pH values during the acidic stage (III) leads to a decrease in solubility of calcium, iron, manganese and heavy metals. Furthermore, the initial high content of sulphates is slowly reduced due to redox potential decrease and metals sulphides are generated. During the stable methanogenic phase (IV), leachate pH is almost neutral and the degradation of organic matter leads to relatively low concentrations of BOD_5 (<100-200 mg/l) and low values of BOD_5/COD ratio (< 0.1-0.2) whereas ammonia may continue to be generated.

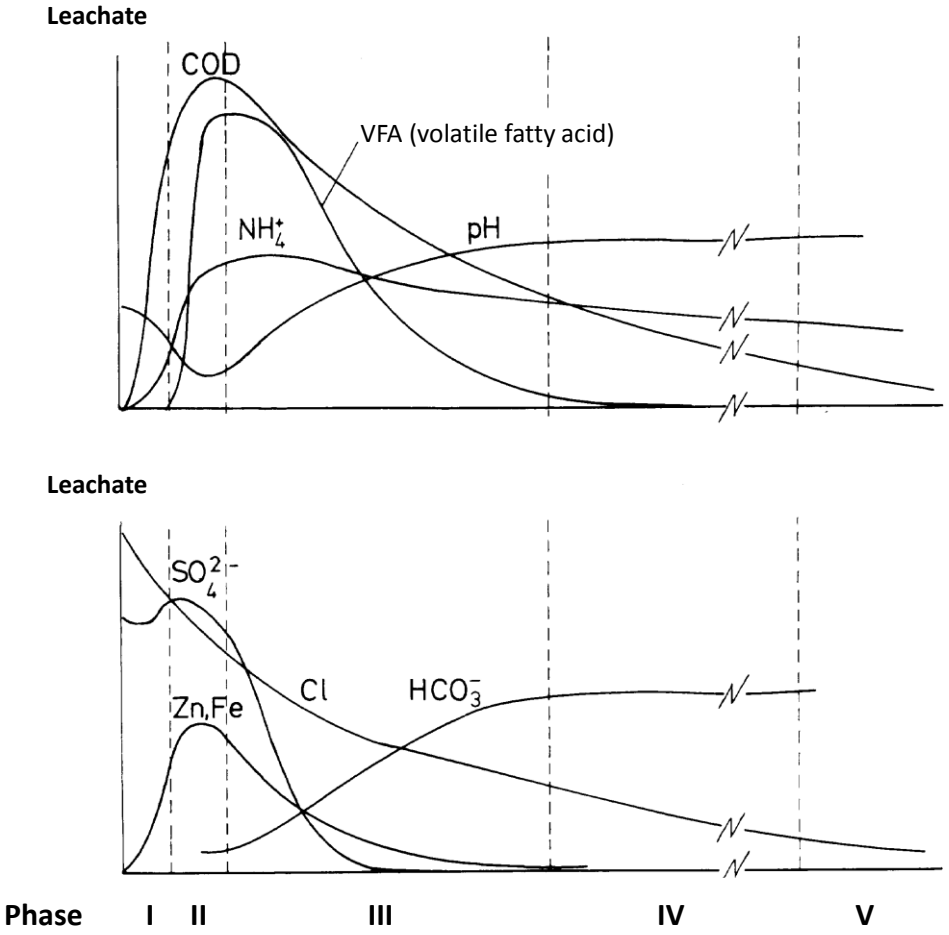

Figure 1.1. Qualitative illustration of leachate composition in landfills. Source: Christensen and Kjeldsen (1989).

Comprehensive dataset on leachate composition correlated to the biological phase based on measurements in actual landfills have rarely been reported in literature (El-Fadel et al., 2002). Recently, Rodriguez et al. (2009) presented field data about leachate characteristics collected from 400 sanitary landfills classified in three different classes, that are acidogenic, intermediate and methanogenic landfills, while providing comprehensive information about waste properties, biogas production and landfill characteristics. They found COD as one of the most discriminating factor between classes, followed by conductivity, total dissolved solids (TDS) and sulphides that may be directly correlated with the evolving of biological processes, as reported in Table 1.1. Similar results can be found in Ehring (1983) and Kylefors et al. (2003); they stated that concentrations of organic compounds (BOD,COD,TOC) as well as Ca, Cl^- Cr, Fe, Mg, Mn, SO_4 and Zn in leachate are determined by the biochemical processes in landfill pointing out striking differences between acidogenic and methanogenic landfills. Hence, the implementation of new waste management strategies and practices, as waste biological pre-treatments before disposal, could have a great impact on chemical characteristics of leachate produced in new landfills, in which only wastes with low organic content or stabilized waste can be disposed of.

Table 1.1. Average values of leachate parameters measured by Rodriguez et al. (2009) in leachates collected from three landfill classes defined as acidogenic, intermediate and methanogenic. Parameters are expressed as mg/l except for pH (dimensionless) and electrical conductivity (μS/cm).

Landfill phase	**Acidogenic**	**Intermediate**	**Methanogenic**
Parameter	*Mean*	*Mean*	*Mean*
pH	5.97	7.49	7.1
BOD_5	24,825	1,995	312
COD	61,265	5,955	732
TDS	579	322	96
VFA	12,027	2,195	316
NH_4^+-N	1,483	937	170
Conducivity	22,509	26,920	3,914
SO_4^-	1135	169	135
Ca^{2+}	3265	367	230
Mn^{2+}	76	3.87	2.82
Fe	819	72	32
Cu	0.13	0.26	1.98
Pb	0.29	0.22	0.17
Zn	32	2.28	5.68

1.3 LANDFILL GAS (LFG) GENERATION PROCESS

Landfill gas (LFG) production within emplaced waste is a result of the anaerobic degradation process of waste organic fraction which involves complex biochemical reactions carried out by various bacteria species, namely hydrolytic, acid forming, acetogenic and methanogenic bacteria. From a qualitative point of view, LFG composition is mainly affected by several physical-chemical factors and changes with time following the typical pattern shown in Figure 1.2.

After an initial aerobic degradation, which occurs for short time period (less than one month), until oxygen contained in deposited waste is completely depleted, the environmental conditions within the landfill body become favourable for the anaerobic process. An initial lag-phase, which may last for several months up to a year (Gregory et al., 2003; Oonk, 2010; US EPA, 2010), is commonly observed in traditional MSW landfills before all biological processes have started up and biogas has being stably generated. Theoretically, the LFG generation process proceeds through four distinct phases. Each of them accounts for the degradation of a different type of compounds, the activity of a specific bacteria group and the formation of different intermediates (Shah et al., 2014). These phases may coexist simultaneously within a landfill, due to the fact that wastes are disposed at different time and are composed of organic substrates with different biodegradability, and are classified as:

- *Aerobic phase (I)* During this initial short stage the aerobic microbes uses the oxygen contained in refuse to produce carbon dioxide and heat.
- *Hydrolysis (II)* During the hydrolysis stage mostly organic compounds are decomposed into soluble monomers and dimers, that are, monosaccharides, amino acids, and fatty acids, through extracellular enzymes produced by appropriate strain of hydrolytic bacteria.
- *Acid phase (III)* The microbial activity during the acid phase includes two distinct stages, that are, acidogenesis and acetogenesis. During the *Acidogenesis* stage, the acidifying bacteria convert water-soluble substances to short-chain organic acids (formic, acetic, propionic, butyric and pentanoic), alcohols (methanol, ethanol), aldehydes, carbon dioxide and hydrogen. As a

consequence, landfill environment becomes strongly acidic. In the *Acetogenesis* the acetate bacteria covert the acid phase products into acetates and hydrogen which may be directly used by methanogenic bacteria and, thus, pH starts to increase.

- *Methanogenesis (IV).* This phase consists in the transformation of the intermediate products formed in the previous stage into methane and carbon dioxide by methanogenic bacteria.. During this stage, gas is produced at a stable rate and composition. This step lasts for long time period, until most of nutrients and organic substrates have been removed from wastes and gas production rate decreases (*maturation, V*).

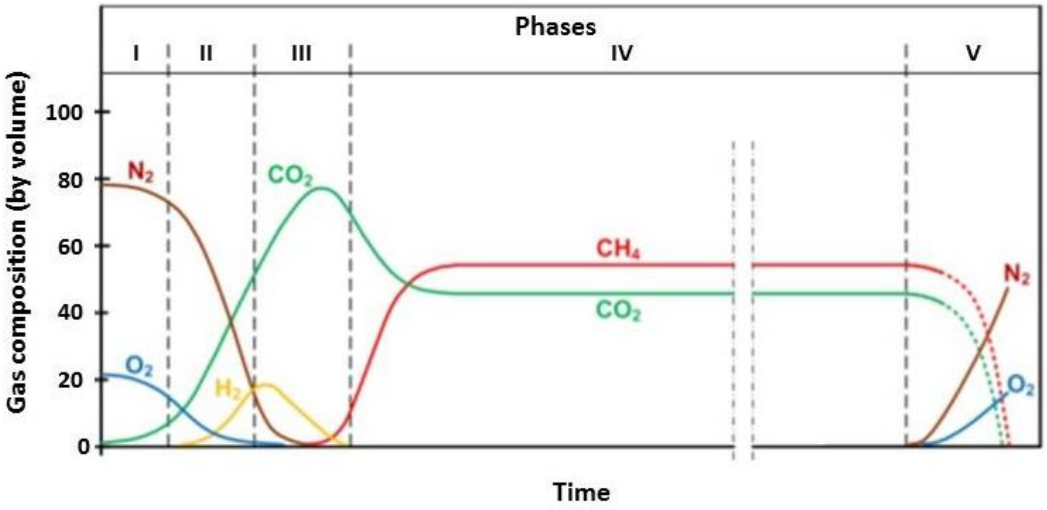

Figure 1.2. Sanitary landfill gas production pattern. Available at www.slideshare.net/HOFSTGAS (accessed on April 2015).

Typically, during the steady methanogenic phase of a MSW landfill, the LFG is mainly composed of methane (45-60 %v/v), carbon dioxide (40-60 %v/v) and tracer compounds (US EPA 2005), such as hydrogen sulphide, hydrogen, carbon monoxide, nitrogen, ammonia, water vapour (<1 %v/v). Nevertheless, the rate and volume of produced LFG, as well as LFG composition (% of methane in biogas) and the duration of each anaerobic phase, depend on several factors (Rawat et al., 2011; Gowing, 2001), that vary from the intrinsic characteristics of emplaced waste (organic content, solubility and degradability of organic matter, particle size) to the environmental condition (pH, temperature, water content, nutrient availability, toxic compounds) and landfill

operation (permeability of intermediate/final cover system, co-disposal of different type of waste, emplacement waste density). It is well documented that pH in the optimal range 6.4-7.5 (Adani et al., 2004; Argun et al., 2008; Fotidis et al., 2012; Lo et al., 2010), enhance the methane emission when the water content in landfill is not limiting. High value of pH would result in increased toxicity due to the shift to higher concentration of ammonia, which is identified as one of the most toxic agent for methanogenic bacteria (Chen et al., 2008; Bernet et al., 2007). On the contrary, low pH values are indicative of the accumulation of volatile fatty acids (VFAs) within the system (Bouallagui et al., 2005; Khalid et al., 2011; Li et al., 2011). VFAs represent the main intermediate products during the initial acidogenic stage of the anaerobic process that are successively converted into methane and carbon dioxide. However, the increasing of VFAs concentration at high level may result in an inhibition of the methanization process, as observed by several authors (Argun et al., 2008; Cabbai et al., 2013). It is also widely recognized that an increase of waste temperature has a positive effect on the microbial growth and activity (Chen et al., 2008; Heyer et al., 2013), thus leading to a faster gas generation process. This implies that gas emissions rates may increase with the increasing landfill height/depth, since the heat transfer is reduced and the average temperature inside the waste body becomes higher (Heyer et al., 2013). Even more, the amount and composition of gas produced is strongly affected by the water content in landfills. Moisture is beneficial for gas yield since it enhances the solute transport of nutrients, the organic matter solubilisation and the microorganism mobilization within microenvironments, as well as dilutes the concentration of inhibitors (Donovan et al., 2010; Mora-Naranjo et al., 2004). Pitchel (2014) and Khalid et al. (2011) reported that the maximum methane production occured at a moisture content of 60 %-80 % (wet weight). However, when water content becomes limiting for the anaerobic process is not completely elucidated and strongly depends on the type of waste. For instance, Heyer et al. (2013) stated that when the moisture content in MBT landfills is lower than 35 % not all the biologically degradable carbon can be mineralized based on field investigation. Similarly, Pommier and Lefebvre (2009) reported a threshold value of waste water content, under which no biodegradation activity is observed, in the range 15 % - 50 % on dry weight basis (which correspond to 13 %-33 % on wet weight). Thus, in very dry climate or when capping system with a

low permeable layer (geomembrane) are installed, the possibility to enhance biological process may be drastically reduced due to the limiting available water (MBT waste usually has own water content below 35%). On the other hand, higher infiltration rate within the landfill body, in case of absence/damage of temporary/final cover systems, may reduce methane production due to the generation of large amount of leachate and to the wash out of substrates and nutrients which are essential for microbial activity (Mudau, 2012). Finally, the particle size of materials influences the process kinetic; it is widely accepted that particle size reduction results in higher methane generation rate due to the high surface area to mass ratio (Esposito et al., 2012; Lesteur et al., 2010) whereas the effect on biogas yield is not completely proved (Nopharatana et al., 2007; Mshandete et al., 2006).

1.4 RESEARCH AIMS AND CONTENTS

Up to now several mathematical models have been developed to evaluate landfill emissions over time. Some of them are mainly focused on the estimation of gas generation and are commonly based on a first order decay model. Other models aim at evaluating exclusively the leachate production in landfills by applying the water balance method without considering waste degradation. Very few, instead, implement an integrated approach which simulates jointly hydrological and biological processes and their mutually dependence. However, these complex models use a fine detailed sequence of calculation and thus require unrealistic amounts of data input that are not usually available at landfill sites, leading to winding calibration processes. In this context, the main objective of this Ph.D. thesis was to develop a simplified model for quantitative estimations of gas and leachate volumes during the lifetime of a landfill, that, based on simplifying analytical and empirical equations, allows to represent the main processes naturally occurring in landfills while limiting the input data requirements. Model architecture, principal features, basic equations and assumptions, as well as some practical applications to real MSW landfill sites are presented in **Chapter 2.** As for the qualitative analysis and modelling of landfill emissions over time, this aspect still represents a challenge for modellers due to the physical, biological and geochemical complexity of a landfill system. Hence, a laboratory methodology was

applied to mechanically biologically treated (MBT) waste in order to gain new insight on the key factors governing contaminants release from this type of residues which, nowadays, constitute the main flow waste disposed of in Italian landfills. In fact, MBT plants represent the main municipal waste management strategy to treat waste before landfilling in central Italian Regions (ARPA Lazio, 2013) in order to meet the new European legal requirements (Landfill Directive 1999/31/EC). Indeed, owing to the relatively recent introduction of the MBT plants within the waste management system, very few field data on long term behaviour of this type of waste in landfills are available. In fact, up to now, leachate and gas emissions from MBT waste have rarely been measured on a full-scale MBT landfill (Harborth et al., 2013). The current knowledge results from several laboratory studies aimed at determining the fundamental characteristics of MBT waste, with regards to its physical-chemical properties (e.g. volatile solids, total and dissolved organic carbon, heavy metals content) and the biological characteristics (Bayard et al., 2010; De Gioannis et al., 2009; Di Lonardo et al., 2014; Ponsà et al., 2008). Instead, very few studies dealt with the heavy metals mobility from this type of waste under different environmental conditions. Hence, the leaching behaviour of MBT waste was assessed by combining pH static-batch test, pH dependent tests and dynamic up-flow column percolation experiments, in order to highlight the effect of pH and liquid to solid ratio (L/S) on the compounds release. Results of this study, shown in **Chapter 3**, were used to develop a simplified screening model for metals release which may provide useful indications for the evaluation of long-term leachate composition expected in MBT landfills. Finally, in order to complete the study on MBT waste environmental behaviour, the gas generation from MBT waste was investigated (**Chapter 4**), by performing anaerobic batch experiments under different operative conditions. Specifically, incubation tests were performed at a wide range of water contents and temperatures in order to simulate different landfill management options (dry tomb or bioreactor landfills) and to deduce a reasonable range for the key factors required in the gas production modelling.

CHAPTER 2

DEVELOPMENT OF A SCREENING MODEL FOR LANDFILL EMISSIONS ASSESSMENT

This chapter is partially taken from:

Pantini S., Verginelli I., Lombardi F. (2014). A new screening model for leachate production assessment at landfill sites. *International Journal of Environmental Science and Technology*, 11, 1503-1516.

Grugnaletti M., Pantini S., Verginelli I., Lombardi F. (2015). An easy-to-use tool for the evaluation of leachate production at landfill sites. In preparation.

Pantini S., Law H.J., Verginelli I., Lombardi F. (2013). Predicting and comparing infiltration rates through various landfill cap systems using Water-Balance models – A case study. *Proceedings of the ISWA 2013 conference*. Florence.

2.1 BACKGROUND

As discussed in the introduction, the pollutant load to the environment is strictly dependent on the quantity and the quality of the water that percolates through the landfill and on the amount of gas generated from waste degradation (Kale et al., 2010; Papadopoulou et al., 2007; Renou et al., 2008) that, in turn, are strongly related to the chemical characteristics, physical properties and degradability of the emplaced waste. Hence, for a correct design and management of landfill systems, reliable emission forecasts are required (Oonk and Boom, 1995; Thompson et al., 2009). To this end, an useful tool is represented by simulation models based on the water-balance method. However, the development of a model which is suitable to different specific landfills contexts is complex (De Cortázar and Monzón, 2007; Han et al., 2011) because of the influence of site-specific factors and complex interaction of several processes on leachate generation. Basically, the water balance method consists of computing all inputs and outputs of water within the landfill system as well as moisture changing due to different processes that lead to water consumption/release over time. The main assumption of this method is that leachate is generated when the waste water content exceeds its field capacity. By definition, field capacity is the maximum amount of moisture that a porous media can retain against gravitational forces without producing downward percolating seepage. However, some studies have highlighted that leachate generation can occur even when waste moisture content is below field capacity due to effects of fast flow channelling through macro-pores and spatial heterogeneity (Bendz et al., 1998; Fellner and Brunner, 2010).

In the last decades several mathematical models have been developed to simulate the generation and transport of leachate and gas in landfills. For instance, the first attempts to evaluate leachate generation using simplified water balance approaches have been developed by Straub and Lynch (1982), Korfiatis et al. (1984) and El-Fadel et al. (1997). Demirekler et al. (1999) introduced a three dimensional mathematical model to estimate the moisture and leachate distribution through the landfill, accounting for the effects of variable hydraulic conductivity with overburden pressure and time dependent landfill configuration. De Velásquez et al. (2003) proposed a model based on the water balance method, in order to evaluate the total leachate likely to be produced, introducing

the interaction effects between different wastes cells. Currently, the most widely used package is the Hydrologic Evaluation of Landfill Performance, HELP (Schroeder et al., 1994), even though in the last years its use is questioned as a number of limitations have been detected (Berger, 2000; De Cortázar et al., 2003; Murthy et al., 2009; Oni, 2010; São Mateus et al., 2012; Shariatmadari et al., 2010). The HELP model has been designed to conduct water balance analyses of open, partially closed and fully closed landfills (Schroeder et al., 1994) but actually it does not allow to reproduce the progressive disposition of waste, the aging of materials and other important processes that affect leachate generation (e.g. waste biodegradation, waste compression and consolidation, change in waste physical-mechanical properties). Indeed, the HELP model assumes constant parameters and simulates the leachate transport and generation after all solid wastes are placed and stability conditions of refuse are reached. In order to overcome these limitations several integrated models have been developed (e.g. De Velásquez et al., 2003; Kindlein et al., 2003; White et al., 2004; Zacharof and Butler, 2004; De Cortázar and Monzón, 2007; São Mateus et al., 2012) that consider both leachate and gas generation due to biological transformation of organic matter, simulating jointly hydrological and degradation phenomena. Zacharof and Butler (2004) presented a mathematical model that simulates water transport and biochemical processes, performing a parameter perturbation model sensitivity analysis; they found a high sensitivity to key parameters and a high uncertainty associated to input data. De Cortázar and Monzon (2007) developed MODUELO, one of the most complete option for water balance modelling, which estimates the leachate flow and organic pollutants as a consequence of the water flowing through the waste and the degradation of organic matter in the landfill. Fellner and Brunner (2010) presented a mathematical model that pointed out the importance of the heterogeneity of the flow within landfill volume, due to the highly non-uniformity of waste mass and to the presence of preferential pathways. Very recently, São Mateus et al. (2012) presented an attempt to model the water balance in a Brazilian MSW landfill, focusing on aspects such as the effects of the waste compression and the distinction of the stored water between free water and water attached to the waste. All the above mentioned models differ by the underlying assumptions, the conditions at which they can be applied and the amount of input data required. Specifically, the more sophisticated models (e.g. Fellner and Brunner, 2010;

De Cortázar and Monzon, 2007) account in details for the physical and biochemical complexity of landfill system but they however require massive amounts of data, most of them not easily available at landfill sites. This may lead to a winding calibration process without a clear improvement in simulation results when compared to field data (Zacharof and Butler, 2004). On the contrary, simplified approaches (e.g. De Velásquez et al., 2003; São Mateus et al, 2012), may fail to represent the key processes leading to less reliable leachate prediction (Zacharof and Butler, 2004). Therefore, it is necessary to find a good compromise between the need to limit data requirements and the need to represent all the fundamental processes occurring in landfills. In view of such need, a new landfill screening model (*Landfill Water Balance* model, *LWB*) was developed. The model, based on simplified analytical and empirical equations, provides a quantitative estimation of gas and leachate volumes during the lifetime of a landfill, taking into account for the main factors and processes affecting leachate generation (see Table 2.1) while limiting the input data requirements.

Table 2.1. Main features of the LWB model and comparison with other available models. Y:Yes. N:No. NS: Not specified

Features	**HELP (1994)**	**Sao Mateus et al. (2012)**	**MODUELO (2007)**	**De Velásquez et al. (2003)**	**LWB (2014)**
Operative stage (progressive waste disposal)	N	NS	Y	Y	Y
Aftercare period	Y	Y	Y	Y	Y
Landfill discretization	Y	Y	Y	Y	Y
Vertical flow	Y	Y	Y	Y	Y
Horizontal flow	Y	N	Y	N	Y
Multilayer capping system	Y	NS	Y	NS	Y
Different waste type	Y	Y	Y	Y	Y
Waste initial moisture	Y	Y	Y	Y	Y
Potential evapotranspiration	Y	Y	Y	Y	Y
Actual evapotranspiration	Y	Y	Y	Y	Y
Surface runoff	Y	Y	Y	Y	Y
Retained/released water by cover soil	Y	Y	N	Y	Y
Water storage capacity	Y	Y	Y	Y	Y
Waste compression	N	Y	Y	Y	Y
Released water	N	Y	Y	Y	Y
Biodegradation	N	Y	Y	N	Y
Biogas production	N	Y	Y	N	Y
Wastes mass reduction due to biodegradation	N	Y	N	N	Y
Biotic consumption	N	Y	N	N	Y
Vapour losses	N	Y	N	N	Y
Temporal changes of waste properties	N	Y	Y	Y	Y

The LWB model has also been coded in MATLAB language and integrated within a graphical interface that helps the user to easy handle the input and output data (Grugnaletti et al., 2015). In this chapter, after a brief introduction of the model architecture, different applications to some hypothetical scenarios and to four real landfill sites are presented. Specifically, the first simulations aimed at highlighting the effects of waste compression and biodegradation on leachate production. To this end, the simulation results obtained by applying the LWB model are compared with those returned by HELP which neglects both these processes. Thereafter, applications of the developed model to four different landfill sites are presented; in this section, simulated leachate volumes were compared with the landfill measurements of the leachate flows in the final collection pipes in order to evaluate the accuracy of model predictions. Finally, the applicability of the proposed model for the analysis of closed landfills was evaluated by simulating three different alternative capping systems and by comparing the results with those returned by HELP, since no field data were available for the analysed landfill site.

2.2 MODEL DEVELOPMENT

2.2.1 LANDFILL DISCRETIZATION

The developed model accounts for the progressive variation of landfill configuration, during the operative stage, as well as for temporal changes of waste hydraulic and physical-mechanical properties since they have been emplaced. To simulate the schedule of waste disposition during landfilling, the overall landfill volume is discretized in elements of waste forming vertical cells and horizontal layers (Fig. 2.1). For each cell the number of layers *k*, the surface area, the thickness, the progressive time of layers disposal, the hydrological properties and type of wastes (e.g. municipal solid wastes, mechanically-biologically treated waste, MBT scraps, etc.) can be defined. The implementation of such a landfill discretization enables the incorporation of spatial changes in physical and hydraulic properties of the landfill and thus allows to represent the spatial and temporal leachate distribution. For the aftercare period, further

information related to the capping system (i.e. vegetation and soil cover, lateral drain layers, low permeability barrier soils and geomembrane liners) can be introduced.

2.2.2 WATER BALANCE OF OPEN LANDFILLS

The developed model provides a quantitative estimation of leachate volumes by applying the water balance to each layer *k* composing the single cell, at every time *t*, as follows:

$$\Delta W(t,k) = \begin{cases} P(t) - R(t) - ET_r(t) + W_{rel}(t,k) - W_{ret}(t,k) - W_{bio}(t,k) - W_{vap}(t,k) - L_{out}(t,k) & \text{for exposed layer} \\ L(t,k+1) + W_{rel}(t,k) - W_{ret}(t,k) - W_{bio}(t,k) - W_{vap}(t,k) - L_{out}(t,k) & \text{for covered layer} \end{cases} \quad (2.1)$$

Where ΔW is the change in water volume (m^3), P the rainfall (m^3), R the surface runoff (m^3), ET_r the actual evaporation (m^3), $L(t,k+1)$ the leachate incoming from the upper layer (m^3), W_{rel} and W_{ret} the released and retained water from waste (m^3), W_{bio} the biotic consumption (m^3), W_{vap} the loss of water as vapour in biogas (m^3), and L_{out} the leachate (m^3) that passes through the bottom liner (different from zero only for the bottom layer). Note that in Eq. (2.1) a different computation for the change in water volume is performed if the layer *k* is exposed to atmosphere or covered by another layer *k+1* (see Fig. 2.1).

When ΔW obtained from Eq. (2.1) is positive, it means that leachate is produced (L); otherwise ΔW represents a reduction of the moisture content in the waste (ΔC):

$$\begin{cases} L(t,k) = \Delta W(t,k) & \text{if } \Delta W(t,k) \geq 0 \\ \Delta C(t,k) = |\Delta W(t,k)| & \text{if } \Delta W(t,k) < 0 \end{cases} \quad (2.2)$$

Here below a short description of the different terms considered in the water balance (Eq. 2.1) is reported.

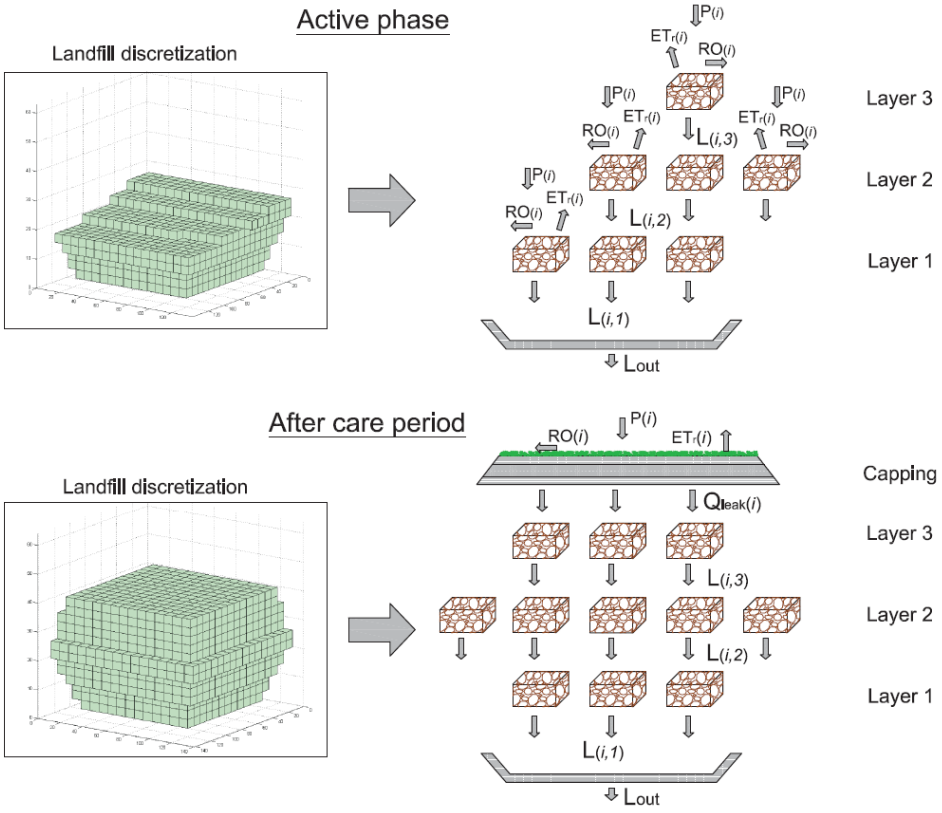

Figure 2.1. Example of water balance application and landfill discretization in three layers and five cells for the active phase and for the aftercare period.

Runoff and evaporation/ evapotranspiration

Runoff and actual evapotranspiration are evaluated applying the water balance to the evaporative layer of the exposed material on daily scale, taking into account for the actual moisture content of this layer. Specifically, runoff is computed using the well known SCS Curve Number method (USDA, Soil Conservation Service, 1972), with the adjustment of curve number (CN) for the type of material, the antecedent moisture condition (dry, average condition, saturated)[1] , the surface slope and the vegetation class. In analogy with the HELP model, firstly, an initial average CN value is computed from the CN curves represented in Fig. 2.2, depending on the textural class of the material and the type of cover (bare ground, fair stand of grass and good stand of grass). Up to now, 5 soil textural classes are implemented within the software (Fig. 2.2): coarse sand

[1] Dry condition: water content at wilting point. Average condition: water content between wilting point and field capacity. Saturated condition: water content at field capacity.

(soil texture number 1), loamy sand (soil texture number 5), loam (soil texture number 9), clay loam (soil texture number 11) and clay (soil texture number 15). The initial average CN value can be directly defined by the user or computed by the model using the mathematical formulation of the selected CN-curve for the specific texture number and vegetation cover (in Figure 2.2 a graphical representation of model computational procedure is represented).

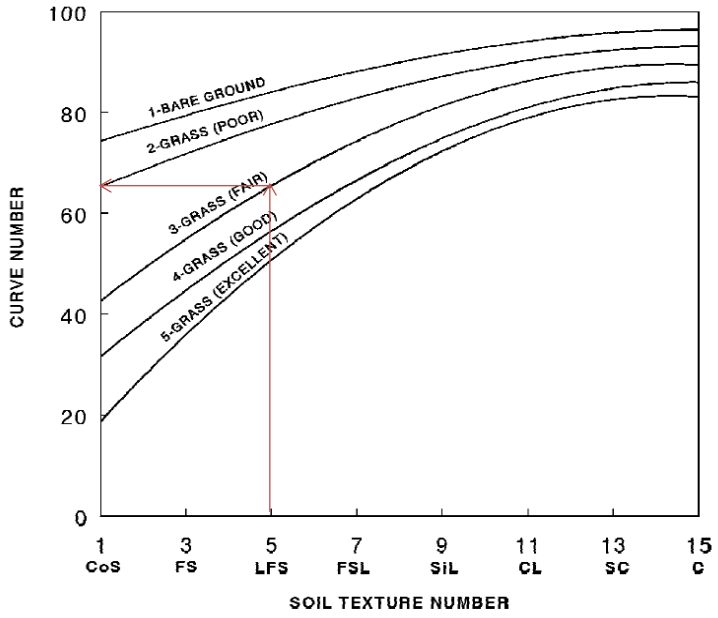

Figure 2.2. Relation between SCS Curve Number and soil texture number for various type of vegetation cover. Source: Schroeder et al. (1994).

Since the initial CN value refers to an average moisture condition of the surface layer (water content between wilting point and field capacity), thereafter, this value is corrected considering the antecedent moisture condition of the layer and its slope, as reported in Schroeder et al. (1994). The corrected CN value is then used to determine the potential maximum water retention of the soil and the runoff depth through the empirical formulations proposed by USDA SCS (1972). Note that the curve number CN may theoretically range from zero, for highly permeable flat soil (all rainfall will infiltrate and no runoff will be generated), to one hundred, for very low permeable soil (all rainfall will become runoff) but, in reality, it will be somewhere in between (USDA SCS 1972).

Different models are implemented in the tool in order to compute potential evapotranspiration/evaporation, which can be selected depending on the weather data available and the model requirements. The actual evapotranspiration is then calculated using the approach proposed by Allen et al. (1998), which accounts for the moisture availability and correction for the crop, if present. Table 2.2 reports a summary of the different models implemented in the tool and the required parameters for the estimation of R and ET_r. For more details about the computational approach, mathematical formulations, assumptions and input data required in the estimation of potential and actual evaporation/evapotranspiration readers are directed to Thornthwaite (1948), Hargreaves and Samani (1985), Allen et al. (1998), Priestley and Taylor (1972), Makkink (1957) and Turc (1961).

Table 2.2. Summary of models implemented and input data requirements for the computation of actual evaporation /evapotranspiration and runoff.

Term	Model	Required parameters
Evaporation/ Evapotranspiration (ET_r)	- Potential evapotranspiration. Seven models incorporated: Thornthwaite (1948), Hargreaves and Samani (1985), FAO Penman-Monteith (Allen et al., 1998), Priestley and Taylor (1972), Makkink (1957), Turc (1961). - Actual evapotranspiration: Evaporative layer / Root layer - water balance with crop coefficient approach, as proposed by Allen et al. (1998). Daily computing.	- Weather data - Potential evapotranspiration model - Evaporative zone depth (for waste and/or soil) - Latitude of landfill
Runoff (R)	SCS Curve Number method (USDA, Soil Conservation Service, 1972) modified with CREAMS approach (Knisel et al. 1980). Snowmelt term (Jenicek et al., 2012). Daily computing.	- Automatic calculation of Curve Number CN (based on waste/soil characteristics) or user's fixed CN

Released and retained water by wastes

Changes in water content, ΔU (m^3), are due to temporal variation of hydraulic retention capacity of waste layers as well as to the waste water content in excess/defect compared to the retention capacity, CS_{max}(m^3):

$$\Delta U\ \ t,k\ \ = W_w\ \ t,k\ \ - CS_{\max}\ \ t,k \tag{2.3}$$

Where W_w is the initial water content of waste (m^3) at the time *t*:

$$W_w\ \ t,k\ \ = \begin{cases} W_{res}\ \text{(t-1,k)} & \text{unsatured} \\ \text{CS}_{\max}\text{(t-1,k)} & \text{saturated} \end{cases} \tag{2.4}$$

W_{res} is the residual water content (m^3) at the previous time t_{i-1} which is equal to the final retention capacity (CS_{max}) if the layer has become saturated. Otherwise, leaching does not occur and water is stored within wastes.
The released (W_{rel}) and retained water (W_{ret}) reported in Eq. (2.1) are calculated from Eq. (2.3) as follows:

$$\begin{aligned} W_{rel}\ \ t,k\ \ &= \max\ \ \Delta U\ \ t,k\ \ ;0 \\ W_{ret}\ \ t,k\ \ &= \left|\min\ \ \Delta U\ \ t,k\ \ ;0\right| \end{aligned} \tag{2.5}$$

The water retention capacity of each layer, $CS_{max}(k)$, at any time *t* can be estimated as:

$$CS_{\max}\ \ t,k\ \ = FC_w\ \ t,k\ \ \cdot V_w\ \ t,k \tag{2.6}$$

Where V_w (t,k) is the waste volume (m^3) and FC_w (t,k) the waste field capacity (% v/v) both varying with time due to waste compression and biodegradation processes.
The field capacity of the waste depends on the porosity *n* (% v/v) and the effective stress σ_s (kPa) induced by upper layers (De Cortázar et al., 2002); the former can be evaluated using the followings expressions (Stoltz et al., 2010):

$$\Delta e\ \ t,k\ \ = C_c \cdot \log \frac{\sigma_s\ \ t,k}{\sigma_S\ \ t-1,k} \tag{2.7}$$

$$n\ \ t,k\ \ = \frac{e\ \ t,k}{1+e\ \ t,k} \tag{2.8}$$

Where *e* is the void ratio (% v/v) and C_c is the compression index (adm). The compression index C_c shown in Eq. (2.7) is a parameter commonly used in engineering practice to characterize the compressibility of a porous medium (Chen et al., 2009; Durmusoglu et al., 2006; Stoltz et al., 2010). Namely, C_c (also indicated as primary compression index) is defined as the slope of the compression curve that represents the trend of void ratio as a function of the applied vertical pressure, experimentally determined from confined compression test. A wide literature range exists for the MSW waste compression index (0.02–7.5), since it strongly depends on waste composition and properties such as the percentage of incompressible material, the organic matter content, the initial waste moisture, the unit weight, the void ratio and waste age (Bareither et al., 2012; Chen et al., 2009; Stoltz et al., 2010).

It is worth noting that the effect of biodegradation on waste compression is implicitly considered in the LWB model in relation to gas formation. Specifically, the reduction in waste solid mass, due to the conversion of organic matter in CH_4 and CO_2, was evaluated following the same trend of gas production. Hence, mass losses could be expressed by a first order decay model, Gompertz model or triangular model and used to compute the residual volume of waste dry matter at the time step *t* (assuming average constitutive dry densities of each fractions). The sum of this contribution and the residual pore volume allows to evaluate the residual total waste volume $V_w(t,k)$ shown in Eq. (2.6).

Using Eqs. (2.7), (2.8) the temporal trend of waste field capacity is estimated as follows:

$$FC_w\ t,k\ = FC_0\ t,k\ + n\ t,k\ - n_{in} \tag{2.9}$$

Where FC_{w0} is the initial waste field capacity (% v/v) and n_{in} the initial waste porosity (% v/v).

Alternatively, the waste field capacity can be evaluated as a function of the applied stress through the formulation proposed by De Cortázar et al. (2002):

$$FC_{w}\ t,k\ = FC_{0} -\ FC_{0} - FC_{\lim}\ \cdot \frac{\sigma_{s}\ t,k}{CC_{c} + \sigma_{s}\ t,k} \tag{2.10}$$

Where FC_{lim} is the waste field capacity (% v/v) corresponding to the infinite pressure on the layer (assumed equal to the waste wilting point) and CC_c is an empirical parameter (kg/m^2) that defines the field capacity variation with mean stress σ_s. CC_c values proposed by authors are in the range 5,000-30,000 kg/m^2 (De Cortázar et al., 2002; Sirini et al., 2010) but are closely related to the nature and composition of waste. Note that the empirical constant CC_c only links the field capacity to the applied stress σ_s but it is somehow indicative of the compressibility behaviour of a waste. Indeed, for a fixed applied stress, the higher CC_c value is, the lower field capacity reduction is; hence, small changes in the final waste porosity and volume are associated to higher CC_c that could be considered representative of a low compressible waste. For instance, assuming a waste layer with the initial characteristics of FC_0=40 % and FC_{lim}=7 % that, at the time *t*, is subjected to a vertical stress of 40 kPa (4080 kg/m^2) due to the emplacement of an upper waste layer (height: 4.5 m, density: 900 kg/m^3), the final waste field capacity FC_w will be 25.2 % (for CC_c=5,000 kg/m^2) or 36% (for CC_c=30,000 kg/m^2) according to Eq. 2.10.

However, CC_c should not be confused with the compression index C_c shown in Eq. 2.7;. in fact, the higher C_c is, the higher the reduction in void ratio is, leading to a lower final volume of the waste layer. Conversely, higher CC_c values implies smaller reduction in waste porosity.

The retention capacity shown in Eq. (2.6) is also related to waste volume V_w (m^3), which depends on the compression effects that reduces the porosity, as well as on waste biodegradation, that reduces the residual material volume, V_m:

$$V_{w}\ t,k\ = n\ t,k\ \cdot \frac{V_{m}\ t,k}{1 - n\ t,k} + V_{m} \tag{2.11}$$

Finally, the mean pressure σ_s (kPa) in Eqs.(2.7), (2.10) is calculated at the average height of the layer and it depends on the landfill profile, the waste residual dry mass and the water content at the time *t*:

$$\sigma_s\ t,k\ = \frac{0.5\left[M_{H2O}\ t,k\ + M_{dry,w}\ t,k\ \right] + M_{soil}\ t,k}{A\ k} + \sum_{j=1}^{N-j} \frac{M_{tot}\ t,k+j}{A\ k} \quad (2.12)$$

Where $M_{dry,w}$ (kg) is the waste dry mass, which decreases with the degradation process development; M_{H2O} (kg) is the water mass contained in the *k* layer at the time *t*, M_{soil} (kg) is the mass of the intermediate soil cover and the second term on the right side is the total mass of the upper layers at time *t*.

Biotic consumption and vapour losses

Water losses due to biotic consumption and vapour in biogas are directly related to the volume of gas produced at time *t*, *Q(t,k)*. The temporal trend of gas production *Q(t,k)* is computed based on the theoretical value, which is related to the reaction stoichiometry of the readily (RBOF) and slowly (SBOF) biodegradable fraction contained in wastes:

$$\begin{cases} \text{RBOF} : C_a H_b O_c N_d + \alpha^{RBOF} \cdot H_2O \rightarrow \beta CH_4 + \gamma CO_2 + \delta NH_3 \\ \text{SBOF} : C_{a'} H_{b'} O_{c'} N_{d'} + \alpha^{SBOF} \cdot H_2O \rightarrow \beta' CH_4 + \gamma' CO_2 + \delta' NH_3 \end{cases} \quad (2.13)$$

To describe the temporal trend *Q(t,k)* of landfill gas generation the modified triangular model (Tchobanoglous et al., 1993), the exponential model based on FOD equation (Mor et al., 2006) and the modified Gompertz model (Lo et al., 2010) can be used, as described in **Section 2.2.4.**

Hence, water biotic consumption (m^3) at the time step *t* is computed as follows:

$$W_{bio}\ t,k\ = \alpha^{RBOF} \frac{PM_{H2O} \cdot \%RBOF \cdot M_w}{PM_{RBOF} \cdot \rho_{H2O}} \cdot \frac{Q_{RBOF}\ t,k\ \Delta t}{V_{gas,RBOF}} + \alpha^{SBOF} \frac{PM_{H2O} \cdot \%_M SBOF \cdot M_w}{PM_{SBOF} \cdot \rho_{H2O}} \cdot \frac{Q_{SBOF}\ t,k\ \Delta t}{V_{gas,SBOF}} \quad (2.14)$$

And vapour losses (W_{vap}) are calculated by assuming gas saturation condition (i.e. u_r =1):

$$W_{vap}\ \ t,k\ = \left(\frac{PM_{H2O} \cdot P_{v,sat}}{R_g \cdot T_L \cdot \rho_{H2O}} \right) \cdot\ Q_{RBOF}\ \ t,k\ \cdot \Delta t + Q_{SBOF}\ \ t,k\ \cdot \Delta t \tag{2.15}$$

Where α^{RBOF} (mol H_2O/mol RBOF) and α^{SBOF} (mol H_2O/mol SBOF) are respectively the stoichiometric water consumption of RBOF and SBOF, PM_{H2O}, PM_{RBOF} and PM_{SBOF} the molecular weight (g/mol) of water, RBOF and SBOF, M_w the emplaced waste mass in the layer (kg), $V_{gas,RBOF}$ and $V_{gas,SBOF}$ (m^3) the theoretical amount of biogas generated by RBOF and SBOF, Q_{RBOF} and Q_{SBOF} (m^3/y) the gas flow by RBOF and SBOF at the time t, ρ_{H2O} the density of water (kg/m^3), $\%_{RBOF}$ and $\%_{SBOF}$ the percentage of biodegradable mass fraction in waste (kg RBOF/kg waste), R_g the universal gas constant (8314 m^3·Pa/K·kmol), T_L the temperature inside the landfill (308 K) and Δt the step length (e.g. 1 month or 1 year). It should be noticed that the gas flow Q_{RBOF} and Q_{SBOF} can also be corrected using a formation factor ζ (Mor et al., 2006) to take into account for unfavourable conditions inside the landfill, as shown in **Section 2.2.4**.

Leakage through bottom liner

Leakage, L_{out}(m^3), through the composite bottom liner, which is typically composed by a drainage layer of sand/gravel, HDPE geomembrane and a clay layer, may be computed assuming that the geomembrane governs the flow rate through the composite barrier and the validity of Darcy's law:

$$\mathrm{L}_{out}\ (t,k) = S_b \cdot \left[K_g \cdot \frac{\Delta H(t,k) + s_g}{s_g} + K_c \cdot \eta \cdot \frac{\Delta H(t,k)}{s_g} \right] \tag{2.16}$$

Where S_b is the bottom area of landfill (m^2), K_c the hydraulic conductivity of clay (m/s), K_g the equivalent hydraulic conductivity of geomembrane (m/s), s_g the geomembrane thickness (m), η the percentage of cracked of the geosynthetic sheet (adm), ΔH the water head (m), which depends on the volume of leachate produced and the efficiency of leachate extraction systems. A deeper explanation of all the parameters shown in Eq.

(2.16) is presented in the next section since leakage through the bottom liner system is substantially equivalent to Eq. 2.21.

2.2.3 WATER BALANCE OF CLOSED LANDFILLS

The aftercare period of a landfill starts when the final cover (*capping*) is realized. The main task of a surface cover system is to minimize the infiltration of rain water into wastes, promoting surface water runoff, evapotranspiration and lateral drainage, and thus reducing leachate production and contaminants transfer (Laner et al., 2011; Schnabel et al. 2012; Venkatraman et al., 2011). To ensure isolation of waste body against surface water infiltration, different type of capping systems can be designed, which vary from a simple soil cover to a multiple-barrier layers of natural and geosynthetic materials (Kampf and Montenegro, 1997), depending on the standard regulatory requirements. The simplest configuration consist of either a geomembrane (GM), a compacted clay liner (CCL) or a geosynthetic clay liner (GCL), that involves a thin layer of bentonite clay between two geotextiles. Nowadays, composite liners (CLs), which combine two or more of these components, have become widely used in solid waste and hazardous waste landfills (Foose 2010; Giroud et al. 1992). Alternative configurations for composite liners include, for example, a GM over a CCL, a GM over a GCL or a GM over a GCL over a CCL (Barroso et al. 2006). Depending on the specific configuration realized and the hydrology of the site, the degree of protection may significantly vary. Hence, water balance analysis of the composite liner is useful in order to estimate its efficiency in reducing infiltration rates or compare alternative designs and/or optimize a specific capping system based on cost-benefit considerations.
Different type of capping systems can be simulated in the LWB model, through the definition of the properties of each natural/artificial material involved. Basically, the model considers the resistance exerted to the water flow by each layer composing the cover system and assumes that the percolation rate is determined by the lower permeable layer. The general formulation of the water balance applied to a cover system is:

$$Q_{\text{inf}}\ \ t,k\ + Q_{lat}\ \ t,k\ = Q_{u}\ \ t,k\ + Q_{leak}\ \ t,k \tag{2.17}$$

Where Q_{inf} is the effective infiltration (m^3) in the surface layer of the cover (computed as *P(t)- R(t) - ETr(t)*), Q_{lat} and Q_u are the incoming and out-coming horizontal flow in the drainage layer (m^3) and Q_{leak} is the water flow infiltrating in waste (m^3).
Incoming water (Q_{lat}) corresponds to the drained flow coming from the adjacent layer ($Q_{u,ad}$):

$$Q_{lat}(t,k) = Q_{u,ad} \quad t \tag{2.18}$$

Out-coming horizontal flow in the drainage layer, Q_u (m^3), which moves away without infiltrating in the underlying layers, is computed through Darcy's equation as a function of the distance between the cell and the water collection system, D_c(m), the hydraulic conductivity of drain, K_d (m/s), the water head, ΔH (m) and the cell-size along orthogonal direction to the main direction of flow, B (m):

$$\mathrm{Q}_u(t,k) = K_d \cdot \frac{B(t,k)}{D_c(t,k)} \cdot \frac{\Delta \mathrm{H}^2(t,k)}{2} \tag{2.19}$$

Water flow, Q_{leak} (m^3) that leaks from the cover and infiltrates in the wastes layer is computed differently depending on the configuration of the cover system. Specifically, if the capping is composed of a natural soil barrier (i.e. no geosynthetic sheet), as compacted clay, $Q_{leak,c}$ is calculated through Darcy's equation depending on the hydraulic conductivity of clay, K_c (m/s), the water head, ΔH (m) and the clay thickness, s_c(m):

$$\mathrm{Q}_{leak,c}(t,k) = K_c \cdot \frac{\Delta H(t,k) + s_c}{s_c} \cdot \mathrm{A} \quad k \tag{2.20}$$

Leakage through a composite liners including a GM is mainly due to the advective flow through geomembrane holes, since this component is essentially impervious to water diffusion (Katsumi et al. 2001, Foose 2010, Rowe 2012). Nevertheless, leakage $Q_{leak,g}$ through GM is computed accounting for both diffusive flux through geosynthetic

material (first term on the right side) and the advective flow through pinholes and installation defects of geosynthetic sheet (second term on the right side):

$$Q_{leak,g}\ (t,k) = K_g \cdot A_g(t,k) \cdot \frac{\Delta H(t,k) + s_g}{s_g} + K_c \cdot \eta \cdot A_g(t,k) \cdot \frac{\Delta H(t,k)}{s_g} \qquad (2.21)$$

Where K_g is the equivalent geosynthetic hydraulic conductivity (m/s), A_g the intact area of geosynthetic (computed through the percentage of cracked of the geosynthetic sheet η) and s_g the sheet thickness (m). The percentage of cracked of the geosynthetic sheet η is computed multiplying the defects frequency (number of defects per hectare) by the area of each defects (m^2).

Note that permeation through a geomembrane was described through Darcy's formulation, even though it is not physically valid for water transport through an intact geomembrane. However, this approach can be adopted so long as an equivalent hydraulic conductivity K_g is utilized (Schroeder et al., 1994; Giroud and Bonaparte, 1989) that should be derived from interpretation of water vapour transmission test. Specifically, Giroud and Bonaparte (1989) have experimentally determined K_g values through a combination of Fick's and Darcy's laws results in a relationship between geomembrane water vapour diffusion coefficient, obtained from vapour transmission tests, and the equivalent geomembrane hydraulic conductivity K_g.

In Table 2.3, a list of K_g values determined by Giroud and Bonaparte (1989) for different types of polymers and geomembrane thickness based on the aforementioned experimental procedure is reported.

It is also worth noting that leakage through the clay layer located directly beneath the geomembrane is estimated assuming vertical Darcian flow only in the clay area below the defects. Schroeder et al. (1994) indicated that this computation may represent a lower bound estimate of leakage for perfect contact conditions between the geosynthetic liner and the controlling soil (clay) layer below; an upper bound prediction can be obtained by assuming radial flow in the clay layer and integrating Darcy's law in spherical coordinates. However, other empirical equations have been developed to describe leakages through damage geomembrane, that take into account for the quality

of the contact between geomembrane and soil below as well as for the type/dimension of holes (Giroud and Bonaparte, 1989; Giroud et al., 1992; Schroeder et al., 1994).

Table 2.3. Water vapour transmission (g/(m^2 d)) and equivalent hydraulic conductivity, K_g (m/s), for different type of polymers and geomembrane thickness. Source: Giroud and Bonaparte (1989).

Polymer	**GM thickness (mm)**	**Water vapour transmission (g/(m^2 d)) (*)**	**Equivalent hydraulic conductivity K_g (m/s) (*)**
Butyl rubber	0.85	0.02	1.4E-15
	1.85	0.097	1.5E-14
Chlorinated Polyethilene (CPE)	0.53	0.643	2.8E-14
	0.94	0.305	2.3E-14
Ethylene-Propylene Diene Monomer (EPDM)	0.51	0.27	1.1E-14
	1.7	0.172	2.4E-14
Neoprene	0.51	0.304	1.3E-14
	0.91	0.473	3.5E-14
Nitrile rubber	0.76	5.51	3.4E-13
Polybutylene	0.69	0.088	4.7E-15
Polyester Elastomer	0.2	10.5	1.7E-15
Low-Density Polyethylene (LDPE)	0.76	0.057	3.5E-15
High-Density Polyethylene (HDPE)	0.8	0.0017	1.1E-15
	2.44	0.006	1.2E-15
Polyvinyl Chloride (PVC)	0.28	4.42	1.0E-13
	0.51	2.97	1.2E-13
	0.79	1.85	1.2E-13

(*) Values of water vapour transmission and equivalent hydraulic conductivity determined by experimental tests carried out at 23 °C with a relative humidity difference of 50%, which is equivalent to a vapour pressure difference of 1.4 kPa (Giroud and Bonaparte, 1989).

Moreover, Eq. 2.21 requires the user to define the frequency of geomembrane defects (number of defects per hectare) and the defect area that should be evaluated on a

project-specific basis (Erickson and Thiel, 2002). For instance, Giroud and Bonaparte (1989) recommend using a defect area of 1 cm^2 for conservatively reasons and adopting a defect density of 3-5 defects per hectare, if an intensive quality control monitoring during liner construction has been performed. A flaw density of 30 defects per hectare or more is recommended if quality assurance is limited to spot checks or when environmental difficulties have been encountered during installation. Forget et al. (2005) reported in their study on leaks density on geomembranes (HDPE, PVC and bituminous geomembrane) measured for more than 89 project sites that 80 % of projects where the liner installation was performed under a rigorous construction quality assurance program showed a very low leaks density, ranging from 0 to 7 leaks per hectare (4 leaks per hectare as average) and the remaining 20 % had density in the range 8-20 leaks per hectare. Instead, density from 14 up to 52 leaks per hectare were measured in project sites without quality assurance program.

To simplify the model computation, the geosynthetic time-dependent deterioration due to aging or external elements, such as chemicals, temperature and mechanical actions that can create sheet flaws or increase the size of existing flaws, resulting in higher infiltration rates within the landfill, is neglected in the current version of the LWB model.

The general formulation for the water head, ΔH, can be derived by rearranging Eq.(2.17) with Eqs.(2.18)-(2.21):

$$\Delta H(Z_j,t_i) = \frac{-\left(\frac{K_x}{s_x}\cdot A_x+\xi\right)+\sqrt{\left(\frac{K_x}{s_x}A_x+\xi\right)^2+2\cdot B\cdot\frac{K_d}{D_c}\cdot\left[Q_{\inf}(t)\cdot A(k)+Q_{lat}(t)\right]-K_x\cdot A_x}}{B\cdot\frac{K_d}{D_c}} \tag{2.22}$$

Where:

$$\begin{cases}\xi=0; \quad K_x=K_c; \quad s_x=s_c & \text{no synthetic layer}\\ \xi=K_c\cdot\eta\cdot A_g\left[Z_j,t_i\right]/s_g; \quad K_x=K_g; \quad s_x=s_g & \text{synthetic layer}\end{cases}$$

It is worth noting that Eq.(2.22) can be also used to estimate the amount of water which leaks through the bottom liner system simply replacing $Q_{inf}(t)$ with L (t,k) and assuming D_c equal to the effective distance between leachate pipes accounting for the slope.

2.2.4 LANDFILL GAS (LFG) GENERATION MODELLING

As discussed in **Section 1.3**, landfill gas generation depends on several factors, such as waste composition and density, water availability and others site-specific conditions (e.g. temperature, pH, nutrients), that may reduce the gas yield compared to the theoretical value (Bicheldey and Latushkina 2010, Rawat and Ramanathan 2011, Behera et al. 2010, Machado et al. 2009).
Several landfill gas models have been developed to describe waste anaerobic degradation and to estimate gas generation over time in landfills. Basically, a gas generation model consists of two parts:

- Stoichiometric module, which uses bio-chemical characteristics of input waste (e.g elemental composition or degradable organic content) to compute the gas generation potential, L_0 (Nl per kg of waste). It represents the maximum amount of gas that can be produced during the entire life of a landfill, when all organic substances have been converted into CH_4 and CO_2.
- Kinetic module, which describes the trend of gas potential release over time. Depending on the kinetic order assumption (0, 1, 2 or saturated) or the temporal function applied (linear, exponential or bi-exponential empirical formulation), the emission profiles greatly vary.

As an example, Table 2.4 gives an overview of the different LFG predictive models and main parameters required. First order decay (FOD) landfill gas generation model is currently the most applied for the estimation of LFG emission from landfill sites (Thompson et al., 2009; Mou et al., 2015). The FOD model assumes that the degradable organic carbon in waste decays by following the first-order reaction kinetic, as shown in Eq. (2.23):

$$C\ t = C_0 \cdot \exp^{-kt} \tag{2.23}$$

Where C is the residual amount of degradable organic carbon at time t (kg), C_0 the initial quantity of organic carbon in wastes (at t=0), and k the first-order kinetic constant

(y^{-1}). By assuming a certain amount of degraded organic carbon would generate a constant amount of CH_4, Eq. (2.24) could be derived from Eq. (2.23):

$$Q\ t\ = \delta \cdot \frac{d\left[C_0 - C\ t\ \right]}{dt} = \delta \cdot\ k \cdot C_0 \cdot \exp^{-kt} \tag{2.24}$$

Where $Q(t)$ is the annual methane generation (kg/y) and δ is the correlation factor, which expresses the ratio between CH_4 generated and degraded organic carbon. Under ideal gas condition, considering that landfill gas contains 50 % of methane, δ is equal to 0.933 m^3 (CH_4)/kg (or 1.87 m^3 (LFG)/kg C).

Almost all of the software developed to estimate gas emissions from landfills are based on the FOD model, such as GasSim 2 (latest version 2.5, Golder Associates, 2012), LandGem 3.02 (US-EPA 2010) and TNO model (Oonk and Boom, 1995). Some of them are single-phase model (TNO, LandGEM), which implies that they do not distinguish between waste categories. Other models (GasSim, MTM) are based on a multi-phase approach that involves partitioning of MSW wastes into fractions characterized by different degradability (fast, medium and low).

As shown in Table 2.4, FOD models provide a time-dependent emission profile taking into account for the amount of deposited waste per year, waste composition (multi-phase model), its degradability characteristics (degradable organic content and degradation rate *k*), and, in some cases, other parameters such as waste water content, disposal practice, gas recovery efficiency and methane oxidation in soil cover. Usually, FOD models assume that the only factor which determines the gas generation rate in landfills is the amount of degradable carbon remaining within the waste mass. Indeed, they consider that other factors affecting the gas generation process, mainly the water content in landfills, are not limiting the rate of LFG production. However, since the waste mass and the water transport in landfills could be very heterogeneous, anaerobic decomposition can be hindered in specific microenvironments due to unsuitable environmental conditions (Mor et al., 2006). This could lead to overestimation of gas generation rates compared to values measured in real landfill site, since only a fraction of substrate can actually be converted into landfill gas (Mor et al., 2006).

Table 2.4. Overview of some available models for estimating gas generation over time.

TNO model	$Q\ t\ = DOC_f \cdot 1.87 \cdot M \cdot DOC \cdot k \cdot \exp^{-kt}$	Q=methane production (kt/y) DOC_f=fraction of assimilated DOC M= waste generation (Mt/y) DOC= degradable organic carbon (kg/t) k=decay rate (y^{-1}) t=time of waste disposal (y)
LandGEM 3.02	$Q\ t\ = \left(\frac{M}{10}\right) \cdot k \cdot L_0 \cdot \exp^{-kt}$	Q=methane production (kt/y) M= waste generation (Mt/y) k=decay rate (y^{-1}) L_0=methane generation potential (kg/t) t=time of waste disposal (y)
GasSim 2	$Q(t) = \varsigma \sum_i 1.87 \cdot A \cdot C_{0,i} \cdot k_i \cdot \exp^{-k_i t}$	Q=gas production at time *t* (m^3/y) ζ=fraction of organic carbon ultimately converted in LFG (-) *i*=waste fraction with degradation rate k_i A=amount of waste in place (t) $C_{0,i}$= organic carbon in waste fraction *i* (kgC/t) k_i=decay rate of fraction *i* (y^{-1}) t=time elapsed since depositing (y)
Modified Triangular Model (MTM)	$Q^f\ t\ = \begin{cases} \frac{2V_0^f}{t^f_{\deg}} \cdot \frac{t}{t^f_{peak}} & \text{for } t_i \le t^f_{peak} \\ \frac{2V_0^f}{t^f_{\deg}} \cdot \frac{t^f_{\deg} - t}{t^f_{\deg} - t^f_{peak}} & \text{for } t_i > t^f_{peak} \end{cases}$	Q=gas production at time t (m^3/y) V_0= methane generation potential (m^3) t= time elapsed since waste deposition (y) f=organic fraction (readily or slowly) $t^f_{\deg}$ = decomposition time of fraction *f* t^f_{peak} = peak time of gas production for fraction *f*
Modified Gompertz equation (empirical)	$y(t) = A \cdot \exp\left\{-\exp\left[\frac{\mu_m e}{A}\ \lambda - t\ +1\right]\right\}$	y=biogas accumulation at time t (l/kg) t=time (d) A= biogas production potential (l/kg) μ_m=maximal production rate (l/kg d) λ=lag-phase (d) e=2.7183

To take into account also for the moisture condition within landfills, which affects both the gas generation rate (*k*) and the amount of gas being formed per unit weight of waste (L_0), a range for k-values can be assumed depending on the mean precipitation and temperature of the climate region of landfill sites and a formation factor (ζ) can be introduced to reduce gas yield compared to the theoretical value.

In the proposed model, firstly, the maximum theoretical volume of landfill gas that can be produced by waste degradation is calculated from molecular formula ($C_aH_bO_cN_d$) of the readily (RBOF) and slowly (SBOF) biodegradable fraction contained in wastes, as shown in Eq. (2.13) (*stoichiometric module*). Then, the moles of methane, β (mol CH_4/mol RBOF) and carbon dioxide, γ (mol CO_2/mol RBOF) are converted in volumes using the ideal gas law and the theoretical landfill gas generation is determined as follows:

$$V_{gas} = V_{gas,RBOF} + V_{gas,SBOF} = \beta + \gamma \left(\frac{R_g \cdot T_L}{p} \cdot \frac{\%RBOF}{PM_{RBOF}} M_w \right) + \beta' + \gamma' \left(\frac{R_g \cdot T_L}{p} \cdot \frac{\%SBOF}{PM_{SBOF}} M_w \right) \quad (2.25)$$

where PM_{RBOF} and PM_{SBOF} are the molecular weight of RBOF and SBOF (g/mol), $\%_{RBOF}$ and $\%_{SBOF}$ the percentage of biodegradable mass fraction in waste (kgRBOF/kg waste), R_g the universal gas constant (8314 m^3·Pa/K·kmol), p the gas pressure (Pa), T_L the temperature inside the landfill (308 K) and M_w the wet waste mass (kg).

Hence, the gas volume generated at the time t can be determined by using different kinetic modules: the modified triangular model (Tchobanoglous et al., 1993), the exponential model based on first order kinetic equation (Mor et al., 2006) and the modified Gompertz model (Lo et al., 2010) whose general formulation are reported in Table 2.4.

For instance, if the first-order model is selected by the user, the following equation is applied:

$$Q\ t = \varsigma \left[V_{gas,RBOF} \cdot 1 - \exp^{-k_{RBOF} t} + V_{gas,SBOF} \cdot 1 - \exp^{-k_{SBOF} t} \right] \quad (2.26)$$

Where ζ is the formation factor (-), k_{RBOF} and k_{SBOF} the first order kinetic constant (y^{-1}) for RBOF and SBOF fractions, respectively. Namely, the formation factor ζ allows to reduce the rate of theoretical gas production due to heterogeneity of waste composition as well as unfavourable conditions inside the landfill (heterogeneous water distribution, inhibitors, toxic elements, pH) that may inhibit the microbial activity and hence waste degradation. Bogner and Matthews (2003) proposed a value of ζ between 0.5 and 0.7. Values of k_{RBOF} and k_{SBOF} can be assumed from the range recommended by IPCC 2006,

shown in Table 2.5, depending on the climate region and the moisture condition inside the landfill.

Table 2.5. Default k-values recommended by IPCC 2006 as a function of the climate zone and moisture conditions in landfills. MAT= Mean Annual Temperature; MAP= Mean Annual Precipitation; PET= Potential Evapotranspiration.

	Climate zone	Boreal -Temperate (MAT≤ 20°C)		Tropical (MAT>20°C)	
Type of waste		DRY	WET	DRY	WET
		MAP/PET <1	MAP/PET >1	MAP<1000 mm	MAP>1000 mm
Slowly	Paper/textile waste	0.03-0.05	0.05-0.07	0.04-0.06	0.06-0.085
	Wood/straw waste	0.01-0.03	0.02-0.04	0.02-0.04	0.03-0.05
Moderately	Organic (no-food) and garden waste	0.04-0.06	0.06-0.1	0.05-0.08	0.15-0.2
Rapidly	Food waste/sludge	0.05-0.08	0.1-0.2	0.07-0.1	0.17-0.7
	Bulk waste	0.04-0.06	0.08-0.1	0.05-0.08	0.15-0.2

2.3 RESULTS AND DISCUSSIONS

2.3.1 INFLUENCE OF WASTE BIODEGRADATION AND COMPRESSION ON LEACHATE PRODUCTION

In order to better understand how biodegradation and compression processes may affect the expected leachate production in landfills, several simulations assuming different MSW properties were carried out (see Table 2.6). Specifically, 4 tests assuming saturated (Test 1 and 3) or unsaturated wastes conditions (Test 2 and 4) were performed. Furthermore, the waste compressibility has been progressively modified to assess the influence of waste consolidation processes on leachate prediction by varying the empirical parameter CC_c within the literature range reported for MSW waste (5,000-30,000 kg/m^2). Specifically, three different conditions were assumed, that are high compressible waste (CC_c=5,000 kg/m^2), low compressible waste (CC_c=30,000 kg/m^2) and incompressible waste (for which $CC_c=10^9$ kg/m^2 is assumed), and the temporal trend of field capacity was estimated using Eq. (2.10). It should be highlighted that the classification of waste in high/low compressible and incompressible waste is only qualitative and it is not based on literature. However, the general concept of

compressibility, as the material's ability to reduce its volume when subjected to a compressive stress, was considered for this classification. Specifically, according to Eq. 2.10 (in case of 60 % initial porosity; 25 % initial field capacity and 7.7 % wilting point) and assuming a vertical stress of 100 kPa, a pore volume reduction ($\Delta n/n_{in}$) of 20 %, 7 % and 0 % can be computed in case of CC_c=5,000 kg/m^2 (high compressible), CC_c=30,000 kg/m^2 (low compressible) and CC_c=10^9 kg/m^2 (incompressible), respectively.

Table 2.6. Parameters values set for landfill simulations (Tests 1,2,3,4). The parameters modified in the different tests are highlighted in red. High Compressibility: CC_c=5,000 kg/m^2; Low Compressibility: CC_c=30,000 kg/m^2; Incompressible: CC_c=10^9 kg/m^2.

PARAMETERS	TEST 1	TEST 2	TEST 3	TEST 4
LANDFILL AREA (ha)	1	1	1	1
OPERATIVE STAGE (y)	1	1	1	1
POST-OPERATIVE STAGE (y)	10	10	10	10
NUMBER OF CELLS	1	1	1	1
NUMBER OF LAYERS	1	1	1	1
LAYER THICKNESS (m)	3	3	3	3
INTERMEDIATE COVER SOIL	NONE	NONE	NONE	NONE
WASTE TYPE	MSW	MSW	MSW	MSW
BIODEGRADATION	YES	YES	NO	NO
TOTAL POROSITY (%V/V)	60	60	60	60
FIELD CAPACITY (%V/V)	25	35	25	35
WASTE INITIAL MOISTURE (% V/V)	25	25	25	25
WASTE DENSITY (kg/m^3)	810	810	810	810
WILTING POINT (%V/V)	7.7	7.7	7.7	7.7
COMPRESSIBILITY	High/Low/None	High/Low/None	High/Low/None	High/Low/None
RAINFALL (mm)	965	965	965	965
EVAPORATION (mm)	420	420	420	420
EVAPOTRANSPIRATION ACP (mm)	465	465	465	465
RUNOFF (mm)	170	170	170	170
RUNOFF ACP (mm)	410	410	410	410

It is worth noting that the different simulations were performed assuming constant values of runoff and evapotranspiration and a simple landfill configuration (see Table 2.6), since the sensitivity analysis was only focused on biodegradation and waste compression.

Moreover, the contribution of different processes on the overall leachate production is highlighted by comparing the model results with those obtained by applying the HELP model which neglects both biodegradation and compression. Note that the landfill aftercare period was simulated only for 10 years that is generally a too short time scale for the analysis of closed landfill. However, since the main purpose of this study was to evaluate the effects of waste biodegradation and compression on leachate predictions, simulations were stopped as soon as leachate generation becomes "stable" and no more significant differences between the two models were detected.

Main results of this comparison are reported in Fig. 2.3 that shows the annual leachate production returned by the developed model for the condition assumed in Test 1 (Fig. 2.3a), Test 2 (Fig. 2.3b), Test 3 (Fig. 2.3c) and Test 4 (Fig. 2.3d). For reference, the results obtained by running the HELP model with the same input data are also reported as dashed line. With reference to Fig. 2.2 it can be noticed that leachate volumes predicted by the developed model are generally higher than those returned by HELP. Namely, the main differences are observed in the early part of the simulation (first and second year), corresponding to the operative stage of the landfill, and are more evident for unsaturated waste (Fig. 2.3b, Fig. 2.3d) and for high compressible waste (HC). On the contrary, in the latest part of simulation the two models approached each other. The differences observed in the first years of simulation can be mainly attributed to the waste compression effect which is neglected in the HELP model. In fact, the wastes are initially subjected to a rapid compression as a consequence of their own weight and of final cover system (which is assumed to be realized at the second year of simulations) leading to water release.

Fig. 2.3 also shows that even in the case of almost incompressible wastes (see NC in Fig.2.3 a-d) the two models provide quite different results. This can be attributed to the difficulty of applying HELP for a landfill in evolution.

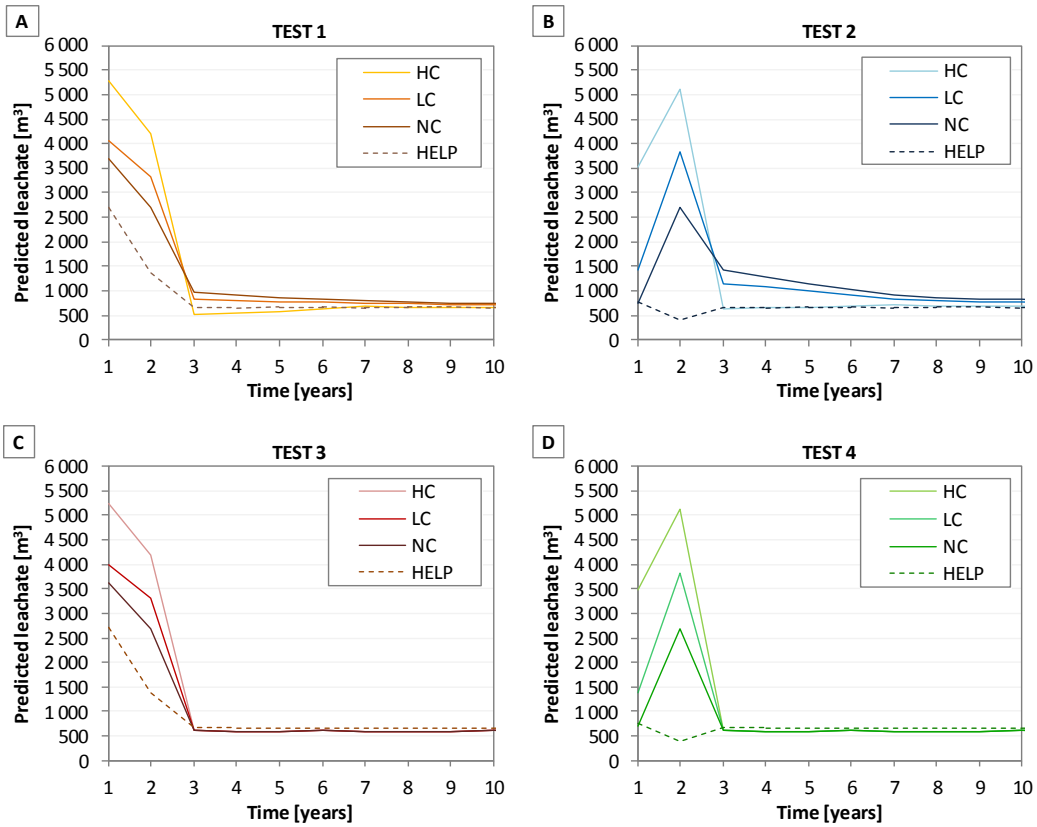

Figure 2.3. Annual trend of leachate produced within the landfill for the different scenarios simulated in Test 1(A), 2(B), 3(C), 4(D). For reference, the results obtained with HELP are also reported. HC = High Compressible waste (CC_c=5,000 kg/m^2); LC = Low Compressible waste (CC_c=30,000 kg/m^2); NC = Incompressible waste (CC_c=10^9 kg/m^2).

In fact, in order to reproduce the filling operation of the active landfill, two different simulations were carried out with the HELP model: one (first year) corresponding to the disposal of the waste layer and the other one (2^{nd}-10^{th} year of the simulation) simulating the landfill aftercare period. Hence, a discontinuity in model computation was actually introduced in HELP simulations to represent the two distinct phases of landfilling. Moreover, as pointed out by the State of Ohio EPA (2005), for short simulations (less than 5 years) the values returned by HELP may be unrepresentative since it is possible that flow equilibrium has not been reached. Schroeder et al. (1994) also indicated that HELP tends to overestimate the water storage in waste during the early part of simulation and overestimates the time required for leachate to be generated, causing an underestimation of the amount of predicted leachate. Thus, the discrepancies observed

between the two models in the first part of the simulation can be also ascribed to the different underlying assumptions related to the occurrence of equilibrium conditions.
Instead, in the latest part of simulation the two models approach each other (see Fig. 2.3), even though slight differences in the expected leachate production are still observed (see Fig. 2.3 a-b). These discrepancies, which are more evident for unsaturated waste (Fig. 2.3 b), are presumably due to the fact that HELP neglects biodegradation. In fact, biodegradation processes lead, on the one hand, to a water consumption to sustain the oxide-reductive reactions and, on the other hand, to a mass reduction in residual organic matter and, consequently, in water retention capacity leading to higher leachate volumes. This is in line with the results presented by Powrie et al. (2000) which have observed that the volume of water that can be hold by wastes progressively decreases as a consequence of biological processes.
Overall, results obtained from these hypothetical scenarios suggest that waste compression phenomena may greatly affect the leachate prediction, especially during the operative stage of a landfill, and neglecting these processes could lead to underestimation up to one order of magnitude, depending on the nature of the emplacement waste. Moreover, results reveal that biodegradation of waste organic matter may result relevant for leachate volumes assessment, influencing water storage capacity of wastes and leading to a leachate production 2-3 times higher than those obtained neglecting these phenomena.

2.3.2 MODEL APPLICATION TO REAL MUNICIPAL SOLID WASTE LANDFILLS

In order to assess the capability of the model to describe the leachate production over time, several simulations on four existing landfills were carried out. The considered landfill sites, located in Italy (landfill A in north Italy and landfills B, C, D in centre Italy), are in the operative management stage and receive municipal solid wastes (MSW) from surrounding areas. Table 2.7 reports a short description of the different landfill sites analysed in this section with regard to surface area, total landfill height, filling period and waste amounts, average rainfall and weather data source.

Table 2.7. Main characteristics of the 4 landfill sites analysed in this study.

Landfill	Exposed surface	Total height	Landfill type	Filling period	Quantity of waste	Weather data source	Average rainfall
A	19,000 m^2	15 m	Fill	Jan-06 / Jun-10 (54 months)	4,300 ton/month	In situ station	660 mm/year
B	14,000 m^2	25 m	Trench and fill	Jan-09 / Oct-12 (46 months)	9,600 ton/month	In situ station	885 mm/year
C	25,000 m^2	40 m	Trench and fill	Jan-05 / Dec-13 (108 months)	9,200 ton/month	ESRL database	1220 mm/year
D	28,000 m^2	14 m	Trench and fill	Jan-06 / Dec-08 (36 months) (*)	8,100 ton/month	ESRL database	1270 mm/year

(*) simulation until Dec-13, no final cover

Data about quantity of emplaced wastes, extracted leachate, dimensions and design characteristics of each landfill have been supplied by landfills managing companies or extrapolated by periodic reports about landfill management. Weather data have been collected from in situ weather station or downloaded by NOAA/ESRL database.

In all simulations, the waste parameters not provided by the landfill management companies (e.g. waste compression index, moisture, field capacity, wilting point and porosity of emplaced waste) were initially selected as average values based on the literature ranges reported for MSW waste. Table 2.8 shows the reference values assumed for these parameters and the corresponding literature range derived from previous studies.

Furthermore, the MSW material composition (Fig. 2.4), required as input data, was assumed the same for all the landfill sites. This composition, expressed as percentage on wet weight basis and shown in Fig. 2.4, was provided by the managing company of Landfill B. However, it was considered representative of the average composition of municipal solid waste in northern and central Italy.

Finally, for all simulations, the configuration of landfills bottom liner system was defined following the minimum Italian regulatory design requirements for non-hazardous waste landfills. In particular, the barrier liner system used in all simulations include an HDPE geomembrane with a thickness of 2 mm, a density of 4 defects per hectare above a clay layer with a permeability of 10^{-9} m/s and thickness of 1 m.

Produced leachate was assumed to be totally extracted by the pump without accumulation within the landfill.

Table 2.8. Parameters, models and waste characteristics used as reference values for MSW waste in different simulations. RBOF: Readily Degradable Organic Fraction. SBOF: Slowly Degradable Organic Fraction.

Parameter	Symbol	Selected value	Literature range	Units	Reference
Compression index	C_c	0.5	0.02 ÷ 7.5 0.08 ÷ 1.4 0.26 ÷ 0.99	-	Bareither et al. (2012) Chen et al. (2009) Stoltz et al. (2010)
Waste moisture	MC	30	30 21.5 ÷ 39.2 28 ÷ 69	% v/v	Sirini et al. (2010) Staub et al. (2009) Stoltz et al. (2012)
Waste porosity	n_{in}	50	45 ÷ 55 43 ÷ 63.7	% v/v	Han et al. (2006) Stoltz et al. (2012)
Waste field capacity	FC_{w0}	35	20 ÷ 35 37.7 27 ÷ 33.6	% v/v	Oweis et al. (1990) Oni (2010) Shariatmadari et al. (2010)
Waste wilting point	WP_w	7.7	7 [(a)] 7 [(a)]	% v/v	Lopez et al. (2009) Tchobanoglous et al. (1993)
Wet waste density	ρ_w	900	900 ÷ 1070 530 ÷ 1090 900	kg/m^3	Dixon and Jones (2005) Hanson et al. (2010) Olivier et al. (2005)
Biogas production	QRBOF, QSBOF		Triangular model		-
Biogas formation factor	ζ	55	50 ÷ 70	%	Mor et al. (2006)
RBOF decomposition time	-	60	-	month	Sirini et al. (2010)
RBOF peak time	-	12	-	month	Sirini et al. (2010)
SBOF decomposition time	-	60	-	month	Sirini et al. (2010)
SBOF peak time	-	180	-	month	Sirini et al. (2010)
Biogas lapse time	-	1	-	month	Sirini et al. (2010)
Potential evapotranspiration	ET_0		Thornthwaite model		-
Waste evaporative zone depth	EZD_w	0.15	0.10 ÷ 0.15	m	Allen et al. (2005) [(b)]
Horizontal cell size	-	8	-	m	-
Vertical cell size	-	3	-	m	-

[(a)] Computed from values reported by Lopez et al. (2009) and Tchobanoglous et al. (1993) (WP_w=7 % wet weight) assuming the waste density of 900 kg/m^3.

[(b)] Referred to a soil.

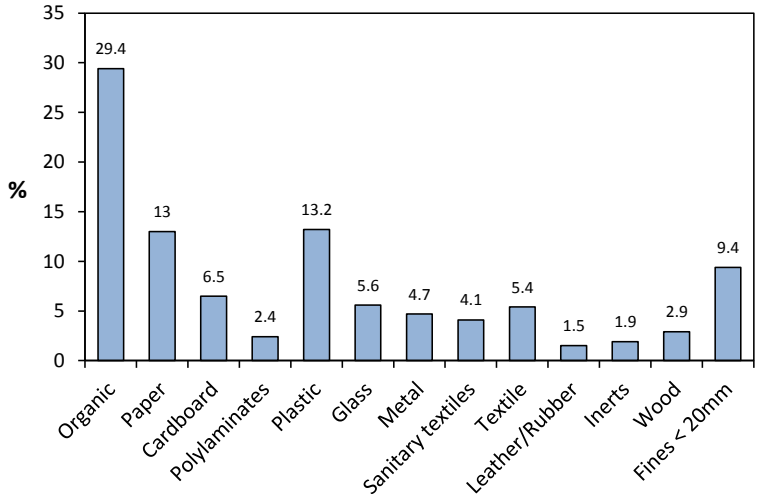

Figure 2.4. Mean composition of MSW waste (expressed as percentage by wet weight) provided by the managing company of Landfill B. The same average waste composition was assumed for all other landfills.

In Figs. 2.5-2.8, a comparison of the predicted leachate volumes (lines) with data measured in the field (black dots) is presented for each landfill analysed in this study. Namely, the reported simulated leachate trend refer to the results obtained performing 4 different types of simulations. The first one (Fig. 2.5) was carried out using average literature values for the physical and mechanical characteristics of waste (Table 2.8) without any preliminary calibration of the model. The second simulation (Fig. 2.6) was performed adopting constant values for the waste input parameters that, based on a preliminary model calibration, allowed to minimize the normalized root-mean-square error (NRMSE) between predictions and measured data. The normalized root-mean-square error (NRMSE) is defined as:

$$NRMSE = \frac{\sqrt{\frac{1}{N}\sum_{i=1}^{N} y_{meas,i} - y_{sim,i}^{2}}}{\overline{y}_{meas}} \qquad (2.26)$$

Where $y_{meas,i}$ and $y_{sim,i}$ are, respectively, the measured and the simulated leachate volumes at month i, $\overline{y}_{meas}$ is the average leachate measured for the N months of simulations.

The third simulation, shown in Fig. 2.7, was carried out varying step by step all the unknown waste parameters within the range reported in Table 2.9 and assuming the same occurrence probability for each variable. This simulation allowed to find out the parameters values of the model that step by step minimize the root-mean-square error (NRMSE). Likewise, in the last simulation (Fig. 2.8) a calibration was performed only operating on the waste moisture content and compression index, since they appeared as the key parameters influencing leachate prediction from previous simulations.

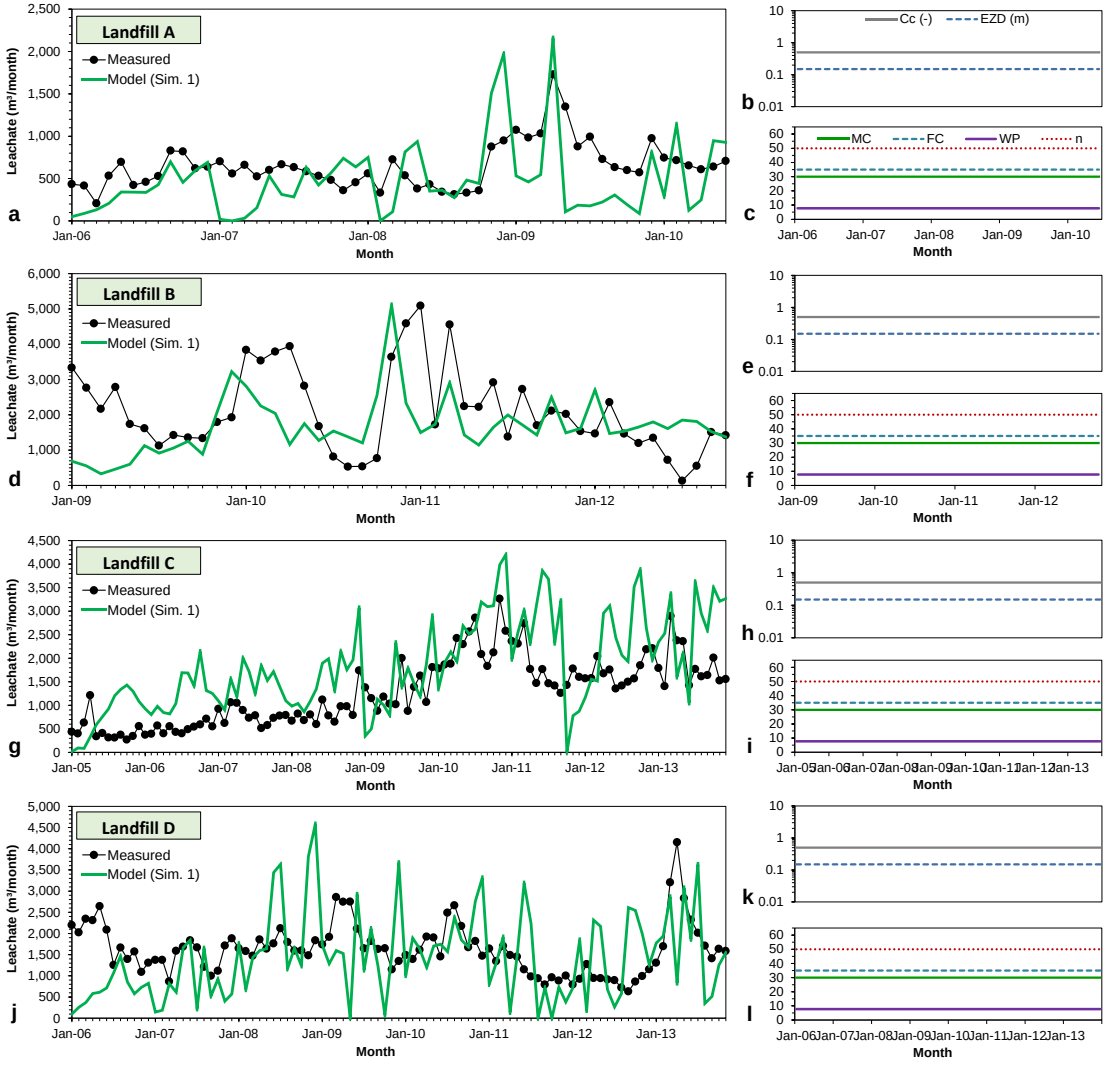

Figure 2.5. Comparison at a monthly scale between measured (black dots) and simulated leachate (green line) obtained using the constant values of waste input parameters reported in Table 2.9 (simulation 1), for landfill A (graphs **a**), landfill B (graphs **d**), landfill C (graphs **g**) and landfill D (graphs **j**). Graphs **b**, **e**, **h**, **k** show waste compression index and evaporative zone depth whereas graphs **c, f, i, l** display waste moisture content (MC), initial waste field capacity (FC), wilting point (WP) and porosity (n).

On the right side of Figs. 2.5-2.8, constant values assumed for waste parameters (Fig. 2.5-2.6) as well as the temporal trends (Fig. 2.7-2.8) returned from the step by step calibration that best fit the measured data are reported.

Making reference to the results reported in Fig. 2.5, it can be noticed that the simulated leachate obtained assuming the reference literature values for waste properties (Table 2.8, Table 2.9 simulation 1) follows the trend measured in the different landfill sites although with a general tendency for the model to underestimate the produced leachate volumes. In fact, for all landfill sites, NRMSE values computed from these simulation runs were quite high, as displayed in Table 2.10 (NRMSE:0.63 ÷ 0.73). These results, hence, suggest that the values selected from literature for the unknown parameters are not representative of the different site-specific scenarios.

Table 2.9. Waste moisture and compression rate values used in different simulations. Simulation 1: constant values selected from literature. Simulation 2: constant values obtained after a preliminary model calibration (by minimizing the root mean square error between measured and simulated leachate data). Simulation 3: all waste parameters values are changed within literature range on monthly basis. Simulation 4: only waste moisture content and compression index were monthly varied within literature ranges.

	Landfill	Moisture (% v/v)	Field capacity (% v/v)	Wilting point (% v/v)	Porosity (% v/v)	Compression index (-)	Waste Evaporative Zone Depth (m)
Simulation 1	A,B,C,D	30	35	7.7	50	0.5	0.15
Simulation 2	A	28.1	29.2	5.4	43.2	0.38	0.04
	B	28	30.1	7.1	46.7	0.48	0.25
	C	35.2	35.7	9.6	48.3	0.16	0.25
	D	34.3	34.5	6.7	41.5	0.3	0.22
Simulation 3	A,B,C,D	7.7 ÷ 37	25 ÷ 40	3 ÷ 10	35 ÷ 60	0.05 ÷ 5.0	0.02 ÷ 0.30
Simulation 4	A,B,C,D	7.7 ÷ 35	35	7.7	50	0.05 ÷ 5.0	0.15

Indeed, a better correlation among predicted and measured leachate was observed in Fig. 2.6, when a preliminary calibration of the waste properties was carried out. In this case, by adopting for each landfill the waste characteristics reported in Table 2.9 (simulation 2), the model provides results that better describe the observed trend compared to the previous simulation 1, as confirmed by the lower NRMSE values shown in Table 2.10 for simulation 2 (NRMSE: 0.45÷0.67). From Table 2.9 it also quite

interesting to note that the initial moisture content of waste that allowed to get a more reliable description of the produced leachate were quite similar in all landfills (MC =28 ÷ 35 %v/v) suggesting that a narrow range could be used as reference for the average moisture content of MSW waste in a screening phase. The waste compression index, instead, exhibited a wider variation among landfill sites (0.16 ÷ 0.48) but the relative magnitude appears coherent with the literature range (see Table 2.8).

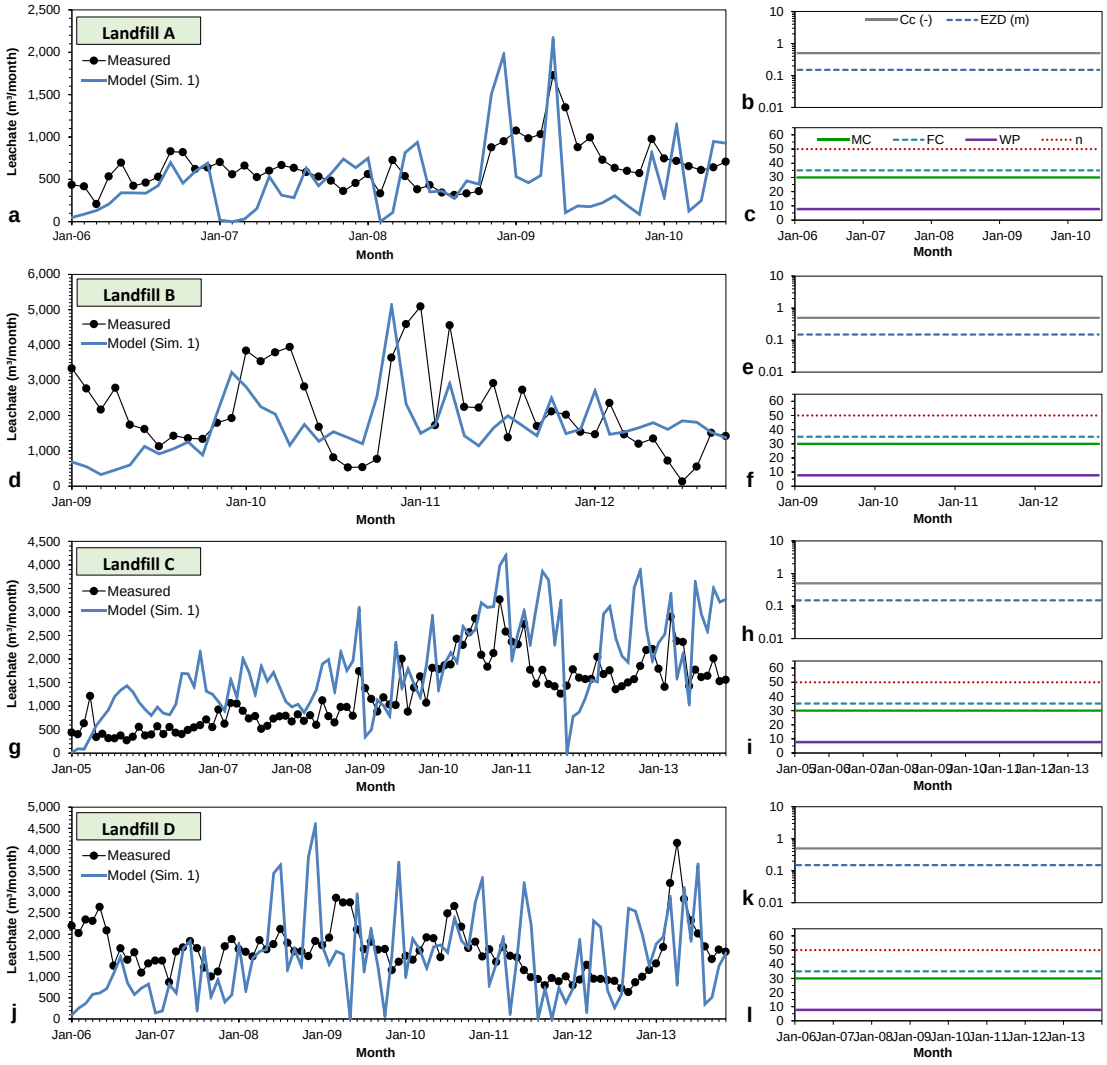

Figure 2.6. Comparison at a monthly scale between measured (black dots) and simulated leachate data (blue line) obtained using the constant values of waste input parameters reported in Table 2.9 (simulation 2), for landfill A (graphs **a**), landfill B (graphs **d**), landfill C (graphs **g**) and landfill D (graphs **j**). Graphs **b**, **e**, **h**, **k** show waste compression index and evaporative zone depth whereas graphs **c, f, i, l** display waste moisture content (MC), initial waste field capacity (FC), wilting point (WP) and porosity (n) resulting from a preliminary model calibration (by minimizing the root mean square error between measured and simulated leachate data).

However, it should be considered that the deviation observed after this calibration step (simulation 2) is still significant. This could be due to the fact that, in these simulations, the waste parameters were assumed to be constant for the entire period of disposal. Instead, MSW waste composition and properties may exhibit significant temporal variation due to seasonal changing of weather conditions (rainfall, air humidity) as well as seasonal variability in the amount and the type of specific waste fractions produced (Gidarakos et al., 2006; Hanson et al., 2010; Oni 2010; Park et al., 2014). Hence, a simulation was carried out by performing a calibration of all waste parameters on a monthly scale (simulation 3) assuming for them the ranges reported in Table 2.9. Moreover, in order to highlight the contribution of waste water content and compression index to leachate estimations, a further simulation (simulation 4) was performed only varying these two parameters within the range shown in Table 2.9. The results of these two simulations are displayed in Fig. 2.7 and Fig. 2.8, respectively. In both cases, it is quite evident that the model provides results that are really in line with leachate volumes measured in the field, with only a few exceptions (see landfill D in Figs. 2.7-2.8). These results suggest that the deviations observed in the previous simulations can be in large part ascribed to the waste input parameters selected. In fact, adopting a step-by-step calibration allowed to achieve a general good agreement between model-calculated and measured leachate trend. Best model performances were associated with landfills B and C; in fact, either performing a full parameter calibration (simulation 3) or only varying waste water content and compression index (simulation 4), very small errors were detected (NRMSE of 0.01-0.03 and 0.02-0.04, respectively). Thus, by comparing the results reported in Fig. 2.7 and Fig. 2.8 it seemed that just operating on the waste moisture content and the waste compression index allowed to get predictions that fit fairly well measured data. On the contrary, the model performances in simulating landfills A and D appeared less accurate. Despite a better correlation with field data was achieved after model calibration (simulation 2), larger underestimations were still observed by varying waste properties on monthly basis, as confirmed by higher NRMSE values (NRMSE: 0.11 – 0.29, Table 2.10). These deviations appeared to be restricted to particular time periods (Jan-Apr, landfill A and D in Figs. 2.7, 2.8) and were more evident for landfill D, where very few information were available. Thus, these deviations could be ascribed to uncertainties related to other input parameters such

as weather data, exposed landfill area and waste height that were not measured in landfill D but were extrapolated from annual report.

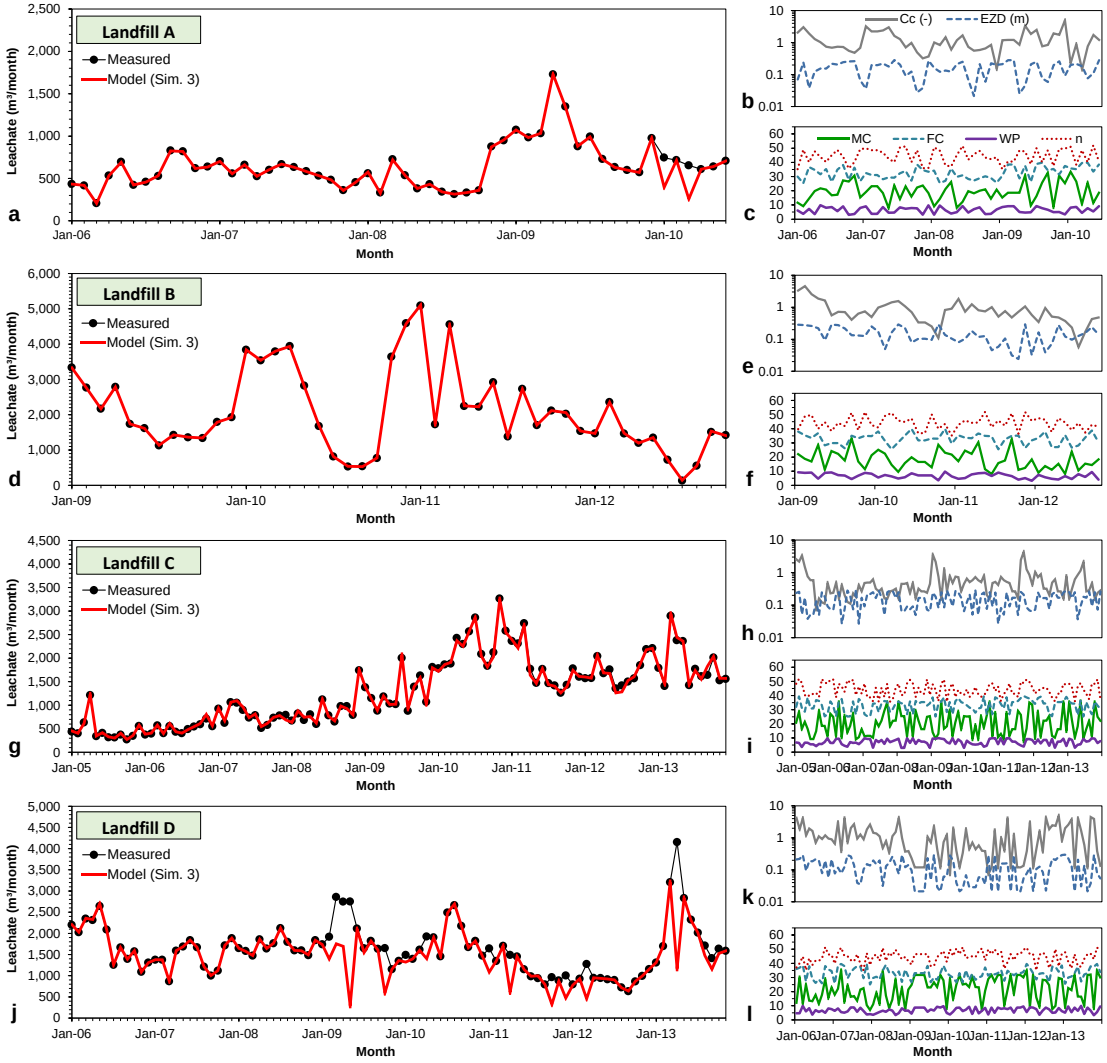

Figure 2.7. Comparison at a monthly scale between measured (black dots) and simulated leachate data (red line) obtained changing the waste input parameters within the range reported in Table 2.9 (simulation 3), for landfill A (graphs **a**), landfill B (graphs **d**), landfill C (graphs **g**) and landfill D (graphs **j**). Graphs **b**, **e**, **h**, **k** show the monthly trend of waste compression index and evaporative zone depth whereas graphs **c, f, i, l** displayed the temporal variation of waste moisture content (MC), initial waste field capacity (FC), wilting point (WP) and porosity (n) resulting from the calibration step-by-step (by minimizing the root mean square error between measured and simulated leachate data).

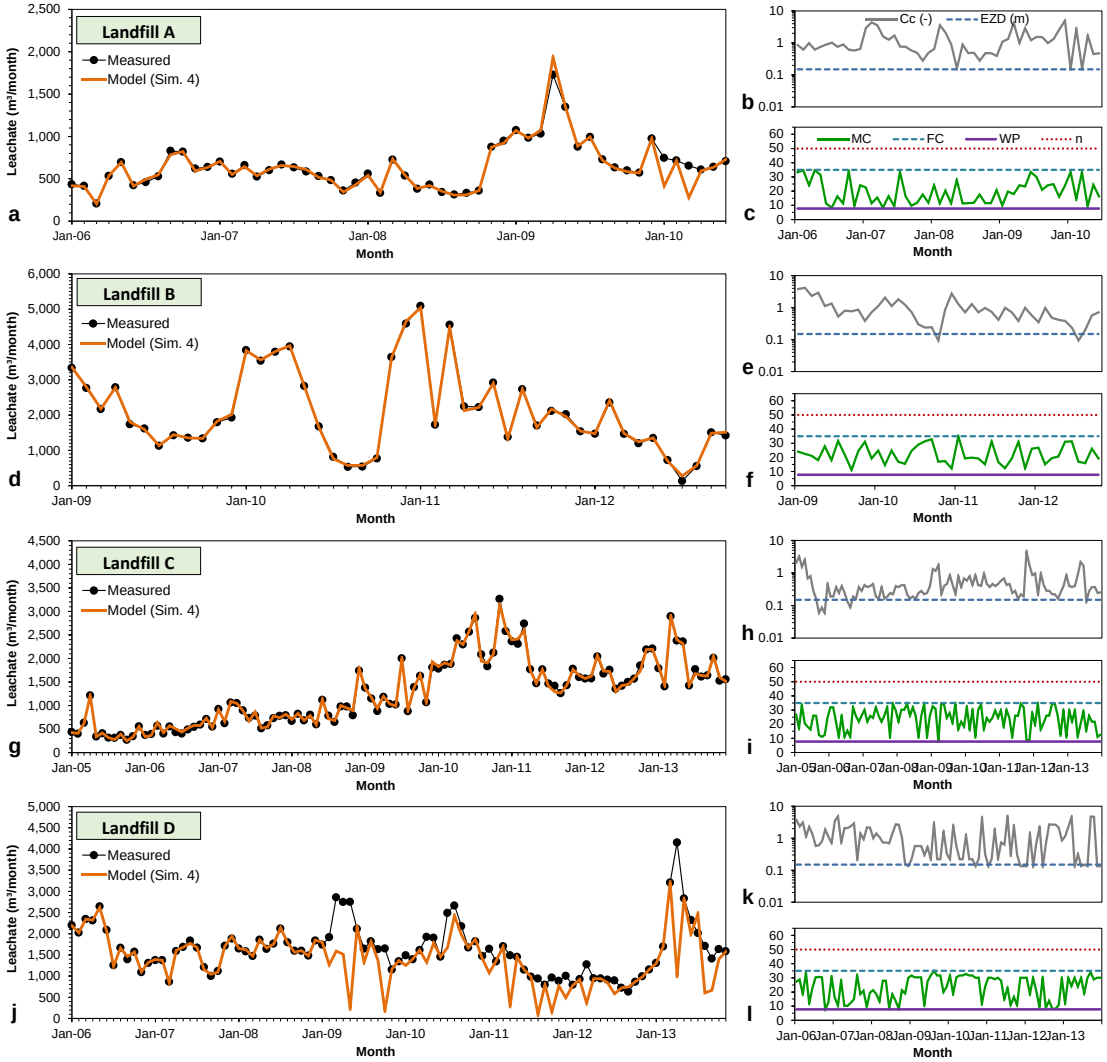

Figure 2.8. Comparison at a monthly scale between measured (black dots) and simulated leachate (orange line) obtained changing the waste compression index and moisture within the range reported in Table 2.9 (simulation 4), for landfill A (graphs a), landfill B (graphs d), landfill C (graphs g) and landfill D (graphs j). Graphs b, e, h, k show the monthly trend of waste compression index and evaporative zone depth whereas graphs c, f, i, l displayed the temporal variation of waste moisture content (MC), initial waste field capacity (FC), wilting point (WP) and porosity (n) resulting from the calibration step-by-step (by minimizing the root mean square error between measured and simulated leachate data).

Overall, these results pointed out that the proposed model, which is based on simple analytical and semi-empirical equations, could be able to describe quite well the leachate production observed at a monthly scale, provided that the waste properties, especially water content and compression index, have been accurately chosen. Moreover, comparing results of simulations 1,2 against those of simulations 3,4 highlighted that the predictive performances could be significantly improved if the

variability related to waste input parameters are considered within the model rather than using constant values for them. The relatively high variability of waste properties returned by the developed model and shown in Figs. 2.7-2.8 could take into account for the seasonal variation in intrinsic waste characteristics as well as for the influence of specific landfill operation practices (waste compaction and fill speed) and weather condition occurring at the site during waste landfilling (not directly implemented in the LWB model).

Table 2.10. Normalized root mean square error (NRMSE) computed from simulations results of landfills. The total number of leachate measured data available for each landfill site is also displayed.

Landfill	N° data	NRMSE Simulation 1	NRMSE Simulation 2	NRMSE Simulation 3	NRMSE Simulation 4
A	54	0.67	0.54	0.11	0.12
B	46	0.63	0.59	0.01	0.02
C	108	0.73	0.44	0.03	0.04
D	96	0.69	0.64	0.29	0.34

Main findings

The results of these case studies showed that the accuracy of the model simulations strongly depends on the quality of input parameters, especially if field data are not available (see landfill D). Indeed, using input data reported in literature, it could be noticed that the simulation follows the general trend, even if many values are underestimated (Fig. 2.5). However, having performed a preliminary calibration only on the initial moisture content and on the compression index of the emplaced waste, the results have achieved a better correlation with the field data (Fig. 2.6), finding parameters quite similar for all landfills, and suggesting these values as reference for MSW wastes in a screening phase. Overall, these findings highlight that using a simplified model such as the one presented in this thesis, that requires a relatively limited number of unknown input parameters, could lead however to a realistic estimation of the produced leachate in landfills avoiding the winding calibration step typical of more sophisticated models. As a remark, performing a step-by-step calibration either varying all waste properties or only changing the waste water content and the waste compression index, allows to get a perfect match among the simulated

values and the measured data for many months at almost all of the landfills (Figs. 2.7-2.8). These findings also reveal that the waste initial moisture content and waste compression index represent key parameters affecting leachate predictions, and show the advantages to use a simplified model, which allows to easily manage the uncertainties related to the input data. Moreover, taking into account for temporal changing of waste input parameters instead of using constant values for them led to a significant improvement in leachate model predictions compared with field measured data. This suggests that further investigation could be direct towards quantifying the uncertainty and the variability associated to waste properties in the field, especially with regards to the moisture content and compression index of emplaced waste.

2.3.3 EVALUATION OF INFILTRATION AND LEAKAGE RATES IN CLOSED LANDFILLS

In this section, the capability of the LWB model to predict the effective infiltration and leakage rates through different capping systems is evaluated by comparing the simulation results with those of HELP, which is widely adopted to determine comparative effectiveness of different alternative composite liners. Specifically, these two models were applied for assessing the performances of three different cover options over a period of 30 years. The different alternative capping systems, named as CAP 1, CAP 2 and CAP 3, are displayed in Figure 2.9.

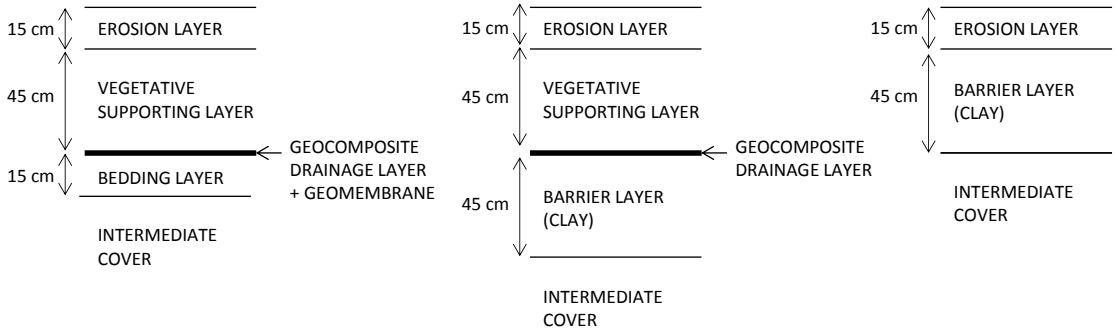

Figure 2.9. Alternative capping system configurations assumed in simulations carried out with HELP and LWB models.

Specific details about the analysed cover systems and the values of main parameters assumed in HELP and LWB model simulations are shown in Table 2.11. The project site is in Howard County, Maryland, where two cap systems were eventually installed; the soil cap on the plateau area (CAP 3) and the geomembrane on the slope (CAP 1).

Table 2.11. Configurations and main parameters of different alternative capping systems analysed in this study.

	Cap 1	**Cap 2**	**Cap 3**
Erosion layer		*moderately compacted loam*	
thickness (cm)	15	15	15
porosity (%v/v)	42	42	42
field capacity (%v/v)	31	31	31
wilting point (%v/v)	18	18	18
initial water content (%v/v)	27	30	27
saturated hydraulic conductivity (m/s)	1.9E-07	1.9E-07	1.9E-07
Vegetative support layer		*silty clay loam*	*Absent*
thickness (cm)	45	45	
porosity (%v/v)	47	47	
field capacity (%v/v)	34	34	
wilting point (%v/v)	21	21	
initial water content (%v/v)	38	38	
saturated hydraulic conductivity (m/s)	4.2E-07	4.2E-07	
Geocomposite liner			*Absent*
geocomposite drainage layer, hydraulic conductivity (m/s)	5E-02	5E-02	
LLDPE geomembrane (*), hydraulic conductivity (m/s)	4.0E-15		
soil barrier liner (compacted clay) hydraulic conductivity (m/s)		1.0E-07 /1.0 E-09	
Compacted clay layer	*Not used*	*Not used*	
thickness (cm)			45
porosity (%v/v)			43
field capacity (%v/v)			42
wilting point (%v/v)			37
initial water content (%v/v)			43
saturated hydraulic conductivity (m/s)			1.0E-07
Support layer		*silty clay loam*	
thickness (cm)	15	15	15
porosity (%v/v)	47	47	47
field capacity (%v/v)	34	34	34
wilting point (%v/v)	21	21	21
initial water content (%v/v)	38	40	38
saturated hydraulic conductivity (m/s)	4.2E-07	4.2E-07	4.2E-07

(*)geomembrane with pinhole density of 2/ha, defect density of 5/ha, good placement quality, η of 4 10^{-6} %, over a bedding layer of compacted soil.

Moreover, in order to evaluate the effect of clay conductivity on the performance of different capping alternatives in reducing infiltration and leakage rates, other simulations were conducted changing the conductivity of the clay layer from 10^{-7} m/s to 10^{-9} m/s.

For all the alternative covers, a total area of 1 hectare was assumed and weather data were generated for a thirty-year period using the HELP synthetic generator program WGEN, using the latitude of the site (39°18' N). Table 2.12 shows the average monthly values of rainfall and air temperature for the considered site, used as input parameters in both models.

Table 2.12. Average monthly values of rainfall and air temperature used in HELP and LWB simulations.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Rainfall (mm)	76.2	75.7	94.5	85.1	87.4	95.5	98.8	117.3	87.9	79.0	79.0	86.4
Temperature (°C)	0.4	1.5	6.3	12.2	17.5	22.4	24.9	24.2	20.5	13.8	8.0	2.5

Finally, runoff was estimated using the SCS curve number (CN) method in both models; the computed curve number from the characteristics of the surface cover layer (moderately compacted loam) was equal to 90 and 89 in HELP and LWB model, respectively.

Modelling results

A summary of the simulation results obtained for the different alternative capping systems by applying the HELP and LWB model is reported in Table 2.13. Values of runoff, evapotranspiration, effective infiltration, leakage and lateral drainage are expressed as average values over the thirty-year period of simulations.

Based on the results shown in Table 2.13, it can be observed that the LWB model predicted higher values of effective infiltration (Q_{inf}) compared to HELP, maybe due to lower evapotranspiration losses and also possibly limitation in the use of Darcy's law. Moreover, it is interesting to note that the two models provide quite different values of surface runoff, which is probably due to a different implementation of the SCS curve number method within the two models.

Table 2.13. Comparison of averaged values of runoff (R), actual evapotranspiration (ET_r), effective infiltration (Q_{inf}), leakage (Q_{leak}) and lateral drainage (Q_{lat}) simulated by the HELP and the LWB models for the different alternative cap systems. Average annual precipitation:1051 mm/y (not reported).

	HELP model				**LWB model**			
	Cap 1	**Cap 2**		**Cap 3**	**Cap 1**	**Cap 2**		**Cap 3**
Parameter		**$K_c=10^{-7}$m/s**	**$K_c=10^{-9}$m/s**			**$K_c=10^{-7}$ m/s**	**$K_c=10^{-9}$ m/s**	
R (mm/y)	178	178	178	194	225	225	225	225
ET_r (mm/y)	737	737	737	590	645	645	645	578
Q_{inf} (m^3/ha/y)	1 355	1 355	1 355	2 663	1 797	1 797	1 797	2 473
Q_{leak} (m^3/ha/y)	0.06	1 095	83	2 663	0.09	1 779	48	2 466
Q_{lat} (m^3/ha/y)	1 357	262	1 274	---	1 797	18	1 749	---

Indeed, surface runoff computed in LWB seems not to be affected by the cover configuration, since it essentially depends on the characteristics of the surface soil layer which is the same in all the alternatives. On the contrary, slightly difference of runoff values between alternative Cap 3 and alternatives Cap 1, Cap 2 can be found in HELP simulations. Hence, due to average higher infiltration rates, leakage (Q_{leak}) and later drainage (Q_{lat}) are generally higher in LWB predictions than in HELP ones. However, temporal trends of infiltration and leakage rates simulated by the two models are fairly similar. For instance, Fig. 2.10 reports the annual trends of leakage through the GM computed in CAP 1 using the HELP (purple) and the LWB (green) models. Annual values of effective infiltrations predicted with the two models are also reported as bars. With reference to Fig. 2.10 it can be noticed that, in both models, the leakage through GM is about 0.005-0.01 % of the effective infiltration, even though the net infiltrations predicted with the LWB model are averagely 1.4 times higher than those provided by HELP. This is probably due, on the one hand, to the lower evapotranspiration rate obtained with the Thornthwaite's method (1948) with respect to Penman's method (1963) and, on the other hand, to the differences in modelling leakage through geomembrane's holes.

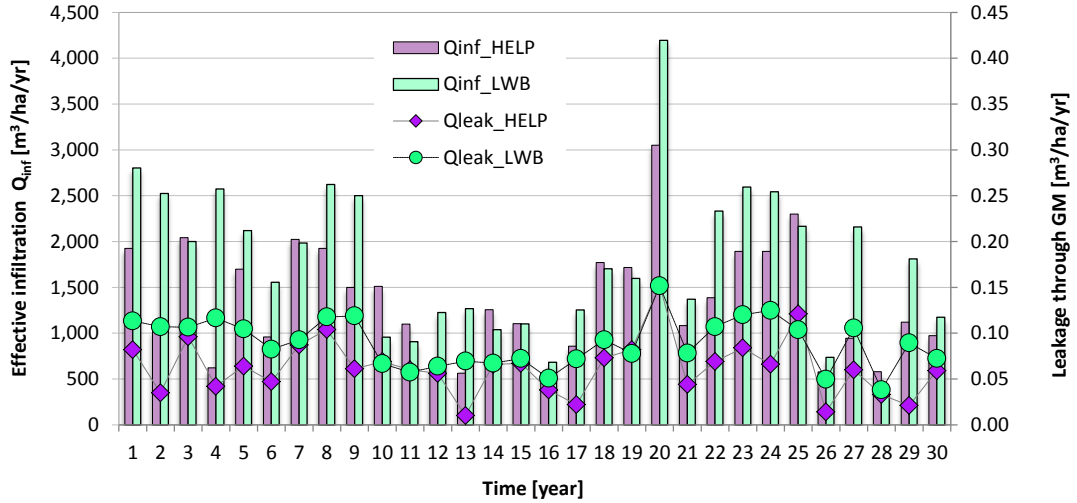

Figure 2.10. Annual trend of effective infiltration (bars) and leakage through GM (symbols) provided by the HELP and LWB models for the cover system CAP 1.

Results of CAP 2 are presented in Fig. 2.11, which refers to the conditions of a clay hydraulic conductivity (K_c) of 10^{-7} m/s (Fig. 2.11a) and of 10^{-9} m/s (Fig 2.11b), respectively. According to the results provided by the LWB model, this capping configuration, using a K_c of 10^{-7} m/s, ensures a slight reduction of water infiltration. In fact, leakage through the bottom cover layer corresponds to 97-100 % of the effective infiltration and lateral drainage occurs only in a few years.

On the contrary, reducing the clay conductivity to 10^{-9} m/s (Fig. 2.11b), the LWB model estimates very low annual leakage rates, about 1-8 % of the infiltration, while promoting water removal in the drainage layer (average Q_{lat} of 1.8 10^3 m^3/ha/y). A similar trend is also predicted by the HELP model. Even though percolation rates through the bottom liner in HELP are higher than those of LWB (Fig. 2.11b), HELP results suggest that decreasing the clay hydraulic conductivity by two orders of magnitude, from 10^{-7} to 10^{-9} m/s, reduce leakage rates to about 92 % (vs 97 % obtained with the LWB model).

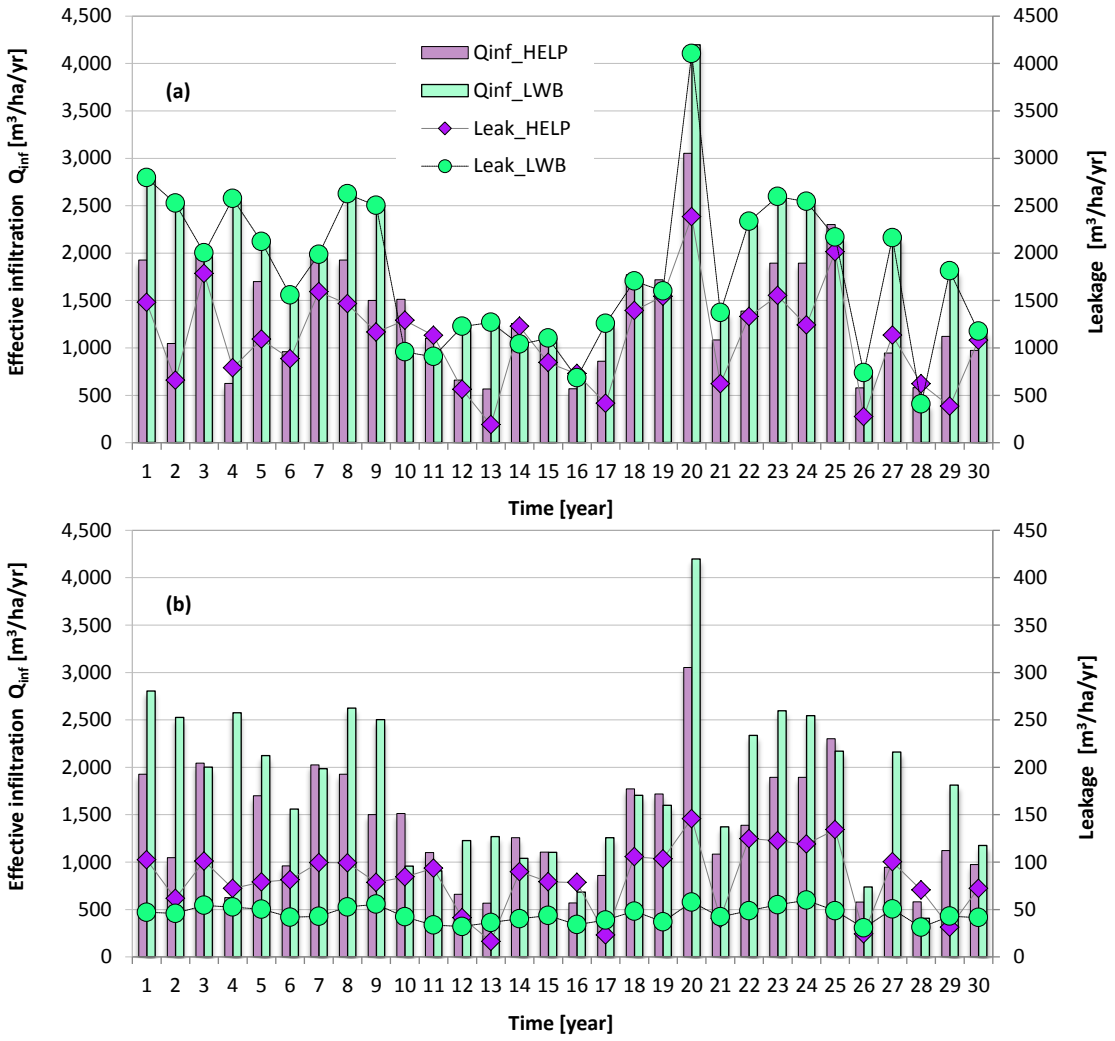

Figure 2.11. Annual trend of effective infiltration (bars) and leakage through GM (symbols) provided by HELP and LWB models for the alternative CAP 2, assuming the hydraulic conductivity of clay of 10^{-7} m/s (a) and 10^{-9} m/s (b), respectively.

Finally, simulation results of alternative CAP 3 (K_c of 10^{-7} m/s) are reported in Fig. 2.12. As expected, this capping configuration produces the worst performance in limiting water infiltration. In fact, according to both models' predictions, nearly all the amount of water that infiltrates the upper layer manage to overcome the hydraulic barrier and therefore enters the landfill body. Moreover, the ability of the superficial soil to act as a water reservoir enhancing evapotranspiration is more restricted comparing to alternatives CAP 1 and CAP 2. In fact, in the cover system CAP 3 the lower thickness of surface soil over the soil barrier liner corresponds to a lower water holding capacity and leads to minor evapotranspiration losses and thus greater infiltration rates.

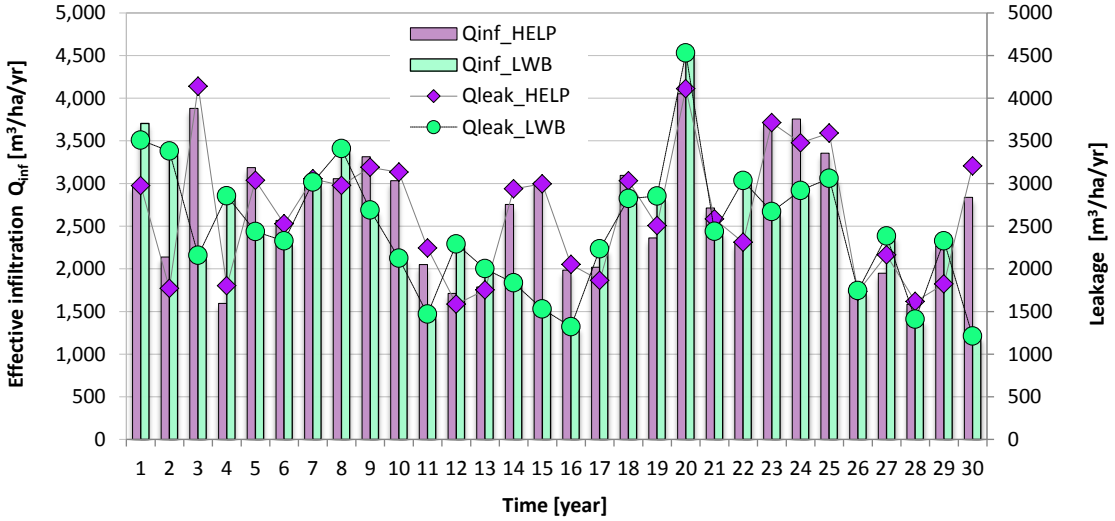

Figure 2.12. Annual trend of effective infiltration (bars) and leakage through GM (symbols) provided by the HELP and LWB models for the capping system CAP 3, assuming the hydraulic conductivity of clay of 10^{-7} m/s.

Main findings

From the analysis of different hypothetical closure scenarios presented in this section, it can be noticed that HELP and LWB models predicted similar values of infiltration and leakage rates through the capping systems analysed, even though they use different computational approaches. In fact, the results indicate that leakage through the GM in CAP 1 is a very small fraction of water budget (from 0.0005 % to 0.001 % of annual rainfall for the LWB and from 0.0001 % to 0.001 % for HELP) whereas lateral drainage contributes greatly (from 5 % to 30 % of precipitations in LWB simulations and from 2 % to 25 % in HELP ones). Both in HELP and LWB simulations, surface runoff has a quite influence on water budget, accounting for approximately 10-30 %, whereas evapotranspiration comprises the largest fraction, 60-80 % in HELP and 50-80 % in LWB. One of the most evident difference between the two models is related to the alternative CAP 2 with the hydraulic conductivity of clay of 10^{-7} m/s. In the LWB model predictions, this value of hydraulic conductivity seems not to prevent the infiltration of water into underlying layers and thus lateral drainage occurs very rarely with low values (leakage ranges from 5 % to 30 % of annual rainfall and lateral drainage from 0 % to 3 %). On the contrary, in HELP simulations, lateral drainage is one order of magnitude greater (0.3 %- 6 % of annual rainfall). However, reducing the

hydraulic conductivity of the clay allows to attenuate percolation up to one order of magnitude according to both models predictions (from 1779 to 48 m^3/ha/y in LWB and from 1095 to 83 m^3/ha/y in HELP). In fact, leakage through the cover contributes for less than 1.5% of annual rainfall in HELP and 1 % in LWB whereas the lateral drainage (together with the evapotranspiration) becomes the major contribution to the water budget (2-25 % in HELP and 10-40 % in LWB).

The results obtained from both models show that, as expected, conventional covers with soil barriers only (CAP 3) are not effective for limiting water infiltration whereas the best protective action is guarantee by a composite liner system with a geomembrane (CAP 1), even though much depends on its integrity and on the quality of contact with the soil below. Moreover, results of both model simulations indicate that, to ensure the protective action of a composite liners (CLs) cap (CAP 2), the hydraulic conductivity of the clay layer plays a key role in reducing water infiltration. For a higher hydraulic conductivity (10^{-7} m/s), the performance of CLs are very poor and are comparable to those of a soil barrier. Instead, when a lower clay hydraulic conductivity is assured (10^{-9} cm/s), the performance of CLs appear successful, with leakage close to those of geomembrane liners. In addition, the results suggest that the effectiveness of a cover system could be also strongly enhanced by the water storage capacity of the surface soil layer and by the type of vegetation cover which have a great influence on evapotranspiration and surface runoff losses. Nevertheless, these results only confirm that water balance models could be useful tools for comparing alternative options for liner systems but do not provide indications about the accuracy of these approaches to estimate the infiltration rates through the different cover layers, since no field data were available for this case study.

2.3.4 FINAL REMARKS

Results obtained from the model simulations of four landfill sites and of some hypothetical scenarios revealed that the LBW model is applicable to open as well as closed landfill. Specifically, once an appropriate calibration was carried out, the results show a good agreement with the measured data, despite the limitations and the

simplifying assumptions of the model. In view of these results, it can be stated that the proposed water balance model can be used as screening tool for a quantitative estimation of leachate production in landfills. However, it should be kept in mind that this model does not account for the heterogeneity of the waste materials and the preferential pathways of leaching within the landfill body, which may locally change the moisture distribution. In fact, landfilling practices (intermediate covers, filling procedure and speed) and field compaction procedures of waste layers may lead to horizontal stratification within the landfill and the orientation of impermeable materials, such as plastic sheets, may increase the anisotropic behaviour of waste. Consequently, the horizontal permeability could become greater than vertical permeability and the hypothesis of one dimensional homogeneous flow within the waste mass could be not more valid. Moreover, many landfill operations and practices could be taken in account in order to better model all types of site-specific conditions, such as daily cover, cells and lots interaction, leachate accumulation.

Bearing in mind these limitations, the obtained results, however, show that the developed model was able to describe quite well the leachate trend observed at a monthly scale in the field. Moreover, the different simulations carried out highlighted that the model can be calibrated on field observations simply operating on the initial waste humidity and on the waste compression index. Assuming a monthly variability of waste input parameters instead of using constant values for them led to a significant improvement in leachate model predictions compared with field measured data. Hence, based on the obtained results it can be concluded that further investigation could be direct towards quantifying the uncertainty and the variability associated to waste properties in the field, especially with regards to the moisture content and compression index of emplaced waste

CHAPTER 3

QUALITATIVE ASSESSMENT OF LIQUID EMISSIONS FROM MECHANICALLY-BIOLOGICALLY TREATED (MBT) WASTE

This chapter is partially taken from:

Pantini S., Verginelli I., Lombardi F. (2015). Analysis and modelling of metals release from MBT wastes through batch and up-flow column tests. *Waste Management* 38, 22-32.

3.1 BACKGROUND

Municipal solid wastes (MSW) contain large quantities of organic materials that, depending on the country economy and on the waste management policies in place, may range from 25 up to 70 % of the produced MSW (Di Lonardo et al., 2012; Farrell and Jones, 2009; Montejo et al., 2010). The need to avoid direct landfilling of biodegradable wastes is shared by the whole technical community in view of reducing the environmental impacts mainly due to methane emissions and generation of strongly polluted leachate associated with their final disposal (De Gioannis et al., 2009). This principle was legally formalized by the Landfill Directive 1999/31/EC (European Commission, 1999) that imposed limits on the amount of biodegradable fraction disposable in landfills. To meet the European targets, the different member states have applied several strategies such as source separation of recyclable and compostable materials, biological treatments of source separated organic wastes or Mechanical Biological Treatment (MBT) plant of raw MSW (Lornage et al., 2007). In the last decades, MBT has been playing a key role in waste management of residual wastes due to its capacity to divert/reduce organic waste materials from landfill while producing a bio-stabilized product that has a lower impact when landfilled (Adani et al., 2004; Farrell and Jones, 2009; Montejo et al., 2013). Usually, a MBT plant consists of a mechanical pre-processing stage including crushing, sieving and recovering of recyclable materials (such as metals, glass or plastics). This mechanical stage results in two distinct flows: the oversize fraction, which is further processed to produce refuse-derived fuel, and the undersize fraction, rich in organic putrescible matter. The latter is biologically treated using an anaerobic and/or aerobic process in order to stabilize it against degradation. All over Europe, MBT facilities differ in the sequence of process steps and whether the biological treatment is designed to produce dry stabilized waste or biologically stabilized materials (Pan and Voulvoulis, 2007). In most of the European countries, such as Switzerland, Austria, France and Italy, aerobic systems are mainly in use. These systems usually consist of a primary intensive treatment stage (closed system with forced aeration) followed by a ripening phase in open or closed systems, with a typical retention time of 4 weeks for the first stage and 6-12 weeks for the second one (Bayard et al., 2010; Morais et al., 2008; Report APAT 2007; Stegmann, 2005; Steiner,

2005; Tintner et al., 2010). MBT plants adopting anaerobic process are quite common in Spain as well as in Germany. Here, the fine fraction is usually digested using dry or wet fermentation processes (3-4 weeks) and the digestate is generally treated in a tunnel composting system for 3-6 weeks (Ponsà et al., 2008; Stegmann, 2005).

The quality of MBT wastes may significantly vary depending on the MBT facility configuration, the feedstock source, the biological treatment and the duration of the ripening stage (Di Lonardo et al., 2012; Hargreaves et al., 2008; Robinson et al., 2005). It is widely recognized that pre-treatment of MSW organic fraction affects the environmental behaviour of these materials in terms of both biogas emissions and leachate quality and quantity (Farrell and Jones, 2009; Lou and Nair, 2009; Pan and Voulvoulis, 2007; Robinson et al., 2005; Siddiqui et al., 2013; Van Praagh et al., 2009). In the last years, several studies aimed to assess the fundamental characteristics of MBT wastes such as the physical-chemical properties (e.g. volatile solids, total and dissolved organic carbon, heavy metals content) and the biological characteristics (e.g. respiration activity, biomethane potential emissions) were carried out (Bayard et al., 2010; Binner and Zach, 1998; De Gioannis et al., 2009; Di Lonardo et al., 2014; Ponsà et al., 2008). All these studies were mainly focused on the evaluation of biogas/biomethane potential capacity (BP) in terms of volume and composition of the gas generated from these samples. On the contrary, the assessment of the leaching characteristics of these materials and the evaluation of the pre-treatment effects on the heavy metals mobility and thus leachate emissions is still poorly investigated (Robinson et al., 2005; Siddiqui et al., 2013; Siddiqui et al., 2012). Generally, two distinct approaches may be adopted in order to assess the leaching behaviour of wastes: lab-scale experiments by coupling different testing procedures (e.g. batch tests or up-flow column percolation tests) and sampling campaign at real scale landfill sites. Regarding the latter approach, there are no data on the performance of landfills completely filled with MBT wastes (Siddiqui et al., 2012) and only few data on landfills that received varying proportion of MBT wastes (Robinson et al., 2005), due to relatively recent introduction of the MBT technology within the waste management policy. Among the different leaching tests, the static batch leaching test at natural pH (UNI EN 12457-2, 2004) is the most widely used method for assessing the potential release of pollutants from a wide variety of solids and waste materials (Grathwohl and Susset, 2009). However, single batch extraction tests

give an indication of metal leachability under specific experimental conditions and do not allow an extrapolation of the long-term behaviour (Van Der Sloot, 1990). Hence, these tests are generally used as a simple tool for compliance or quality control reasons (Lopez-Meza et al., 2008). In order to overcome this limitation, in the last years, new methodologies such as multiple batch extraction tests, pH dependent and up-flow column percolation tests were developed in order to assess the influence of pH and liquid to solid ratio (L/S) on metal release. Nowadays, column percolation tests are preferred as they are able to simulate the water flow through the material and to assess the leaching behaviour over an extended time period (Gratwohl and Susset, 2009; Lopez-Meza et al., 2008; Van der Sloot, 2004). In this view, column experiments resemble natural field conditions better than other laboratory tests (Grathwohl and Susset, 2009). Nevertheless, attention must be paid on the interpretation of the data obtained from these tests, especially if experimental results will be modelled for the prediction of elements release over time.

In this section, a first attempt to address this issue for MBT wastes is presented. To this end, pH static batch test, pH dependent tests and column percolation experiments on waste samples collected from an Italian MBT plant were performed. The obtained results were first used to assess the extent of heavy metals release with respect to the total content in the material. Then, the observed trends were analysed to identify some key factors and mechanism governing the mobility of heavy metals from this type of waste. This was made by using a simplistic model that describes the release kinetics observed in the different column tests. Finally, combining the model with the experimental data allowed extrapolating some useful consideration about the expected long term emissions of MBT wastes in landfill disposal scenarios.

3.2 PHYSICAL AND CHEMICAL CHARACTERIZATION OF MBT WASTE SAMPLES

The analysed material is the mechanically-biologically treated waste produced by an Italian MBT plant which receives raw MSW waste. The average composition of the

waste feedstock is reported in Table 3.1. These data, provided by the MBT plant managing company, were collected during the year 2011.

In this MBT facility, the biodegradable fraction, coming out from the primary screening unit at 80 mm, is sent to a biostabilization basin. Here, the aerobic biodegradation occurs for 28 days at forced aeration conditions; furthermore, the material is daily turned and water is added. Thereafter, in order to separate the improper materials from the undersize fraction consisting of the final treated MBT waste, the flow outgoing from the stabilization basin is sieved in a trommel screen with a mesh opening of 20 mm (secondary refining unit). In order to account for the seasonal variation of waste characteristics, the MBT samples were collected at the discharge point of the conveyor belt from the secondary refining unit during three different campaigns. These samples are indicated as MBT 1 (February 2013), MBT 2 (April 2013) and MBT 3 (November 2013).

Table 3.1. Average composition (% wet weight) of incoming MSW waste feeding the MBT plant.

	Mean (%)	**SD (%)**
fines < 20mm	13.4	3.8
organic waste	28.0	7.3
paper	16.0	4.7
cardboard	7.7	3.2
coupled packaging	1.8	0.5
textiles	3.0	1.1
diapers	4.8	2.0
plastics	14.4	2.8
rubber	0.4	0.3
glass	3.7	1.9
metals	2.9	1.1
inert materials	1.2	1.0
hazardous waste	0.4	0.3
wood	1.9	1.7
leather	0.1	0.2
others	0.4	0.4

A quantity of approximately 25 kg for each MBT sample, after being homogenized and quartered (according to UNI 10802:2013), was transported to the laboratory. From the laboratory sample (25 kg), two representative sub-samples were obtained after homogenizing and quartering; one sub-sample (2 kg) was used to determine the initial gravimetric moisture content of the MBT waste (which was in the range of 24-26 % by

wet weight) and the other one (5 kg) was air dried at room temperature (20-25 °C) before performing particle size analysis. Thereafter, the latter (5 kg) was shredded below 4 mm and split again into two samples of which, one (4.5 kg) is used in column and batch tests and the other one (0.5 kg) is successively grinded below 0.25 mm in order to determine the organic matter content and the chemical composition.

3.2.1 PARTICLE SIZE DISTRIBUTION

The particle size analysis (ASTM, 2007) was performed by sieving an amount of roughly 5 kg for each air-dried MBT sample. The following sieve sizes were used: 25.4 mm, 19.1 mm, 10 mm, 4 mm, 2 mm, 0.84 mm and 0.125 mm. Materials retained by each sieve were progressively weighed and the cumulative passing, P (% dry matter), was then calculated. Results of these analyses, shown in Fig. 3.1, revealed that about 70-80 % of MBT particles passed through the 10 mm sieve and roughly 40 % of particles had a diameter less than 4 mm.

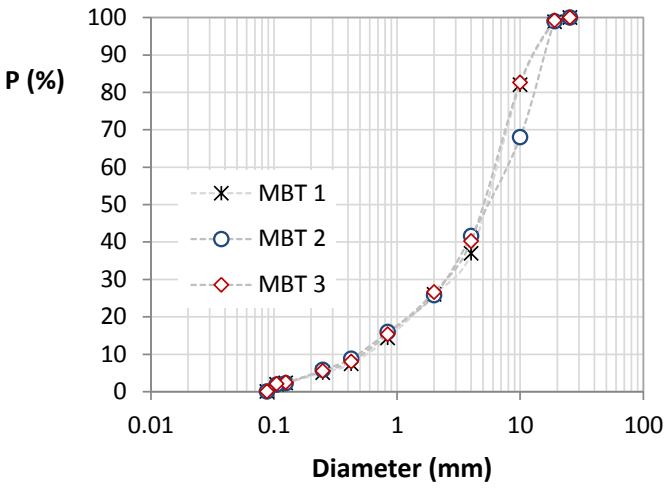

Figure 3.1. Particle size distribution analyses performed on MBT waste samples.

3.2.2 ORGANIC MATTER CONTENT

The volatile solids (VS) content was determined by loss-on-ignition (LOI) at 550°C for 8 h (UNI/TS 11184, 2006). Each sample, of about 10 g, from a representative mixed MBT sample previously grinded to 0.25 mm, was pre-dried in oven at 105°C for 4 h. Total organic carbon (TOC) content was analysed by means of Shimadzu SSM-5000A instrument on approximately 0.15 g of dried sample grinded to 0.25 mm (UNI 13137, 2002). All analyses were carried out in triplicate and the obtained average values, expressed on a dry weight basis, are reported in Table 3.3 together with the relative standard deviation.

3.2.3 CHEMICAL COMPOSITION

Heavy metals content of MBT waste samples was determined by acid digestion with HNO_3, H_2O_2 and HCl, according to EPA method 3050B (1996). Namely, 1 g of air-dried sample grinded to 0.25 mm was used for the analysis that was carried out in triplicate. The obtained solution, after filtration at 0.45 μm, was analysed by inductively coupled plasma optical emission spectrometer (Varian ICP-OES).

3.3 LEACHING TEST

As introduced above, in order to evaluate the leaching behaviour of MBT waste and to identify the key factors affecting the contaminants release from this type of material, a combination of pH static batch tests, pH-dependent test and up-flow column percolation experiments were carried out.

3.3.1 BATCH LEACHING TEST

Batch leaching test were performed according to the test method UNI EN 12457-2 (2004). MBT samples were air-dried and ground to obtain a particle size lower than 4 mm. Around 8 -10 g of MBT were put in contact with a solution of 0.001M $CaCl_2$ at a liquid to solid ratio (L/S) of 10 l/kgDM for 24 hours under constant agitation. The

obtained leachate, after pH measurement (Hanna Instrument pH-meter), was separated by centrifugation (SL 16R Tecnovetro Monza) at 10,000 g for 10 min and then filtered with a 0.45 μm cellulose acetate filter (Sartorius Stedim biotech) using a vacuum pump. Filtered leachate was then analysed to obtain the heavy metal concentrations (Varian ICP-OES analyser) and the dissolved organic carbon (DOC) (Shimadzu TOC-V CPH/CPN analyser). Note that, in order to compare the batch with the column tests, a solution of 0.001M $CaCl_2$ was used as leachant instead of demineralized water (standard method UNI EN 12457). However, as reference, in one of the collected samples a standard batch test with demineralized water was also carried out. All experiments were conducted in triplicate, at room temperature (20-25 °C).

3.3.2 COLUMN TEST

In order to assess the influence of the L/S ratio on the contaminant release, up-flow column percolation tests were carried out according to the method UNI CEN ISO/TS 21268:3 (2010). The apparatus consisted of plexiglas columns with a height of 35 cm and an inner diameter of 5 cm. Note that in the method UNI CEN ISO/TS 21268:3 (2010) is recommended, in order to avoid preferential flow pathways along the material-wall interface, that the maximum particle size should be at least 10 times smaller than the column diameter. For this reason, MBT samples were previously ground in order to get a particle size below 4 mm. The columns were closed with flanges sealed with polypropylene O-rings, stainless steel nuts and bolts. The bottom section was equipped with a perforate plate to ensure a homogeneous flux into the packed material to avoid preferential pathways. For the same reason, and to prevent the solid particle transport into the PVC tubing, a 2-cm high layer of fine quartz sand, embedded in two glass-microfiber discs (1.2 μm, Munktell filter), was inserted at the bottom and at the upper section of the column. Each column was filled with 0.3–0.4 kg of MBT waste samples, which were introduced in consecutive thin layers (2-3 cm) and compacted with a rammer. A final dry bulk density of materials ranging from 0.54 to 0.62 g/cm^3 was obtained (see Table 3.2). The packed columns were subjected to an upward flow (15 ± 2 cm/day) of demineralized water with 0.001 M of $CaCl_2$ by connecting the inlet pipe to a peristaltic pump. Since the main condition for this type of test is to ensure local

equilibrium between solid matrix and liquid phase is reached, the columns were saturated at the same linear velocity of the test (15 ± 2 cm/day) and, after saturation, maintained disconnected from the pump for 4 days. Thereafter, the pump was started again and the outlet pipe was connected to an eluate collection graduate bottle which was replaced once a water volume corresponding to the required L/S ratio was measured. Seven distinct leachates were collected at different cumulative L/S ratios (0.1, 0.2, 0.5, 1, 2, 5, and 10 l/kg of dry matter). Water volume for each L/S ratio was preliminary computed weighing the amount of sample in the column and determining the dry matter content according to UNI EN 14346 (2007). Measurements were done in triplicate. Dry matter content was equal to 87.4 %, 94.6 % and 92.9 % for MBT 1, MBT 2 and MBT 3, respectively (see Table 3.2). MBT column tests were carried out in duplicate, except the MBT 1. Table 3.2 summarizes the test conditions adopted for MBT 1, MBT 2 and MBT 3 samples. Table 3.2 also reports the average value of the contact time T_c (h) between the eluent and the matrix in each column experiments. Since this parameter could affect the contaminants release from wastes (Kylefors et al., 2003; Lopez-Meza et al., 2010; Parodi et al., 2011), T_c (h) values were calculated, at every test condition, according to Eq. (3.1) (Lopez- Meza et al., 2010):

$$T_c = \frac{V \cdot \theta}{q_{average}} \tag{3.1}$$

where V is the filling volume of the column (ml), θ the porosity (-) and $q_{average}$ the average flow rate (ml/h).

Table 3.2. Characteristics of up-flow column percolation tests carried out for the MBT waste samples. D= column inner diameter; W_{MBT}=wet weight of MBT sample in column; H_{MBT}=height of MBT material in the column; ρ = MBT bulk dry density; DM=dry matter; S_w=water volume for MBT saturation; θ= estimated porosity; $q_{average}$= average flow; T_c = contact time eluate/sample.

Test	D_i (cm)	W_{MBT} (g)	H_{MBT} (cm)	ρ (g/cm^3)	DM (%w/w)	S_w (ml)	θ (%v/v)	$q_{average}$ (ml/h)	Tc (h)
MBT 1	5	430	30.8	0.62	87.4	340	56.2	10.35	33
MBT 2.1	5	405	32.3	0.60	94.6	450	71.0	11.23	40
MBT 2.2	5	360	31.8	0.55	94.6	390	62.6	11.92	33
MBT 3.1	5	330	29.0	0.54	92.9	390	68.5	9.01	43
MBT 3.2	5	330	28.5	0.55	92.9	360	64.4	8.13	44

Column eluates were pre-filtered (after pH measurements) with 0.7 μm glass fiber (Whatman) to facilitate the subsequent filtration at 0.45 μm. Samples were split in two sub-samples; one part was kept untreated for determining concentration of chlorides and DOC and the other one was acidified to ensure pH <2 (using a solution of 1:1 v/v HNO_3:deionized water) for measuring the heavy metals content (Varian ICP-OES analyser).

3.3.3 pH DEPENDENT TEST

The standardized UNI CEN ISO/TS 21268-4 (2010) leaching test procedure was carried out to evaluate the base/acid neutralization capacity (BNC/ANC) of the MBT waste samples as well as the release of major and trace elements as a function of pH. Basically, the test consists of different parallel batch experiments with a fixed L/S ratio of 10 l/kgDM, in which 8 g of MBT waste samples (particle size reduced below 1 mm) were put in contact with 80 ml of solution containing different aliquots of deionized water (DI) and sodium hydroxide (NaOH) or nitric acid (HNO_3) to obtain eluates with end-pH values spanning within a wide pH range (4-12). Each suspension was equilibrated and stirred on a tumbler for 48 h. The pH values of each eluate was then measured (Hanna Instrument pH-meter) and the leachate solutions were filtered through 0.45 μm pore size filters before performing the chemical analyses. The samples collected were separated in two sub-samples: one acidified with nitric acid for metal analysis and the other directly analysed to determine its chlorides and Dissolved Organic Carbon (DOC) contents. Concentrations of major compounds and trace elements were measured by ICP-OES (Varian ICP-OES analyser). The leaching of soluble chlorides were evaluated by titration with $AgNO_3$ (ISO 9297:1989) and concentrations of DOC was determined with a Shimadzu TOC–V CPH/CPN analyser.

3.4 MODELLING THE CONSTITUENT MASS RELEASE IN COLUMN TESTS

As described above, in order to achieve the equilibrium between the concentration in the solids and in the pore water, before performing each test, the columns were saturated and maintained disconnected from the pump for 4 days. Under these conditions, in the early stages of the test (i.e. low L/S ratios) the mass transfer can be considered negligible and the mass release is governed by an advection-controlled transport where the cumulative mass release per unit mass of waste, $M_{cum,adv}$ (mg/kgDM), can be estimated as a function of the L/S ratio (Kosson et al., 2002):

$$M_{cum,adv} = L/S \cdot C_{sol} = \frac{L/S \cdot C_0}{K_d} \tag{3.2}$$

where C_{sol} is the concentration in the liquid phase, C_0 the total content of the contaminant in the solid matrix (mg/kgDM) and K_d (l/kgDM) the solid-water partition coefficient.

The liquid to solid ratio, L/S (l/kgDM), is the amount of water percolated through the column after a certain time relative to the dry weight of the solids in the column (Grathwohl and Susset, 2009):

$$L/S = \frac{v \cdot \theta \cdot t}{h_c \cdot \rho} \tag{3.3}$$

where v is the average flow velocity (m/s), t the time (s), θ the porosity (-), h_c the column height (m) and ρ the dry bulk density of the waste in the column (kgDM/l).

Eq. (3.2) is valid up to low L/S ratios as for extended leaching times non-equilibrium conditions, resulting from a switch to a mass transfer-controlled scenario, are usually observed, leading to a reduction of pore water concentrations below the equilibrium values (Grathwohl and Susset, 2009; Kosson et al., 2002).

Under a mass transfer-controlled scenario, the cumulative mass release per unit mass of waste, $M_{cum,dif}$ (mg/kgDM), can be estimated using the following simplified expression (Kosson et al., 2002):

$$M_{cum,dif} = 2\frac{C_0}{h_c}\left(\frac{D \cdot t}{\pi}\right)^{1/2} \tag{3.4}$$

where D is the apparent diffusion coefficient of the constituent in the porous medium (m^2/s).

Hence, the cumulative mass release per unit mass of waste expected during the entire duration of the column test, M_{cum} (mg/kgDM), can be estimated as follows:

$$\begin{cases} M_{cum} = L/S \cdot C_{sol} & \text{for L/S} \le \text{L/S}^* \\ M_{cum} = L/S^* \cdot C_{sol} + 2\frac{C_0}{h_c}\left(\frac{D \cdot \ t - t^*}{\pi}\right)^{1/2} & \text{for L/S} > \text{L/S}^* \end{cases} \tag{3.5}$$

where L/S^* and t^* are the critical liquid to solid ratio and time, respectively, above which the mass release switches to a mass transfer-controlled scenario.

L/S^* can be estimated assuming the critical number of pore volumes delivered in the column required to achieve a mass transfer-controlled release condition (e.g. $n_{pv} = 0.5$):

$$L/S^* = \frac{n_{pv} \cdot S_w}{\rho \cdot V_c} \tag{3.6}$$

where S_w is the water required to saturate the column (l), V_c the column volume (l) and n_{pv} the number of pore volumes delivered.

Consequently, the t^* can be calculated from Eq. (3.3) as follows:

$$t^* = L/S^* \cdot \frac{h_c \cdot \rho}{v \cdot \theta} \tag{3.7}$$

Note that the simplistic models described here do not account for biodegradation and geochemical processes that can occur in landfill and that can influence the DOC and metal release over time.

3.5 RESULTS AND DISCUSSION

3.5.1 MBT WASTE COMPOSITION AND CHARACTERISTICS

Table 3.3 reports the chemical composition and organic matter content of the different MBT waste samples analysed. From Table 3.3 it can be noticed that MBT wastes, even though subjected to a biological stabilization process, were characterized by a relevant organic matter content. In fact, in all the analysed samples volatile solid content (VS) was higher than 50% of dry matter. As far as metals are concerned, results indicate that Cu, Ni, Pb and Zn are numerically the major elements among the trace compounds in the different MBT waste samples. Similar results were obtained by Smith (2009), Alvarenga et al. (2007) and Farrell and Jones (2009).

Table 3.3. Chemical composition and organic matter content of MBT samples (mean ± SD).

	MBT 1	**MBT 2**	**MBT 3**
Macro- constituents (g/kgDM)			
Al	10.6 ± 2.3	14.2 ± 0.1	14.1 ± 0.1
Ca	62.7 ± 4.9	72.7 ± 14.5	53.8 ± 2.0
Fe	9.9 ± 0.5	9.3 ± 0.5	8.0 ± 0.2
K	8.9 ± 0.6	10.7 ± 0.1	7.4 ± 0.3
Mg	4.1 ± 0.0	3.9 ± 0.1	4.1 ± 0.1
Na	5.7 ± 0.3	7.5 ± 1.3	5.6 ± 0.1
Trace elements (mg/kgDM)			
Ba	307 ± 56	383 ± 32	305 ± 17
Co	3.3 ± 0.7	2.4 ± 0.1	1.6 ± 0.3
Cr	18.8 ± 3.9	30.3 ± 15.2	29.3 ± 1.3
Cu	154 ± 6	172 ± 110	108 ± 18
Li	3.8 ± 0.5	5.4 ± 0.4	5.1 ± 0.2
Mn	201 ± 5	212 ± 9	176 ± 16
Mo	2.2 ± 0.1	1.7 ± 0.1	2.3 ± 0.1
Ni	17.9 ± 2.6	15.7 ± 0.4	24.2 ± 1.2
Pb	390 ± 67	350 ± 120	251 ± 16
V	18.8 ± 2.4	21.7 ± 1.1	18.2 ± 0.7
Zn	322 ± 21	370 ± 7	307 ± 12
TOC (% DM)	28.1 ± 0.1	27.0 ± 0.5	26.9 ± 1.3
VS (% DM)	56.3 ± 0.7	54.2 ± 1.6	53.3 ± 1.3

High concentrations of Cu, Ni, Pb and Zn are probably due to the nature of the feedstock (e.g. heterogeneous mixed/residual MSW). In fact, as reported by Amlinger et al. (2004), Di Lonardo et al. (2012), Farrell and Jones (2009) and Smith (2009), there are many sources of heavy metals in municipal solid wastes (such as dust, batteries, plastics and paints).

3.5.2 RESULTS OF BATCH TESTS

Table 3.4 shows the average metal concentrations measured in the eluates of batch leaching tests (L/S = 10 l/kg) carried out on the analysed MBT samples using the procedure described in **Section 3.3.1**. Reported values are expressed as g/kg or mg/kg of dry matter for macro-constituents and trace elements, respectively. Standard deviations (SD) are also shown. Note that the results reported in Table 3.4 are the ones obtained from batch leaching tests carried out with a solution of 0.001 M $CaCl_2$ as leachant. As reference, for the MBT 2 sample the results of standard batch test with deionized (DI) water are also shown. The obtained results show that, in this specific case, the batch tests performed using $CaCl_2$ or DI water are basically the same. Referring to the results reported in Table 3.4, it can be noticed that although MBT samples contain relatively high heavy metal contents (see Table 3.3), only a small amount of metals was actually leachable under the test conditions (natural pH, ambient temperature) and thus environmentally available. For instance, with reference to MBT 1, the total Cr content was 18.8 mg/kgDM whereas the leached Cr measured in the batch test was 0.47 mg/kgDM that corresponds to a very low percentage release (i.e. 2.5 %). These results are in line with those reported by Farrell and Jones (2009), Iwegbue et al. (2007) and Smith (2009) for MSW-derived compost. The relatively low availability observed for the different metals is presumably due to the aerobic composting process that may increase the complexation of metals within the solid matrix. It is widely recognized, in fact, that solubility and bioavailability of most metals decrease during the evolving of aerobic biological process as they may be strongly bound to the organic residual material in a more stable form (Amir et al., 2005; Farrell and Jones, 2009; Smith, 2009).

Table 3.4. Results of batch leaching tests carried out with 0.001 M $CaCl_2$ solution on MBT samples (mean ± SD). In the last column of the table the results of standard batch test with deionized (DI) water on MBT 2 sample are also reported.

Parameter	Batch $CaCl_2$ solution			Batch DI water
	MBT 1	**MBT 2**	**MBT 3**	**MBT 2**
pH	6.5	6.8	7	6.5
DOC (g/kgDM)	25.7 ± 0.9	16.2 ± 0.3	14.1 ± 0.6	14.8 ± 0.4
Cl^- (g/kgDM)	7.3 ± 0.1	7.2 ± 0.2	5.3 ± 0.3	7.3 ± 0.4
Macro- constituents (g/kgDM)				
Al	0.03 ± 0.00	0.03 ± 0.01	0.01 ± 0.00	0.02 ± 0.00
Ca	7.8 ± 0.3	6.0 ± 0.8	4.5 ± 0.1	5.6 ± 0.7
Fe	0.05 ± 0.00	0.07 ± 0.01	0.02 ± 0.00	0.06 ± 0.00
K	2.6 ± 0.0	3.8 ± 0.5	2.5 ± 0.1	3.2 ± 0.1
Mg	0.7 ± 0.0	0.7 ± 0.1	0.4 ± 0.0	0.6 ± 0.0
Na	3.0 ± 0.0	3.8 ± 0.0	2.9 ± 0.1	3.6 ± 0.1
Trace elements (mg/kgDM)				
Ba	7.8 ± 1.2	18.2 ± 3.8	10.8 ± 0.4	11.8 ± 1.3
Co	0.24 ± 0.01	0.24 ± 0.02	0.10 ± 0.04	0.19 ± 0.01
Cr	0.47 ± 0.09	0.81 ± 0.07	0.48 ± 0.02	0.76 ± 0.01
Cu	5.03 ± 0.05	5.91 ± 0.45	3.68 ± 0.13	6.26 ± 0.15
Li	0.29 ± 0.01	0.16 ± 0.01	0.08 ± 0.04	---
Mn	15.0 ± 0.4	10.2 ± 0.5	4.9 ± 0.2	9.5 ± 0.2
Mo	0.42 ± 0.10	0.33 ± 0.06	0.24 ± 0.01	0.40 ± 0.02
Ni	2.2 ± 0.1	2.5 ± 0.1	1.6 ± 0.1	2.4 ± 0.0
Pb	3.4 ± 0.2	3.3 ± 0.4	1.1 ± 0.0	2.9 ± 0.2
V	0.16 ± 0.01	0.32 ± 0.02	0.18 ± 0.01	0.34 ± 0.01
Zn	37.8 ± 1.1	45.4 ± 4.6	25.0 ± 0.9	38.3 ± 0.8

3.5.3 RESULTS OF COLUMN TESTS

Fig. 3.2 shows the cumulative mass release (mg/kgDM) as a function of the liquid to solid ratio (L/S) for DOC and some heavy metals measured in the different column tests. In the same figure, the total content (lines) and the results of batch leaching tests carried out with 0.001 M $CaCl_2$ solution (black symbols) are also reported. Although many different elements were measured, for sake of conciseness, the attention was focused on the leaching of DOC, Co, Cr, Cu, Mg, Ni, Pb, V and Zn, since they exhibited most significant results. Looking at the results reported in Fig. 3.2, it can be noticed that, even if MBT waste is a heterogeneous material, the trends of mass release

provided by column tests for the different MBT waste samples are quite similar. This reveals on the one hand, a similar behaviour of the samples collected in the different campaigns, and, on the other hand, a good reproducibility of the column tests and the consistency of leaching data. The only exceptions are represented by Co and Pb that have shown a wider variation, presumably due to the different total content in MBT samples (lines).

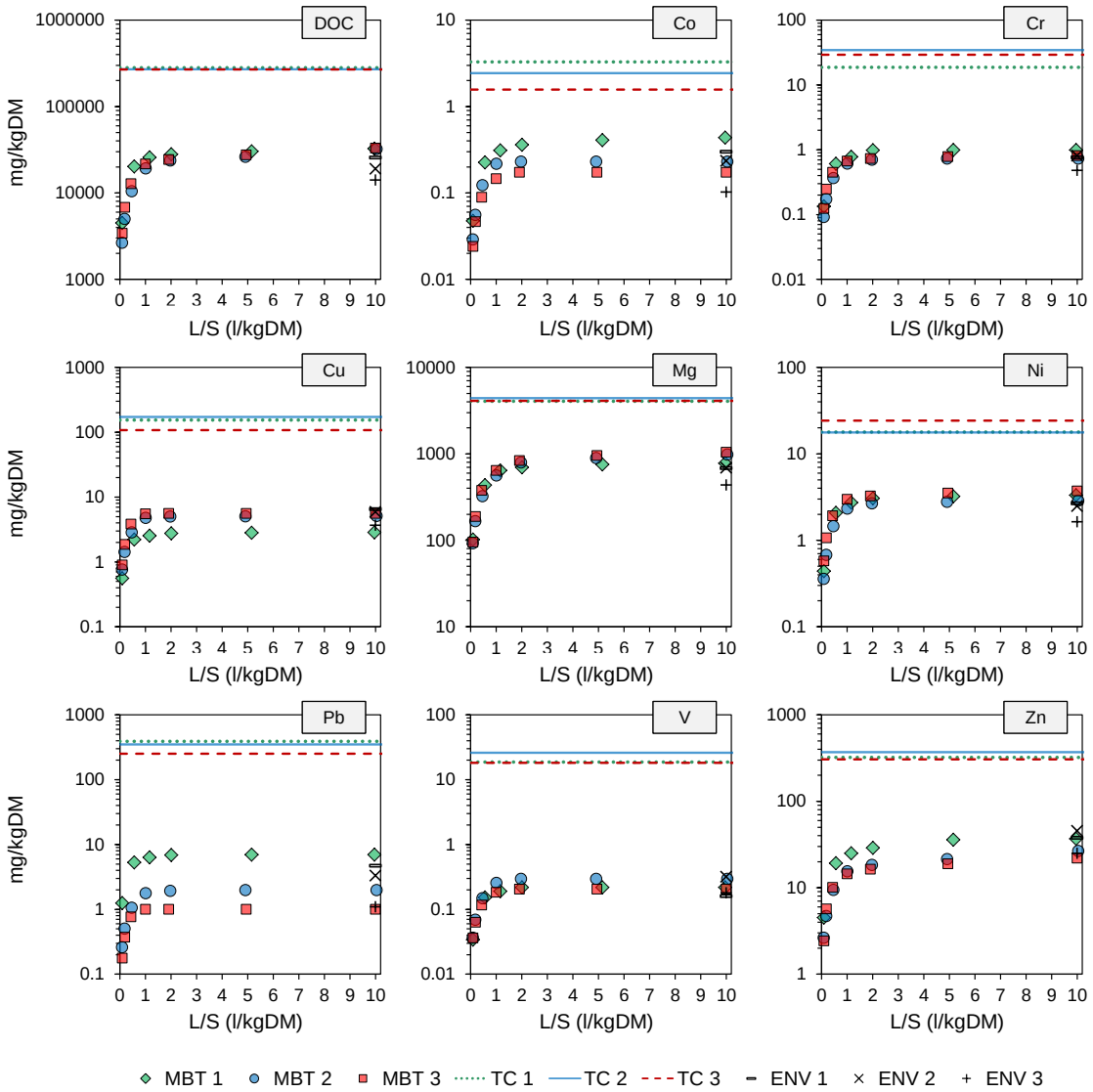

Figure 3.2. Total content (lines) and cumulative element release (dots) measured in the column tests MBT 1 (green), MBT 2 (blue) and MBT 3 (red). Black signs represent constituent concentrations measured in batch leaching tests carried out with 0.001M $CaCl_2$ solution (ENV 1, 2, 3).

Trends reported in Fig. 3.2 also indicate that the cumulative release of compounds is much lower than the total content. Namely, by comparing the total release of each metal provided by column tests with the total content, it is evident that only a small amount of these elements is mobilized, at least if the environmental conditions (pH, temperature) are similar to the tested ones. In fact, the release percentage was about 11-13 % for DOC, 7-11 % for Zn, 2-5 % for Cr and Cu and < 1 % for Pb and V. The highest mobility was observed for Ni and Co with release percentages up to 15–19 % and 9–13 %, respectively.

Furthermore, from Fig. 3.2 it can also be noticed that the cumulative concentrations of DOC, Co, Cr, Mg and Ni obtained at the end of column tests (corresponding to a L/S ratio of 10) are clearly higher than those provided by the batch leaching test (performed at the same L/S ratio of 10). This means that probably the batch test may underestimate the actual release of contaminants from this type of waste. This result may be due to the longer duration of the column experiment (Cappuyns and Swennen, 2008; Kalbe et al., 2007) compared to the batch one (2-3 weeks instead of 24 hours). Moreover, in dynamic column tests there is a continuous renewal of the leachant that maintains the driving force of leaching (Cappuyns and Swennen, 2008). In Fig. 3.3, pH trends and DOC, Co, Cr and V concentrations (mg/l) measured in column and batch tests for MBT 2.2 (Fig. 3.3a) and MBT 3.2 (Fig. 3.3b) samples are plotted as a function of the L/S ratios. Note that in Fig. 3.3, for illustration purposes only, the values lower than the quantification limit (QL) were reported as QL/2 (Dashed symbols). From Fig. 3.3a, it can be noticed that in the MBT 2.2 test, the DOC concentration showed an increasing trend at the beginning of the test and a rapid decrease for L/S ratios greater than 1. On the contrary, in the MBT 3.2 test (Fig. 3.3b), DOC exhibited a sharp descending trend, which is indicative of a rapid wash-out mechanism, until reaching a stable concentration of about 1000 mg/l for L/S ratios greater than 5. It is likely that in test MBT 2.2, the initial equilibrium condition (at the beginning of the test) between solid matrix and leachant had not been completely established, presumably due to the lower contact time (see Table 3.2). This may explain the delay time that was observed before measuring the DOC peak concentration. However, this different behaviour in DOC mass release allowed to find out the key parameter governing metals release from this type of waste.

Indeed, the results reported in Fig. 3.3 highlight that the elution profiles of Co, Cr and V followed a very similar trend to the one observed for DOC.

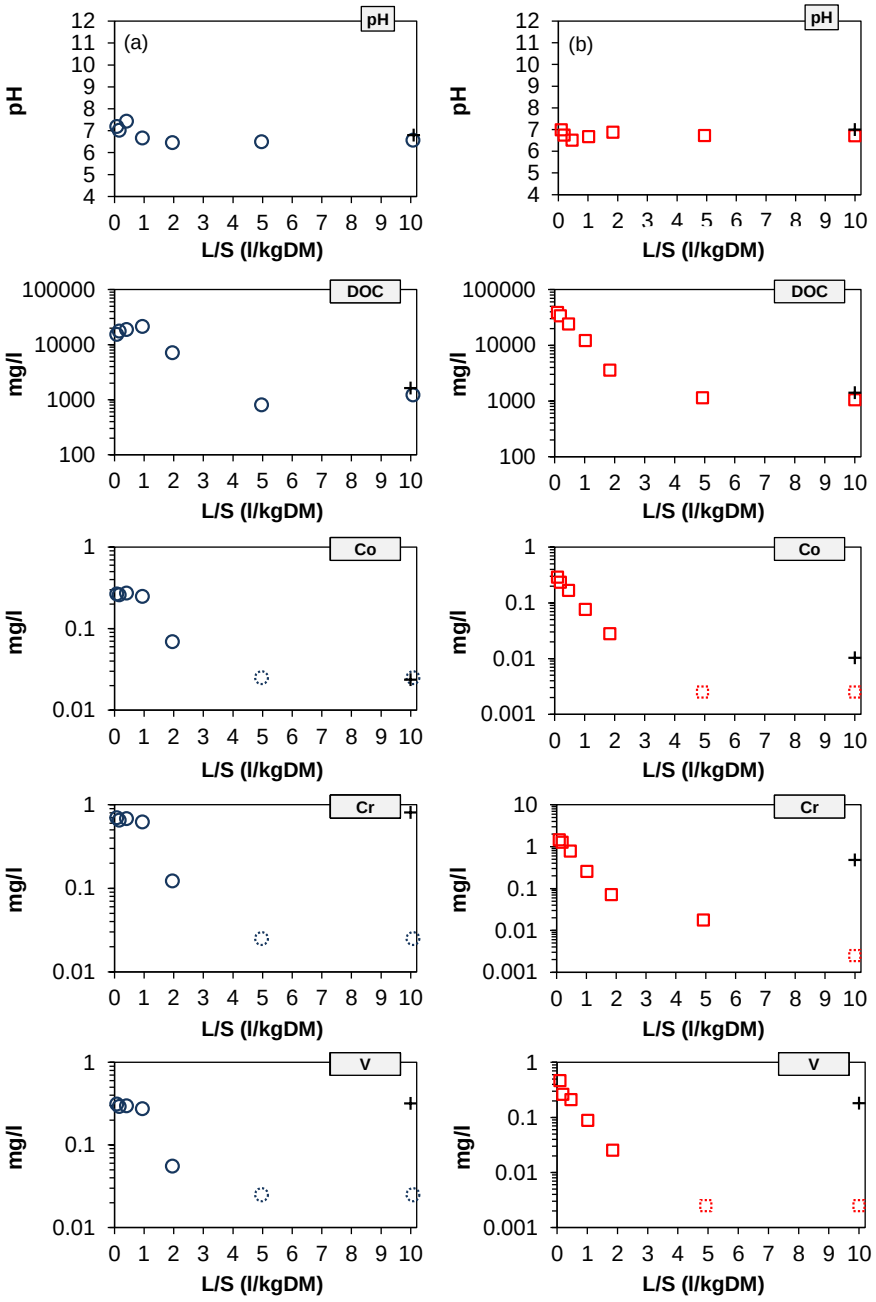

Figure 3.3. Elution profiles of DOC, Co, Cr, V and pH trend measured in column test MBT 2.2 (a) and MBT 3.2 (b). Black sign (+, -): values from batch leaching tests performed with 0.001M $CaCl_2$. For illustration purposes only, the concentrations lower than the detection limit (DL) were substituted with the DL/2 (dashed symbols).

Conversely, pH cannot be evoked to explain the different compounds release. Indeed, during all column tests, the pH of emplaced sample showed a slight variation compared to the initial native pH value of these materials (e.g. pH measured in batch test and reported in Table 3.4). Namely, as reported in Fig. 3.3, pH values measured during column tests were very close to the native pH (dotted line) and differences did not exceed ±0.5 unit. On the contrary, a clear correspondence between metals and the DOC concentrations in eluates is observed, revealing that metals release essentially reflects the leaching pattern of the dissolved organic carbon.

To verify this hypothesis, the results of batch and column tests were combined to obtain information about the correlation between metals concentration and DOC. In Fig. 3.4 the eluate concentrations of Co, Cr, Cu, Mg, Ni, Pb, V and Zn are reported as a function of the DOC measured in column (blue, green and red dots) and in batch tests (yellow triangles). As shown in these graphs, a strong linear correlation between DOC and metals concentrations was observed ($R^2 > 0.8$), with the only exception of Pb that showed a lesser dependence on DOC. These findings suggest that these elements were mainly released as organo-compounds due to complexation of heavy metals with dissolved organic matter. Actually, it is widely recognized that, in organic-rich materials such as sludge and biowaste, the DOC is one of the key factor controlling the release (especially of Cu, Cr, Ni and Zn), due to its high solubility and its ability to form stable soluble organic complexes with metal ions (Ashworth and Alloway, 2007; Ashworth and Alloway, 2004; Van Der Sloot, 2004). For instance, Ashworth and Alloway (2007) investigated the mobility of sewage-sludge showing that Ni and Cu were readily leached and strongly correlated with DOC whereas Zn tends to be adsorbed to the solid matrix. Hsu and Lo (2001) found that in composted swine manure the concentrations of Cu and Zn in water extract were highly correlated to water soluble organic carbon, with a correlation coefficient of 0.98 and 0.99, respectively. Zheng et al. (2007) noticed a strong positive correlation between the DOC and Cr. Antoniadis and Alloway (2002) observed that increasing DOC concentration in sewage sludge amended soils resulted in increasing availability of Cr and Zn; they conclude that DOC has an important influence on the chemical reaction and probably competes with solid surfaces for adsorbing heavy metals, leading to higher metal concentrations in solution. Zhao et al. (2007) observed, by performing soil-polluted column experiments, that Cu mobilization was controlled

by DOC whereas Zn mobility was primarily governed by Ca and to a lesser extent by DOC. Results presented by Ashworth and Alloway (2008) revealed a high affinity of Cu, Ni and Pb with DOC due to the formation of organically complex forms. Their results disclosed the existence of a strong linear relation between these elements and the solubility of organic matter, particularly at pH greater than 6. Hence, the obtained results (Fig. 3.4) are consistent with the above mentioned studies on organic-rich materials.

Based on these results, it can be assumed that metal concentrations vary proportionally to DOC and, thus, metal release could be modelled as a function of the dissolved organic carbon through a partition coefficient ($K_{DOC,Me}$) between metal (Me) and DOC:

$$Me = K_{DOC,Me} \cdot DOC \tag{3.8}$$

In this case, the partition coefficient of each metal, $K_{DOC,Me}$, was deduced by interpolating all the data provided by batch and column tests performed on MBT samples (48 samples). The obtained $K_{DOC,Me}$ values together with the determination coefficients (R^2) are reported in Fig. 3.4.

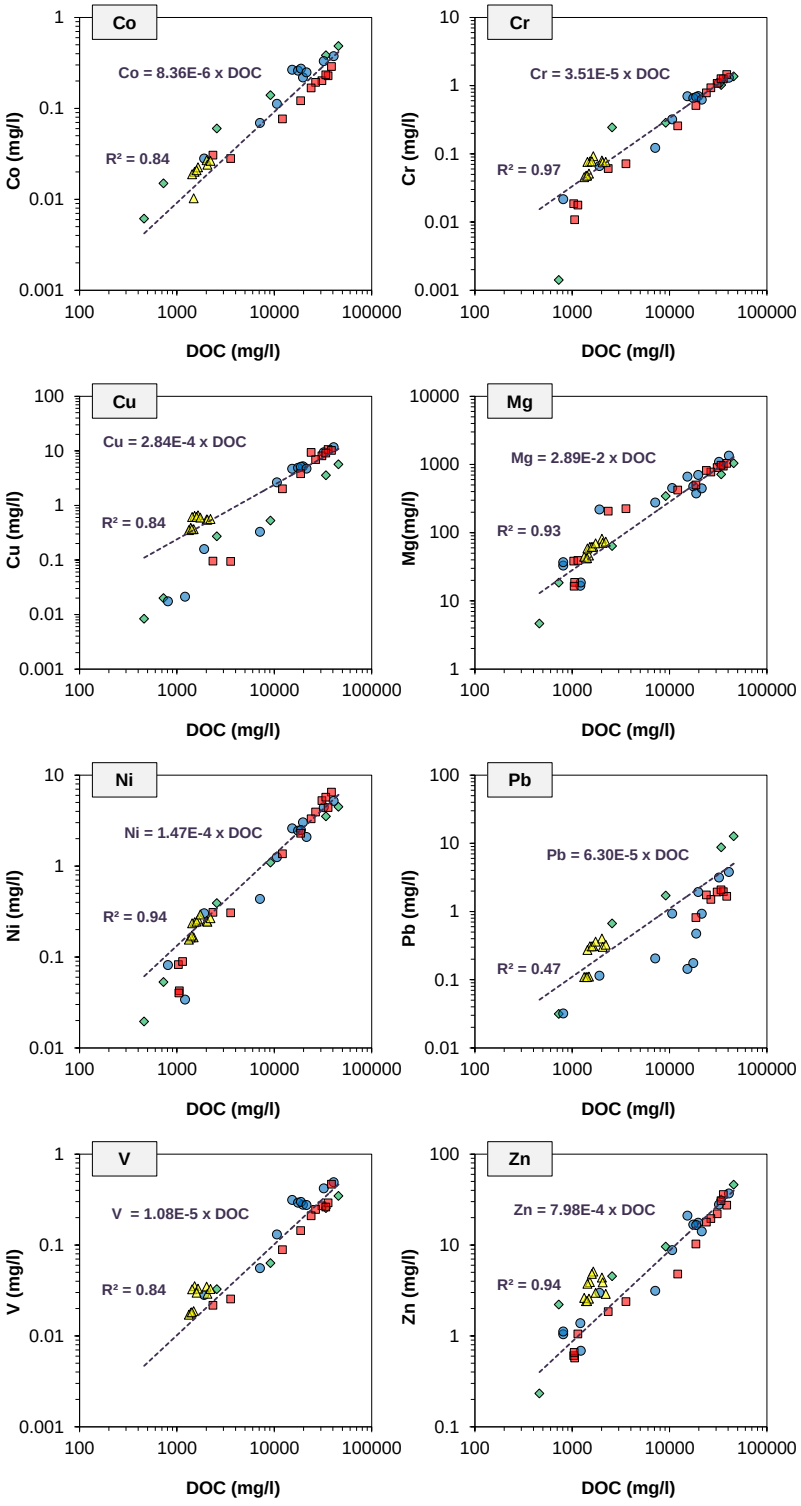

Figure 3.4. Correlation between DOC and Co, Cr, Cu, Mg, Ni, Pb, V and Zn concentrations in column tests (green, blue and red dots) and batch tests (yellow triangle). The dotted lines represent the regression lines assuming a zero value for the intercept (Eq. (3.8)).

3.5.4 LEACHING MODELLING AND IMPLICATIONS FOR LONG-TERM EVALUATIONS

3.5.4.1 DOC RELEASE AS A FUNCTION OF L/S

The previous results showed that the metals release from the MBT waste is closely related to the amount of DOC in the eluate (see Fig. 3.3 and Fig. 3.4). This suggests that the prediction of metal release from the tested material can be carried out by simulating the leaching behaviour of DOC during the test. This can be done by using the simplified model described in Eqs. (3.4)-(3.6). To this end, all the available parameters measured for each sample (see Table 3.2 and Table 3.3) were used. The other parameters required in the model were estimated after a preliminary calibration step. Specifically, the DOC diffusion coefficient in porous waste (D) was set equal to 10^{-6} cm^2/s. This value, however, is not so far from the range of diffusivity coefficients in water typically assumed for organic compounds (Verginelli and Baciocchi, 2013). Moreover, a critical pore volume number (n_{pv}) of 0.5, which can be considered as an average condition of water renewal in the column, was set. This value is reasonable assuming that the switch to a mass-transfer controlled scenario is not linear along the whole column, but rather occurs first at the bottom, where the water is fluxed, and, progressively, takes place moving vertically in the column. Finally, the organic carbon (OC) solubility was estimated as a function of the total carbon content (TOC) in the solid sample through the partition coefficient K_d (i.e. the ratio of the sorbed OC per unit mass of solid to the amount of DOC at equilibrium). Based on the measured TOC data (Table 3.3) and the first eluate concentrations of DOC measured in the outlet of the column, an average K_d value of 0.15 l/kgDM was determined for OC. This value could be assumed as representative of this specific MBT waste e.g. coming from a 4-weeks aerobic process without the ripening stage. However, it is likely that K_d is strongly influenced by the stability degree of the MBT waste material as well as by the characteristics of the incoming MSW waste feeding the MBT plant and, hence, it should be estimated for each specific plant configuration and/or biological treatment procedure.

Fig. 3.5 reports the results of the model application for the different tests carried out. Namely, the figure shows the DOC cumulative trend modelled assuming a flux-

controlled transport (red dotted line), a mass transfer-controlled scenario (blue dotted line) and a combined transport scenario (green line). Furthermore, the DOC cumulative concentrations measured in each test are also reported (black dots). Making reference to the obtained results, it can be noticed that assuming either a simple flux-controlled transport (Eq. (3.2)) or a mass-transfer controlled scenario (Eq. (3.4)), the model provides results quite different from the ones measured in the column tests leading to an overestimation and underestimation of the cumulative DOC release prediction, respectively. On the contrary, very good results are obtained using the combined model described in Eq. (3.5). It is worth noting that most of the model parameters required in Eq. (3.5) were derived from results of column experiments (S_w, ρ, θ and ν, see Table 3.2), using the column device dimension (column height h_c: 3.5 dm; column inner diameter D_i: 0.5 dm; column volume V_c: 0.69 l) and the MBT waste chemical characteristics (total carbon content TOC, C_0 (mg/kgDM), shown in Table 3.3 and the DOC concentration in the liquid phase, C_{sol}, estimated as a function of C_0 through the OC solid-water partition coefficient K_d).

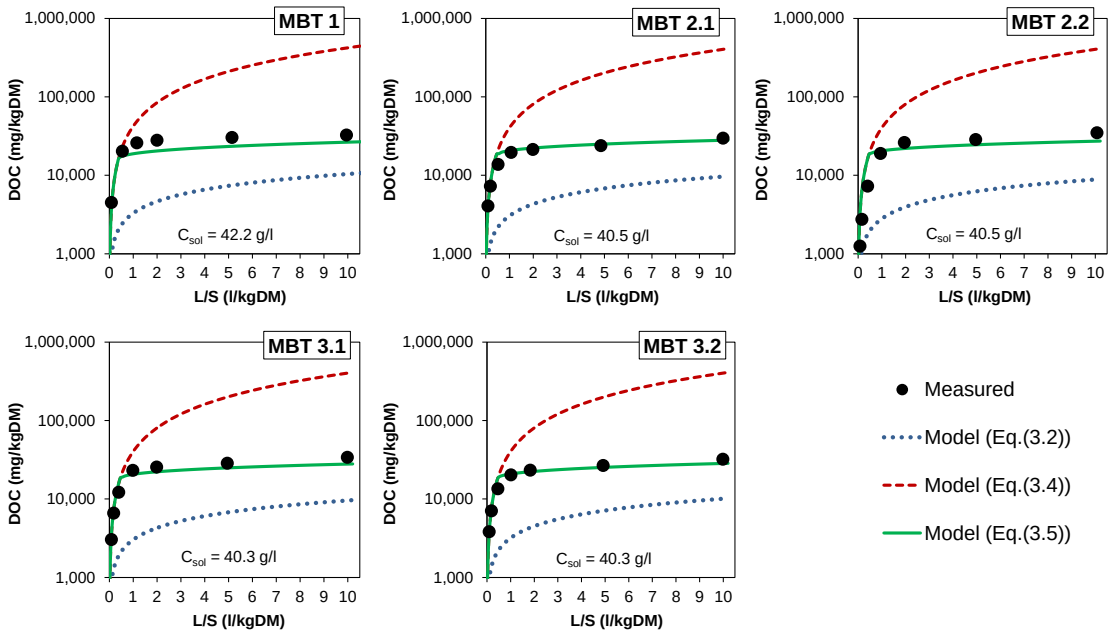

Figure 3.5. Cumulative mass release of DOC (mg/kg) in column experiments: comparison of measured data (black dots) with model predictions (green lines). Red and blue dotted lines represent the DOC mass release due to flux-controlled (red dotted lines) or mass-transfer controlled transport (blue dotted lines), respectively.

The only unknown parameters in Eq. (3.5) were the critical pore volume, n_{pv}, and the apparent diffusion coefficient of DOC in waste, D, that were set equal to 0.5 and 10^{-6} cm^2/s, respectively, and assumed the same in all column experiments. Moreover, the OC solid-water partition coefficient K_d, assumed equal to 0.15 l/kgDM for each test, was estimated as average of ratios between the TOC of the MBT waste sample in the considered column experiments and the DOC concentration measured in the first column eluate.

Overall, the results displayed in Fig. 3.5 indicate that the flux-controlled scenario is valid only for low L/S ratios, whereas for higher L/S a non-equilibrium conditions, which can be described by a mass-transfer controlled model, are observed. This is a key issue to be accounted for long-term evaluations of leaching behaviour since implies that for L/S approximately higher than 0.5 l/kgDM, Eq. (3.3), used to switch from L/S to time, is not more valid but the mass release should be estimated as a function of time (see Eq. (3.5b)). As a result, the overall mass release expected for long-term scenarios (e.g. after 50 or 100 years) will be definitely higher than the values reported in Fig. 3.5 for high L/S ratios.

3.5.4.2 METAL RELEASE AS A FUNCTION OF L/S

The metals release observed during the different column tests can be described by combining the model used to predict the DOC release (Eq. (3.5)) with the empirical equation (Eq. (3.8)) that links the metal release to DOC:

$$\begin{cases} M_{cum(Me)} = \left(L/S \cdot \dfrac{TOC}{K_d} \right) \cdot \mathrm{K_{DOC,Me}} & \text{for L/S} \le \text{L/S}^* \\ M_{cum(Me)} = \left(L/S^* \cdot \dfrac{TOC}{K_d} + 2\dfrac{TOC}{h_c}\left(\dfrac{D \cdot t - t^*}{\pi} \right)^{1/2} \right) \cdot \mathrm{K_{DOC,Me}} & \text{for L/S} > \text{L/S}^* \end{cases} \quad (3.9)$$

where TOC is the total organic carbon content, K_d the partition coefficient between TOC and DOC (i.e. DOC=TOC/K_d) and $K_{DOC,Me}$ the empirical partition coefficient between metal (Me) and DOC (reported in Fig. 3.4).

Fig. 3.6 displays a comparison between the cumulative mass release of metals measured in the column test MBT 3.1 (blue circles) and the values predicted by the model (dotted grey line). The obtained results clearly show that the simplified approach proposed in this work (Eq. (3.9)) allows to get a very good prediction of the metal release during the column test. This is particularly true for the metals that showed the strongest correlation with DOC (i.e. Cr, Ni and Zn). Similar results (not shown for sake of conciseness) were also obtained for the other performed column tests, confirming the ability of the simplified approach to describe the metal release from the tested material.

However, it is worth pointing out that for long-term field predictions the proposed simplified approach could be improved since it neglects different geochemical and biological processes, which are likely to occur in landfill and that can influence the DOC release, the form of soluble organic matter and its ability to bind metals (Van der Sloot, 1996).

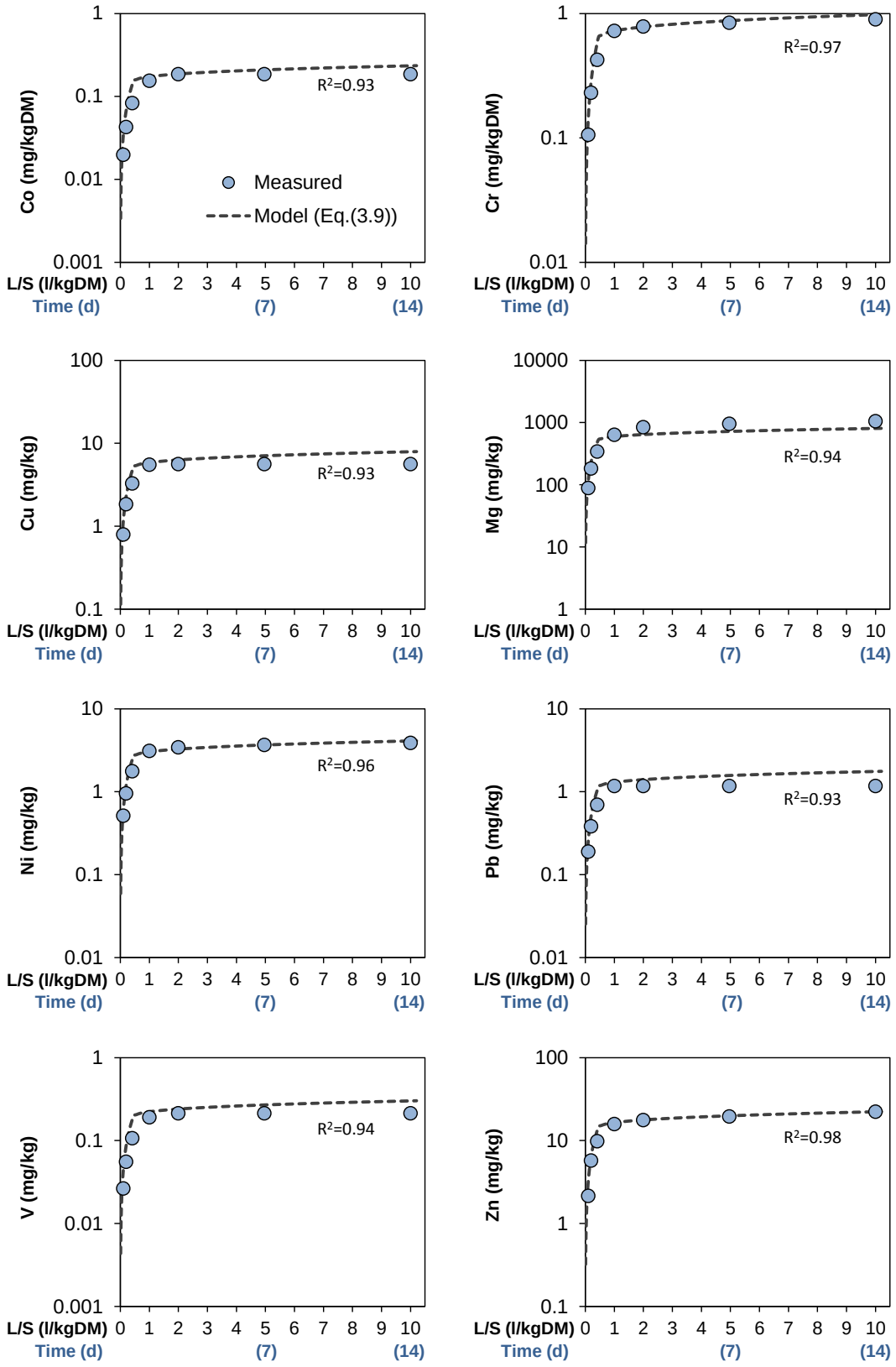

Figure 3.6. Metal cumulative mass release as a function of L/S ratio: comparison between measured data (blue dots) and predicted values (grey dotted lines) for the MBT 3.1 column test. Secondary x axis (blue): Test duration (days) used in Eq. (3.9) for L/S > L/S*.

3.5.4.3 DOC AND METAL RELEASE AS A FUNCTION OF PH

The acid/base neutralization behaviour gives an estimation on how fast the pH of the material and, subsequently, the release of constituents, will be altered due to changing in local environmental conditions. The acid/base neutralization capacity (ANC/BNC) curve obtained for the MBT 2 waste sample by applying the test procedure described in **Section 3.3.3** is shown in Figure 3.7. This curve shows the measured pH in eluates after the addition of different aliquots of base/acid, expressed as milliequivalents of base/acid per dry weight of the material. As can be noted from Fig. 3.7, the MBT waste exhibited a good acid neutralization capacity whereas a very low base buffer capacity was observed for pH between 6.5 and 12.

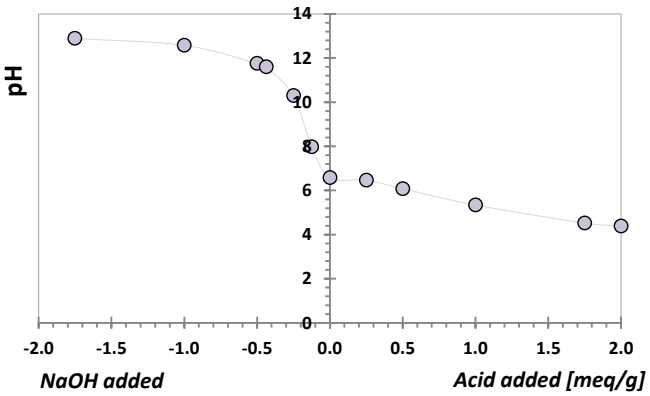

Figure 3.7. Acid/base neutralization capacity curve obtained for MBT 2 waste sample.

The initial pH of MBT waste was 6.5 and gradually decreased with the addition of acid to the solution. In fact, the addition of 0.5 meqH^+/g entailed a very small pH reduction (from 6.5 to 6.1) and after the addition of 1.0 meqH^+/g, the pH in eluates reach the value of 5.3. When 2.0 meqH^+/g were added, the pH decreased to the lowest value of 4.4. Therefore, the MBT waste has the potential capacity to neutralize the acidification effect, as a result, for instance, of VFAs accumulation during the organic matter degradation in landfills.

The overall buffer capacity of MBT waste has a huge influence on the leaching mechanism of different metals from this type of material. Indeed, the influence of pH on the release of contaminants is directly related to the nature of a particular element of concern as well as to the characteristics of the phases in which it is bound. Fig. 3.8

shows the pH dependent release of DOC and some elements obtained from this type of test. Concentrations measured in eluates (blue dots) are expressed as mg per kg of dry matter in order to compare them with the total content in the matrix (dotted line). It is worth noting from Fig. 3.8 that DOC release pattern is almost constant and not influenced by pH values, as observed by van Der Sloot et al. (2001) for mechanically separated organic material. In fact, as reported in Table 3.5, variations in DOC concentrations with pH are less meaningful compared to other elements (see for instance Al, Ca, Mg and Zn in Table 3.5).

Table 3.5. Concentrations of DOC, Al, Ca, Mg and Zn, expressed as mg/kgDM, as a function of pH in eluates. Results from pH dependent test carried out on MBT 2 waste sample.

Sample	pH	DOC (mg/kgDM)	Al (mg/kgDM)	Ca (mg/kgDM)	Mg (mg/kgDM)	Zn (mg/kgDM)
ANC 1	11.6	23,520	700	138	31	15
ANC 2	10.3	20,390	209	176	35	19
ANC 3	8	21,940	24	410	418	22
ANC 4	6.6	22,390	19	645	716	30
ANC 5	6.5	15,085	15	977	761	26
ANC 6	6.1	17,260	26	2,372	1,048	45
ANC 7	5.3	16,770	61	1,496	849	34
ANC 9	4.4	14,943	82	3,873	1,537	121

A similar trend characterized also other elements such as Co, Cr, Cu and Ni for which the leaching behaviour seemed to be independent from pH, thus confirming that their release is mainly governed by complexation-controlled mechanism. This means that the partitioning coefficient and the modelling presented in **Section 3.5.3** could be representative not only for the natural pH maintained during column experiments but also for a wider pH range.

On the other hand, strongly acidic pH values (4-5) enhanced the leaching of Ca, Mg, Mn and Zn, leading to concentrations very close to the total content (dotted line). This result implies that the correlation between Mg and DOC and Zn and DOC found in **Section 3.5.3** can be considered valid only for pH values close to the initial natural pH of MBT waste. Differently, Al and Pb exhibited the release pattern typical of amphoteric metals (V-shaped curve) with higher solubility under both strongly acidic and strongly alkaline conditions. Hence, in order to predict the leaching behaviour of

these elements, a major concern relates the ability to evaluate pH conditions for the application at a real landfill site.

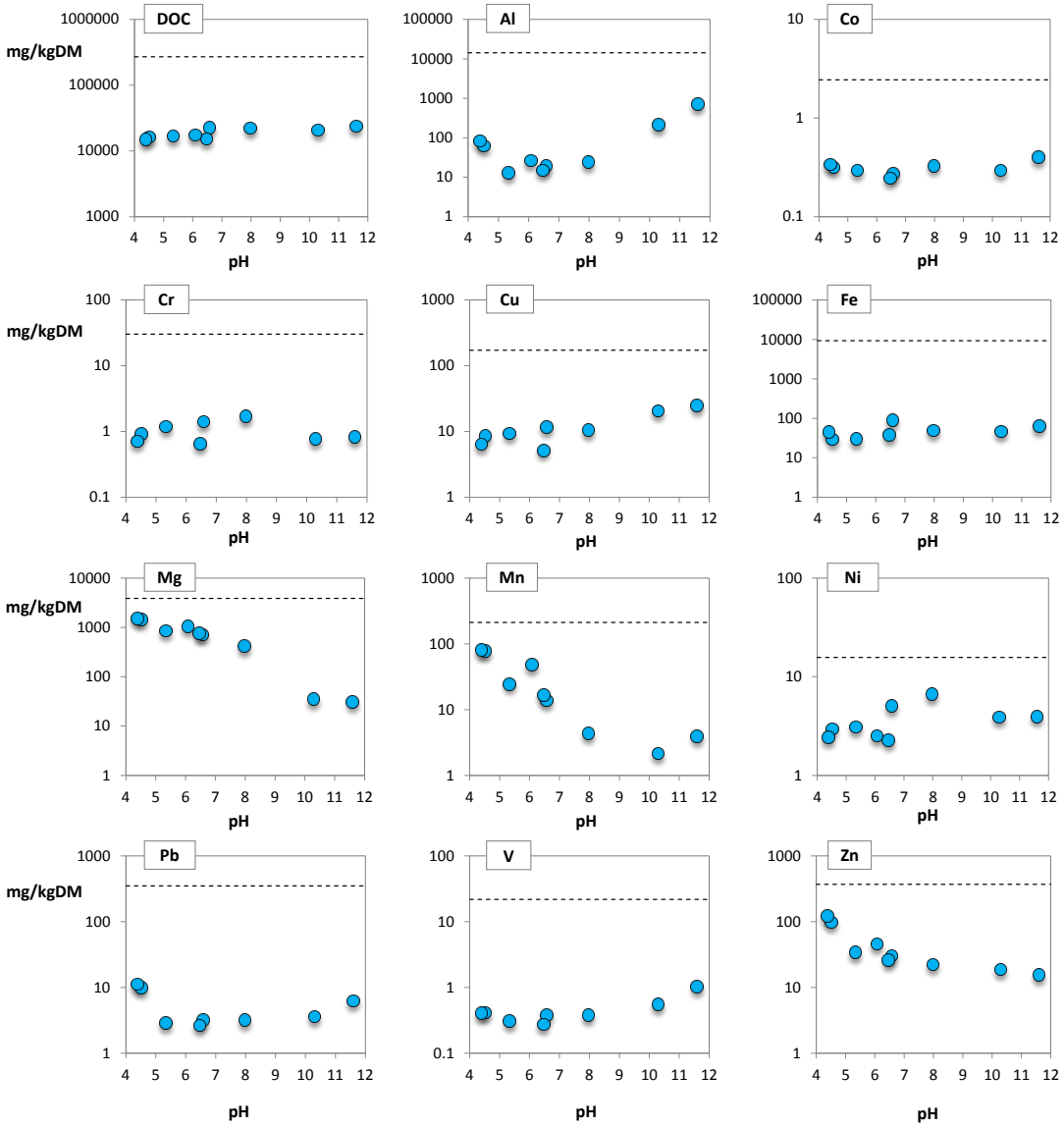

Figure 3.8. Release curves (mg per kg of dry matter) of DOC, Al, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn as a function of pH for MBT 2 waste sample.

3.6 MAIN FINDINGS

The leaching behaviour of mechanically biologically treated waste samples coming out from an Italian MBT plant was investigated by applying different pH-static batch test, pH dependent tests and dynamic up-flow column percolation experiments.

The obtained results show that, despite the MBT wastes are characterized by relatively high heavy metals content, only a limited amount was actually soluble and thus bioavailable under the specific test conditions. Namely, the release percentage was generally lower than 5 % of the total content with the only exception of dissolved organic carbon (DOC), Zn, Ni and Co with percentages up to 20 %. Furthermore, comparing the results of static pH batch test and dynamic up-flow column experiment, it was observed that the batch test, which is the compliance method commonly used for landfill disposal, may underestimate the actual release of DOC and Co, Cr, Mg and Ni from this type of waste. This result may be due, on one hand, to the longer duration of the column experiment compared to the batch one and, on the other hand, to the different test conditions that may affect metals leaching (e.g. with respect to static batch tests in dynamic column tests there is a continuous renewal of the leachant that could maintain the driving force of leaching). Overall, experimental findings provided by different tests allowed to highlight some key factors governing the kinetic release of DOC and metals from this type of waste. Specifically, results of column percolation tests disclosed that the elution profiles of some metals (Co, Cr, Ni, Zn) essentially followed the leaching trend of DOC suggesting that these elements were mainly released as organo-compounds. Similar results were provided by pH dependent tests; in fact, release curves determined for Co, Cr, Cu and Ni, as well as for DOC, appeared almost independent from pH values, confirming that DOC complexation is the prevalent mechanism controlling their release. Finally, combining the results of batch and up-flow column percolation tests, partition coefficients DOC-Me specific for each element were derived that, coupled with a simplistic screening model for DOC release allowed to obtain a very good prediction of metals release during the different column tests. However, these results only refer to a particular type of MBT waste i.e. coming from a 4-weeks aerobic process without the ripening stage. Hence, it would be interesting to investigate the leaching properties of waste coming out from different MBT plants in

order to evaluate how the stability degree of the MBT waste material, the specific plant configuration and/or biological treatment procedure applied, the duration of treatment as well as the characteristics of the MSW waste feeding the MBT plant may influence metals release from the solid matrix and, hence, the model parameters such as K_d and $K_{DOC,Me}$.

CHAPTER 4

ANALYSIS OF GAS GENERATION FROM MBT WASTE UNDER DIFFERENT OPERATING CONDITIONS

This chapter is partially taken from:

Pantini S., Verginelli I., Lombardi F., Scheutz C., Kjeldsen, P. (2015). Assessment of biogas production from MBT waste under different operating conditions. Submitted to Waste Management.

4.1 BACKGROUND

Landfill has been recognized as one of the main source of anthropogenic methane emission and a significant contributor to global warming (Bogner et al, 2008). As already described in the **Section 1.3**, methane is generated from the anaerobic conversion of organic matter in waste as a result of biological processes naturally occurring in landfill sites. It is well documented that mechanically biologically treated waste are characterised by lower gas generation potential compared to untreated waste owing to the removal of readily degradable fraction during the biological treatment. Moreover, the reduction in gas emission potential is closely related to the type and duration of the stabilization processes applied in MBT plants. Currently, few data on the gas emission from MBT waste at real landfill sites are available (Harborth et al., 2013), whereas several experimental studies, based either on small scale laboratory tests or on large scale experiments such as lysimeters (Sormunen et al., 2008) have been performed. However, depending on the specific aim of the test, lab scale studies on gas emissions from MBT wastes and solid organic wastes are usually carried out using different procedures and operative conditions (see Table 4.1). As highlighted by Lornage et al. (2007), the differences in the experimental procedure adopted may modify the biogas yield and kinetics, thus leading to results that are not always comparable. The anaerobic process is indeed sensitive to several factors such as pH, water content, temperature, particle size, as well as by the presence of inhibitors such as volatile fatty acids (VFAs), ammonia and heavy metals (Cabbai et al., 2013; Labatut et al., 2011; Lornage et al., 2007; Elbeshbishy et al., 2012; Raposo et al., 2011). Among these, pH is recognised as the key parameter to be maintained in an appropriate range (6.4-7.5) in order to enhance the methane yield (Adani et al. 2004; Argun et al., 2008; Lo et al., 2010). High pH values would result in increased toxicity due to the shift to higher concentrations of ammonia, which is identified as one of the most toxic agent for methanogenic bacteria (Chen et al., 2008; Bernet et al., 2007). In contrast, low pH values are indicative of the accumulation of VFAs within the system (Bouallagui et al., 2005; Li et al., 2011) that may result in an inhibition of the methanogenic activity, as observed by several authors (Argun et al., 2008; Borzacconi et al., 1997; Cabbai et al., 2013). Regarding the other operative conditions, an increase of temperature has a

positive effect on the microbial growth and activity (Chen et al., 2008) thus leading to a faster gas generation process. Similarly, increasing the water content of incubated waste is beneficial for methane yield since it enhances the solute transport of nutrient, the organic matter solubilisation and the microorganism mobilization within micro-environments, as well as dilutes the concentration of inhibitors (Donovan et al., 2010; Mora-Naranjo et al., 2004). Finally, the particle size of materials exerts a relevant influence on the process kinetic; it is well accepted that particle size reduction results in higher methane generation rate (Esposito et al., 2012; Lesteur et al., 2010, Mata-Alvarez et al., 2000), whereas its effect on biogas yield is still not completely elucidated (Nopharatana et al., 2007; Mshandete et al., 2006).

Table 4.1. Literature overview on the anaerobic digestion experiments performed on MBT wastes.

Reference	Amount	Particle size	Water addition	Inoculum	Temperature (°C)	Test duration (d)	Aim
Binner & Zach (1999)	50 g DM	<20 mm	1 l demineralized water	Used	35	42	Cumulative gas
De Araujo-Morais et al. (2008)	20 g	<20 mm	1.2 l nutrient medium	Used	35	90	Cumulative gas
Sormunen et al. (2008)	2 gVS_w/gVS_{in}	<40 mm	up to 95%	Used	20-22	70-100	Methane potential
Barrena et al. (2008)	200 g	ns	Not added	Used	35	100	Gas production in solid state test
Barrena et al. (2008)	1 g DM	<1 mm	up to 50%	Used	35	75	Gas production in liquid state test
Binner & Zach (1999)	1 kg DM	<20 mm	up to water holding capacity	Not used	40	90	Determining gas generation in landfills
De Gioannis et al. (2009)	500 g	ns	up to water holding capacity	Not used	30	240-390	Modelling gas generation
Panepinto et al. (2013) (**)	ns	ns	0%-20%-40%-150%(*)	Used	40	370	Modelling gas generation
Sormunen et al (2008)	96 t	<40 mm	ns	Used	40	640	Simulate landfill emissions

ns=not specified

(*) water added on wet weight basis
(**) MBT waste (biodrying)

The objective of this study was to evaluate the effects of temperature, water content and inoculum addition on biogas production from mechanically-biologically treated waste by performing anaerobic batch tests at different operating conditions. Furthermore, in order to determine the potential gas generation capacity under optimal conditions, biomethane potential tests (BMP) were carried out. All these tests were then compared in terms of cumulative biogas yield and rates. Besides, where applicable, a first-order kinetic model was used to compute the biogas rate constants from the cumulative gas generation curves observed in each experiment. Finally, the obtained results were addressed to assess the possible implications resulting from the different environmental conditions expected in the field.

4.2 MATERIALS AND METHODS

4.2.1 MBT WASTE MATERIAL

Mechanically-biologically treated waste samples were collected at the belt discharge point of the secondary refinement unit of a full-scale MBT plant operating in Italy. This MBT plant receives residual municipal solid waste (226,000 ton/y in 2013), with the average composition shown in Table 3.1.

The MBT waste sample was collected in May 2014 using standard procedures (UNI 10802:2013). A final MBT waste sample of about 80 kg was sent to the laboratory and stored at 4 °C. In the laboratory, three representative sub-samples were obtained by the "coning and quartering" method. One sub-sample was analysed to determine the moisture content (W), dry matter (DM) and volatile solids (VS), pH, total (TC) and organic carbon (TOC) content, total Kjeldahl (TKN) and soluble nitrogen (NH_4-N), the Chemical Oxygen Demand (COD) and the water content at field capacity (FC) of waste (i.e. the water-retaining capacity including both the hygroscopic and capillary water). All measurements were performed at least in triplicate; initial waste water content, dry matter and waste field capacity are expressed as percentage of wet weight whereas the other parameters are computed on dry weight basis. Average values and standard deviations are reported in Table 4.2. A sub-sample (3-4 kg) was used for BMP tests. Before performing the BMP analysis, the sub-sample was dried at room temperature (25

°C) to avoid losses of volatile organic compound and then shredded to 1 mm particle size. The last sub-sample was used in the incubation tests as received since, currently, the MBT waste is not subjected to further treatment before landfilling it.

4.2.2 ANALYTICAL METHODS

In order to characterize the MBT waste with regards to its physical and chemical properties, different analytical methods were applied. These tests provide basic information that are essential for the interpretation of the biological test results.

4.2.2.1 MOISTURE CONTENT (W), TOTAL (TS) AND VOLATILE SOLIDS (VS), TOTAL (TC) AND ORGANIC CARBON (TOC) CONTENT

The moisture content was determined by weighing the waste sample (100 g) before and after drying it at 105 °C for 24 hours (UNI EN 14346, 2007) until a constant weight was achieved. The dry matter (DM) content was then computed as difference. The volatile solids (VS) were measured by loss-on-ignition (LOI) at 550 °C for 8 h (UNI/TS 11184, 2006) on 5 g of sample grinded to 0.25 mm and pre-dried in oven at 105 °C for 12 h. Total (TC) and organic carbon (TOC) content was analysed by means of Shimadzu SSM-5000A instrument on approximately 0.15 g of dried sample grinded to 0.25 mm (UNI 13137, 2002).

4.2.2.2 pH

The pH of MBT waste was determined on the eluates according to UNI EN 12457-2 (2004). Around 80 g of the received material were put in contact with deionized water at a liquid to solid ratio (L/S) of 10 l/kgDM, for 24 hours, under constant agitation. After elution, pH was measured in each sample (triplicate).

4.2.2.3 TOTAL (TKN) AND SOLUBLE NITROGEN (NH_4-N)

Total Kjeldahl Nitrogen (TKN) was measured on solid waste samples through digestion and distillation method. Approximately 2.5-3 g of MBT waste sample (at own water content), a Kjeldahl catalyst (31108-250 EA Sigma Aldrich, Fluka analytical), glass beads and 14 ml of 97 % sulphuric acid were added to each Kjeldahl flask. Blank and control tests were performed simultaneously, in triplicate. In blank tests, 4 ml of deionized water were used whereas in control tests, to evaluate the efficiency of ammonia recovery, 4 ml of L-glutamic acid (1000 mg/l) were utilized. Samples were digested in FOSS 2020 Digestor at 180 °C for 1 h and thereafter at 350 °C for 1-2 hours (warm-up time excluded). After cooling, samples were distilled using FOSS Kjeltec 8100 distillation unit. In the distillation method, 30 ml of deionized water and 70 ml of the alkaline solution (32 %w/w NaOH) were added to each tube. The steam supply was set to 60 % and the distillation time was 5 minutes. A solution consisting of 50 ml deionized water, 4 ml boric acid (40 g/l) and 3-4 drops of Kjeldhal indicator (mixture of methyl red indicator and Bromocresol green indicator, MERCK KGaA) was used as absorbent solution during distillation. The ammonia content was determined by tritation of distillate with 0.1 M H_2SO_4.

Determination analyses of soluble nitrogen (NH_4-N) were carried out on 2.5-3 g of solid sample (as it is) using FOSS Kjeltec 8100 distillation unit. For the distillation method, 30 ml of deionized water and 50 ml of the alkaline solution (32 %w/w NaOH) were added to each tube. Steam supply and distillation time were the same as mentioned above, as well as the titration method. The ammonia recovery of the instrument was evaluated by adding 4 ml of a known solution (1000 mg/l NH_4-N) to 50 ml of deionized water. An efficiency up to 100 % was detected.

4.2.2.4 CHEMICAL OXYGEN DEMAND (COD)

COD measurements were carried out on 1.0 g of air-dried MBT waste sample (ground < 1 mm), adding 6 ml of 97 % sulphuric acid and 30 ml of deionized water to the flask while stirring it for 30 minutes. Samples were then transferred to a 500 ml graduate glass balloon. The solution was further diluted using deionized water (7:50 by volume).

From this solution, 3.5 ml sample were transferred to the reaction glass flask and 5 mm diameter glass beads were placed in each tube in order to avoid aggressive boiling. Then, 2.0 ml of Potassium Dichromate 0.025 M (for high range detection) and 4.5 ml of silver sulphate sulphuric acid solution were added to each flask which was immediately closed and mixed. Sample measurements were performed in triplicate. The reaction mixtures were boiled in a Holm & Halby Techne Dri Block at 148 °C ± 2 °C for 110 minutes. After cooling, 5.0 ml of deionized water and 3-4 drops of ferroin indicator were added and samples were titrated with 0.035 M Ferrous Ammonium Sulphate solution (high range: 100 - 600 mg/l COD). The five blanks (3.5 ml of deionized water) and the three control tests (3.5 ml of High range 500 mg COD/l solution) were carried out simultaneously.

4.2.2.5 VOLATILE FATTY ACIDS (VFA)

VFA were measured in fresh solid waste as well as in waste samples at different incubation time. Samples were prepared weighing about 5 g of MBT waste, adding 12.5 ml of deionized water and acidifying them with 0.4 ml of 97 % sulphuric acid to ensure pH< 2. A magnet was inserted and samples stirred for approximatively 10-15 minutes to homogenize them. Then, 1.5 ml of each sample was placed in an Eppendorf tube and centrifuged at Eppendorf mini spin table centrifuge at 13,400 rpm for 10 min. After centrifugation, 1.0 ml sample was transferred to a GC glass vial and 0.100 ml of internal standard (2.2 mM 4-Methyl valeric acid) was added. Concentrations of acetate, propionate, iso-butyrate, butyrate, iso-valerate, valerate, hexanoic acids were determined by using GC Shimadzu GC – 2010 equipped with and FID (flame-ionization-detector). VFA compounds were separated by a capillary column (ZB – FFAP, 30 m, 0,53 mm I.D x 1,0 µm) and concentrations were computed by means of a linear calibration curve obtained after standards injection (range: 5-1500 mg/l). All measurements were performed in triplicate.

4.2.2.6 MBT WASTE FIELD CAPACITY (FC)

Water content of MBT waste at field capacity was determined by performing column tests. A plexiglas column with an inner diameter of 3.5 cm and a total height of 15 cm was packed with about 70 g of MBT waste and weighted (M_{in}). Then, the packed column was saturated from the bottom section until a water head of few centimetres formed at the top and the pump was stopped. After saturation, the column was let drain until no significant outgoing flow was detected and weighted again (M_{end}). The difference in weight (M_{end} - M_{in}) is the adsorbed water ($M_{w,ads}$). The ratio between the total water in the column at the end of the experiment (i.e. sum of adsorbed water and initial moisture water, W) and the final mass of MBT material in the column ($M_{in,MBT}$ + $M_{w,ads}$), shown in Eq. (4.1), represents a rough estimation of the water field capacity of the studied MBT waste (expressed as percentage of wet weight):

$$FC\ \%w/w = \left(\frac{M_{w,ads} + W\ \% \cdot M_{in,MBT}}{M_{in,MBT} + M_{w,ads}} \right) * 100 \qquad (4.1)$$

4.2.3 GAS GENERATION TESTS

4.2.3.1 BIOCHEMICAL METHANE POTENTIAL TEST (BMP)

Since there is no standard protocol for performing a BMP test, the potential biogas yield was determined following the procedure described by Hansen et al. (2004). Glass bottles (1 l) with a thick rubber septum were used as reactors. Approximatively 1 g of air dried waste sample (particle size < 1 mm), 80 ml of deionized water and 320 ml of a fresh de-gased inoculum were used in the experiments in order to achieve an organic load of 1.4 gVS/l (weight of VS in substrate per unit volume of inoculum). Tests were carried out for 30 days with six replicates, due to the relatively high heterogeneity of the MBT material. Thermophilically digested material from a full-scale biogas plant was used as inoculum. Three blanks with only water and inoculum were run to test the biogas production from the inoculum itself. Control tests, containing 0.8 g of AVICEL (Fluka, Sigma Aldrich, Vallensbæk Strand, Denmark) as a standard substrate, were performed to check the quality of the inoculum. After set-up, the reactors were flushed

with N_2 for 10 minutes, to ensure the establishment of anaerobic conditions in the headspace of the glass bottles, then sealed and placed in the incubator at 55 °C (± 1 °C). The methane concentration in the reactors was measured every two days during the first two weeks, and later once per week. Gas samples (0.2 – 0.5 ml) were taken from the headspace of the reactors by using a syringe with a pressure lock and directly injected into the gas chromatograph for methane determination (Shimadzu GC 14A) and for qualitative analysis of gas composition in terms of % CH_4 and % CO_2 (Mikrolab GC Aarhus). In order to avoid build-up of high pressure inside the reactors, the gas was released during the experiment. Based on the difference of CH_4 concentration before and after release of excess gas, the generated amount of CH_4 was computed.

4.2.3.2 ANAEROBIC GAS GENERATION TESTS

In order to evaluate the effects of temperature and water content on the gas generation rate and yield, anaerobic batch tests were performed at three different temperatures: room temperature (20-25 °C), 37 °C and 55 °C. At each operational temperature, the water content of waste sample was artificially adjusted to values of 26 %, 32 %, 38 %, 43 % w/w (expressed on wet weight basis) that correspond to 63 %, 78 %, 93 % and 105% of water holding capacity of the analysed MBT waste (assuming FC equal to 41% w/w). The values set for temperature and water content aimed at covering the actual ranges generally observed at real scale landfill sites (Mora-Naranjo et al., 2004; Mor et al., 2006). Moreover, 37 °C and 55 °C represent optima temperatures for mesophilic and thermophilic inoculum, respectively. Incubation tests at 37 °C and 55 °C consisted of 1 l glass bottle filled with waste sample (0.5-0.7 kg as received material), sealed with a rubber septum and equipped with a PVC pipe, which connected it to a 3 l SKC Tedlar Sampling Bag (SKC Inc., Eighty Four, PA, US) for gas collection. At each measurement, 5 ml of gas were sampled with a syringe and injected into evacuated glass vials fitted with pierceable rubber septa (Exetainer Vail, Labco Ltd, Lampeter, UK), which were then analysed for determining gas composition. A 490-PRO Micro GC (Agilent Technologies Denmark Aps, Glostrup, Denmark) equipped with two columns (PoraPLOT Q PLOT, 0.25 mm, 10 m, and Molecular Sieve 5A PLOT, 0.25 mm, 20 m) was used to measure CH_4, CO_2 and O_2 in gas samples with a detection limit of 0.1 % for

all gases. In the incubation tests at room temperature, 12 l steel drums with airtight lids were used as reactors. Drums were filled with as received material (5-8 kg) wetted to three different water content (26 %, 34 %, 43 % w/w) and flushed with nitrogen for 30 minutes before sealing them. Lids were equipped with T-shaped sampling ports and connected to 5 l SKC Tedlar Sampling Bags. More information about tests conditions and experimental activities are reported in Table 4.2.

Table 4.2. Summary of the test conditions and activity stage of the anaerobic batch experiments performed on the MBT waste samples.

ID TEST	Reactor volume (l)	T (°C)	MBT weight (kgDM)	Water content (% w/w)	Inoculum addition (g)	Duration (d)
R1A **R1B**	12	20-25	4.0-4.5	26%	not used	**Stage I**: 167
R2A **R2B**				34% (**Stage I**) 75% (**Stage III**)	**Stage III**: 800 g mesophilic inoc. (DM=3.8% wet weight, VS=60% DM) + 6.1 kg water [(a)]	**Stage I**: 94 **Stage III**: 73
R3A **R3B**				43%	not used	**Stage I**: 167
T1A **T1B**	1	37	0.36-0.39	26%	**Stage II**:20 g mesophilic inoc. (DM=3.8% wet weight, VS=60%DM)	**Stage I**: 38 **Stage II**: 94
T2A				32% (**Stage I**) 75% (**Stage III**)	**Stage II**:20 g mesop. inoc. ; **Stage III**: 70 g mesop. inoc. + 530 g water [(b)]	**Stage I**: 38 **Stage II**: 20 **Stage III**: 74
T2B				32%	**Stage II**: 20 g mesop. inoc. (DM=3.8% wet weight, VS=60%DM)	**Stage I**: 38 **Stage II**: 94
T3A **T3B**				38% (**Stage I**) 75% (**Stage III**)	**Stage III**: 70 g mesop. inoc. + 530 g water [(b)]	**Stage I**: 58 **Stage III**: 74
T4A				43%	not used	**Stage I**: 132
T4B				43% (**Stage I**) 48% (**Stage III**)	**Stage III**: 70 g mesop. inoc. (same), no water addition [(c)]	**Stage I**: 50 **Stage III**: 82
T5A **T5B**	1	55	0.36-0.39	26%	**Stage II**:20 g thermophilic inoc. (DM=3% wet weight, VS=65%DM)	**Stage I**: 24 **Stage II**: 76
T6A				32% (**Stage I**) 75% (**Stage III**)	**Stage II**:20 g thermop.inoc. **Stage III**: 70 g thermop. Inoc. + 530 g water [(d)]	**Stage I**: 24 **Stage II**: 19 **Stage III**: 57
T6B				32%	**Stage II**:20 g thermop. inoc.	**Stage I**: 24 **Stage II**: 76
T7A **T7B**				38% (**Stage I**) 75% (**Stage III**)	**Stage III**: 70 g thermop. Inoc. + 530 g water [(d)]	**Stage I**: 43 **Stage III**: 57
T8A **T8B**				43%	Not used	**Stage I**: 103

(a) Waste removed from reactor before inoculum and water addition. DM content Stage III: 2.66 kgDM

(b) Waste removed from reactor before inoculum and water addition. DM content Stage III: 0.21 kgDM (T3A/B)-0.24 kgDM (T2A)

(c) Waste removed from reactor before inoculum addition. DM content Stage III: 0.36 kgDM

(d) Waste removed from reactor before inoculum and water addition. DM content Stage III: 0.22 kgDM (T7A/B)-0.24 kgDM (T6A)

With reference to Table 4.2, it can be noticed that the anaerobic gas generation tests were carried out in three sequential stages. In the first stage, no inoculum was used. During the second stage of experimental activity, a low amount of mesophilic and thermophilic inoculum (20 g of inoculum, i.e. approximately 5 %w/w of the waste dry matter used in the test) was introduced into the incubation bottles with lower water contents (T1, T2, T5, T6) to enhance the microbial activity.

In the following stage III, due to the unexpected very low biogas production, some reactors were opened (R2, T2A, T3A/B, T4B, T6A, T7A/B) in order to partially remove the material, which was then analysed with regard to pH, VFA, TKN and NH_4-N. In this stage, inoculum (about 30 % of waste dry matter in reactor after waste removal) and water (230 % of waste dry matter, to obtain a final moisture content of 75 % w/w) were introduced within these reactors that were successively purged with nitrogen and incubated again. A triplicate measurement of the biogas production from the added inoculum was performed on blank experiments and deduced from the biogas yield of waste samples.

The gas volume produced by each reactor was computed timing the emptying of gas bags using a Fluid Metering Inc. laboratory pump (QG, Fluid Metering Inc., Syosset, NY, US). The flow rate of the pump was tested several times during the experiment and an average flow of 0.5 l/min was measured.

4.3 MODELLING GAS FORMATION

As mentioned in **Section 2.2.4**, several equations can be used to describe the temporal evolution of gas generation in landfills. In this study, experimental data were interpolated using the first-order kinetic model (Mor et al., 2006) and the modified Gompertz equation.

The generic formulation of the first-order kinetic model was modified to take into account for the lag-time observed in the test, as follows:

$$L = L_0 \left[1 - \exp\left(k \cdot \left(t_{lag} - t \right) \right) \right] \quad (4.2)$$

where L is the biogas accumulation (l/kgDM) at the time t (d), L_0 the potential biogas production (l/kgDM) for the tested conditions (at optimal conditions, L_0 approaches the potential gas generation capacity measured in the BMP experiments), t the time over the digestion period, t_{lag} the lag-phase (d) and k the first-order kinetic constant (d^{-1}).
Another method commonly used to simulate biogas accumulation over time is the modified Gompertz equation (Lo et al., 2010), reported in Eq. (4.3).

$$L\ t\ = L_0 \exp\left\{-\exp\left[\frac{\mu_m \cdot 2.7182}{L_0}\cdot\ \lambda - t\ +1\right]\right\} + b \tag{4.3}$$

Where μ_m is the maximal production rate [l/(kgDM d)], λ the lag phase (d) and b is a constant (l/kgDM).
Hence, the cumulative biogas volume measured during the anaerobic batch experiments were correlated with the Eqs. (4.2), (4.3) and the equation parameters were determined by regression analysis for each specific operational condition.

4.4 RESULTS AND DISCUSSIONS

4.4.1 MBT WASTE CHARACTERIZATION RESULTS

Results of the characterization analysis performed on the MBT waste are reported in Table 4.3. Moisture content (W), as well as water field capacity, were slightly lower than the values usually measured for this type of waste (Di Lonardo et al., 2014; Zach et al., 2000). Despite the waste underwent an aerobic treatment process in the MBT plant, the organic matter of waste is still quite high, as confirmed by VS, TOC and COD contents.
As shown in Table 4.3, the pH was almost neutral and in the optimal range for the anaerobic process. It is also interesting to point out that values of TKN and NH_4-N were quite high, close to the range usually observed for untreated waste or poorly treated waste (Modin 2007; Pognani et al., 2010).

Table 4.3. Characterization of the MBT waste. Mean value ± standard deviation.

	Mean	Unit
Initial water content, W (*)	19.4 ± 1.1	(%w/w)
Water content at field capacity, FC (*)	41 ± 5	(%w/w)
Dry matter, DM (*)	80.6 ± 1.0	(%w/w)
Volatile solids, VS	47.3 ± 1.0	(%DM)
Organic carbon, TOC	23.9 ± 0.3	(%DM)
pH	6.7	--
TKN	14.1± 2.0	g/kgDM
NH_4-N	2.0 ± 0.2	g/kgDM
COD	520 ± 40	g/kgDM
Total VFA	0.18 ± 0.05	g/l

(*) expressed on wet weight basis

4.4.2 BIOCHEMICAL METHANE POTENTIALS

Figure 4.1 shows the cumulative CH_4 generation curve measured in control (red dots) and in MBT waste tests (green dots) as a function of the incubation time. The results reported in this figure, expressed as cumulative volume of methane per gDM at standard temperature and pressure (STP) conditions (0 °C, 1 atm), represent the average values measured in the different replicates obtained after subtracting the CH_4 measured in the blank experiments. The solid red line and the dotted green line depict the theoretical methane potential for the cellulose substrate (control) and the MBT waste, respectively. The latter was estimated from the total organic carbon (TOC) of the substrate (Table 4.3), as shown in Eq. (4.4). Based on the carbon balance equation of the degradation reactions and assuming that the biogas formed by a complete degradation of TOC contains 60% of methane (that corresponds to the average CH_4 concentration measured during the BMP test), a theoretical value of 268 NmlCH_4/gDM was computed (i.e. 60% of CH_4 in biogas implies that 1 g of TOC generates 1.12 Nl of CH_4 at STP).

$$L_{theoretical,TOC}\left(\frac{NmlCH_4}{g_{DM}}\right) = 60\%CH_4 \cdot \frac{1}{12\frac{g_C}{mol_C}} \cdot 22.414\left(\frac{Nl}{mol}\right) \cdot 0.239\frac{g_{TOC}}{g_{DM}} \cdot 1000 \qquad (4.4)$$

The theoretical methane determined through Eq. (4.4) is slightly higher than the value that can be computed from the initial chemical oxygen demand (0.52 gCOD/gDM) of the waste. Indeed, assuming that 1 g of COD produces 0.35 l of methane at STP (Angelidaki and Sanders, 2004; Labatut et al., 2011; Lesteur et al., 2010; Lin et al. 1999) a theoretical value of 182 NmlCH_4/gDM can be estimated from COD content in MBT waste.

From Figure 4.1, it can be noticed that the cumulative CH_4 curves observed for control and waste samples showed a rapid increase in the first two weeks and then achieved an asymptotic value. The lag phase was absent, confirming that the BMP test was run under optimal conditions. The average cumulative methane generation in controls resulted in an average gas generation of 367 NmlCH_4/gDM on the 13th day after starting the batch tests and reached the theoretical potential value of 415 NmlCH_4/gDM in 27 days. Within the first two weeks, the methane generation curve observed in control tests appeared linear (R^2=0.99), with an average slope of 27.5 NmlCH_4/(gDM·d). Similarly, in the first stages of the MBT waste sample test a linear methane production rate of 8.4 NmlCH_4/(gDM·d) was observed. Thereafter, the slope rapidly decreased and the cumulative CH_4 generation curve asymptotically approached a constant level of 121 NmlCH_4/gDM. Hence, it seems that, on average, only 45 % of the theoretical methane generation (268 NmlCH_4/gDM) was achieved during the BMP experiment of the MBT waste sample, most likely due to the presence of non-biodegradable fractions (plastics), recalcitrant organic substances or lower degradable compounds, such as hemicellulose and lignocellulose complexes (Bayard et al., 2010), which is plausible owing to the high content of paper, cardboard and wood in the raw MSW treated in the MBT plant (totally 25.6 % w/w in MSW, see Table 3.3). Moreover, it should be noted that the theoretical methane (Eq. 4.4) was computed neglecting the biomass synthesis and, thus, it could be overestimated. Some authors indicate that 5-10 % of organic matter is consumed by bacteria to grow (Elbeshbihy et al., 2012; Labatut et al., 2011; Raposo et al., 2011) and, hence, does not contribute to CH_4 production.

Even though the extent of degradation achieved in a BMP test is strongly dependent on the composition of the analysed substrate as well as on the test methodology applied (substrate to inoculum ratio, test duration, inoculum characteristics), the 45% degradability estimated for the analysed MBT waste based on TOC content is consistent

with other previous studies on organic substrates. For instance, Elbeshbihy et al. (2012) reported that the biodegradability of food waste in 35-days BMP tests (37 °C) may range from 27 % to 87% based on the initial total COD of the substrate, depending on the substrate to inoculum ratio and the specific inoculum used in the BMP test. Using experimental results (TOC, BMP, % CH_4 in biogas) presented by Bayard et al. (2010) for different MBT wastes, degradability was estimated within the range 10% - 36% in 90-days BMP tests.

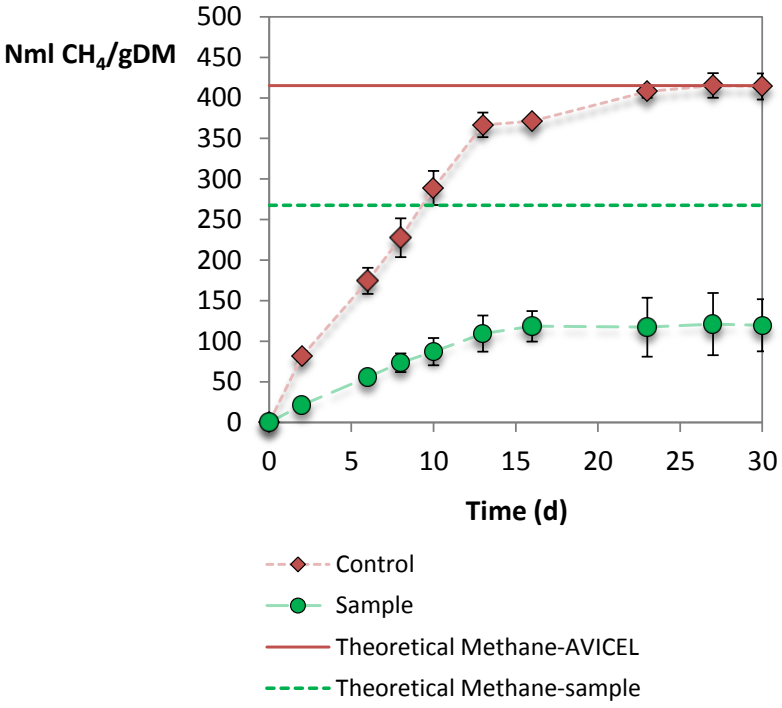

Figure 4.1. BMP cumulative methane production measured in control (red dots) and MBT waste (green dots) tests, expressed as Nml CH_4 per g of total solids. Solid red line: theoretical methane generation of control. Dotted green line: theoretical methane generation of MBT waste, computed according to Eq. (4.4). Bars: standard deviation. The results is the average of 6 and 3 bottles for MBT waste and controls, respectively.

Making reference to Figure 4.1, some variations of accumulated CH_4 volumes were observed between the replicate of MBT waste tests (coefficient of variation in the range of 12.4-23.3 %), probably due to its relatively high heterogeneity and to the low amount

of material tested in the BMP experiment. On the contrary, both substrate (control) and inoculum (blank) showed a good internal homogeneity with coefficients of variation in the range of 0.5-7.0 % and 1.9-4.9 %, respectively.

From the qualitative analyses of gas composition, an average value of 60.8 ± 1.1 % and 62.4 ± 1.4 % of methane concentration in biogas was detected for sample and control, respectively. Assuming this percentage, a potential CO_2 yield of 78 ± 25 NmlCO_2/gDM for MBT waste and 250 ± 9 NmlCO_2/gDM for control was computed.

Hence, a maximum potential gas production of 199.2±63 Nml_{gas} /gDM was estimated for the analysed MBT waste. This result is consistent with some BMP studies performed on aerobically treated MBT wastes. For instance, Barrena et al. (2008) measured a total gas production of 187±16 Nl/kgDM, with an average methane content of 57%v/v, from MBT wastes after 32 days of aerobic treatment. Bayard et al. (2010) analysed the gas generation potential of different flows in a French MBT plant; they observed that the intermediate fraction (< 50 mm), after 6 weeks forced-aerobic treatment, still exhibited high gas generation potential (232±23 Nl/kgDM). Lornage et al. (2007) measured a gas potential of about 160 Nl/kgDM from MBT wastes subjected to 4-weeks aerobic treatment process.

4.4.3 ANAEROBIC GAS GENERATION TESTS

Figs. 4.2-4.3 show the cumulative generation curve of methane (red circles) and carbon dioxide (black squares dots) obtained for the MBT waste samples at room temperature (Fig. 4.2), 37°C (Fig. 4.3) and 55°C (Fig. 4.4), and for different initial water content of waste, as a function of the incubation time. Results are expressed as cumulative volume of gas per kg of dry matter (DM) at STP. For comparison purposes only, the potential CH_4 and CO_2 values computed in BMP test have also been reported in these figures. From Figs. 4.2-4.4 it can be noticed that, for all operational conditions, a long lag-phase was detected. During this stage, the microbial population needed to get adapted to the micro-environment and to be acclimatized to the organic substrate in order to be able to grow until a sufficient active population established and the anaerobic degradation could stably evolve. Results shown in Figs. 4.2-4.4 suggested that the duration of the lag-phase was strongly affected by both the water content of waste and the process

temperature. Regarding the former parameter, it widely documented that water enhances nutrients and substrates solubilisation in the liquid phase as well as supports bacteria movement and facilitates substrate and products diffusion through the porous medium (Donovan et al., 2010; Khalid et al., 2011; Liotta et al., 2014). However, the water content of waste in a landfill disposal scenario could be quite far from the optimum value for degradation (60 % -80 %) and, thus, may become limiting for the anaerobic process. Indeed, experimental results confirmed that the water content of waste could be considered as one of the most important factors limiting methane generation and, the probability of achieving a stable methanogenic stage is significantly reduced for water contents below 32 %w/w (wet weight) at any temperature for this type of waste.

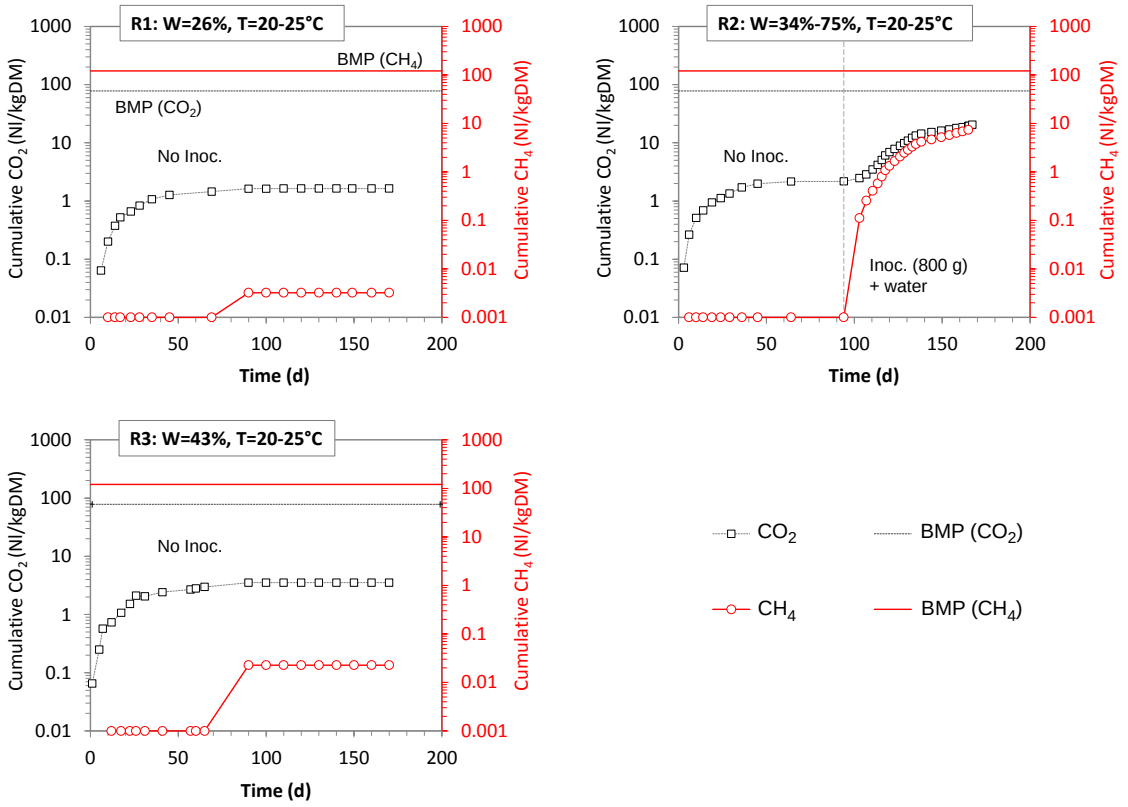

Figure 4.2. Cumulative methane (red circles) and carbon dioxide (black square dots) curves as a function of the incubation time, obtained during anaerobic batch tests carried out on MBT waste samples at room temperature (20-25 °C) and different values of initial water content (26 %, 34 % -75 % and 43 % w/w). Solid red line: CH_4 potential obtained from BMP tests. Dotted black line: CO_2 potential obtained from BMP tests. Dotted grey line: starting point of stage III (increasing water content up to 75 %w/w and adding 800 g of inoculum).

Increasing the operative temperature would enhance both the substrate solubilisation and the microbial activity (Raposo et al., 2011). It is likely that higher temperature allowed moving from non-equilibrium state towards more suitable conditions for methanogenic bacteria growth, thus favouring a more rapid establishment of the methanogenic phase (Lesteur et al., 2010; Li et al., 2011; Mata-Alvarez et al., 2000). Indeed, as shown in Fig. 4.2 in all the experiments at room temperature methane was not detected within the first three months but only CO_2 was generated at high levels (80% of gas produced). A similar behaviour was observed by Adani et al. (2004) during 90 days incubation tests carried out on fresh and partially treated wastes (10 days of aerobic treatment). The high CO_2 concentration without CH_4 production suggested that the biological process was completely inhibited at every water content in tests at room temperature, probably due to acidification effects, and revealed the poor stability degree of the analysed MBT waste. Furthermore, even though the methanogenic activity was observed in tests at higher temperature and water content, a clear instability associated with the anaerobic process was still detected.

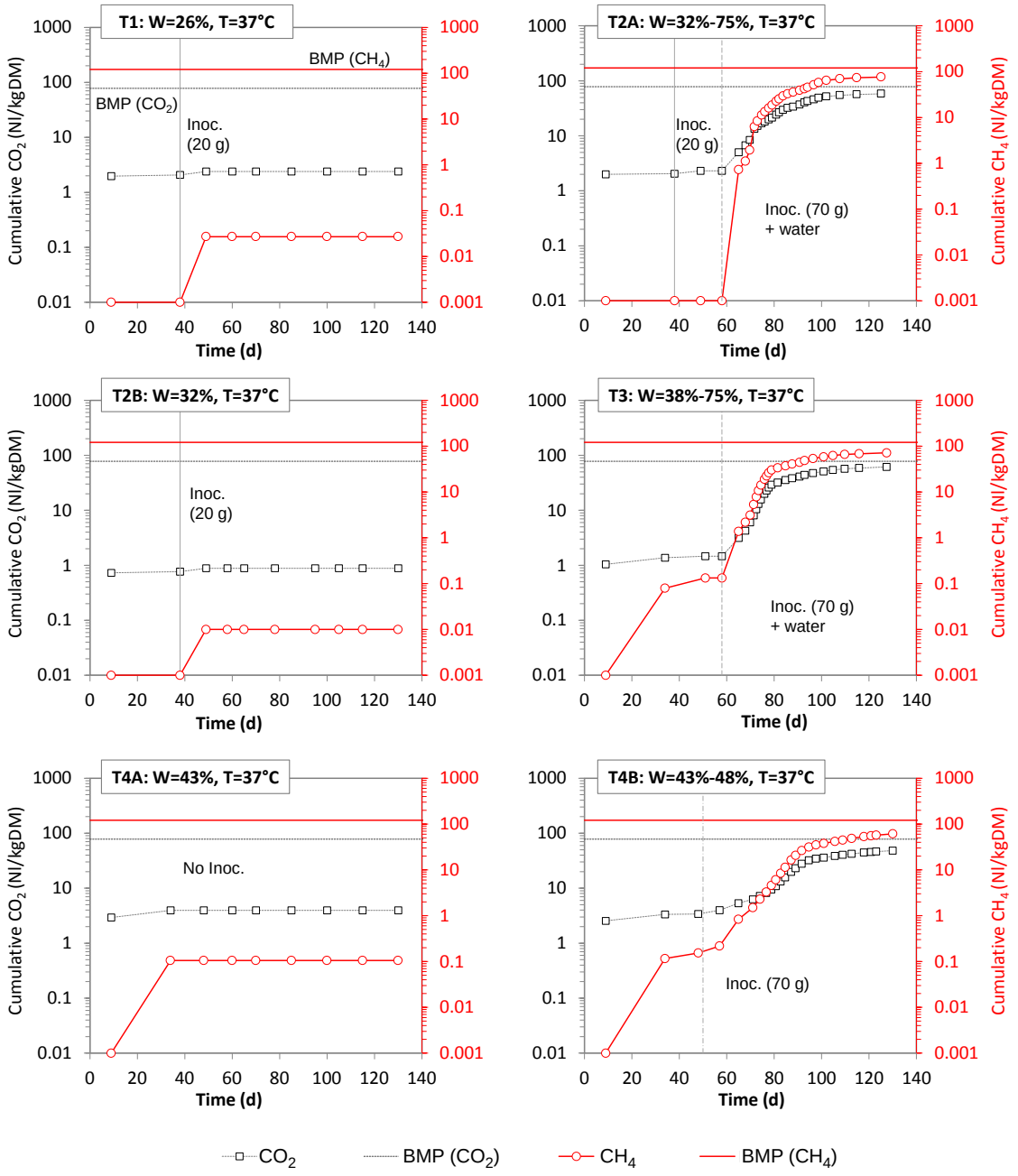

Figure 4.3. Cumulative methane (red circles) and carbon dioxide (black square dots) curves as a function of the incubation time, obtained during anaerobic batch tests carried out on MBT waste samples at 37 °C and different values of the initial water content (26 %, 32 %, 32 %-75 %, 38 %–75 %, 43 % and 43 %- 48 % w/w). Solid red line: CH_4 potential from BMP. Dotted black line: CO_2 potential from BMP. Solid grey line: starting point of stage II (20 g inoculum addition). Dotted grey line: starting point of stage III (increasing water content up to 75 % w/w and adding 70 g of inoculum, with the exception of reactor T4B in which only 70 g of inoculum were added).

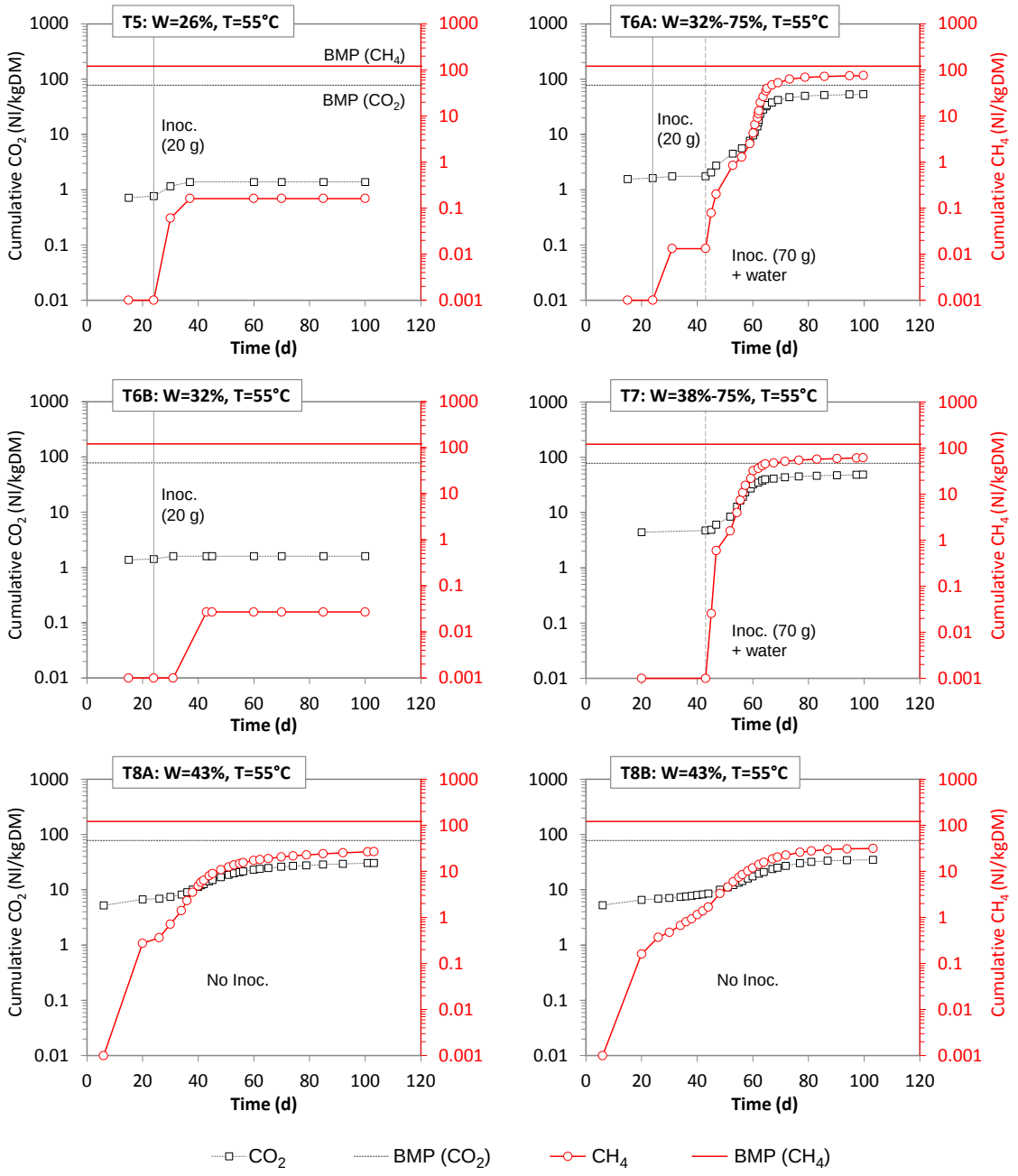

Figure 4.4. Cumulative methane (red circles) and carbon dioxide (black square dots) curves as a function of the incubation time, obtained during anaerobic batch tests carried out on MBT waste samples at 55°C and different values of the initial water content (26 %, 32 %, 32 %-75 %, 38 %-75 %,43 % w/w). Solid red line: CH_4 potential from BMP. Dotted black line: CO_2 potential from BMP. Solid grey line: starting point of stage II (20 g inoculum addition). Dotted grey line: starting point of stage III (increasing water content up to 75 % w/w and adding 70 g inoculum).

In fact, as reported in Fig. 4.3, reactors at 37 °C and water content of 38 %w/w (T3) – 43 %w/w (T4) started producing methane after 27 days but CH_4 concentrations in the

generated gas were very low (below 20 %v/v). A similar trend was observed for batch tests at 55 °C (Fig. 4.4) where methane generation started after 22 days and 13 days for tests at moisture content of 38 %w/w (T7) and 43 %w/w (T8), respectively. However, in all these reactors (except T8), just after few days, biogas generation slowed down. Only the experiment at higher water content and temperature (T8) managed to reach the stable methanogenic phase during the experiment (without inoculum addition), as confirmed by the CH_4 concentration measured in biogas, which was in the range 45-60 %v/v (See Fig. 4.7). Even if a lag phase of 40 days was observed in these tests before the stable methanogenic stage has been achieved, the cumulative gas generation approached an asymptotic value of 29.1±2.2 $NlCH_4$/kgDM and 32.6±2.1 $NlCO_2$/kgDM within 100 days (Fig. 4.4). These values are in line with previous studies on treated MBT waste wetted to a water holding capacity in which no inoculum was added (Adani et al., 2004; De Gioannis et al., 2009). However, compared to the maximum gas generation measured in the BMP experiment (199.2 Nlgas/kgDM), a very low conversion degree was achieved (31% of BMP value) indicating that the anaerobic process was severely restricted under these test conditions.

Overall, the results obtained during the initial experimental activity suggested that, in most of test conditions, the anaerobic process was slowed down either due to high levels of inhibiting factors (low water content) or to a limited amount of active biomass inside the reactors compared to the organic load. Hence, during stage II, a small amount of inoculum (20 g) was introduced into reactors at lower water contents (T1, T2, T5, T6) and the evolvement of degradation was monitored for 20 days. After the addition of the inoculum, methane started to be produced in all reactors but its concentration still remained very low (below 10% v/v) and then decreased again (see Tests T2B and T6B in Figs. 4.6, 4.7). Thus, it seems that the microorganism population inside the MBT waste was not sufficient to sustain the anaerobic degradation process. For this reason, during stage III, in reactor T4B (W=43 %w/w, T=37 °C) a higher amount of inoculum was introduced (70 g) and, in two weeks, methane concentration achieved the typical range of the stable methanogenic phase (50-70 %v/v, see Fig. 4.6).

Results shown in Figs. 4.3-4.4 also highlighted the different behaviour for tests at water field capacity (W=43 %w/w at 37 °C and 55 °C, see T4 vs. T8). In fact, even if the water content was the same in these reactors, only tests at 55 °C (see T8 in Fig. 4.4)

manage to achieve the stable methanogenic phase without the inoculum addition. Instead, at 37 °C, a very low methane volume was measured in test where no inoculum was used (see T4A in Fig. 4.3), whereas methane was stably produced only after the addition of a significant amount (70 g) of mesophilic inoculum (T4B). This may be ascribed, on the one hand, to a lower active mass of mesophilic bacteria in the MBT waste compared to the thermophilic ones, presumably due to the type of biological process performed in the MBT facility. Indeed, temperatures up to 70 °C were achieved in the biostabilization basin of the MBT plant during the aerobic treatment. This sanitation process may have drastically reduced the microorganism population inside the waste, especially the mesophilic bacteria, which are more sensitive to high temperatures than the thermophilic ones. On the other hand, the lower gas generation at 37 °C may be explained considering that the methanogenic mesophilic bacteria could be more vulnerable to unfavourable environmental conditions (high VFA and ammonia content) and have lower growth rates (van Lier et al., 1997; Amani et al., 2011) compared to the thermophilic bacteria, that implies the adapting period could last longer. For instance, Gallert and Winter (1997) have observed that thermophilic bacteria tolerated twice as much of free ammonia than the mesophilic flora. In conclusion, results obtained during stage I and II suggested that the capability of the MBT waste to generate methane is drastically limited due to inhibition effects, which are emphasized due to low initial water contents, also because the initial bacteria population inside the waste mass could not contain a sufficient level of methanogens to sustain the anaerobic process under the specific test condition (high organic content). For a better understanding of these results, during stage III of the experimental activity, reactors were opened and waste was partially removed in order to measure pH, VFA and ammonia. Then, inoculum (30 % of final DM in reactors after waste removal) and water (up to a final moisture content of 75 %w/w) were added in reactors R2, T2A, T3, T6A, T7 that were flushed with N_2 and incubated again. The beneficial effects were evident, resulting in an immediate growth of the biogas yield, with increasing gas generation rates at higher temperature. On the one hand, the supplemental water addition may have reduced the inhibitory effect by diluting potential toxic substances such as heavy metals (copper, chromium or zinc), ammonia and VFAs. (Chen et al., 2008; Yenigun and Demirel, 2013; Poggi-Varaldo et al., 1997). On the other hand, a proper balance

between acidogens and methanogens could have been achieved by lowering the organic load (through waste removal) and increasing the active bacteria mass within the anaerobic reactors (through inoculum addition). Indeed, after water and inoculum addition tests at 55 °C achieved the asymptotical value of 66.7 ± 6.3 Nl CH_4/kgDM and 50 ±2.3 Nl CO_2/kgDM within 30-40 days after the inoculum and water addition. In tests carried out at 37 °C, a cumulative volume of 73.1 ± 2.1 Nl CH_4/kgDM and 54.9 ±1.8 Nl CO_2/kgDM was measured after 60-70 days from inoculum and water addition.

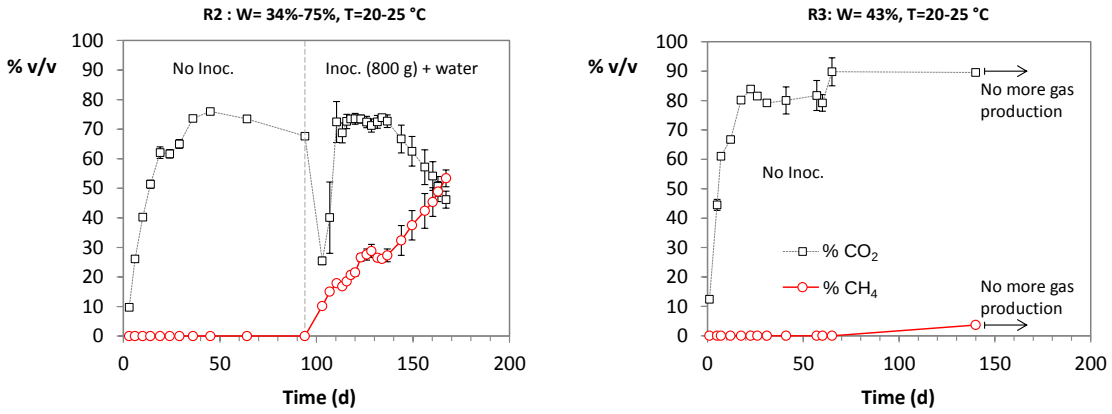

Figure 4.5. Gas composition (percentage by volume) measured in tests at room temperature (20-25°C) and initial water content of 34 % -75 % w/w (R2) and 43 % w/w (R3). Red dots: CH_4 concentration (% v/v). Black square: CO_2 concentration (% v/v). Dotted grey line: starting point of stage III (increasing water content up to 75 % w/w and adding 800 g of inoculum).

These results showed that the biodegradability of the MBT waste in terms of methane and carbon dioxide yields did not vary significantly between 37 °C and 55 °C when moisture conditions were not limiting, as also observed by other authors (Liu et al., 2009; Veeken and Hamelers 1999; Hejnfelt and Angelidaki, 2009). In fact, in both cases, the total biogas yield at the end of these tests was in the range of 55–60 % of the methane potential value (66.7 and 71.9 against 121 Nl CH_4/kgDM). However, from the results obtained at room temperature, it is evident that the temperature surely affects the gas generation rate but also seems to influence the gas generation capacity. Indeed, in test with water and inoculum addition (see R2 test in Fig. 4.2), the gas production achieved a value of 8.5 ± 1.0 Nl CH_4/kgDM and 19.3 ± 0.3 Nl CO_2/kgDM after 70 days

from inoculum and water addition but was still increasing, indicating that the stable methanogenic phase has not been reached yet (see Fig. 4.5).

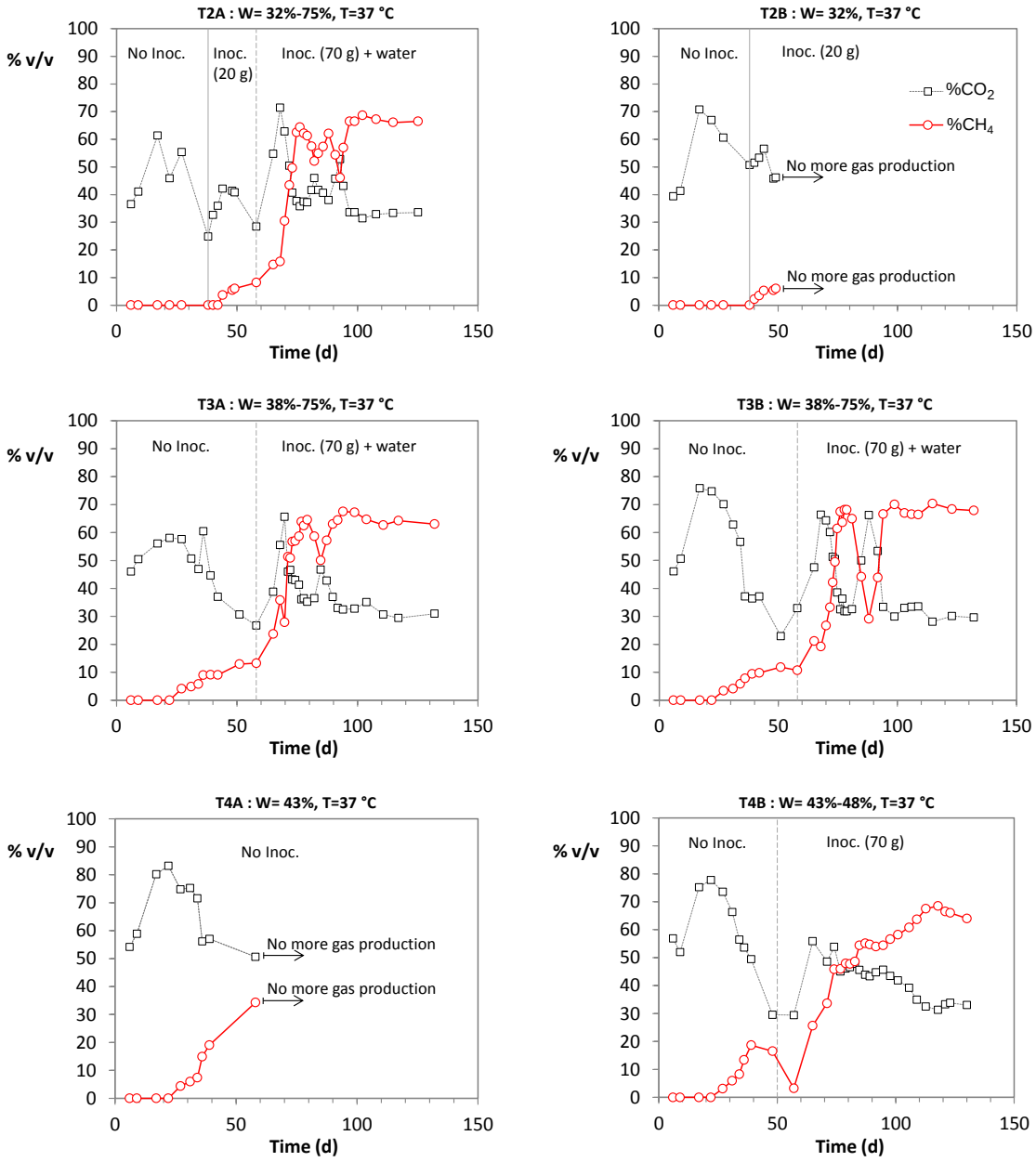

Figure 4.6. Gas composition (percentage by volume) measured in tests at 37 °C and initial water content of 32-75% (T2A), 32% (T2B), 38-75% (T3A/B), 43% (T4A) and 43-48% (T4B) on wet weight. Red dots: CH_4 concentration (% v/v). Black square: CO_2 concentration (% v/v). Solid grey line: starting point of stage II (20 g inoculum addition). Dotted grey line: starting point of stage III (increasing water content up to 75 % w/w and adding 70 g of inoculum, with the exception of reactor T4B in which only 70 g of inoculum were added).

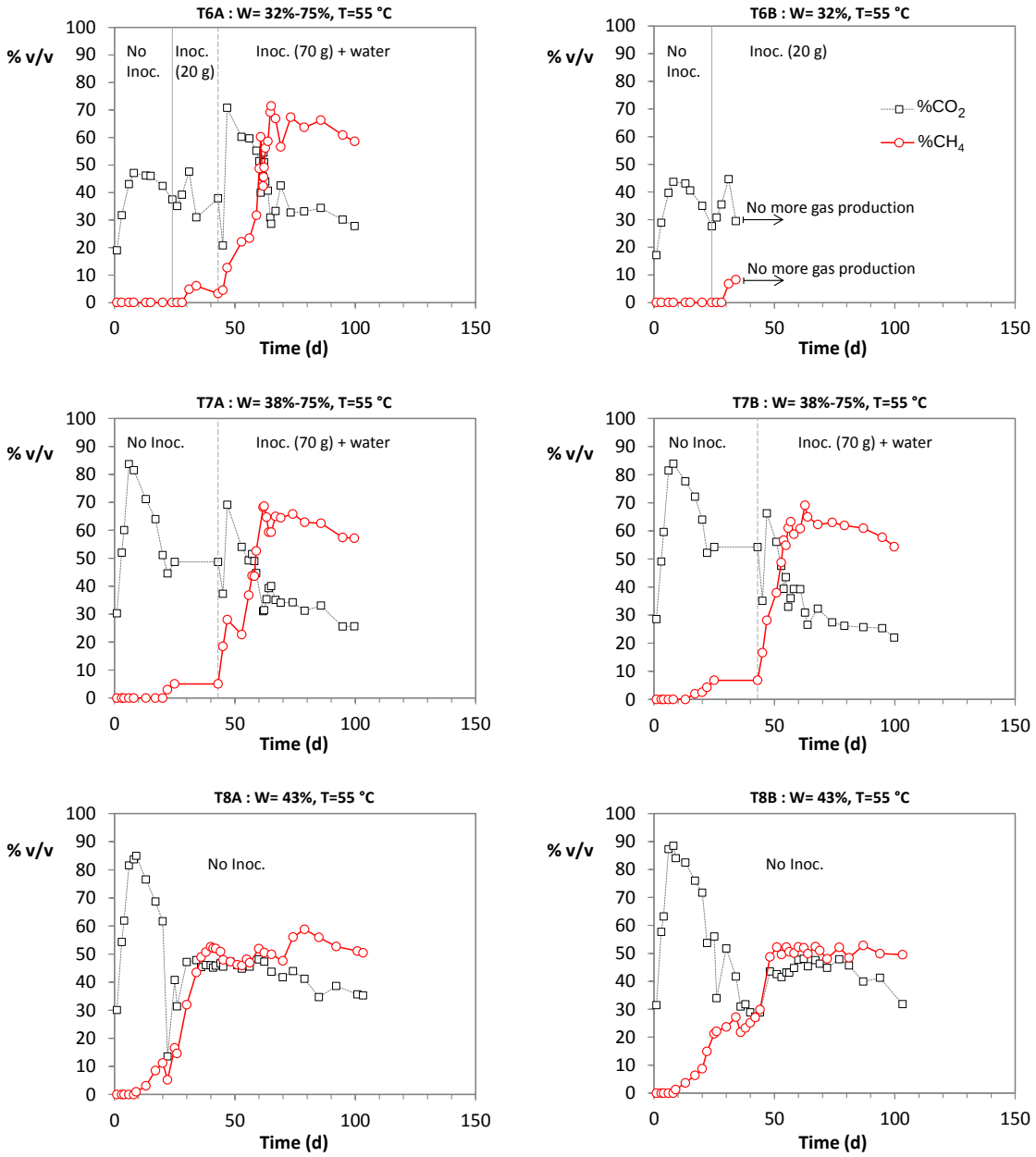

Figure 4.7. Gas composition (percentage by volume) measured in tests at 55 °C and initial water content of 32-75% (T6A), 32% (T6B), 38-75% (T7A/B), 43% (T8A/B) on wet weight. Red dots: CH_4 concentration (% v/v). Black square: CO_2 concentration (% v/v). Solid grey line: starting point of stage II (20 g inoculum addition). Dotted grey line: starting point of stage III (increasing water content up to 75 % w/w and adding 70 g of inoculum).

4.4.3.1 ESTIMATION OF GAS GENERATION MODEL PARAMETERS

Fig. 4.8 shows, for the tests that achieved the stable methanogenic phase, the cumulative biogas production simulated with the first order kinetic model (lines) fitted to the measured data (dots). Each data point represents the average of replicated experiments performed at each set of operating conditions.

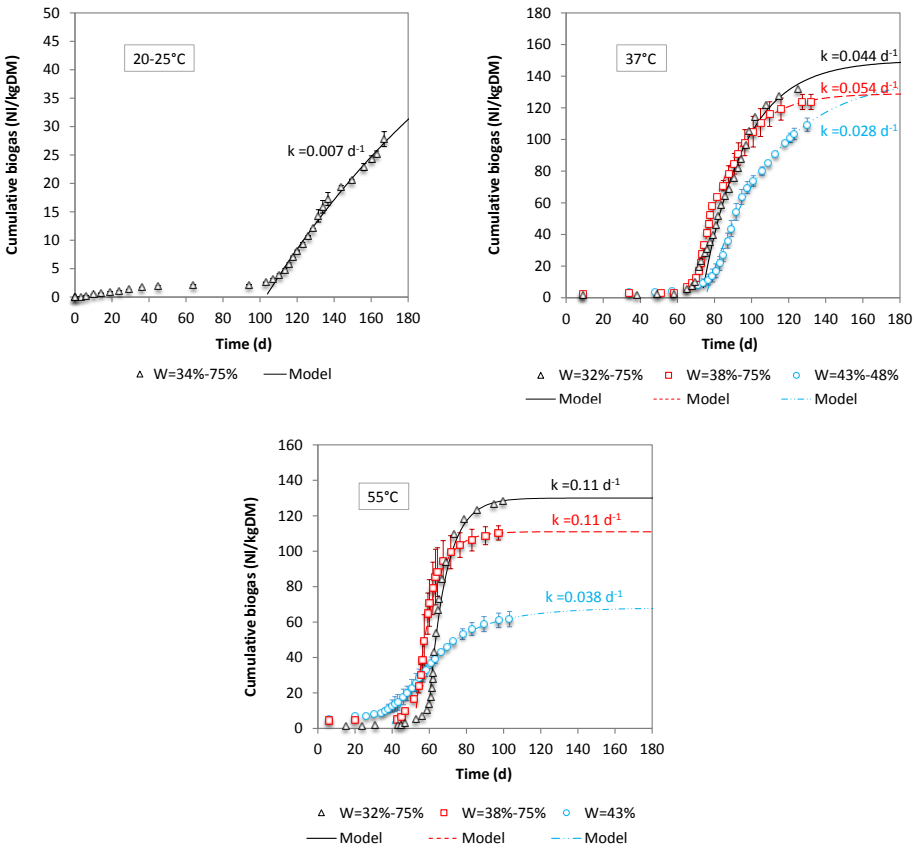

Figure 4.8. Cumulative biogas volume (Nl/kgDM) as a function of the incubation time: comparison between measured data (dots) and modelling results (lines) obtained with a first-order kinetic model, Eq. (4.2).

The same analysis was carried out using the modified Gompertz equation (Eq. 4.3); the simulated (lines) and measured (dots) trends of gas accumulation as a function of the incubation time are reported in Fig. 4.9. Furthermore, the best-fit parameters used in both models are reported in Table 4.4; in almost all simulations, except for test at room temperature (R2), the modified Gompertz (Eq.4.3) plots exhibited slightly better results

compared to the first order model (Eq.4.2), as confirmed by the R^2 values reported in Table 4.4.

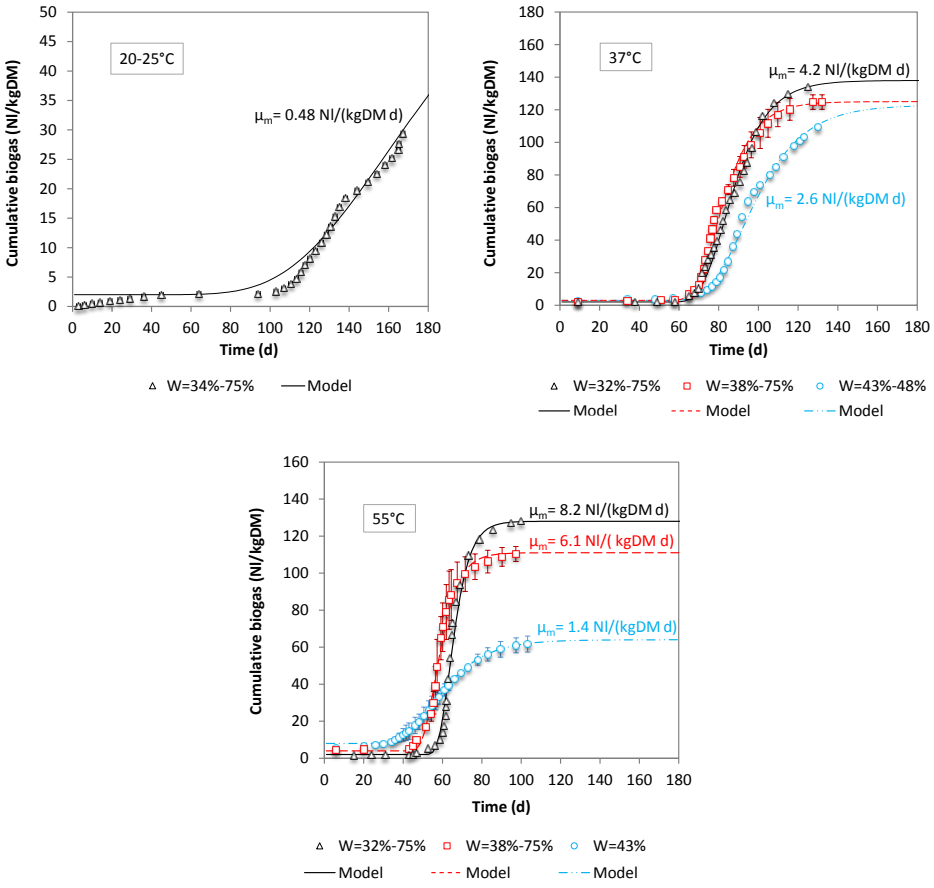

Figure 4.9. Cumulative biogas volume (Nl/kgDM) as a function of the incubation time: comparison between measured data (dots) and modelling results (lines) obtained with the modified Gompertz equation, Eq. (4.3).

From Table 4.4 it can be also observed that values of the maximum generation capacity (L_0) determined by applying the Gompertz formulation were slightly lower than those computed with the first order kinetic model. Hence, modelling the experimental results revealed that the biodegradability of the MBT waste, which was expressed as $\%L_0$/BMP, ranged between 56%-75% and 56%-69% at optimal conditions (75% water content) according to the first order model and Gompertz equation, respectively. When the experimental conditions become limiting for the biological process (see R2 and T8 tests) the biodegradability decreases to 34 %-38 %, in the first order model, and to 32 %-34 % in Gompertz simulations. This range is lower than the typical values usually

observed in solid state incubation tests of MBT residues, presumably due to the poor stability degree of the MBT waste analysed in this study. For example, Binner and Zach (1999) found that the gas generated within 90 days was about 75 % to 90 % of the potential gas generation capacity (measured after 240 days) for well treated wastes (duration of pre-treatment >10 weeks).

Table 4.4. First-order kinetic and Gompertz model parameters derived by interpolating experimental data for different test conditions. L_0: maximum biogas production (Nl/kgDM). t_{lag}: lag time (d). k: first-order kinetic constant (d^{-1}). R^2: correlation factor. $\%L_0$/BMP: percentage of gas generated compared to the potential value measured in BMP test. $T_{99\%}$: time (d) to reach 99% of maximum gas generation L_0. μ_m: maximal generation rate (Nl/(kgDM d)). b: Gompertz equation constant (Nl/kgDM).

	T= 20-25°C	T= 37°C			T= 55°C		
	R2	**T4B**	**T2A**	**T3**	**T8**	**T6A**	**T7**
	(W=34%-75%)	(W=43%-48%)	(W=32%-75%)	(W=39%-75%)	(W=43%)	(W=32%-75%)	(W=39%-75%)
First order kinetic model parameters							
L_0 (Nl/kgDM)	75	140	150	129	68	130	111
T_{lag} (d)	103	75	73	69	39	59	52
k (d^{-1})	0.007	0.028	0.044	0.054	0.038	0.11	0.11
R^2	0.993	0.991	0.972	0.996	0.992	0.981	0.986
% L_0/BMP	37.7	70.3	75.3	64.8	34.1	65.3	55.7
$T_{99\%}$ (d)	631	165	100	82	121	42	42
Modified Gompertz equation parameters							
L_0 (Nl/kgDM)	65	120	136	122	56	126	107
μ_m (Nl/kgDM d)	0.48	2.6	4.2	4.2	1.4	8.2	6.1
T_{lag} (d)	109	75	71	68	40	58	50
b (Nl/kgDM)	2	2	2	3	8	2	4
R^2	0.983	0.989	0.989	0.992	0.999	0.983	0.99
% L_0/BMP	33.6	61.3	69.3	62.8	32.1	64.3	55.7

As already discussed above, higher operative temperature leads to a faster gas production and to a shorter lag phase. Indeed, the maximal production rates determined with Gompertz equation, μ_m, were found in the ranges 0.54 Nl/(kgDM d) at room temperature, 2.6 - 4.2 Nl/(kgDM d) at 37 °C and 1.4 - 8.2 Nl/(kgDM d) at 55 °C.
Similarly, the first order k-values vary from 0.007 d^{-1} at room temperature, 0.03-0.05 d^{-1} at 37 °C and 0.04-0.11 d^{-1} at 55 °C. Moreover, a linear correlation of k-values with the operative temperature was observed for tests at 75 % w/w water content, as shown in Fig. 4.10. Making reference to this figure, each point is computed as average of tests

performed at the corresponding temperature and 75 % w/w water content (i.e. the k-value at 55 °C is determined as average of k-values estimated for tests T6A, T7A and T7B).

As for the duration of lag-phase, according to both models it decreases with increasing temperature, from more than 100 days at room temperature to 50 days at 55°C.

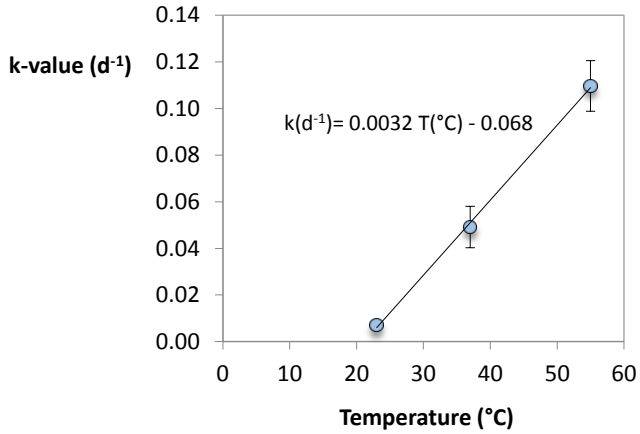

Figure 4.10. Empirical linear correlation of the k-value (d^{-1}) with the operative temperature (°C) obtained for tests at higher water content (75 % w/w).

The k-values estimated with the first order kinetic model were also used to compute the time required to reach the 99 % of the maximum biogas generation L_0, as follows:

$$T_{99\%} = \frac{\ln\ 1-0.99}{k} \tag{4}$$

Due to quite high k-values, a relatively short time period $T_{99\%}$ (Table 4.4), ranging from few months up to 2 years, was determined.

Table 4.5 reports a brief literature review of the kinetic constants and gas yields experimentally determined for different types of organic substrates. As shown in Table 4.5, these parameters vary substantially between different substrates, experimental procedures and tests conditions. Even if a direct comparison is not possible, the k-values obtained in this work are in line with most of these studies. For instance, the k-value of 0.007 d^{-1} determined at T=20-25 °C and water content of 75 %w/w, is consistent with

the results obtained by Vavilin et al., 2004 for MSW waste at 65 % of water content and T=30 °C (k=0.007-0.08 d^{-1}).

Table 4.5. Literature values of gas yield and first-order kinetic constant (k) for different types of organic substrates.

Gas yield	k-value(d^{-1})	Substrate	Experimental assay	Reference
75 Nl/kgDM	0.007 (T=20-25°C)	MBT waste (different water content)	anaerobic batch digester	*This work*
129-150 Nl/kgDM	0.03-0.06 (T=37°C)			
68(*)-130 Nl/kgDM	0.04(*)-0.11 (T=55°C)			
52 -70 gCH_4/kg	$4.3 \cdot 10^{-4}$-$5.2 \cdot 10^{-4}$	sludge	anaerobic batch digester	Mou et al. (2015)
107-117 Nl/kg	$6.6 \cdot 10^{-5}$-$6.8 \cdot 10^{-5}$	combustible waste		
37.6 lCH_4/kg	0.013 (T=55°C)	lignocellulosic biomass	batch reactor (BMP)	Ghatak and Mahanta (2014)
26.6 lCH_4/kg	0.004 (T=35°C)			
350 $NlCH_4/kgDM$	0.068 (T=35°C)	mixed waste from landfill (44% w/w organic)	lamdfill reactor with recirculation	Bilgili et al. (2009)
425 $NlCH_4/kgDM$	0.056 (T=35°C)		reactor without recirculation	
19 Nl/kg	$9.6 \cdot 10^{-5}$ (T=30°C)	MBT waste (water=50% w/w)	anaerobic batch digester	De Gioannis et al. (2009)
550 Nl/kgVS	0.1	hay (no comminution)	anaerobic batch digester	Vavilin et al. (2008)
590 Nl/kgVS	0.15	hay (comminution)		
240-280 $NlCH_4/kgVS$	0.035-0.063 (T=37°C)	co-digested organic waste and sewage sludge	anaerobic batch digester	Neves et al. (2006)
163 $NlCH_4/kgVS$	0.0311 (T=35°C)	grey waste (residual MSW, 41% w/w biodegradable)	batch reactor (BMP)	Vavilin et al. (2004)
---	0.007 - 0.08 (T=30°C)	MSW (water=65% w/w)	landfill reactors	Vavilin et al. (2004)
---	0.06-0.245 (T=28°C)	biowaste	continuous anaerobic digester	Veeken et al. (2000)
---	0.03-0.15 (T=20°C)	selected biowaste components	anaerobic batch digester	Veeken and Hamelers (1999)
---	0.24-0.47 (T=40°C)			
140 lCH4/kgVS	0.405 (T=35°C)	mechanically separated OF-MSW	continuous anaerobic digester	Mata-Alvarez et al. (1990)

(*) values refer to 103-days experiments performed at 55 °C and 43% (wet weight) water content, without inoculum addition.

Similarly, the k-values range (0.028-0.054 d^{-1}) observed at 37 °C is really close to the one reported by Neves et al. (2006), which refer to a co-digestion of organic waste and sewage sludge (0.035-0.063 d^{-1}) confirming that the analysed MBT waste is poorly treated. On the contrary, significant differences can be observed referring to the results presented by De Gioannis et al. (2009) and Mou et al. (2015). Indeed, the k-values reported by those authors are up to one-two orders of magnitude lower than the ones obtained in this work. This difference can be due to the higher content of readily

degradable organic matter in the analysed MBT waste compared to the low-organic wastes of Mou et al. (2015) and De Gioannis et al. (2009).

Nevertheless, it should be kept in mind that the high water content as well as the inoculum addition had accelerated the biodegradation process during the anaerobic experiments. Hence, the gas generation rate and yield listed in Table 4.4 may be overestimated in comparison to real landfill conditions. For example, Heyer et al. (2013) stated that the biological conversion process within lysimeters filled with MBT waste could be accelerated by a factor 3-10 compared to MBT landfills due to water addition or leachate recirculation.

4.4.3.2 INHIBITION OF ANAEROBIC DIGESTION PROCESS

Analysis carried out on the MBT waste samples removed from the reactors at the different stages of the tests revealed that pH was still suitable for the anaerobic digestion (6.6-7.0). Hence, in this specific case, pH alone did not give a clear indication of process inhibition. However, it should be considered that pH changes may be very small in highly buffered system even when the process is severely stressed (Ahring et al., 1995). Thus, it is likely that pH was buffered due to contrasting effects of VFA accumulation, which could have led to acidic conditions, and proteins degradation that could have favoured an increase of waste buffer capacity through the ammonia release (Veeken et al. 2000). In fact, as shown in Table 4.6, high VFAs and ammonia concentrations were measured in all MBT samples. Specifically, Table 4.6 reports the average values of total TKN and soluble nitrogen NH_4-N, the ratio between NH_4-N and TKN, and the total VFAs concentration measured in the fresh MBT sample and in the MBT samples removed from the anaerobic batch experiments at room temperature R2, at 37 °C (T2A and T3) and at 55 °C (T6A and T7). As shown in this table, the ratio of NH_4-N/TKN exhibited a twofold increase compared to what measured in the fresh waste. Moreover, VFAs concentrations in all samples were more than one order of magnitude higher than the ones measured in the fresh sample. This result indicates that the MBT waste still contains a certain amount of readily and medium-degradable organic matter, which was not expected, since the easily degradable fraction was supposed to be mineralised during the stabilization process in the MBT plant. Thus, it is

likely that the 4-week aerobic treatment process performed by the MBT plant is not sufficient to obtain a well stabilized waste, as also observed by Di Lonardo et al. (2014). Referring to Table 4.6, it can also be noticed that total VFAs content, as well as ammonia, exhibited an increasing trend with temperature (T7, T6 > T3, T2 > R2) reflecting the different extent of the biological process reached at different operational conditions. Namely, a total VFAs content ranging from 5.4 to 7.9 g/l was measured and the acetate was found as the predominant compound (see Table 4.7). Tests at room temperature also exhibited high concentration of propionate (1.5 g/l) that has been recognized as one of the main inhibitors of methanogens by some authors (Mawson et al., 1991; Weiland 2010; Wang et al., 2009). Even if it is widely documented that VFAs concentration can serve as a good indicator of process imbalances, controversy still exists about the specific role of individual VFA on overall anaerobic process as well as on threshold levels (Ahring et al., 1995; Nielsen et al., 2007) since it is strictly related to the type of substrate to be degraded.

Table 4.6. Average value and (±) standard deviation of total nitrogen, TKN (mg/gDM), soluble nitrogen, NH_4-N (mg/gDM), % NH_4-N/TKN and total VFAs concentration (g/l) measured in fresh MBT waste and in samples removed from anaerobic batch reactors.

SAMPLE	TKN (g/kgDM)	NH_4-N (g/kgDM)	NH_4-N/TKN (%)	VFA (g/l)
FRESH WASTE	14.1 ± 2.0	2.0 ± 0.2	14.4	0.18 ± 0.05
R2 (20-25 °C, W= 34 %w/w)	15.2 ± 1.2	3.4 ± 0.1	22.7	5.42 ± 0.24
T2A (37 °C, W=32 %w/w)	15.2 ± 0.6	4.2 ± 0.2	27.4	6.28 ± 0.58
T3 (37 °C, W= 38 %w/w)	14.1 ± 0.9	4.2 ± 0.3	30.1	7.57 ± 0.31
T6A (55 °C, W= 32 %w/w)	14.1 ± 1.4	4.6 ± 0.3	32.4	7.94 ± 0.93
T7 (55 °C, W= 38 %w/w)	15.0 ± 1.3	5.0 ± 0.2	33.6	7.56 ± 0.83

Overall, the high VFAs production suggests that the hydrolysis was rather fast, especially at the higher temperature. Hence, it seems that the hydrolytic-acidogenic bacteria did not limit the substrate degradation and the process was held at the acetogenic and methanogenic stage (a similar result was obtained by Palatsi et al., 2011). Therefore, the inhibition was likely due to an imbalance in the growth rate of acidogenic bacteria, which led to an accumulation of degradation by-products in reactors, as also observed by Adani et al. (2004). On the other hand, the inhibition of methanogenic bacteria may be also due to the high TKN and ammonia content observed

in the MBT samples (see Table 4.6). Thus, it is likely that the interaction between ammonia, VFAs and pH could have led to an "inhibited steady state" condition in which the process was running stably but a very low methane yield (Chen et al., 2008).

Table 4.7. Average concentration of acetate, propionate, isobutyrate, butyrate and isovalerate (g/l) measured in fresh MBT waste and in samples removed from anaerobic batch reactors.

	FRESH WASTE	T = 20-25 °C	T = 37 °C		T = 55 °C	
		R2	T2A	T3	T6A	T7
Acetate (g/l)	0.17	2.54	2.17	4.55	4.50	5.16
Propionate (g/l)	0.003	1.50	0.74	0.62	0.65	0.62
Iso-butyrate (g/l)	0.003	0.06	0.12	0.11	0.19	0.17
Butyrate (g/l)	0.001	1.26	3.03	2.10	2.24	1.25
Iso-valerate (g/l)	0.007	0.07	0.22	0.19	0.37	0.35
Total VFA (g/l)	0.18	5.42	6.28	7.57	7.94	7.56

4.4.4 EXPERIMENTAL FINDINGS AND PRACTICAL IMPLICATIONS

The BMP experiments, performed at optimal operational conditions, highlighted that for the analysed MBT waste, only 45 % of the theoretical gas generation potential can be achieved within 3-weeks experiment. This may be due to the presence of less soluble/degradable or more recalcitrant organic substances in the solid matrix, which cannot be mineralized during the limited duration of the lab-scale experiment. Hence, BMP tests, with respect to a simple theoretical estimation based on the available organic carbon measured in the solid matrix (TOC), can provide useful indications on the expected maximal potential gas generation capacity of landfilled waste under optimal conditions. On the contrary, the results obtained in this work highlighted that particular caution should be paid when the anaerobic batch tests are carried out under limiting operational conditions, e.g. low water content and temperature, high organic load, no inoculum addition. This is particularly true when the material of concern is, as in the present case, a waste with high organic content and a poor stability degree. In fact, although the tests performed under these limiting conditions may better resemble the environmental conditions expected in the field, the presence of inhibitory substances at

high level (such as ammonia, VFA accumulation, heavy metal content) may slow down or stop the anaerobic microbial process leading to an underestimation of the gas yield and generation rate. Indeed, as already shown in Table 4.6, in all experiments which exhibited very low gas generation rate and methane content, high concentrations of VFA and ammonia were measured within the systems, revealing an imbalanced kinetic between acids producers and consumers. Nevertheless, small pH changes were detected due to high protein degradation, which have increased buffer capacity of the analysed waste sample as a result of ammonia release, as well as due to the acid neutralization capacity characterizing the analysed MBT waste (see **Section 3.5.4.3**). Hence, it is likely that the interaction between ammonia, VFA and pH lead to an "inhibited steady state" condition in which the anaerobic process may run stably but at a very low gas yield. In particular, the experimental results suggested that the microbial activity could be completely inhibited when the water content of MBT waste was less than 32 % (on wet weight) and severely reduced for higher water content (up to the field capacity of approximately 41 %) depending on the operating temperature. These findings suggest that a stable gas generation process could be delayed for a long time until the environmental conditions within MBT waste landfills become favourable to the establishment of a stable methanogenic activity. Thus, it is not possible to predict how long the lag-phase can last in a landfill disposal scenario, where the boundary conditions significantly vary depending on the climate, the landfill geometry (surface, height), the operative management strategies in place (e.g. leachate recirculation, waste disposal methods), the presence and type of temporary and final cover systems. Indeed, the experimental results of this study revealed that, as soon as the anaerobic process starts, a relative short time period, ranging from few months up to two years depending on the water content and temperature, is required to deplete the gas generation. However, small scale experiments performed under controlled conditions may not provide a gas generation trend that is completely representative of full-scale landfill sites. Here, higher heterogeneous and variable conditions are expected due to greater amounts of waste mass, miscellaneous nature of emplaced waste as well as the heterogeneity of water flow patterns inside the landfill body that are also affected by different operational strategies (such as waste emplacement density, permeability and thickness of daily cover).

CONCLUSIONS AND FINAL REMARKS

Landfills can represent a source of persistent environmental impacts and risks for human health due to the potential seepage of liquid and gas emissions in the surrounding areas. Indeed, the pollutant load to the environment and related impacts are strictly dependent on the quantity and the quality of the water that percolates through the landfill and on the amount of gas generated from waste degradation. Thus, understanding leachate and gas generation processes and assessing their temporal evolution is a key issue for a correct landfill design and management. To this end, valuable information can be obtained by using landfill simulation models as well as by performing experimental investigations either at a small/large laboratory scale or at a full-scale MBT landfills.

Hence, the main goal of this Ph.D. thesis was, on the one hand, to develop a landfill screening model that, based on simplified analytical and empirical equations, enables the incorporation of main processes leading to landfill emissions generation as well as their spatial and temporal variation while limiting the input data requirements. On the other hand, the research study was focused on the characterization of leachate and gas emissions generated from MBT waste, since it currently represents the main flow waste disposed of in Italian landfill facilities due to new legal requirements. To this aim, a comprehensive laboratory study on physical, chemical and biological properties of MBT waste produced in Italian MBT plants was carried out. The experimental results were used to identify the key factors governing the leaching mechanism and gas formation from landfilled MBT waste. Based on laboratory results, a reasonable range for these parameters was proposed that may be assumed in a screening analysis of a full-scale MBT landfill along with some advices concerning the use of these values in practical applications.

Hereafter, a discussion on the main findings of the specific issues covered in the PhD thesis is briefly presented.

4.5 EVALUATION ON THE LWB MODEL APPLICABILITY

During this research study, a new landfill screening model (LWB) was developed to provide quantitative estimations of leachate and gas generation over time. The LWB model is based on a simplified approach and takes into account for physical, mechanical, hydrological and biological processes that previous models have usually tackled individually or through complex numerical computations, thus allowing an easier calibration process if field data are available. An essential precondition for practical uses of a simulation model, as screening tool for supporting landfill design, management and monitoring, is its comprehensive validation including theoretical and applicative steps. Hence, some simulations of hypothetical scenarios were performed in order to assess the conceptual model validity and to highlight more sensitive parameters. Results obtained during this step reveal that waste compression phenomena may greatly affect the leachate prediction, especially during the operative stage of a landfill, and neglecting these processes could lead to leachate underestimation up to one order of magnitude depending on waste properties. Moreover, biodegradation of waste organic matter may be relevant in leachate volumes assessment, influencing water storage capacity of wastes and leading to leachate productions higher than those obtained neglecting these phenomena.

The model capability in simulating closed landfills was evaluated considering different alternative cover systems and comparing predictive values of infiltration and percolation rates with the widely adopted HELP model. The results showed that, as expected, conventional covers composed of only soil barriers are not effective for limiting water infiltration whereas the best protective action is guarantee by a composite liner system with a geomembrane, even though very much depends on its integrity and on the quality of contact with the soil below. In addition, the effectiveness of a cover system could be also strongly affected by the water storage capacity of the surface soil layer and by the type of vegetation cover that have a huge influence on evapotranspiration and surface runoff losses. Despite some differences with the HELP predictions were detected, in a general perspective, the developed model was able to compare the long term performances of the analysed capping systems, demonstrating its applicability as screening tool for comparing alternative options of liner systems, even though these

results do not provide indications about the model accuracy since no field data were available for this case study.

In a second step, the applicability and accuracy of the developed model was partially verified using leachate data measured at four different real scale landfills currently in operative management stage. Good performances of the developed model in simulating leachate generated volumes in landfills were attained, especially once an appropriate calibration was performed, despite the limitations and simplifying assumptions of the model. Results of the model application to these case studies suggest that the accuracy of predictions strongly depends on the quality of input data and particular attention should be paid on selection of representative input values used in model simulations. In particular, the waste initial water content and the waste compression index were identified as the key unknown parameters affecting the leachate assessment from a quantitative point of view. Indeed, using the values reported in literature for MSW waste as input parameters leads to a general underestimation of leachate volumes in landfills compared to measured data. Hence, waste moisture and compression index were determined for each landfill site through a preliminary calibration procedure; the values computed appeared quite similar for all analysed landfills, suggesting these values may be assumed as representative for MSW waste in a screening phase modelling. As a remark, the best predictive performances were obtained when a step-by-step calibration was carried out; considering that waste properties may change monthly instead of assuming them constant throughout a year (which is a basic assumption of most landfill predictive models) allows to get, for many months, a perfect match between the simulated leachate values and the measured data for almost all the landfills. These findings highlight the huge influence of the key parameters on model predictions and show the advantages to use a simplified model which allows to easily manage the uncertainties related to the input data.

4.6 LEACHING BEHAVIOUR OF MBT WASTE

The leaching behaviour of biologically treated waste samples collected from an Italian MBT plant was investigated by applying pH static-batch, pH dependent tests and dynamic up-flow column percolation experiments, in order to highlight the effects of

the environmental condition, mainly pH and liquid to solid ratio (L/S), on the mobility of major and minor constituents from this solid matrix. Comparing the results of batch and column tests, it was observed that the static batch test, which is the compliance method commonly used for landfill disposal, may underestimate the actual release of dissolved organic carbon (DOC) and Co, Cr, Mg and Ni from this type of waste. This result may be due, on one hand, to the longer duration of the column experiment compared to the batch one and, on the other hand, to the different test conditions that may affect the compounds release (e.g. with respect to static batch tests in dynamic column tests there is a continuous renewal of the leachant that could maintain the driving force of leaching). On the contrary, the column tests performed on different MBT samples provided robust results and useful information about the kinetics of compounds release, allowing to highlight the key parameters governing their mobility. In fact, from the comparison of the elution profiles of DOC with those of Co, Cr, Cu, Mg, Ni, V and Zn an evident similarity in the leaching behaviour was observed. These results suggest that the DOC plays a key role in the leachability of these metals probably due to its high solubility and its affinity to form stable metal complexes. Actually, a strong linear correlation (R^2>0.8) between DOC and metals concentration in eluates was observed especially for Cr, Ni and Zn (R^2>0.94). This evidence was further confirmed by the results of pH-dependent tests for most of metals, with the exception of Mg and Zn, for which the influence of pH was not negligible. Thus, combining the results of batch and up-flow column percolation tests, partition coefficients specific for each element were derived. These data coupled with a simplistic screening model for DOC release allowed to obtain a very good prediction of metals release during the different column tests. However, it should be highlighted that the model presented here does not account for long-term processes, such as geochemical and biological processes, which are likely to occur in a landfill and can influence the DOC release, the form of soluble organic matter and its ability to bind metals. Moreover, from the modelling of leaching data it appears that the mass release may be simulated assuming a flux-controlled mechanism only for low L/S ratios, whereas for higher L/S non-equilibrium conditions, which can be described by a mass-transfer controlled model, are observed. This is a key issue to be accounted for long-term evaluations of leaching behaviour since implies that for L/S approximately higher than 0.5 l/kg, the mass release should be

estimated as a function of time. As a result, the overall mass release expected for long-term landfill scenarios (e.g. after 50 or 100 years) will be definitely higher than the values predicted on the basis of experimental results modelling. It should be highlighted that all results refer to a particular type of MBT waste g. coming from a 4-weeks aerobic process without the ripening stage. Since leaching properties (K_d $K_{DOC,Me}$) are likely to be strongly influenced by the stability degree of the MBT waste material as well as by the characteristics of the incoming MSW waste feeding the MBT plant, these parameters should be estimated for different MBT wastes, depending on the specific plant configuration and/or biological treatment process.

Thus, further investigations are needed to clarify all these aspects; to this aim, both laboratory scale tests, performed on different type of MBT wastes as well as field-scale monitoring could be certainly useful.

4.7 GAS GENERATION FROM MBT WASTE

The gas production from MBT wastes was evaluated by performing anaerobic batch tests under different operating conditions. In order to characterize the MBT material regarding its long-term gas emission in different landfill disposal scenarios, a wide range of water contents (26-43 %w/w up to 75 %w/w) and temperatures (from 20-25°C up to 55°C) were investigated. The obtained results display that the analysed MBT material still contains a large amount of readily degradable organic matter, as confirmed by the long duration of the lag-phase (several months), the high values of gas production potential (199.2±63 Nml_{gas}/gDM), the gas generation rates (ranging from 0.007 d^{-1} at room temperature, 0.03-0.05 d^{-1} at 37°C and 0.04-0.11 d^{-1} at 55°C), as well as the strong inhibition effects observed due to high concentrations of VFAs and soluble ammonia.

Based on the results presented in this study, the following conclusions and perspectives can be drawn:

- it is very difficult to predict how long the lag-phase can last in MBT waste landfills where the boundary conditions change continuously and vary significantly depending on the climate, the landfill geometry (surface, height), the operative management strategies in place (e.g. leachate recirculation, waste

disposal methods) and the presence and type of temporary and final cover systems.

- The water content of emplaced MBT waste is the most important factor limiting the anaerobic biological process. Experimental results showed that, for this specific MBT waste, when the waste moisture was lower than 32 %w/w, the methanogenic microbial activity was completely inhibited whereas for values in the range 38-43 %w/w only a limited amount of the degradable organic matter was converted into biogas (32 -34 % of the maximum potential gas generation capacity). Moreover, even in the case of higher water content (75 %w/w), the measured potential generation capacity (BMP values) was not achieved, presumably due to the effect of waste particle size and low substrate to inoculum ratio on the gas yield. Hence, a wide range for the gas formation factor was determined (0.3-0.75) as a function of the waste water content and temperature that could be used for gas generation modelling in a screening phase.
- As soon as the environmental conditions inside the waste mass become favourable to the establishment of the stable methanogenic phase, a relatively short time period, ranging from few months up to two years is required to deplete the MBT waste gas generation. However, this result provides just an indication of the actual lifetime of biogas production from MBT wastes disposed of in landfills, where much higher amount of waste are emplaced and the environmental conditions may be quite far from the experimental ones.
- Gas generation model parameters, as the cumulative gas generation and the first order rate constants, determined by performing small scale laboratory tests may be not appropriate for characterizing the whole landfill body and its heterogeneity. Hence, using these values in a screening analysis of a real landfill site could lead to overestimation of gas production over time. Field measurements of produced gas volumes could be helpful to deduce correlation factors between experimental results and real observations that could be used to calibrate the proposed model.
- The benefits of using the MBT technology within a sustainable waste management system strongly depends on the efficiency of the biostabilization process in reducing the gas generation capacity of the residual MBT waste. In

this specific case, experimental data suggest that 4 weeks of aerobic biological treatment do not guarantee a sufficient degree of stability for the analysed MBT waste.

4.8 FINAL REMARKS

A new landfill simulation model was developed to provide quantitative estimation of leachate and gas generation over time taking into account for site-specific conditions and main processes naturally occurring in landfills. Up to now, the use of predictive models as screening analysis tools is still not so widespread in municipal solid waste landfills as in other fields (e.g. risk assessment software for contaminated sites or life cycle analysis), even though a modelling approach can be used to support landfill design and management. Indeed, results of model application to some real case studies demonstrate that the proposed model could appropriately describe leachate generation in landfills. However, despite these results are encouraging, further investigations based on monitoring data from closed and active landfills are needed to verify the model reliability in forecasting future landfill emissions. Moreover, practical and theoretical applications of the developed model suggested that, despite the high complexity of a landfill system and numerous processes affecting field emission behaviour, reliable predictions could be obtained by operating on a limited numbers of calibrating parameters (initial water content and waste compression index). This means that efforts to improve model robustness can be focussed on a better evaluation of only few factors. Furthermore, the model applicability to specific landfill context could be improved by performing experimental studies in order to identify the key factors governing emission generation as well as to highlight possible limiting conditions. In the present study, an experimental investigation was carried out to assess leachate and gas emissions from mechanically biologically treated wastes. The experimental findings revealed that both the leachate composition and the extent of gas emissions are strictly dependent on the amount of readily soluble and degradable organic matter contained in the MBT waste and, hence, on the efficiency of the stabilization process carried out in the MBT plant. However, further investigations on MBT waste samples coming from different MBT plants are needed to confirm these findings.

Specifically, leaching tests combining static and dynamic experiments, indicated that the mass release of some metals (Co, Cr, Ni, Mg, V and Zn) is mainly governed by complexation mechanism with the dissolved organic carbon (DOC) and seemed to be less influenced by environmental condition such as pH (except for Mg and Zn). This implies that more efforts should be direct to elucidate the long-term leaching pattern of DOC in MBT waste landfills.

As for gas production experiments carried out on the same MBT materials, it was observed that for poorly treated MBT waste greater uncertainties are related to the duration of the lag phase, the amount of gas generated and the time required to achieve a complete stabilization of waste organic matter, owing to inhibition effects and strong influence of environmental conditions on biological processes. This suggests that a predictive model of landfill emissions should consider, besides the chemical and biological properties of the emplaced waste, also the specific landfill aspects (climate, waste properties, water flow pattern) and operational strategies (waste compaction, co-disposal, containment systems) in order to provide more reliable estimations of gas generation over time, since all these aspects may drastically affect the kinetic of gas generation processes. In this view, lab-scale results can provide useful information to support model refinement, to facilitate its calibration and to verify its predictive capacity. However, laboratory tests may be not completely representative of the whole landfill and, thus, the experimental results should be carefully interpreted before using them either as model input parameters or for the extrapolation of long-term emission in real scale landfill sites.

LIST OF PUBLICATIONS

Scientific Journals

Pantini, S., Verginelli, I., Lombardi, F., (2014). A new screening model for leachate production assessment at landfill sites. *International Journal of Environmental Science and Technology*, 11, 1503-1516.

Pantini, S., Verginelli, I., Lombardi, F., (2015). Analysis and modelling of metals release from MBT wastes through batch and up-flow column tests. *Waste Management*, 38, 22-32. doi:10.1016/j.wasman.2014.12.002

Pantini, S., Verginelli, I., Lombardi, F., Scheutz C., Kjeldsen, P. (2015). Assessment of biogas production from MBT waste under different operating conditions. Submitted to *Waste Management*.

Di Gianfilippo, M., Costa, G., Pantini, S., Lombardi, F., Allegrini, E., Astrup, F.T., (2015). LCA of management strategies for RDF incineration and gasification bottom ash based on experimental leaching data. Submitted to *Waste Management*.

Grugnaletti, M., Pantini, S., Verginelli, I., Lombardi, F., (2015). An easy-to-use tool for the evaluation of leachate production at landfill sites. In preparation.

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