UNIVERSITÀ DEGLI STUDI DI ROMA "TOR VERGATA"

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DOTTORATO DI RICERCA IN INGEGNERIA AMBIENTALE

EVALUATIONS FOR A POSSIBLE RECOVERY/UTILISATION OF MECHANICALLY-BIOLOGICALLY TREATED MUNICIPAL SOLID WASTE BY MEANS OF DIFFERENT OPERATING CONDITIONS AND RETAINING TIMES

Maria Chiara Di Lonardo

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Evaluations for a possible recovery/utilisation of mechanically-biologically treated municipal solid waste by means of different operating conditions and retaining times

DISSERTATION

Maria Chiara Di Lonardo

Tutor: Prof. Francesco Lombardi

Co-tutor: M.Sc. Erwin Binner

Coordinator: Prof. Renato Gavasci

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ABSTRACT

In the last two decades mechanical-biological treatment (MBT) of residual municipal solid waste (i.e. the remaining MSW after source separate collection) was developed in order to minimise the environmental impacts and reduce the risk to human health associated to landfilling, as required by the European Landfill Directive 1999/31/EC. The goal of MBT broadened over years with the further purpose to utilise significant percentages of the outputs for material and/or energy recovery. One of the output of MBT is the biostabilised waste (BSW) produced from the aerobic biodegradation process of the biodegradable organic fraction mechanically separated from the input MSW. As indicated in the document drafted by the European Commission "Biological treatment of biowaste - 2nd draft", the MBT of MSW shall have the purpose of stabilising and reducing the volume of the biodegradable waste in order to ensure that the resulting BSW can either be used for ecological improvement or has reduced negative environmental impacts when landfilled. Moreover the EC document specifies that Member States may authorise the use of biostabilised waste, fulfilling the requirements indicated in the document, as a component in artificial soils or in those land applications that are not destined to food production (such as final landfill cover, landscape restoration in old and disused quarries and mines, anti-noise barriers, road construction, etc.). Such statement came from the evidence that the content of heavy metals in BSW is generally higher than that in compost produced from source segregated waste.

Italy has a long tradition in MBT but emphasis on recovery of the outputs is mainly focused on the production of solid recovered fuel (SRF), with just some plants producing biostabilised waste suitable for restricted applications. As a result, nowadays, biostabilised waste coming from Italian MBT plants is mainly landfilled. Furthermore specific technical standards defining the quality requirements of the biostabilised waste and its sustainable uses do not have been drafted since 2010, when a legislative proposal on this topic was issued.

In view of such need, the present research study aimed to assess the possible biostabilised waste recovery/utilisation, in alternative to landfilling, by evaluating different operating conditions and treatment times.

Specifically, waste materials were sampled in two MBT plants (plant A and plant B) located in Rome whose maximum treatment capacity is 750 Mg MSW/day per each plant. Residual MSWs feeding such MBT plants were found to be composed by high percentage of biodegradable organic waste (food and garden waste, paper and cardboard, fine organic waste lower than 20 mm) equal to 60 %. A percentage equal to 70 % of such biodegradable waste is separated through a primary mechanical sieving in the MBT facilities and then it is subjected to a biological treatment consisting of aerobic biodegradation at forced aeration conditions for 4 weeks. Afterwards, the biostabilised output is not subjected to a ripening phase but it is directly landfilled.

Firstly, an evaluation on the quality of the biostabilised waste (BSW) as currently treated by the MBT plants of Rome was carried out in order to assess the suitability for a possible recovery. For this purpose, biological and physical-chemical characterisation of the output material was performed. A further characterisation of the material sampled before and after the 1st and the 4th week of the aerobic biodegradation was performed in MBT plant A in order to assess the evolution/changing of the investigated characteristics during the process. Results led to conclude that the BSW did not have a suitable quality for waste recovery, both in terms of biological stability degree and in terms of physical-chemical characteristics.

Given the unsuitability for recovery of the biostabilised waste as currently treated, second step of the research was to evaluate the influence on BSW characteristics of longer duration of the aerobic biological process. Specifically, an extension of the biodegradation process at forced aeration condition occurring in the biostabilisation basin of the MBT plant A from 4 weeks, which is the duration in normal operating conditions of the plant, to 7 weeks was evaluated. Furthermore, a well biostabilised output, coming from the intensive biodegradation lasting 4 weeks, was subjected to a ripening phase in slightly aerated lab test cells in order to analyse and evaluate a possible further increase of the biological stability. Again, biological and physical-chemical characterisation of waste samples, periodically collected during the aerobic biodegradation in the bio-stabilisation basin and during the lab ripening phase, was carried out. Results confirmed that the biostabilised waste was still highly reactive after 4 weeks of intensive biodegradation treatment. By extending the process duration to 7 weeks, a good biological stability degree was reached. It was also observed that an additional ripening phase lasting at least 5 weeks (as indicated by lab-tests, possibly longer duration will be necessary in-situ) should be carried out in order to obtain a highly biostabilised waste, acquiring the characteristics of a biologically mature material. Furthermore heavy metals total content in the BSW outputs, both from the intensive biostabilisation process of 7 weeks and from the lab ripening phase, was found to fulfil the requirements for a potential utilisation in environmental remediation applications restricted to commercial and industrial sites (as indicated by Italian regulatory regime). Differently, contaminants release in water phase showed to increase for some metals (specifically Cu, Pb and Cr) at the end of the two biodegradation stages and to not comply with limit values set by the Italian regulation for the recovery.

In conclusion, the only feasible utilisation for the biostabilised waste showed to be in monitored environments, such as in landfill sites as cover material, where the release of contaminants is controlled through the collection of the percolate and its subsequent treatment. However, it is important to remark that, even in the use as landfill cover, the biostablised waste need to be subjected to a longer duration of the biological process, including a ripening phase, otherwise strong pollutant loading may occur, such as high long-term biogas emissions (as shown by the results of the incubation tests measuring the biogas generation).

Other uses of the biostabilised waste, such as in soil applications for landscape restoration, may be considered under the constraint to apply a risk assessment procedure on a site-specific level in order to evaluate the potential risk for receptors (groundwater and surface water, plants, animals and humans) and to establish at which acceptable levels of pollutants, taking also into account the migration routes, such land application is not harmful to the environment and the human health. Therefore, the observations and evaluations highlighted in the present research thesis could be useful in the development of such risk assessment.

SOMMARIO

Il trattamento meccanico-biologico (TMB) dei rifiuti urbani (RU) residuali dalla raccolta differenziata è stato sviluppato con lo scopo primario di minimizzare gli impatti ambientali e ridurre il rischio per la salute umana associati allo smaltimento dei rifiuti in discarica, in applicazione della Direttiva Europea 1999/31/CE. Nel corso degli anni l’obiettivo del TMB si è ampliato andando a realizzare una effettiva gestione dei flussi di rifiuti tale da produrre materiali in uscita utilizzabili per il recupero di materia e/o di energia. Uno degli output del TMB è la cosiddetta frazione organica stabilizzata (FOS) proveniente dal trattamento biologico aerobico della frazione organica putrescibile (FOP) separata meccanicamente a monte (tramite vagliatura) dal rifiuto urbano in ingresso al trattamento. In un documento della Commissione Europea dal titolo “Biological Treatment of Biowaste - 2nd draft”, viene indicato come il TMB dei rifiuti urbani debba assicurare la stabilizzazione e la riduzione del volume dei rifiuti biodegradabili in modo tale che la FOS risultante possa essere utilizzata in applicazioni ambientali per miglioramenti ecologici o comunque che venga smaltita in discarica con ridotti impatti negativi sull’ambiente. Inoltre viene specificato che gli Stati Membri possono autorizzare l’uso del rifiuto biostabilizzato, qualora rispondente ai requisiti stabiliti nel documento stesso, come componente di suoli artificiali o in quelle applicazioni che non sono destinate alle produzioni di beni di consumo umano e animale (come ad es. copertura finale di discariche, recupero paesaggistico di cave e miniere in disuso, barriere anti-rumore, costruzione di strade, ecc.). Tale circostanza è emersa dall’evidenza scientifica che il contenuto di metalli pesanti nella FOS è generalmente più elevato rispetto a quello del compost prodotto dal trattamento biologico dei rifiuti organici separati alla fonte tramite raccolta differenziata.

L'Italia ha una lunga tradizione nel trattamento meccanico-biologico, ma gli impianti TMB sono maggiormente focalizzati sulla produzione di combustibile solido secondario (CSS) per il recupero di energia e solo alcuni producono rifiuti biostabilizzati adatti a

poche applicazioni ambientali. Di conseguenza, ad oggi, la FOS viene principalmente smaltita in discarica. Inoltre, il Decreto Legislativo 205/2010, che ridisciplina l'ambito dei rifiuti in Italia in modifica della parte IV del D.Lvo 152/2006, rimanda la definizione dei requisiti di qualità del rifiuto biostabilizzato e dei suoi utilizzi compatibili con la tutela ambientale e sanitaria ad apposite norme tecniche che ancora non sono tate emanate.

A fronte di ciò, l'obiettivo della presente ricerca è stato quello di valutare il possibile recupero/utilizzo della frazione organica stabilizzata, in alternativa allo smaltimento in discarica, esaminando diverse condizioni operative e diversi tempi di trattamento.

In particolare, i rifiuti sono stati campionati in due impianti TMB (impianto A e impianto B) situati nella città di Roma. Data la bassa percentuale di raccolta differenziata che ancora oggi si registra in questa città (22.4 %), i rifiuti urbani residuali in ingresso a tali impianti sono risultati essere costituti da un'alta percentuale di rifiuti organici biodegradabili (scarti alimentari e verdi, carta e cartone, rifiuti organici di pezzatura inferiore a 20 mm), pari al 60 % in peso. Nei due impianti TMB, una percentuale pari al 70 % di tale frazione biodegradabile viene separata mediante vagliatura meccanica come sottovaglio (< 80 mm) e viene sottoposta ad un processo biologico aerobico in condizioni di aerazione forzata per 4 settimane. Successivamente, a valle di una seconda vagliatura a 20 mm, il rifiuto biostabilizzato viene direttamente inviato allo smaltimento in discarica.

In primo luogo, è stata effettuata un'indagine sulla qualità della FOS così come attualmente trattata dagli impianti TMB di Roma in modo tale da valutarne l'adeguatezza per un possibile recupero. A tale scopo, è stata eseguita una caratterizzazione chimico-fisica e biologica del materiale in uscita dai due impianti TMB di cui sopra. Successivamente, è stata condotta un'ulteriore caratterizzazione del materiale prelevato a monte e a valle della prima e della quarta settimana di biostabilizzazione nell'impianto TMB A al fine di valutare l'evoluzione delle caratteristiche indagate durante il processo. I risultati ottenuti hanno portato a concludere che la FOS non aveva una qualità adatta per un recupero, sia in termini di stabilità biologica che di caratteristiche chimico-fisiche.

Vista l'inadeguatezza per il recupero del rifiuto biostabilizzato così come attualmente prodotto, si è ritenuto necessario andare a valutare la qualità del rifiuto biostabilizzato

considerando una durata maggiore di trattamento. A tal fine, nell’impianto TMB A, una parte del bacino di biostabilizzazione è stata “isolata” e predisposta in modo tale da poter trattare il materiale per un tempo maggiore di 4 settimane, ossia per 7 settimane, e permettere il monitoraggio e il campionamento dello stesso. Inoltre, la FOS proveniente ancora dall’impianto TMB A (a valle del processo di 4 settimane e della vagliatura meccanica a 20 mm) è stata sottoposta ad una fase di maturazione a scala di laboratorio. In particolare, il materiale è stato inserito in un sistema di celle verticali aerate dal fondo con un basso flusso di aria, in modo tale da simulare il sistema “open windrow” ad aerazione naturale. Ancora una volta è stata eseguita una caratterizzazione biologica e fisico-chimica dei campioni di rifiuti prelevati periodicamente durante le 7 settimane di biodegradazione aerobica nel bacino di biostabilizzazione e durante la fase di maturazione in laboratorio. Da tale indagine è stato confermato che il rifiuto biostabilizzato per 4 settimane era molto reattivo biologicamente. Estendendo la durata del processo fino a 7 settimane, è stato invece osservato che può essere raggiunto un buon grado di stabilità biologica. Inoltre, si è visto che, prevedendo una fase aggiuntiva di maturazione della durata di almeno 5 settimane (come indicato dalle prove di laboratorio mentre su scala reale sarà probabilmente necessaria una durata maggiore del processo), si può ottenere un rifiuto altamente biostabilizzato, tale da acquisire le caratteristiche di un materiale biologicamente maturo. In più, i risultati ottenuti sul contenuto totale di metalli pesanti nei due output uscenti dal processo di biostabilizzazione di 7 settimane e dalla fase di maturazione in laboratorio, hanno mostrato che questi rispettavano i requisiti previsti per un potenziale utilizzo nell’ambito dei ripristini ambientali vincolati a siti con destinazione d’uso commerciale e industriale (nel rispetto del regime normativo italiano). Diversamente, il rilascio dei contaminanti in fase acquosa ha mostrato di aumentare per alcuni metalli (in particolare Cu, Pb e Cr) al termine delle due fasi di biodegradazione e di non rispettare i valori limite fissati dalla normativa italiana per il recupero dei rifiuti non pericolosi.

In conclusione, è emerso che l'unico possibile utilizzo del rifiuto biostabilizzato sembra essere limitato ad ambienti controllati, ad esempio come materiale di copertura delle discariche in cui il rilascio di contaminanti è tenuto sotto controllo mediante la raccolta del percolato e il suo successivo trattamento. Tuttavia, è importante sottolineare che, anche in questo caso, la FOS andrebbe sottoposta ad una maggiore durata del processo

biologico, che includa anche una fase di maturazione, andando a ridurre così il forte carico inquinante associato, ad esempio, ad elevate emissioni di biogas a lungo termine (come mostrato dai risultati del test di incubazione per la misura della produzione di biogas).

Altri impieghi della FOS, come ad esempio in recuperi paesaggistici, potrebbero essere considerati sotto il vincolo di applicare una procedura di analisi di rischio sito-specifica al fine di valutare il potenziale rischio per i recettori (acque sotterranee e superficiali, piante, animali ed esseri umani) e per definire dei livelli accettabili di inquinanti, tenendo conto anche delle vie di migrazione degli stessi, che non siano dannosi per l'ambiente e per la salute umana. Pertanto, le osservazioni e le valutazioni evidenziati nella presente tesi potrebbero essere utili nello sviluppo di tale valutazione del rischio.

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CHAPTER 1

BACKGROUND AND GOAL OF THE RESEARCH

This chapter is partly taken from:

Di Lonardo M.C., Lombardi F., Gavasci R. (2012a) Characterization of MBT plants input and outputs: a review. *Review in Environmental Science and Biotechnology* 11, 353-363.

OVERVIEW ON MECHANICAL BIOLOGICAL TREATMENT OF MUNICIPAL SOLID WASTE

In the last two decades, hundreds of large scale mechanical-biological treatment (MBT) facilities of residual municipal solid waste (i.e. the remaining MSW after source separate collection) were developed in Europe (Lornage et al., 2007; Barrena et al., 2009; Bayard et al., 2010; Ponsá et al., 2010; Tintner et al., 2010) in order to minimise the environmental impacts and reduce the risk to human health associated to the disposal in landfill, as required by the European Landfill Directive 1999/31/EC (European Commission, 1999). The Directive specifically requires Member States to only landfill wastes that have been subjected to treatment, leading to a stepwise reduction of the biodegradable organic matter contained in the waste (Robinson et al., 2005).

Mechanical–biological treatment consists in a combination of mechanical processes (shredding, size, density and magnetic separation, densification, etc.) and biological treatment (aerobic or anaerobic process) (Soyez and Plickert, 2002) of the organic fraction mechanically separated. As observed by several authors (Heerenklage and Stegmann, 1995; Rieger and Bidlingmaier, 1995; Scheelhaase and Bidlingmaier, 1997; Komilis et al., 1999; Leikam and Stegman, 1999; Soyez and Plickert, 2002; Cossu et al., 2003; Bockreis and Steinberg, 2005; Fricke et al., 2005; Robinson et al., 2005; Munnich et al., 2006; Lornage et al., 2007; De Gioannis and Muntoni, 2007; de Araujo Morais et al., 2008; Sormunen et al., 2008; Barrena et al., 2009; De Gioannis et al., 2009; Zdanevitch et al,. 2009; Donovan et al., 2010; Montejo et al., 2010; Scaglia et al., 2010; Velis et al., 2010), MBT have beneficial aspects resulting in a more environmentally sound landfill management, including:

- minimisation of volume and mass of waste to be landfilled;
- degradation and stabilisation of landfilled wastes in order to reduce leachate and methane production and odour emissions;
- immobilisation of pollutants of the waste to be landfilled in order to reduce leachate contamination;
- reduction of landfill settlement;

- reduction of the duration of the landfill aftercare period.

The role of MBT broadened over years with the further purpose to utilise significant percentages of the outputs for material and/or energy recovery (Farrell and Jones, 2009; Velis et al., 2010), in such a way to supplement the waste source separation (Calabrò et al., 2007). Specifically, MBT may be designed and optimised for the production of marketable outputs such as metals (that are recycled in the metallurgical industry), high-calorific materials (solid recovered fuel, SRF) that can be used in waste to energy systems or for co-incineration in high energy-demanding industries like cement plants, as well as biologically stabilised organic waste (BSW) to be used for land/soil applications (European Commission, 2001; Amlinger et al., 2004; Soyez and Plickert, 2002; Clemens and Cuhls, 2003; Sanchez-Monedero, et al. 2004; Fricke et al., 2005; Bezama, 2007; ISPRA, 2007; Pahl et al., 2008; Sormunen et al., 2008; De Gioannis et al., 2009; Bayard et al., 2010; Montejo et al., 2010; Velis et al., 2010). The MBT technology is characterised by relatively low costs, high flexibility of the process and the possibility of centralised and decentralised application (Soyez and Plickert, 2002; Fricke et al., 2005; Norbu et al., 2005; Munnich et al., 2006; Bezama et al., 2007; Lornage et al., 2007). However the MBT cost per ton of waste may vary significantly according to the goals that the plant has to achieve, complying with legal requirements (e.g. treating waste air, drying and stabilising the waste as it is; splitting the incoming waste into biodegradable and high calorific fractions and then stabilising the first ones; stabilising the biodegradable fractions and producing SRF and/or recovering materials to be recycled) and to the fate of the sorted and stabilised materials (landfill disposal, use for landscaping after refining, incineration, recycling) (De Gioannis et al., 2009). In fact, quantity and quality of the outputs of a MBT plant vary in function of (Rotter et al., 2004; Robinson et al., 2005):

- the characteristics of the input, which in turn depends on the area (urban or rural) and season of production,
- the type and percentage of materials that are source-separated (e.g.: food and garden waste, paper, plastics and glass) and
- the types of mechanical and biological processing units employed in the plant.

Furthermore the processing objectives for each facility are site specific and influenced by legislative and market demands for the outputs (Velis et al., 2010).

CHARACTERISTICS OF THE BIOSTABILISED WASTE (BSW) AND POSSIBLE USE OPTIONS

One of the output of the mechanical-biological treatment is the biologically stabilised, or biostabilised waste (BSW) produced from the biological treatment of the biodegradable organic fraction mechanically separated from the input MSW. Such organic fraction is characterised by small particle size (usually 50–80 mm), relevant organic matter content (volatile solids content may range from 50 % to 80 % by weight) and high moisture content (usually 40–55 % by weight) (Zach et al., 2000; Adani et al., 2004; Lornage et al., 2007; Di Lonardo et al., 2012b), and, as previously mentioned, has to be biostabilised prior to landfilling (Robinson et al., 2005) and/or recovery (European Commission, 2001). In MBT plants, the biostabilisation is carried out by means of two biological treatment processes, namely aerobic biodegradation and anaerobic digestion coupled to aerobic post-treatment (Montejo et al., 2010). Aerobic systems are in widespread use, even if anaerobic process have the advantages of reduced treatment time and odour emissions and it can be energetically self-sustaining due to the generation of biogas (the energy demand of the aerobic process for the aeration cannot be covered by energy production) (Soyez and Plickert, 2002; Fricke et al., 2005). In this work, only the biostabilised output characteristics produced by the aerobic biological treatment will be discussed.

After aerobic biological treatment, the biostabilised waste can be subjected to an additional mechanical process, generally consisting of a screening unit at 10–20 mm which separates an oversize fraction composed of non-compostable materials (mainly plastics and paper) to be landfilled (Di Lonardo et al., 2012b) or aimed to thermal treatment (Munnich et al., 2006; Di Lonardo et al., 2012c; Franzese et al., 2013). Nevertheless Montejo et al. (2010) found that techniques used in MBT plants showed an inadequate separation of inert waste from biodegradable (prior to the biological treatment) and stabilised fractions which exhibited high levels of improper materials (such as plastics, glass fragments and batteries), which could be a concern when BSW is aimed to recovery, rather than landfilling.

In Table 1.1 (A and B) several data reported by literature studies on biostabilised waste characteristics are shown (columns 1-10), along with the limit values for waste recovery, such as landfill cover, land reclamation, etc. (columns A-D).

More specifically, the following European regulations were considered:

- the document drafted by the European Commission “Biological treatment of biowaste - 2nd draft” (European Commission, 2001);
- the Italian Decree 27/07/1984, i.e. the former quality standard on compost which is taken as a reference in Italy, given the current lack of a technical standard for MBT wastes (as thereafter discussed);
- the Austrian Compost Ordinance (ACO, 2001) which identify the class B of compost as suitable for landfill cover;

Table 1.1A Characteristics of BSW and European Quality Standards for waste recovery

							Quality Standards			
Parameters	**Units**	**[1]**	**[2]**	**[3]**	**[4]**	**[5]**	**EC [A]**	**Italy [B]**	**Austria [C]**	**Scotland [D]**
Particle size	mm			< 20	-	5-10		0.5-25		
Treatment time	weeks			3	25	2-12				
Moisture content	% WM			33.4	37.1	24.3		≤ 45		
VS	% DM				39.4			≥ 40		
TOC	% DM			20.64		13.3				
DOC	gC/l					1.9				
RA_4	mgO2/gDM				16				7	
DRI	mgO2/kgVS h					435-2303	1000			
GS_{21}	Nl/kgDM				12.3				20	
Antimony	mg/kgDM					19.1				
Arsenic	mg/kgDM			< 0.5		3.0		10		
Cadmium	mg/kgDM	2.7	4.8	1.7		1.8	5	10	3	3
Chromium	mg/kgDM	209	122			105.3	600	*	250	400
Cobalt	mg/kgDM					5.5				
Copper	mg/kgDM	247	162	368		239	600	600	500	200
Lead	mg/kgDM	224	385	487		603	500	500	200	200
Manganese	mg/kgDM					278				
Mercury	mg/kgDM	1.3	1.5	< 0.5		2.2	5	10	3	1
Nickel	mg/kgDM	149	69	97		56.2	150	200	100	100
Vanadium	mg/kgDM					10.6				
Zinc	mg/kgDM	769	542	485		397	1500	2500	1800	1000

Table 1.1B Characteristics of BSW and European Quality Standards for recovery

							Quality Standards			
Parameter	**Units**	**[6]**	**[7]**	**[8]**	**[9]**	**[10]**	**EC [A]**	**Italy [B]**	**Austria [C]**	**Scotland [D]**
Particle size	mm	< 50		< 25	< 70	< 20		0.5-25		
Treatment time	weeks	9		9	21	4				
Moisture content	% WM	17.4	29		39.6			≤ 45		
VS	% DM	47.8			38.9	46.9		≥ 40		
TOC	% DM	19.7		11.5	24.3					
DOC	gC/l	1.4				2.8				
RA_4	mgO2/gDM			4.1	11.6				7	
DRI	mgO2/kgVS h	1339				992.6	1000			
GS_{21}	Nl/kgDM	55		6.5	27.7 (90 d)				20	
Antimony	mg/kgDM					0.3				
Arsenic	mg/kgDM		<1			2.4		10		
Cadmium	mg/kgDM		2	11.7		0.3	5	10	3	3
Chromium	mg/kgDM		24	847.1		20.7	600	*	250	400
Cobalt	mg/kgDM					1.6				
Copper	mg/kgDM		387	697.9		97.6	600	600	500	200
Lead	mg/kgDM		886	336.3		163.8	500	500	200	200
Manganese	mg/kgDM									
Mercury	mg/kgDM					0.4	5	10	3	1
Nickel	mg/kgDM		55	467		24.9	150	200	100	100
Vanadium	mg/kgDM					13.9				
Zinc	mg/kgDM		865	1561		241.9	1500	2500	1800	1000

[1] Amlinger et al., 2004; [2] WRAP, 2002; [3] Regione Piemonte, 2004; [4] Lornage et al., 2007; [5] ISPRA, 2007; [6] Barrena et al., 2009; [7] UK Environment Agency, 2009; [8] van Praagh et al., 2009; [9] Bayard et al., 2010; [10] Di Lonardo et al., 2012b; [A] European Commission, 2001; [B] Italian Decree, 1984; [C] Austrian Compost Ordinance, 2001 and Austrian Landfill Ordinance (Binner et al., 2012); [D] Baird et al., 2005

* No limit value for Cr tot but limit values for Cr^{III} < 500 mg/kg and Cr^{VI} < 10 mg/kg

- the Scottish Environmental Protection Agency (SEPA) standard (Baird et al., 2005) which states that "If mixed waste compost (i.e. biostabilised waste) is able to achieve the indicative standards, then it may be possible to consider applying the material to land subject to risk assessment procedures on a site by site basis".

A high variability of the BSW characteristics can be observed in Table 1.1. This is because biological and physical-chemical properties of the biostabilised waste depend on several factors such as the nature of the feedstock (coming from heterogeneous mixed/residual MSW), the type of mechanical pre-treatment, the stabilisation facility design, the operating conditions, the length of biological treatment, etc. (Hamoda et al., 1998; Amlinger et al., 2004; Hargreaves et al., 2008). Furthermore it is important to notice that, since there are many sources of heavy metals within household waste, potentially passing through mechanical screens designed to remove non-biodegradable components, significant heavy metal content is found in biostabilised waste (Richard and Woodbury, 1992; Amlinger et al., 2004), such as copper, lead, nickel and zinc contents which in some cases exceed limit values (Table 1.1).

A fundamental characteristic to evaluate for the biostabilised waste is the biological stability degree, typically measured by respiration indices (dynamic respiration index, DRI, or cumulative oxygen uptake, RA_4) and anaerobic index (biogas production, BP). The respiration indices measure the degradability of the readily available organic matter contained in the waste in a short time period (4 days) under standardised aerobic conditions (Adani et al., 2004). More specifically, the RA_4 index (mgO_2/gDM) measures the cumulative oxygen uptake within a period of 4 days (Binner et al., 2012), whereas DRI ($mgO_2/kgVS$ h) measures the absolute maximum rates of oxygen consumption (Barrena et al. 2009). Differently, the anaerobic index measures the gas generation of treated waste under anaerobic conditions in 21 days (or 90 days) (Binner, 2002). In general, a waste is considered biologically stable if the DRI is lower than 1000 $mgO_2/kgSV \cdot h$ (European Commission, 2001; Adani et al. 2004), the RA_4 is lower than 5 and 7 mgO_2/gDM according to German and Austrian regulations, respectively, and BP_{21} is lower than 20 Nl/kgDM (AbfAblV, 2001; Binner et al., 2012). In Table 1.1, it can be observed that, in some cases, such limit values were not fulfilled.

The above mentioned European Commission document on biowaste (European Commission, 2001) specifies that Member States may authorise the use of the biostabilised waste, fulfilling the requirements indicated in the document, as a component in artificial soils or in those land applications that are not destined to food production (such as final landfill cover, landscape restoration in old and disused quarries and mines, antinoise barriers, road construction, etc.). Such statement came from the evidence that the content of non-compostable materials and heavy metals in BSW, which lead to physical and chemical contamination, is higher than those in compost produced from source segregated waste, as observed by several authors (Richard and Woodbury, 1992; Leikam and Stegmann, 1999; Whittle and Dyson, 2002; Zennaro et al., 2005; Dimambro et al., 2007). However, modern mechanical separation technologies and process improvements have significantly reduced the “impurities” and the metal content in BSW compared with 30 years ago (Zennaro et al., 2005; Dimambro et al., 2007). Nevertheless, from a legal viewpoint, in many countries, the biostabilised waste remains waste (Baird et al., 2005; Farrel and Jones, 2009), rather than a recoverable material, and its subsequent application in landfill restoration or land reclamation uses has to be subjected to appropriate regulatory measures (Baird et al., 2005).

In recent years scientific research focused on the study of BSW use in environmental restoration activities, such as landfill cover (Hilger and Humer, 2003; Kettunen et al., 2006; Einola et al., 2009; Izzo et al., 2009; Scheutz et al., 2009; Huber-Humer et al., 2009; Angermeier et al., 2011) and in the restoration of degraded areas (contaminated sites, quarries, closed landfills, etc.) (Baird et al., 2005; ISPRA, 2006; Partl and Cornander, 2006; UK Environment Agency, 2009). Specifically, it was observed that the main benefits of the BSW use as landfill cover material were the reduction of landfilled waste volume and the use of treated waste instead of natural soils that are often not available or too expensive, as well as the mitigation of greenhouse gas emissions from landfills when BSW is used as a support medium in methane (CH_4) oxidative biocovers. When applied to degraded soils, BSW was found to improve soil properties, such as water retention, porosity, nutrients and organic matter supplying. Nevertheless, all studies recommended to use a well biostabilised material which otherwise could continue to lose organic mass, resulting e.g. in increased concentrations of heavy metals. Furthermore it is pointed out to take into account the risks related to the potential contaminants that can accumulate in the soil where biostabilised waste would be applied and, through release and transfer mechanisms, move towards other receptors (groundwater and surface water, plants, animals and humans).

GOAL AND CONTENTS OF THE PRESENT THESIS

Italy has a long tradition in MBT but emphasis on recovery of the outputs is mainly focused on the production of refuse derived fuel (RDF), nowadays being defined as solid recovered fuel (SRF), with just some plants producing biostabilised waste suitable for restricted applications (Partl and Cornander, 2006). As a result, nowadays, the biostabilised waste coming from the Italian MBT plants is mainly disposed of in landfill. Data provided by the Institute for the Environmental Protection and Research in “Municipal Solid Waste Report – Edition 2013” (Laraia, 2013), show that 84 % of the total quantity of the biostabilised waste produced in 2011 (about 10 % of MSW feeding MBT plants) was sent to landfilling. The Italian Decree 205/2010 which regulates waste field in Italy, delegates the definitions of quality requirements of the biostabilised waste and its uses complying with health and environmental protection to appropriate technical Standards that still do not have been issued. Therefore a detailed investigation is essential for the development of technical guidelines which could provide limit values for characterising the quality of BSW in relation to the specific intended use or disposal (ISPRA, 2007).

In Lazio Region part of waste management system, besides the source separate collection, was arranged for mechanical-biological treatment with 7 MBT plants now in operation. In the year 2011 a percentage by weight equal to 32 % of MSW produced in this Italian Region were treated by MBT facilities (Laraia, 2013). It has to be pointed out that, in 2012, the percentage of separate collection in Rome was still quite low and equal to 22.4 % of the total amount of MSW produced in this city (Laraia, 2013). As a result, residual MSWs feeding MBT plants were found to be composed by high percentage of biodegradable organic waste (food and garden waste, paper and cardboard, fine organic waste lower than 20 mm) equal to 60 % (Di Lonardo et al., 2012b). A percentage equal to 70 % of such biodegradable waste is separated through a primary mechanical sieving in the MBT facilities and then it is subjected to a biological treatment consisting of aerobic biodegradation at forced aeration conditions for 4 weeks. Afterwards, the biostabilised output, after a secondary sieving unit (20 mm), is directly sent to landfilling. Therefore, in order to comply with waste hierarchy (European Commission, 2008), individuation and evaluation of management techniques aimed at ensuring biostabilised waste recovery represent one of the priorities of waste management strategies in this area.

In view of such need, the present research study aimed to assess the possible biostabilised waste recovery/utilisation, in alternative to landfilling, by evaluating different operating conditions and retaining times.

Firstly, an evaluation on the quality of the biostabilised waste (BSW) as currently treated by the MBT plants of Rome was carried out (**Chapter 2**). For this purpose, biological and physical-chemical characterisation (determination of biological stability degree, heavy metal total content and release in water phase) of the biostabilised output was carried out. Such chemical-physical investigations were conducted by an external private laboratory. A further characterisation of the material sampled before and after the 1st and the 4th week of the aerobic biodegradation was performed in the MBT plant A in order to assess the evolution/changing of the investigated characteristics during the process. These activities were conducted at the Sanitary - Environmental Engineering Laboratory of the University of Rome “Tor Vergata”. Results showed that the BSW did not have a suitable quality for waste recovery, both in terms of biological stability degree and in terms of physical-chemical characteristics.

Given the unsuitability for recovery of the biostabilised waste as currently treated, second step of the research was to evaluate the influence on BSW characteristics of longer duration of the aerobic biological process (**Chapter 3**). Specifically, an extension of the biodegradation process at forced aeration conditions occurring in the biostabilisation basin of the MBT plant A from 4 weeks, which is the duration in normal operating conditions of the plant, to 7 weeks was evaluated. Furthermore, a well biostabilised output, coming from the intensive biodegradation lasting 4 weeks, was subjected to a ripening phase in slightly aerated lab test cells in order to analyse and evaluate a possible further increase of the biological stability and the relative changing in physical-chemical characteristics. Such stage of the research was conducted at the Institute of Waste Management of the University of Natural Resources and Life Sciences in Vienna (ABF-BOKU). Again, biological and physical-chemical characterisation of waste samples, periodically collected during the aerobic biodegradation in the bio-stabilisation basin and during the lab ripening phase, was carried out.

CHAPTER 2

QUALITY EVALUATION OF THE BIOSTABILISED WASTE AS CURRENTLY TREATED IN ROME

This chapter is partly taken from:

Di Lonardo M.C., Lombardi F., Gavasci F. (2014) Quality evaluation of mechanically-biologically treated municipal solid waste in view of a possible recovery. Submitted to *International Journal of Environmental Science and Technology* (currently under review)

Di Lonardo M.C., Lombardi F., Gavasci R., Rocca S. (2012b) Characterisation of MSW Organic Fraction flow separated and treated in a Mechanical-Biological Treatment plant. In: Proceedings of SIDISA 2012 (book of abstracts), Sustainable Technology for Environmental Protection, 26-29 June 2012, Milano, IT

OBJECTIVE OF THE STUDY

A first evaluation on the quality of the biostabilised waste (BSW) as currently treated by the MBT plants of Rome was conducted in order to assess the suitability for a possible recovery. For this purpose, biological and physical-chemical characterisation of the biostabilised waste coming from two MBT plants of Rome was performed. Such investigations were conducted by an external private laboratory.

A further characterisation of the material, sampled in one of the two facilities, before and after the 1st and the 4th week of aerobic biodegradation was carried out in order to assess the evolution/changing of the investigated characteristics during the process. These activities were conducted in the Sanitary- Environmental Engineering Laboratory of the University of Rome “Tor Vergata”.

MBT PLANTS OF ROME AND SAMPLING PROCEDURES

Waste materials were sampled in two MBT plants (plant A and plant B) located in south and east areas of Rome, respectively. The maximum treatment capacity is 750 Mg MSW/day per each plant. The two facilities have exactly the same processing units, as showed in Figure 2.1. More specifically, the received MSW are discharged by the collection vehicles into a basin for temporary storage that has the function of equalising the waste input loads and allows also to homogenise the characteristics of the waste prior to the following treatment stages (Sirini et al., 2009). In the same receiving area, the manual/mechanised pre-sorting of bulky materials (such as appliances, tires, furniture, mattresses, etc.) is carried out in order to avoid clogging phenomena in the downstream equipment. The receiving/storage area is covered and maintained under negative pressure conditions in order to minimise dust and odour emissions to the outside. The first treatment unit consists in bag braking and size reduction by means of hammer-mill shredders, after which the waste, placed on belt conveyors, is fed into trommel screens for size separation (grate spacing of 80 mm). From this latter process the following two outputs are obtained:

- *biodegradable fraction* (undersize), presenting a high percentage of organic compounds and moisture content,

- *dry fraction* (oversize), presenting a lower moisture content and typically enriched in materials characterised by a significant heating value (mainly plastics).

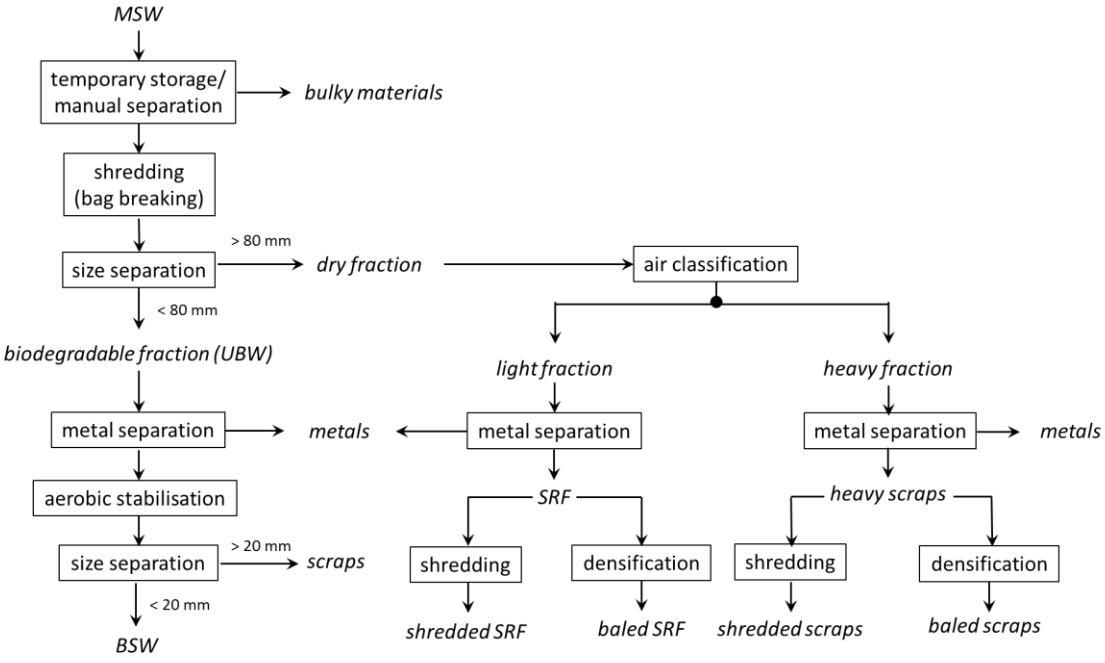

Figure 2.1 Flow diagram of the main MBT units and solid outputs of the MBT plants of Rome

The dry fraction is processed by an air classification unit so to separate the light fraction (solid recovered fuel, SRF) from the heavy fraction (heavy scraps). Ferrous and non-ferrous metals are then separated from these two flows. After this step, densification or shredding of SRF and heavy scraps is carried out in order to facilitate their handling, storage and transport to incineration plant and landfill, respectively.

At the same time, the biodegradable fraction, after metal removal by belt-type electromagnetic separators, is sent to a biostabilisation basin where aerobic biodegradation occurs for 4 weeks at forced aeration conditions. Three augers moved by a crane have a dual function: turning over the material in order to keep proper free air space (pores) for aeration (avoiding the formation of anaerobic conditions, especially at the bottom of the basin) and moving the material along the basin. During the turning/moving, water is added to the material by nozzles fixed on the crane, in order to keep the water content favourable for the microbial activity. The stabilised output then is sieved in a trommel screen with a mesh opening of 20 mm (refining unit) in order to separate an oversized fraction mainly composed of plastics and inert materials (stabilisation scraps disposed of in landfill) from the undersized fraction consisting of the final biostabilised waste (BSW) which is not subjected to a further ripening phase but it is directly landfilled.

The average mass balance of the MBT plants calculated for the year 2012 is showed in Figure 2.2. It can be observed that the biodegradable fraction feeding the biostabilisation process was equal to 56.5 % whereas the percentage of stabilised biowaste was equal to 19.9 % of the input MSW (100 %).

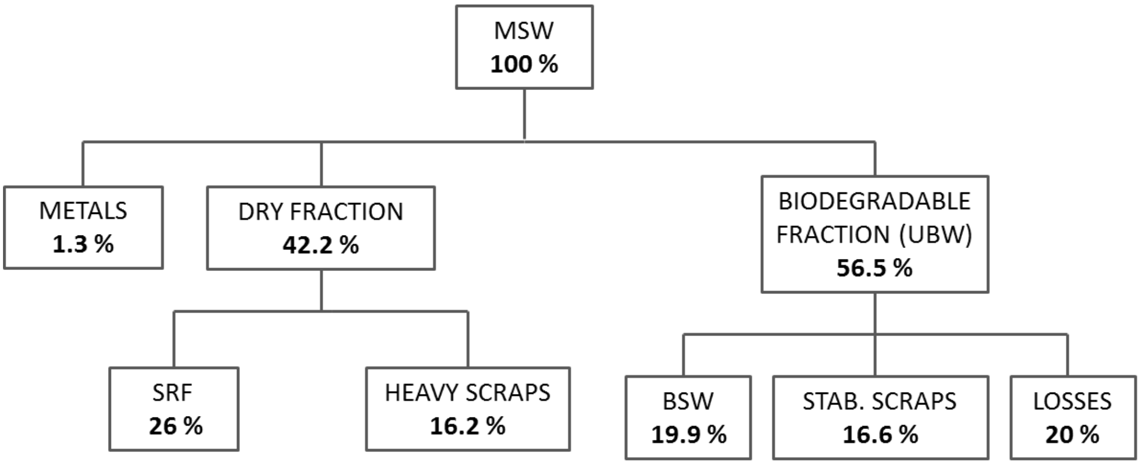

Figure 2.2 Average mass balance of the MBT plants of Rome

The biostabilised waste (BSW_{out}) was sampled in the two MBT plants during several characterisation campaigns performed in the years 2007-2011. The sampling procedure was carried out in accordance with the Italian technical standard UNI 10802 (2004a) which includes collecting random increments, mixing, homogenisation and quartering to obtain the final sample.

Afterwards, in the year 2012, three macro-samples, consisting of the input material feeding the aerobic stabilisation (untreated biodegradable waste, UBW < 80 mm), the biostabilised waste after one week (BSW I) and after four weeks (BSW IV) of treatment, prior to the refining unit, were collected in plant A. The UBW sample was taken from the conveyor belt which moves the biodegradable fraction to the stabilisation basin after the metal separation unit. Partial quantity (increments) of the material were sampled at different time interval while the conveyor belt was moving by feeding the basin. For the sampling of BSW I and BSW IV (ISPRA, 2007), the basin was divided into four parts transversely to the movement direction of the waste, each area corresponding to a progressive week of process. Again partial quantities of the materials were collected at 4 different points along the first area (first week of treatment, BSW I) and along the fourth area (fourth week of treatment, BSW IV) prior to the secondary sieving unit. Afterwards, the different collected increments were mixed in order to obtain the three macro samples of UBW, BSW I and BSW IV which then were homogenised and quartered.

ANALYTICAL METHODS

Biological and physical-chemical characterisation was performed in order to determine the following parameters: biological stability degree (determination of dynamic respiration index, DRI), organic matter content (determination of volatile solids, VS, and total organic carbon, TOC), heavy metal total content, release of contaminants in water phase (leaching test), particle size distribution and the material composition.

A final quantity of roughly 10 kg for each sample was air dried prior to performing all laboratory analysis, with the exception of the biological stability analysis where an additional amount of about 15 kg of as-received samples was used.

The biological stability measures the degradability of the readily available organic matter contained in the waste in a short time period (4 days) under standardised aerobic conditions (Adani et al., 2004). In order to evaluate waste stability degree, a respirometric approach was used by determining the dynamic respiration index (DRI), namely the absolute maximum rate of oxygen consumption due to microbial activity. DRI was measured and calculated according to the procedure reported in the Italian standard UNI/TS 11184 (2006) by using a 30 l adiabatic respirometric reactor (Costech International Respirometer 3024). Prior to the beginning of the respiration test, pH (UNI, 2004b) and moisture content (EN, 2006) were determined on the as-received material.

The volatile solids (VS) content was determined in duplicates by loss-on-ignition at 550°C for 8 h (UNI/TS, 2006) on 10 g of sample grinded to 0.5 mm and pre-dried at 105°C for 4 h. Total organic carbon (TOC) content was analysed in triplicates by means of Shimadzu SSM-5000A instrument on approximately 0.2 g of dried sample grinded to size lower than 200µm (UNI, 2002).

Heavy metal content in solid materials (total content) was determined in triplicates by using two different procedures, namely the microwave assisted digestion with HNO_3 (ISPRA, 2001) for BSW_{out} samples and acid digestion with HNO_3, H_2O_2 and HCl for the UBW, BSW I and BSW IV samples (EPA method 3050B, 1996). Prior to the digestions, the air-dried samples were grinded to size lower than 1 mm. Then, the obtained solutions, after filtration at 0.45 µm, were analysed by inductively coupled plasma atomic emission spectrometry (Varian ICP-AES).

For the leaching test, the air-dried samples were shredded to a particle size lower than 4 mm, as required by the standard procedure EN 12457-2 (2002). A volume equal to 80 ml of deionised water was added to 8 g of each air-dried sample in order to obtain a liquid to solid ratio equal to 10 and bottles containing the mixture were stirred for 24 hours. Such test was conducted in duplicates. The obtained eluates were analysed by determining the pH (Hanna Instrument pH-meter), and, after filtration at 0.45 µm, the heavy metal concentrations (Varian ICP-AES analyser), the dissolved organic carbon (DOC) (Shimadzu TOC-V CPH/CPN analyser) and the chlorides content (Mohr's method; ISO 9297, 1989) were determined as well.

The particle size (PZ) analysis (ASTM, 2007) was performed for BSW I and BSW IV samples. After quartering, an amount of roughly 5 kg for each air dried sample were sieved by means of the following sieve sizes: 38.1 mm, 25.4 mm, 19.1 mm, 10 mm, 4 mm, 2 mm, 0.84 mm. Materials retained by each sieve were progressively weighed and the cumulative passing was calculated through the equations 2.1 and 2.2:

$$P_i = \sum_{n=1}^{i} R_i - R_i \tag{2.1}$$

$$\% \, P_i = 100 \frac{P_i}{\sum_{n=1}^{i} P_i} \tag{2.2}$$

where P_i is the weight, expressed in grams, of the material passed through the i-th sieve and R_i is the weight, in grams, of the material retained by the i-th sieve. The particle size distributions of BSW I and BSW IV were then determined by correlating the percentage by weight of cumulative passing with each sieve size. On the basis of the found PZ distributions, four particle size classes, namely A=[< 2 mm], B=[2–10 mm], C=[10–38.1 mm], D=[38.1–80 mm], were identified and prepared for the subsequent physical-chemical characterisation.

The investigation on material composition was carried out in accordance with the ISPRA method 36/2000 (ISPRA, 2000). Specifically, the different material categories (fines < 20 mm, organics, paper/cardboard, textiles, plastics, composite packaging, wood, glass, metals, inert materials, hazardous) were manually sorted and weighed. The percentage material composition was then determined through the equation 2.3:

$$\%\ \mathrm{F_i} = 100\frac{\mathrm{f_i}}{\sum_{\mathrm{n=1}}^{\mathrm{i}} \mathrm{f_i}} \qquad (2.3)$$

where f_i is the weight, expressed in grams, of the i-th material category.

CHARACTERISATION OF THE BSW$_{\mathrm{OUT}}$: RESULTS AND DISCUSSION

Biological stability degree and organic matter content

Table 2.1 shows the results of DRI, moisture content, pH and volatile solids (VS) of several BSW$_{\mathrm{out}}$ samples coming from plant A and plant B (each samples biologically treated for 4 weeks) measured in 12 characterisation campaigns during the years 2007-2011. A significant variability of the measured parameters can be observed and this is mainly related to the high heterogeneity of the input MSW feeding the two MBT plants. In fact, the material composition investigated for several MSW samples during the same characterisation campaigns showed to be quite variable due to the seasonal period of sampling (summer and winter) and to the different types of production areas (residential and commercial areas), as reported by Di Lonardo et al. (2011).

The values of moisture content, pH and volatile solids, though quite variable, fulfilled the limits set by the Italian Decree (1984). Differently, it has to be noticed that most DRIs were higher than the maximum limit value equal to 1000 mgO_2/kgVS·h, below which the material is considered biologically stable (European Commission, 2001; Adani et al., 2004). As a result the mean DRI value of the 12 determinations was found equal to 2070 mgO_2/kgVS·h with a high standard deviation equal to 931 mgO_2/kgVS·h (Figure 2.3). Therefore BSW$_{\mathrm{out}}$ was found still quite reactive after 4 weeks of aerobic biodegradation.

Table 2.1 Results of DRI, moisture content, pH and VS measured for BSW_{out} samples from plant A and plant B (6 samples per each plant) and limit values

Determinations	**DRI (mgO_2/kgVS h)**	**Moisture (% WM)**	**pH**	**VS (% DM)**
Plant A				
1	2279	19.7	8.0	44.0
2	1177	19.7	6.6	55.3
3	788	19.0	7.9	44.1
4	1147	23.2	8.1	50.8
5	2122	17.6	8.2	51.0
6	3111	28.1	7.2	51.8
Mean ± SD	1770.7 ± 804.7	21.2 ± 3.5	7.7 ± 0.6	49.5 ± 4.1
Plant B				
1	1515	23.3	-	48.4
2	3321	28.8	7.8	54.5
3	710	18.8	7.9	58.1
4	2655	23.0	8.2	43.1
5	2744	28.7	7.1	54.5
6	3275	17.3	8.1	42.9
Mean ± SD	2370.3 ± 951.4	23.3 ± 4.4	7.8 ± 0.4	50.3 ± 5.9
Tot mean ± SD	2070.3 ± 930.7	22.3 ±4.1	7.7 ± 0.5	49.9 ± 5.1
Limits	< 1000 + 20 %	≤ 45	6 – 8.5	≥ 40

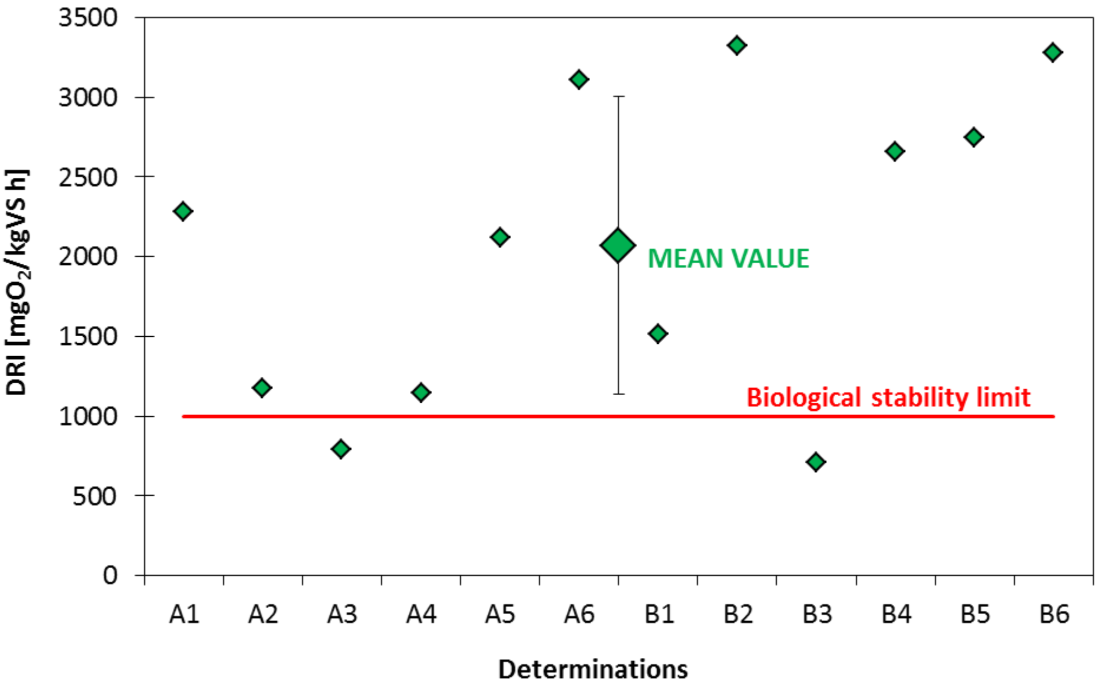

Figure 2.3 DRIs of BSW_{out} samples from plant A and plant B measured in 12 characterisation campaigns

Heavy metals total content and leaching behaviour

In general, there are many potential sources of heavy metals (HM) in mixed MSW such as batteries, electronics, wine bottle tops, cosmetics and medicines, household dust etc. (Richard and Woodbury, 1992; Whittle and Dyson, 2002; ISPRA, 2007). Hence, the content of HM in the biostabilised waste firstly depends on the extent and the type of at source separate collection of hazardous waste, metals, plastics, etc., and on the effectiveness of the upstream mechanical treatments to separate such materials (He et al., 1995; Farrel and Jones, 2009). Residual MSW feeding the MBT plants of Rome, in a previous study (Di Lonardo et al., 2011), was found to be composed by negligible percentage of hazardous waste (0.3 %), low content of metals (3–5 %) and by significant quantity of plastics (15–20 %). Most metals are removed in the mechanical pre-treatment by means of belt-type electromagnetic separators, whereas part of the plastic, which is a significant source of some heavy metals (Richard and Woodbury, 1992), ends up the undersize fraction of the primary screening unit undergoing the aerobic stabilisation. Table 2.2 shows the total heavy metal content (mean ± standard deviation calculated for the different collected samples) found in BSW_{out} samples coming from plant A and plant B.

Table 2.2 Heavy metals total content in BSW_{out} samples from plant A and plant B (6 samples per each plant) and different limit values (all values are expressed in mg/kg DM)

Metals	Plant A	Plant B	Italian Decree 152/2006*		EC doc 2001	AOC 2001	SEPA 2005
			A	B			
As	2.8 ± 1.5	0.7 ± 0.0	20	50			
Cd	0.9 ± 0.4	< 0.5	2	15	5	3	3
Co	0.7 ± 0.5	9.9 ± 8.3	20	250			
Cr	24.3 ± 15.9	17.2 ± 5.9	150	800	600	250	400
Cu	517.5 ± 288.6	315.2 ± 131.2	120	600	600	500	200
Hg	0.5 ± 0.2	< 0.5	1	5	5	3	1
Ni	51.2 ± 39.6	9.6 ± 0.95	120	500	150	100	100
Pb	428.2 ± 246.9	242.8 ± 97.2	100	1000	500	200	200
V	25.4 ± 21.7	21.4 ± 12.8	90	250			
Zn	459.3 ± 259.6	232.5 ± 39.5	150	1500	1500	1800	1000

*Column A – soil contaminant thresholds for use in residential sites; Column B - soil contaminant thresholds for use in coomercial and industrial sites

The results are compared with soil contamination thresholds set by the Italian Decree 152/2006, for the use in residential and public parks sites (column A) and in commercial and industrial sites (column B). Furthermore limit values for environmental applications (for non-food production) set by the European Commission document (European Commission, 2001), by the Austrian Compost Ordinance (ACO, 2001), as well as by the Scottish Environmental Protection Agency (SEPA) standard (Baird et al., 2005) are also reported (regulations described in **Chapter 1**, page 5-6). Firstly, it has to be noticed that significant differences were found between the two MBT plants and in most cases the standard deviations were relatively high. This, again, can be related to the high heterogeneity of the waste. Comparing HM total content with requirements for recovery, it can be observed that Cu , Pb and Zn did not comply with soil contaminant thresholds for the use in residential sites. Moreover Pb and Zn content exceeded limit values set by the Austrian Compost Ordinance and the Scottish EPA.

Generally, regulations on composted/biostabilised waste set limits on total heavy metal content and restrictions on leaching behaviour are not reported. The solely determination of the total composition does not provide useful information about the potential release of contaminants in the environment (van der Sloot et al., 2004), which could occur if, for example, waste are applied to land. In Italy, the only standard which sets limits on waste leaching for the regulation of non-hazardous waste recovery is the Ministerial Decree (MD) 186/2006. It has to be pointed out that the biostabilised waste is not counted in the list of non-hazardous waste that could be subjected to recovery procedure in the case of compliance with the limits. However, the requirements set by this regulation are assumed as reference limits in the next discussions.

Table 2.3 shows the results of metal concentrations (mean ± standard deviation), dissolved organic carbon (DOC), chlorides and pH measured in the eluates of each BSW_{out} sample coming from plant A and plant B. Again, significant differences between the two plants and high standard deviations can be observed due to the heterogeneity of the material influenced by the different collection areas and season of sampling. Comparing the leaching characteristics with the requirements set by MD 186/2006, it can be observed that chromium, copper, nickel, lead, as well as chlorides exceeded the limit values. Hence, biostabilised waste as currently produced by the MBT plants of Rome showed to not have a suitable quality to be recovered.

Table 2.3 Leaching characteristics of BSW_{out} samples from plant A and plant B (6 samples per each plant) and limit values (concentrations are expressed in mg/l)

Parameters	Plant A	Plant B	MD 186/2006
As	0.04 ± 0.03	0.009 ± 0.007	0.05
Ba	0.53 ± 0.38	0.4 ± 0.17	1
Cd	0.004 ± 0.009	0.003 ± 0.0004	0.005
Cr	0.02 ± 0.01	0.06 ± 0.04	0.05
Cu	0.21 ± 0.11	0.59 ± 0.33	0.05
Hg	0.001 ± 0.0007	0.001 ± 0.0006	0.001
Mo	0.03 ± 0.01	0.03 ± 0.02	-
Ni	0.08 ± 0.04	0.13 ± 0.04	0.01
Pb	0.22 ± 0.12	0.17 ± 0.04	0.05
Sb	0.02 ± 0.01	0.014 ± 0.009	-
Zn	0.55 ± 0.30	1.84 ± 1.4	3
DOC	861.3 ± 20.0	792.5 ± 70.5	-
Cl^-	421.3 ± 117.7	497.5 ± 144.1	100
pH (unit)	7.6 ± 0.4	7.4 ± 0.0	5.5 - 12

CHARACTERISATION OF THE WASTE DURING THE BIOLOGICAL PROCESS: RESULTS AND DISCUSSION

Biological stability degree

Table 2.4 shows the results of DRI, moisture content, pH and VS (mean ± standard deviation for the repetitions of the same sample) measured for as-received UBW, BSW I and BSW IV and limit values are also reported. UBW was characterised by significant biological reactivity, much higher than the limit value equal to 1000 $mgO_2/kgVS \cdot h$.

Table 2.4 Results of DRI, moisture content, pH and VS measured for UBW, BSW I and BSW IV samples and limit values

Samples	DRI (mgO_2/kg VS h)	Moisture (% WM)	pH	VS (% DM)
UBW	2266.2	50.1 ± 1.5	6.4	65.9 ± 0.8
BSW I	2397.6	32.0 ± 2.2	6.9	59.2 ± 5.1
BSW IV	1262.2	28.3 ± 0.8	7.9	55.3 ± 1.3
Limits	< 1000 + 20 %	≤ 45	6 – 8.5	≥ 40

During the biodegradation process a reduction in reactivity was observed, even if DRI of BSW IV was found slightly higher than the limit. It has to be noticed that DRI of BSW I was a little bit higher than DRI of UBW. This is likely because of the microbial activity and the related oxygen consumption, after one week of biodegradation, is still quite high and comparable to the beginning of the process whereas organic matter (volatile solids) slightly reduced. As a result, the area under the DRI curve of UBW was greater than that of SBW I even if the latter had a higher max DRI (curve peak), as can be observed in Figure 2.4 which shows the trends of DRIs hourly registered during the respiration test.

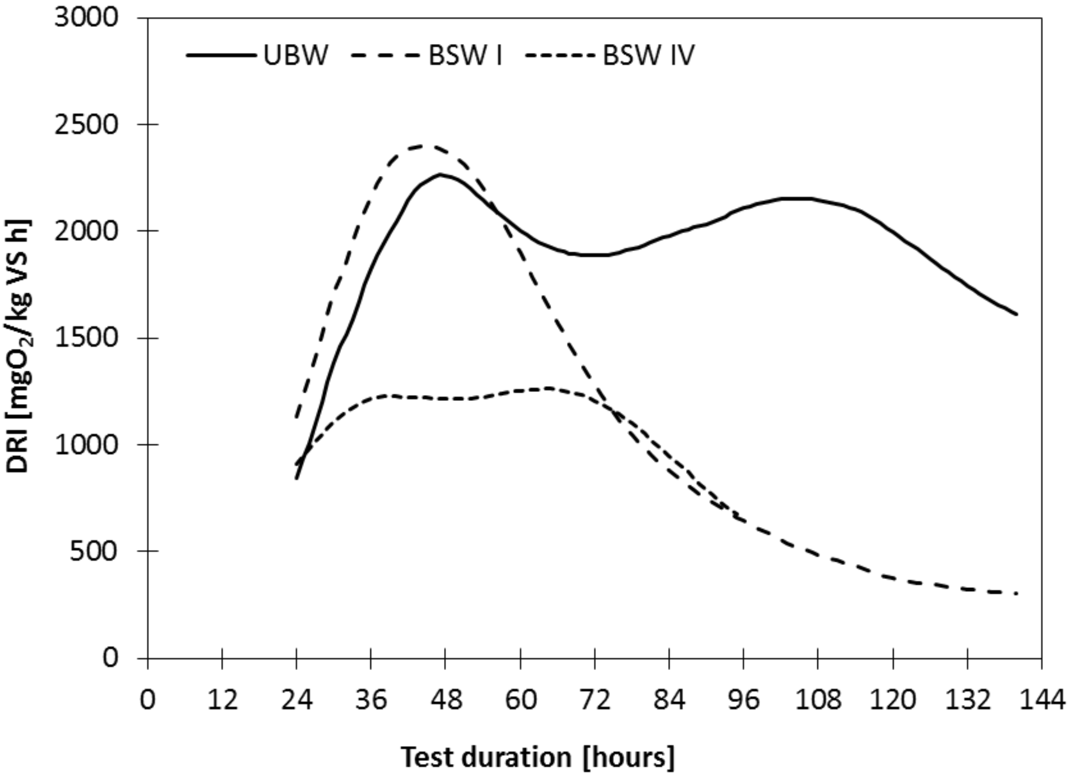

Figure 2.4 Trends of DRIs hourly registered during respiration tests and averaged in 24 hours

Moisture content was quite high for the untreated waste because it was mainly composed of biodegradable organic waste (fines < 20mm plus food and garden waste) with a percentage by weight roughly equal to 50 % by weight (wet matter, WM) of the total UBW, as shown in Figure 2.5. Then moisture tended to decrease in the 4 weeks of biodegradation likely because of the evaporation occurred due to the high temperature reached (50–70°C), even if water was added during the process. The pH values showed to follow the characteristic trend of an aerobic biodegradation lasting 24 days (Sirini et al., 2009), ranging from 6, at the beginning, to 8 at the end of the process.

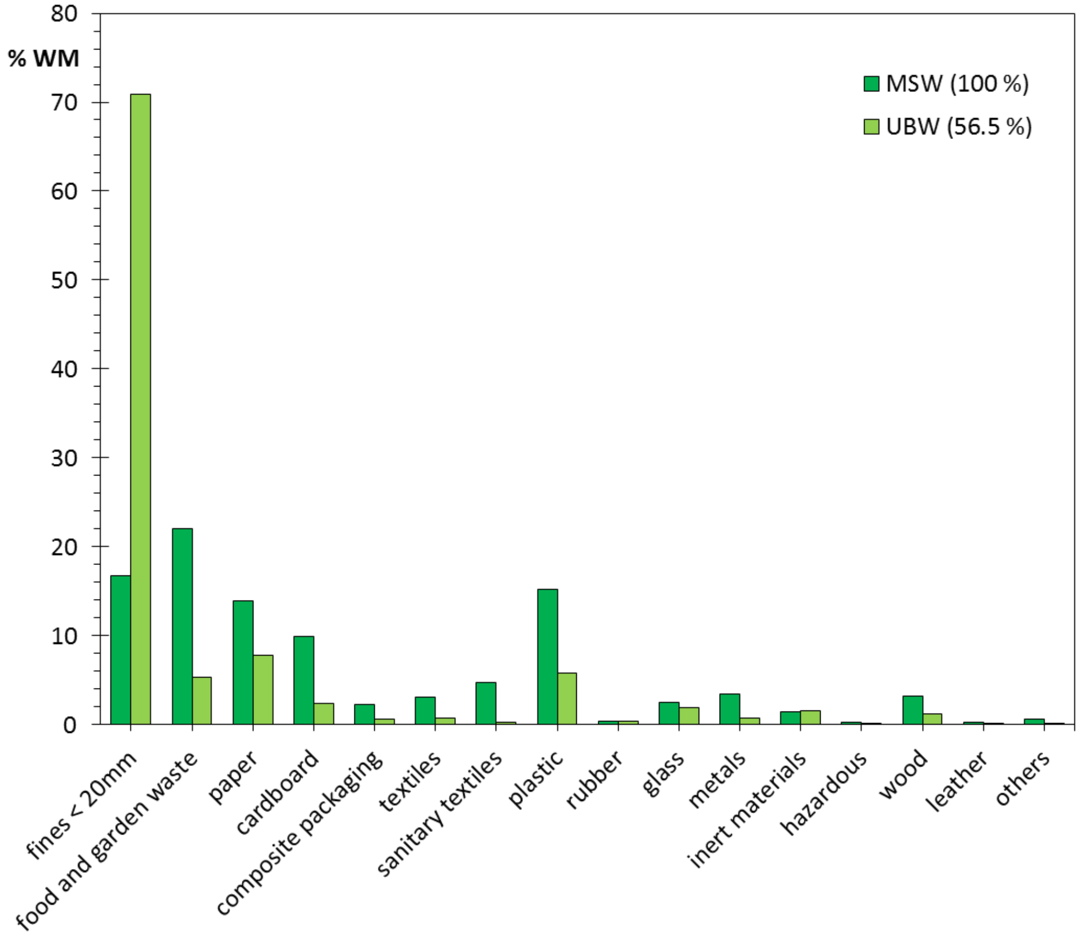

Figure 2.5 Material composition of MSW and UBW

Particle size distribution and material composition

Particle size analysis was carried out in order to investigate the distribution of physical and chemical properties among different particle size classes of the biostabilised waste (Petruzzelli et al., 1989). In Figure 2.6 the particle size distributions of BSW I and BSW IV (sampled prior to the final mechanical screening) are shown and compared. These materials were found to be quite coarse given the low percentages of sizes below 2 mm (approximately 9–14 % by dry matter, DM). Differences between BSW I and BSW IV are clearly visible. More specifically BSW IV was characterised by higher percentages of material at sizes in the range 2–38.1 mm than SBW I. This indicated the progressive degradation of the organic matter during the biostabilisation process which caused a size reduction of the material (Lornage et al., 2007).

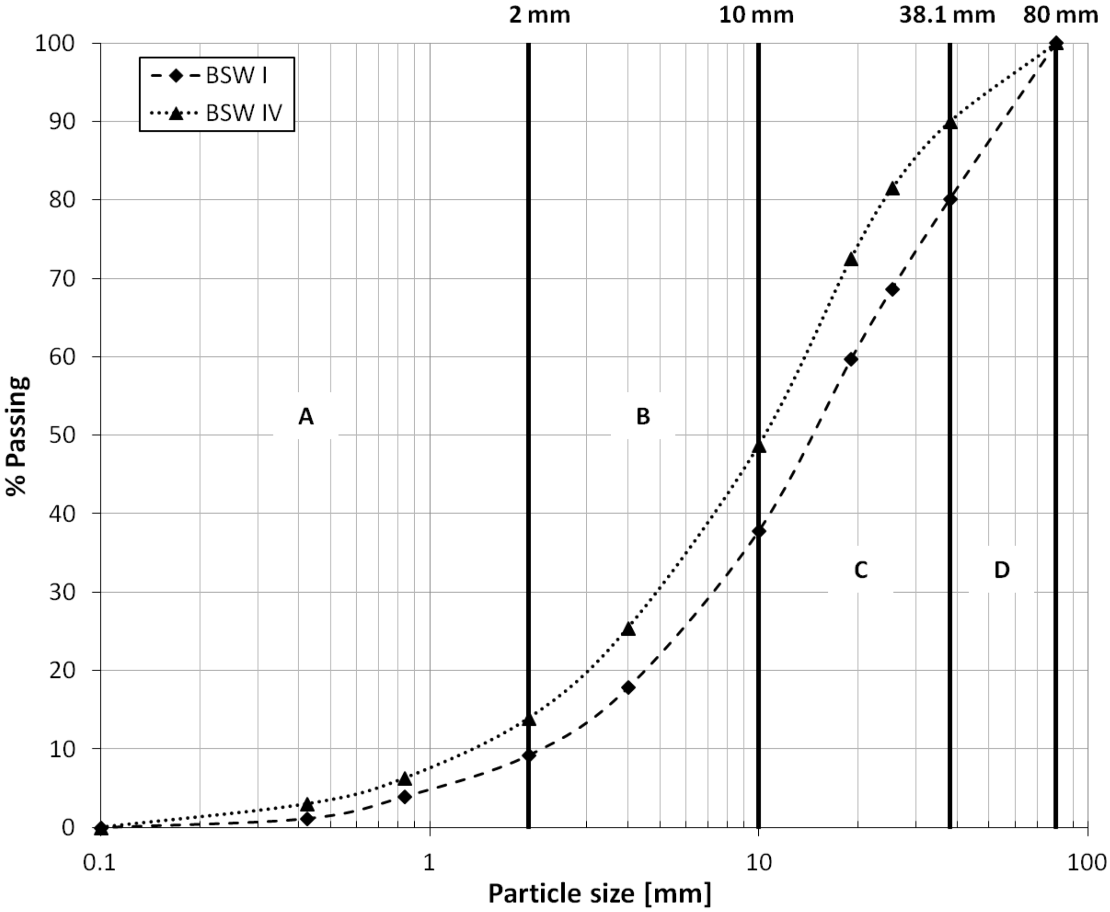

Figure 2.6 Particle size distribution of BSW I and BSW IV

On the basis of the found particle size distributions, four PZ classes, namely A = [< 2 mm], B = [2–10 mm], C = [10–38.1 mm], D = [38.1–80 mm], were identified (see Figure 2.6). The percentages by weight, on a dry matter (DM) basis, of the four classes were: A = 9.2 %, B = 28.6 %. C = 42.3 %, D = 19.8 % for BSW I; A = 13.9 %, B = 34.8 %. C = 41.2 %, D = 10.0 % for BSW IV. It is more evident that the latter was composed of higher percentages of particle size fractions below 10 mm than BSW I.

The analysis of the material composition was carried out in order to investigate the content of non-compostable materials, i.e. plastics, glass, metals, inert and hazardous materials, which may cause a physical contamination (Richard and Woodbury, 1992;

Baird et al., 2005; Dimambro et al., 2007; Farrel and Jones, 2009; Montejo et al., 2010), as well as a chemical contamination due to high heavy metal content (as thereafter discussed) by compromising the final quality of the biostabilised waste. The analysis regarded only classes C and D of BSW I and BSW IV, since, given the small size of classes A and B (< 10 mm), it was difficult to perform the manual sorting of the different materials. However, by a visual inspection, classes A and B showed to be mainly composed of fine organic materials (food and garden waste and small pieces of paper). Results are reported in Table 2.5 and it can be observed that for both BSW I and BSW IV, class D showed a very low content of organics (< 5 %) compared to class C (25 % for BSW I and 15 % for BSW IV).

Table 2.5 Material composition of classes C and D for BSW I and BSW IV (prior to the final screening) (values expressed in % DM)

Categories	**BSW I**		**BSW IV**	
	C	**D**	**C**	**D**
Organics	25.1	4.3	14.9	2.7
Paper/cardboard	26.6	35.7	18.9	32.6
Textiles	1.0	2.5	5.1	3.3
Plastics	10.7	21.1	15.6	17.6
Comp. Packaging	0.0	2.0	0.0	0.0
Wood	4.8	14.5	2.8	4.8
Glass	19.4	2.7	24.7	23.3
Metals	1.4	2.7	6.9	0.9
Inert materials	10.5	14.5	11.1	14.8
Hazardous	0.5	0.0	0.0	0.0
Total	100	100	100	100

Furthermore class D was composed of high quantities of slow and non-biodegradable materials, i.e. paper/cardboard, plastics, glass and inert materials, by total percentages roughly equal to 80 % for BSW I and 90 % for BSW IV. It has to be pointed out that, although paper is a biodegradable material, it is known to have relatively slow kinetics of biodegradation under aerobic conditions (Komilis, 2006), especially if compared to the duration of the biostabilisation treatment (4 weeks). Hence it may influence the performance of the biodegradation by reducing the rate of the whole process (Lornage et al., 2007; Bayard et al., 2010; Montejo et al., 2010). However “impurities” are reduced in the output of the biostabilisation process by means of the secondary mechanical sieving at 20 mm. Concern should be focused on the presence of relative high quantities of glass fragments and inert materials (brick and ceramic pieces) in class C of BSW IV (roughly 25 % glass and 11 % inerts) that in part (size < 20 mm) are not diverted from the undersize of the secondary sieving unit.

Organic matter content

The organic matter content of total UBW, BSW I and BSW IV, as well as of the particle size classes, was determined by measuring the volatile solids (VS) and the total organic carbon (TOC) and results (mean ± standard deviation of 3 repetitions) are shown in Table 2.6.

Table 2.6 VS and TOC content (% DM) measured in UBW, BSW I and BSW IV (prior to the final screening) and in particle size classes of BSW I and BSW IV

Samples	VS (% DM)	TOC (% DM)
UBW	65.9 ± 0.8	27.8 ± 0.3
BSW I	59.2 ± 5.1	23.7 ± 0.1
BSW IV	55.3 ± 1.3	23.6 ± 0.9
BSW I classes		
A	45.6 ± 0.6	21.3 ± 0.2
B	49.9 ± 1.3	24.9 ± 0.3
C	59.7 ± 1.0	23.7 ± 2.8
D	77.5 ± 0.0	23.1 ± 0.5
BSW IV classes		
A	46.5 ± 0.1	22.0 ± 0.1
B	47.3 ± 1.5	22.7 ± 1.7
C	49.3 ± 2.1	25.3 ± 0.6
D	74.7 ± 2.2	21.8 ± 1.0

Comparing UBW, BSW I and BSW IV, low reduction of VS and TOC content during the biodegradation process can be observed (Leikam and Stegmann, 1999; Lornage et al., 2007; Barrena et al., 2009; Bayard et al., 2010). This is because VS and TOC take into account the overall organic matter, including the non-degradable (e.g. plastics), and not-readily degradable. In fact, residual MSW of Rome aimed to MBT, showed to have relative high content of non and slowly degradable organic materials (plastics plus paper and cardboard equal to 39 %) and a significant percentage quantity equal to 25 % of such materials (see Figure 2.5) passed through the primary mechanical sieve. For the same reason, class D (enriched in plastics and paper/cardboard, as previously discussed), for both BSW I and BSW IV, showed a very high content of VS (Table 2.6), as also found by Zennaro et al. (2005) and Bayard et al. (2010) for coarse fraction of MSW undergoing MBT. All other values of VS and TOC showed to be quite comparable among the different particle size classes.

In order to better understand how organic matter was distributed among the different PZ classes, mass balances in terms of VS and TOC were calculated taking into account the percentages by dry weight found for each class and the mass loss compared to the untreated sample, as shown in Figure 2.7.

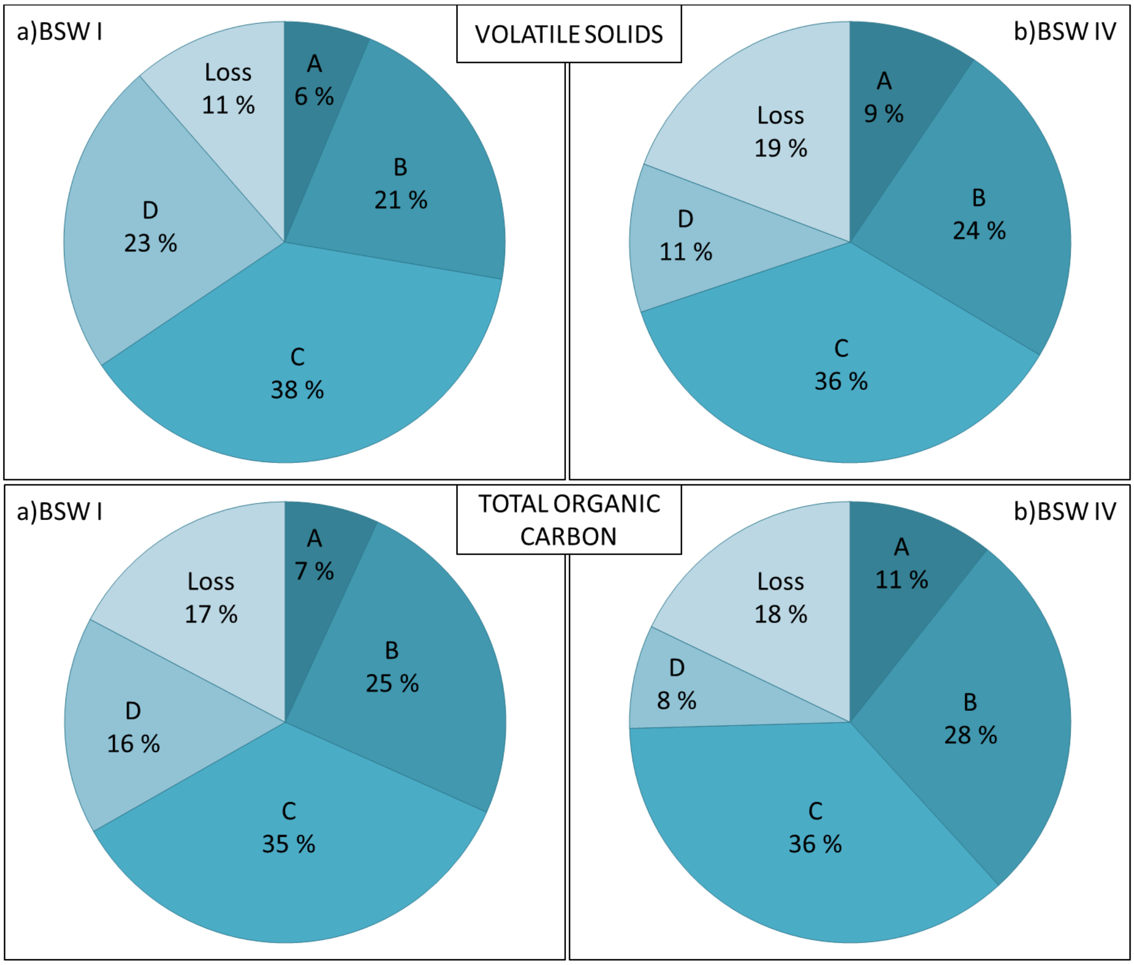

Figure 2.7 Mass balance on the basis of VS and TOC content in the particle size classes composing a) BSW I and b) BSW IV (prior to the final screening)

VS and TOC showed to have roughly the same distribution in BSW I and in BSW IV proving the correlation between these two parameters (Bayard et al., 2010) as they are both directly related to the organic carbon content (Barrena et al., 2009). Differences between BSW I and BSW IV can be noticed since VS and TOC increased in classes A and B and decreased or kept roughly constant in classes C and D for BSW IV compared to BSW I. This confirmed the reduction of the particle size due to degradation of organic matter. Regarding BSW IV, the highest content of organic matter was found in classes B and C. Nevertheless it has to be pointed out that class C was composed of paper/cardboard and plastics by approximately 35 % (see Table 2.5) which highly contribute to increase the VS and TOC values, whereas organic matter in class B was mainly related to fine readily degradable organics.

Heavy metals total content and leaching behaviour

Table 2.7 shows the total heavy metal (HM) content (mean ± standard deviation of 2 repetitions per each sample) found in UBW, BSW I and BSW IV and limit values are also reported. It has to be noticed that arsenic, antimony and mercury were not reported since they were lower than the limit of quantification (LoQ), i.e. the lowest concentration of an element below which the parameter cannot be quantified with sufficient accuracy by the analytical instrument. However a remark on such result worth to be given. Generally As, Sb and Hg are found in waste materials in the order of parts per billion (ppb) therefore they need a specific technique to be measured, e.g. by means of Agilent Vapor Generation Accessory VGA 77 (Agilent Technologies). Specifically the VGA 77 employs continuous flow technology where samples and liquid reagents are pumped together and mixed (Agilent Technologies, 2010). The gaseous reactions products (Hg-vapour and As, Sb-hydrides) are then swept by a flow of argon gas into the ICP-AES spectrometer for the elements determination. Since this method is currently in the starting-up phase, further investigations on As, Sb and Hg determination in BSW materials will need to be carried out.

Comparing HM total content of BSW IV with limit values, it can be seen that all requirements were fulfilled, with the exception of Pb and Zn which exceeded soil contamination thresholds for residential sites. Therefore biostabilised waste could be potentially recovered in environmental applications restricted to commercial and industrial sites.

Table 2.7 Total heavy metal content in UBW, BSW I and BSW IV and limit values (values expressed in mg/kg DM)

				Italian Decree 152/2006*		**EC doc 2001**	**ACO 2001**	**SEPA 2005**
Metals	**UBW**	**BSW I**	**BSW IV**	**A**	**B**			
Al	11503.0 ± 2689.8	9009.9 ± 1108.4	14986.8 ± 2628.5					
Ba	207.8 ± 1.8	220.9 ± 54.7	351.5 ± 32.9					
Ca	78226.7 ± 480.4	53345.1 ± 3228.5	95506.8 ± 4647.3					
Cd	0.3 ± 0.03	0.3 ± 0.03	0.5 ± 0.02	2	15	5	3	3
Co	1.5 ± 0.03	1.6 ± 0.002	1.4 ± 0.3	20	250			
Cr	15.7 ± 4.4	21.2 ± 0.8	15.1 ± 1.3	150	800	600	250	400
Cu	41.2 ± 0.5	97.5 ± 32.1	81.8 ± 1.2	120	600	600	500	200
Fe	7846.0 ± 308.7	5308.3 ± 969.6	9475.5 ± 1568.0					
K	9057.0 ± 1748.8	5629.5 ± 1219.7	9834.0 ± 2955.4					
Li	3.2 ± 0.25	2.7 ± 0.2	3.6 ± 0.4					
Mg	5092.5 ± 1585.9	3192.5 ± 90.8	5528.5 ± 567.8					
Mn	182.4 ± 2.7	135.9 ± 25.7	273.8 ± 73.1					
Na	5356.8 ± 9.0	4312.3 ± 1102.1	5654.5 ± 628.4					
Ni	12.5 ± 3.3	25.4 ± 7.7	27.8 ± 9.9	120	500	150	100	100
Pb	53.0 ± 2.1	163.8 ± 26.0	175.8 ± 4.3	100	1000	500	200	200
Si	1935.6 ± 13.3	2508.2 ± 281.0	1743.2 ± 230.2					
V	20.2 ± 2.3	13.9 ± 1.6	22.0 ± 4.8	90	250			
Zn	226.9 ± 1.6	241.9 ± 30.5	305.7 ± 10.3	150	1500	1500	1800	1000

*Column A – soil contaminant thresholds for use in residential sites; Column B - soil contaminant thresholds for use in coomercial and industrial sites

Heavy metals do not degrade during the aerobic biological process (Richard and Woodbury, 1992), hence roughly constant concentrations might be expected. Results showed some differences between the three analysed samples and this was mainly due to the heterogeneity of the tested materials. Such variations might be reduced by sampling the same input material during the treatment rather than sampling at the same time at different stages (van Praagh et al., 2009). To a lesser extent, besides heterogeneity, other factors might have an influence on the HM changes in concentration during the biostaibilisation. Since most heavy metals are not volatilised at the temperatures occurring during aerobic stabilisation (50-70°C), the loss of mass due to degradation of organic matter causes an increase of the heavy metal concentration in the biostabilised waste (Richard and Woodbury, 1992; Ciavatta et al., 1993; He et al., 1995; Zennaro et al., 2005; Dimambro et al., 2007; van Praagh et al., 2009). In the present work, Al, Ba, Ca, Cd, Cu, Mn, Ni, Pb and Zn showed to be more concentrated in the biostabilised materials (BSW IV) comparing with the untreated waste (UBW).

The other metals (Co, Cr, Fe, K, Li, Mg, Na, Si and V) had roughly the same concentration in the three samples.

In order to overcome the influence of carbon loss on metals content, HM concentrations were recalculated according to the equation 2.4, proposed by Amir et al. (2005):

$$C_{corr} = C_i \cdot \left(\frac{100-VS_{ini}}{100-VS_i}\right) \qquad (2.4)$$

where C_i is the measured heavy metal concentration (mg/kg) at i-th week of the process, and VS_{ini} and VS_i (% DM) are the volatile solids of the untreated material and of the biostabilised waste at i-th week, respectively. The HM corrected concentrations are shown in Figure 2.8 and it can be observed that metals content tended to decrease during the biostabilisation process. This was probably due to metal loss through the combination of degradation/acidification metabolites and percolation (Whittle and Dyson, 2002; Amir et al., 2005; Castaldi et al., 2006), circumstance also promoted by the adding water during the process.

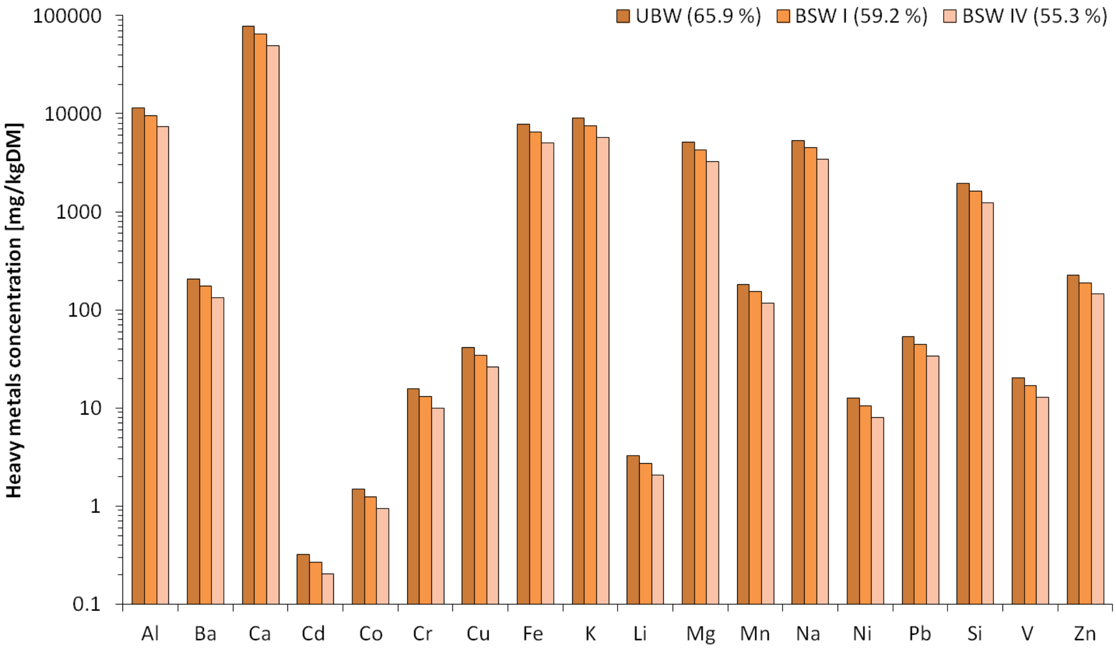

Figure 2.8 Metals corrected concentrations on the basis of VS content in BSW I and BSW IV and comparison with HM content in UBW

Table 2.8 shows the results (mean ± standard deviation of 2 repetition per each sample) of the leaching tests carried out for UBW, BSW I and BSW IV and limit values set by MD 186/2006 are reported. It has to be observed that chromium, copper, nickel, lead and chlorides exceeded limit values. Hence biostabilised waste could not be recovered and this is in contrast with what was found for total heavy metal content.

In order to evaluate how release of contaminants changed during the aerobic biodegradation process, the heavy metals percentage release was calculated by means of the equation 2.5, as follow:

$$\%\ \mathrm{release} = 100 \cdot \mathrm{C_{leach}}/\mathrm{C_{sol}} \qquad (2.5)$$

where C_{leach} is the concentration (mg/kg) measured in the eluates of the three samples and C_{sol} is the total content in solid materials (mg/kg). Results are shown in Figure 2.9.

Table 2.8 Leachate characteristics (L/S = 10) of UBW, BSW I and BSW IV and limit values (metal concentrations expressed in mg/l)

Metals	UBW	BSW I	BSW IV	MD 186/2006
Al	2.1 ± 0.7	2.6 ± 0.7	4.6 ± 0.1	
Ba	0.3 ± 0.02	0.2 ± 0.001	0.1 ± 0.0001	1
Ca	1067.3 ± 91.9	898.5 ± 10.0	757.6 ± 19.5	
Cd	0.001 ± 0.0002	0.001 ± 0.00004	0.002 ± 0.0001	0.01
Co	0.02 ± 0.003	0.02 ± 0.0007	0.02 ± 0.0004	0.25
Cr	0.04 ± 0.001	0.06 ± 0.001	0.1 ± 0.005	0.05
Cu	0.4 ± 0.004	0.6 ± 0.04	0.7 ± 0.02	0.05
Fe	2.9 ± 0.3	2.5 ± 0.04	4.1 ± 0.08	
K	566.5 ± 2.0	344.5 ± 3.0	413.8 ± 27.2	
Li	0.01 ± 0.0001	0.01 ± 0.0004	0.01 ± 0.0002	
Mg	90.0 ± 1.5	68.6 ± 0.5	81.0 ± 2.5	
Mn	2.3 ± 0.8	2.7 ± 1.2	1.5 ± 0.01	
Na	426.4 ± 4.7	356.8 ± 4.7	447.8 ± 16.6	
Ni	0.1 ± 0.001	0.3 ± 0.01	0.3 ± 0.01	0.01
Pb	0.03 ± 0.004	0.1 ± 0.005	0.2 ± 0.01	0.05
Si	85.3 ± 5.7	76.2 ± 5.5	36.6 ± 0.5	
V	0.04 ± 0.001	0.03 ± 0.001	0.03 ± 0.001	0.25
Zn	1.4 ± 0.2	1.4 ± 0.02	1.5 ± 0.02	3
DOC	4912.7 ± 673.8	2317.3 ± 303.6	1561.0 ± 191.2	-
Cl^-	748.6 ± 32.6	895.0 ± 48.8	610.2 ± 40.7	100
pH (unit)	6.1 ± 0.05	6.6 ± 0.03	6.8 ± 0.01	5.5 - 12

Some authors observed that release of metals decreased during the aerobic biodegradation (Baird et al., 2005; Castaldi et al., 2006; van Praagh et al., 2009) as they tend to be bound to solid organic matter. In the present work, the release of most metals (Ba, Ca, Cu, K, Li, Mg, Mn, Si, V and Zn) showed to decrease after 4 weeks of biostabilisation. Differently, the release of Al, Cr, Fe, Ni and Pb was higher for BSW IV comparing to the untreated material, likely because metals were transformed in more mobile forms. Lastly, the release of Cd, Co, Na did not significantly vary among the three analysed samples.

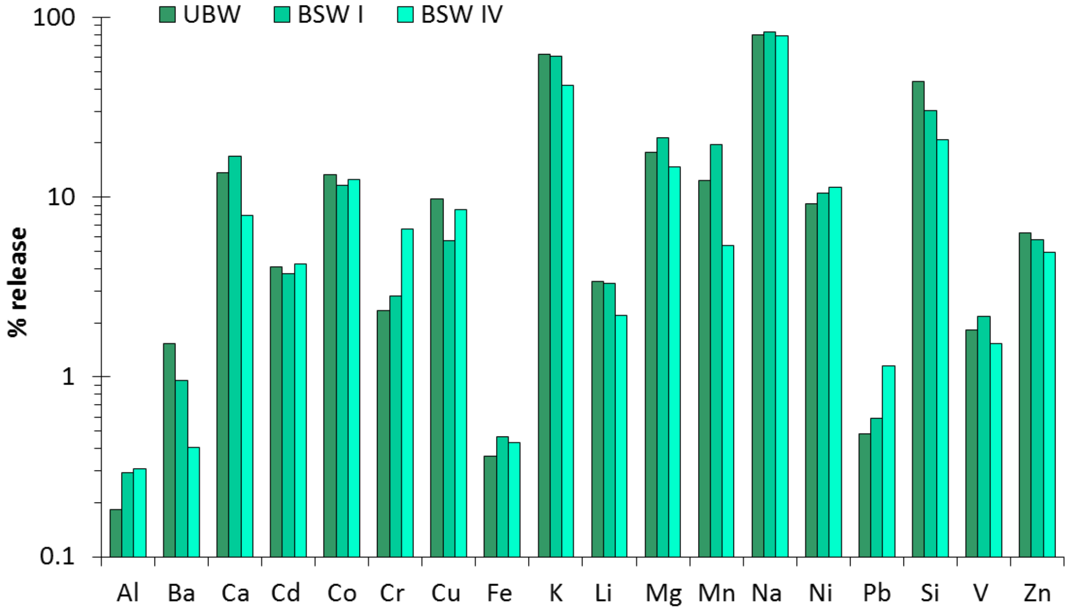

Figure 2.9 Comparison of HM percentage release between UBW, BSW I and BSW IV

Metals content in solid materials was also investigated in the particle size classes in order to evaluate the contributions to the heavy metal content in the entire biostabilised material (Petruzzelli et al., 1989). In Table 2.9 results of total HM contents found in the classes A (< 2 mm), B (2 – 10 mm), C (10 – 38.1 mm) of BSW IV are reported along with the standard deviation (calculated for 2 repetitions per each sample) and the limit values. Since class D was found to be mainly composed of non-biodegradable coarse materials (> 38.1 mm), that are separated from the output of the biostabilisation process by means of the secondary mechanical screening unit, heavy metal content in this class was not determined.

Results showed that the highest concentration of HM was found in the finest class, in agreement with other studies (Petruzzelli et al. 1989; Zennaro et al., 2005). This was probably because metals tend to be mostly bound to the fine solid organic matter. As a result, it can be observed that Pb concentration in class A approached the EC document limit value and exceeded the Austrian Compost Ordinance and SEPA limits.

Furthermore both Pb and Zn contents exceeded the Italian Decree – column A thresholds. Some authors (Petruzzelli et al., 1989; Zennaro et al., 2005) argued that by eliminating the finest fraction, a reduction of heavy metals total content in the biostabilised waste could be obtained without great losses in terms of mass and organic matter. This is true also in this case since BSW IV was composed of class A by roughly 14 % by dry weight and this class had organic content slightly lower than that in class B (see Table 2.6). Nevertheless, the question is on how separating such fraction. For instance, a downstream mechanical sieving would not be very effective since, for wet waste, the fine particles (< 2 mm) would tend to be “glued” to the coarser materials. It has to be observed that, besides class A, also Pb and Zn content of classes B and C did not comply with soil contamination thresholds set for the use in residential sites.

Table 2.9 Total heavy metal content in particle size classes of SBW IV and limit values (all values expressed in mg/kg DM)

Metals	**BSW IV**			**Italian Decree 152/2006***		**EC doc 2001**	**AOC 2001**	**SEPA 2005**
	A	**B**	**C**	**A**	**B**			
Al	23622.5 ± 1447.1	10284.3 ± 1572.0	12420.5 ± 42.2					
Ba	459.4 ± 28.6	247.2 ± 7.8	226.6 ± 15.1					
Ca	4888.8 ± 34.4	4794.1 ± 97.3	4779.8 ± 150.6					
Cd	0.5 ± 0.01	0.3 ± 0.2	0.25 ± 0.06	2	15	5	3	3
Co	3.1 ± 0.2	1.6 ± 0.3	1.7 ± 0.3	20	250			
Cr	79.9 ± 6.4	39.9 ± 24.1	15.0 ± 2.1	150	800	600	250	400
Cu	154.5 ± 17.1	91.3 ± 11.4	79.9 ± 2.1	120	600	600	500	200
Fe	18958.9 ± 1082.3	4384.1 ± 20.0	9817.7 ± 1383.2					
K	14058.6 ± 864.8	9005.9 ± 9.7	10229.0 ± 1450.6					
Li	14.9 ± 0.2	7.8 ± 0.5	9.1 ± 0.9					
Mg	6670.4 ± 376.2	4813.6 ± 1465.2	3953.5 ± 273.3					
Mn	244.1 ± 2.6	140.0 ± 5.8	144.8 ± 1.7					
Na	10195.2 ± 556.3	8794.8 ± 742.9	9024.4 ± 205.8					
Ni	49.3 ± 2.2	36.6 ± 19.3	18.2 ± 1.5	120	500	150	100	100
Pb	499.8 ± 41.9	188.7 ± 26.9	188.1 ± 0.7	100	1000	500	200	200
Si	9189.9 ± 464.2	6969.0 ± 63.4	6238.1 ± 306.3					
V	29.1 ± 0.8	12.6 ± 1.5	16.2 ± 0.3	90	250			
Zn	388.8 ± 7.9	296.5 ± 63.4	275.1 ± 26.5	150	1500	1500	1800	1000

*Column A – soil contaminant thresholds for use in residential sites; Column B - soil contaminant thresholds for use in coomercial and industrial sites

In order to better evaluate the distribution of heavy metals content among the PZ classes of BSW IV, the HM concentrations were recalculate and normalised on the basis of the percentage by dry weight found for each class, as shown in Figure 2.10. In this case, class C showed to have the highest metals content, with the exception of Cr and Ni. Therefore the separation of such class from BSW IV could be taken into consideration also because, as shown by the material composition, class C was composed by 60 % of non-compostable organic materials (see Table 2.5) which might cause a physical contamination in the case of BSW recovery in environmental remediation. Then, materials having particle size higher than 10 mm (classes C and D), once mechanically separated, could be sent to thermal treatment coupled to energy recovery (Di Lonardo et al., 2012c; Franzese et al., 2013), if complying with characteristics set for the different classes defined for Solid Recovered Fuel (SRF) (EN 15359, 2011a), rather than landfilling.

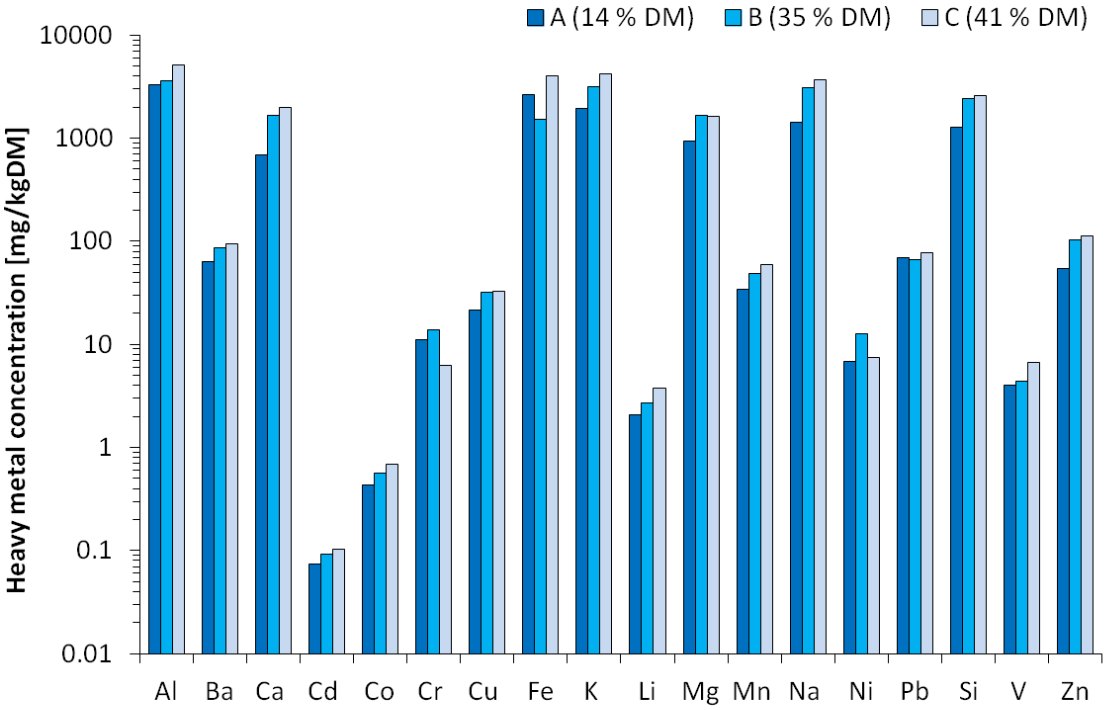

Figure 2.10 HM total content in PZ classes of BSW IV normalised on the percentage by dry weight of each class

CHAPTER 3

QUALITY EVALUATION OF THE BIOSTABILISED WASTE SUBJECTED TO LONGER DURATION OF BIOLOGICAL TREATMENT

This chapter was partly taken from:

Di Lonardo M.C., Binner E., Lombardi F. (2014a) Investigations on biological stability degree of mechanically-biologically treated MSW produced in Rome. Proceedings of EURASIA Waste Management Symposium, 28-30 April 2014, Istanbul, TR, pp. 39-46

Di Lonardo M.C., Lombardi F., Gavasci R. (2014b) Quality evaluation of mechanically-biologically treated MSW subjected to longer duration of biological treatment. Submitted and accepted for oral presentation in ATHENS 2014 - 2nd International Conference on Sustainable Solid Waste Management, 12–14 June 2014, Athens, GR

OBJECTIVE OF THE STUDY

In the previous study, the investigations and evaluations on the characteristics of the biostabilised waste as treated in the MBT plants of Rome, showed that such material did not have a suitable quality to be aimed to recovery procedures. Therefore, second step of the research was to evaluate the influence on BSW characteristics of longer duration of the aerobic biological process.

Specifically, an extension of the biodegradation process duration at forced aeration condition (intensive biodegradation phase) in the biostabilisation basin of the MBT plant A (as described in **Chapter 2**, page 12) from 4 weeks, which is the duration in normal operating conditions of the plant, to 7 weeks was evaluated.

Furthermore, a well biostabilised output, coming from the intensive biodegradation lasting 4 weeks performed in MBT plant A, was subjected to a ripening treatment in slightly aerated lab test cells in order to analyse and evaluate a possible further increase of the biological stability. This stage of the research was conducted at the Institute of Waste Management of the University of Natural Resources and Life Sciences in Vienna (ABF-BOKU).

Again, biological and physical-chemical characterisation of waste samples periodically collected during the aerobic biodegradation lasting 7 weeks and during the lab ripening phase, was carried out in order to evaluate the changing and evolution of the investigated characteristics.

QUALITY EVALUATION OF THE BIOSTABILISED WASTE SUBJECTED TO LONGER PROCESS DURATION IN THE BIOSTABILISATION BASIN

Sampling procedures and analytical methods

In order to evaluate the influence of longer duration of the aerobic biological process on BSW characteristics, the material was kept in the biostabilisation basin of the MBT plant A (as described in **Chapter 2**, page 12) for 3 weeks more, therefore for a total duration equal to 7 weeks. For this purpose, one part of the biostabilisation basin was isolated and set up in order to treat the material for 7 weeks and to allow the process monitoring and the material sampling, as well as to not hinder the normal operating conditions of the facility. Prior to the beginning of the biological process, the input material (biodegradable fraction, BSW0) was sampled from the conveyor belt carrying the biodegradable fraction to the biostabilisation basin. Afterwards, during the aerobic biodegradation process, 7 samples of the biostabilised waste were progressively collected week by week. The 8 collected macro-samples were taken by collecting different increments along the conveyor belt (SBW0) and along the stabilisation basin (BSW1, BSW2, BSW3, BSW4, BSW5, BSW6, BSW7). After mixing and quartering, a final quantity of roughly 20 kg for each sample was sent to the laboratory for the biological and physical-chemical analysis. Then, a secondary quartering in lab was carried out in order to split an amount of approximately 15 kg for the biological analysis, which needed as-received material, from the remaining amount of 5 kg which was air dried prior to perform all physical-chemical tests.

Investigations on biological stability degree, organic matter content, heavy metals total content and contaminant release in water phase (leaching behaviour) of the material periodically sampled during the aerobic biodegradation lasting 7 weeks were performed. Biological stability and organic matter content were measured by means of the same analytical methods previously described (see **Chapter 2**, page 15)

Heavy metal content in solid materials (total content) was determined in triplicates by acid digestion according to the European Standards EN 15410 and 15411 (2011b,c) by making some changes. More specifically 3 ml of HNO_3 and 1 ml of HCl were added to 0.1 g of air dried sample grinded to 0.5 mm. Then the mixture was put in closed vessels (Parr Instrument Company - model 4744) and kept at 150 °C for approximately 15 hours. The obtained solution, after cooling, was firstly filtered by means of Whatman Nr. 41 filter paper so to separate residues and then it was dilute to volume with ultrapure water in 25 ml flask. A final filtration at 0.45 μm (Sartorius cellulose acetate syringe filters) was carried out in order to analyse the heavy metals in the solution by inductively coupled plasma atomic emission spectrometry (Varian ICP-AES).

For the leaching test, air-dried samples were grinded to a particle size lower than 4 mm, as required by the European Standard EN 12457-2 (2002). A volume equal to 80 ml of deionised water was added to 8 g of each sample in order to obtain a liquid to solid ratio equal to 10 ml/g and bottles containing the mixture were stirred for 24 hours. Such test was conducted in duplicates for each sample. The obtained eluate, after decanting for 15 minutes, was firstly analysed by measuring the pH (Eustech Instrument pH 700). Afterwards, three steps of filtration were carried out: (1) centrifugation at 12000 rpm for 10 – 15 min (Thermo Scientific SL 16R Centrifuge), (2) vacuum filtration at 0.7 μm (Munktell AB glass fibre filters) and (3) final filtration at 0.45 μm (as required by the standard method) by means of syringe filters (Sartorius cellulose acetate filters). The dissolved organic carbon (DOC) (Shimadzu TOC-V CPH/CPN analyser) and the chloride content (Mohr's method; ISO 9297, 1989) were then measured in the filtered eluate. Prior to determine heavy metal concentrations, since the dissolved organic matter in the eluate caused interferences during ICP-AES running (as thereafter discussed), an acid digestion procedure was carried out according to APAT - CNR - IRSA Guidelines 29 (2003) in order to oxidise the dissolved organic matter. Specifically, 1 ml of aqua regia was added to 10 ml of eluate and the mixture was put in the above mentioned Parr vessels and kept at 150 °C for 24 h. Then the obtained solution, after dilution to volume in 25 ml flask, was analysed by means of ICP-AES.

Results and discussion

Biological stability degree and organic matter content

Figure 3.1 shows the results of the dynamic respiration index (DRI) measured for weekly samples during the biological process. A progressive reduction of DRI, i.e. an increase of biological stability, during the biodegradation process was observed by following an exponential decreasing trend (Figure 3.1a). Furthermore, DRI was found to be lower than the maximum limit equal to 1000 $mgO_2/kgVS \cdot h$ after 7 weeks of aerobic biodegradation (BSW7) with a percentage reduction equal to roughly 70 % comparing with non-stabilised waste (BSW0). As found in previous determinations (see **Chapter 2**, page 22), DRI of BSW1 was slightly higher than DRI of BSW0. This is because the microbial activity and the related oxygen consumption, after one week of biodegradation, is still quite high and comparable to the beginning of the process whereas volatile solids, i.e. organic matter, slightly reduced (see Table 3.1). As a result, the area under the DRI curve of SBW0 was greater than that of SBW1 even if the latter had a higher max DRI (curve peak), as can be observed in Figure 3.1b. The same was observed for samples SBW2 and SBW3.

In other European Countries, such as Austria, biological reactivity of waste is analysed by means of a different type of respiration test which measures the cumulative oxygen uptake in 4 days (RA_4). Scaglia et al. (2010) found a correlation between the two respiration indices (DRI and RA_4) and derived the regression equation 3.1:

$$\mathrm{DRI} = (15.85 \pm 0.34) \cdot \mathrm{RA}_4 - (1.14 \pm 10.75) \tag{3.1}$$

where DRI is expressed as $mgO_2/kgDM \cdot h$ and RA_4 as mgO_2/gDM.

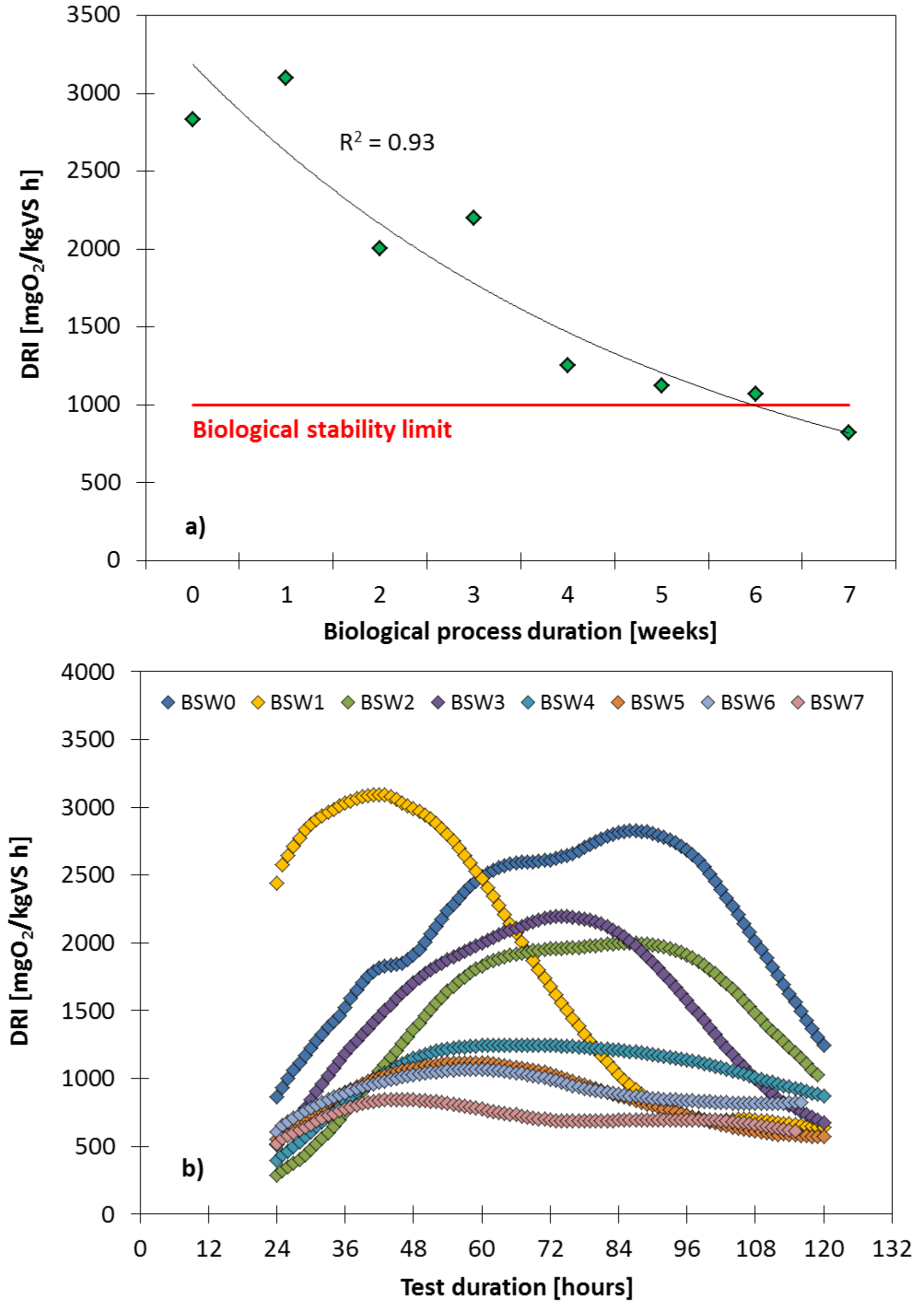

Figure 3.1 a) Max DRIs trend and b) DRI trends hourly registered during the respiration test and averaged in 24 h

The equation 3.1 was used to calculate RA_4, given the DRIs found for all the samples as reported in Table 3.1. RA_4 values showed to be much higher than the maximum limit value equal to 7 mgO_2 g DM^{-1} set by the Austrian Landfill Ordinance (Binner et al., 2012), indicating a high reactivity of the material even after 7 weeks of biodegradation. It has to be pointed out that RA_4 limit is based on a longer duration of biological treatment as carried out in Austrian MBT plants, namely 2 – 6 weeks of intensive decomposition treatment plus a ripening phase ranging from 6 to 12 weeks (Tintner et al., 2010), unlike MBT plants of Rome.

Table 3.1 Results of biological stability indices and organic matter content

BSW samples	DRI (mgO_2/kgVS h)	DRI (mgO_2/kgDM h)	RA_4 (mgO_2/gDM) [a]	VS (% DM)[b]	TOC (% DM)[b]
0	2826	1845.4	116.5 ± 1.9	65.3 ± 0.2	36.3 ± 1.0
1	3093	1699.6	107.3 ± 1.7	55.0 ± 1.0	28.4 ± 0.3
2	1999	1122.4	70.9 ± 0.9	56.1 ± 1.0	30.0 ± 1.1
3	2196	936.7	59.2 ± 0.6	42.7 ± 0.3	18.1 ± 1.6
4	1248	657.0	41.5 ± 0.2	52.7 ± 0.9	22.2 ± 2.2
5	1118	573.6	36.3 ± 0.1	51.3 ± 0.3	23.6 ± 0.9
6	1067	469.9	29.7 ± 0.04	44.0 ± 0.3	18.8 ± 1.1
7	819	354.5	22.4 ± 0.2	42.0 ± 1.3	14.8 ± 0.4
% reduction	70.0	-	-	35.7	59.2

[a] Values calculated by means of equation 3.1; [b] Mean value ± standard deviation

Due to biodegradation, a reduction of organic matter content, in terms of TOC and VS, was observed with an approximately linear decreasing trend (Figure 3.2a). The VS decrease was relatively low, especially comparing with the reduction found for DRI and TOC (Table 3.1). Furthermore for both VS and TOC the decreasing trend was not gradual (Fig. 2a). This is mainly because VS and TOC take into account the overall organic matter, including also non-degradable compounds (such as plastics) (Barrena et al., 2009) and the biodegradable fraction undergoing the biostabilisation process showed to be quite heterogeneous, being composed of not negligible percentage of plastics (roughly 10 %, Di Lonardo et al., 2012b). However TOC and VS showed to have the same trend (Figure 3.2a) during the 7 weeks of biological treatment, as proven by the high linear correlation (R^2 = 0.95) found between the two parameters (Figure 3.2b) since they are both direct indices of the organic matter content.

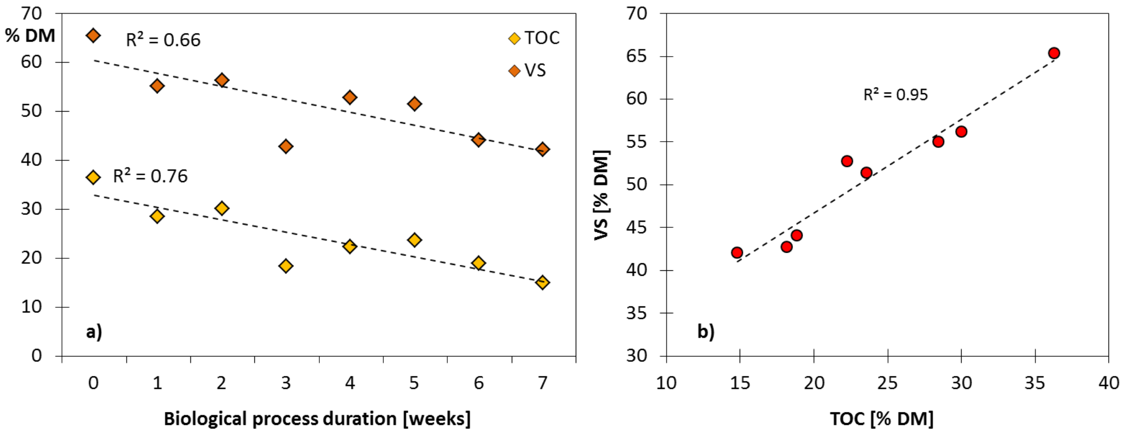

Figure 3.2 a) Organic matter content (TOC and VS) trend during biological process and b) correlation TOC-VS

Heavy metals total content and leaching behaviour

Table 3.2 shows the results of the heavy metals (HM) total content (mean ± standard deviation for 3 repetitions per each sample) measured in the biodegradable fraction (BSW0), in the biostabilised waste after 4 weeks (BSW 4), which is the duration of the biological process in normal operating conditions of the MBT plant A, as well as in the biostabilised waste after 7 weeks of biological treatment (BSW7). The results are compared with limit values reported by the Italian Decree (2006), the European Commission document on biowaste (European Commission, 2001), the Austrian Compost Ordinance (ACO, 2001), as well as by the Scottish Environmental Protection Agency (SEPA) standard (Baird et al., 2005).

The obtained results showed some differences between the three analysed samples (Table 3.2) and this was likely due to three main factors. Firstly, as mentioned above, the heterogeneity of the tested materials (first influencing factor) have a significant influence on the HM changes in concentration during the biostabilisation, as highlighted by the significant standard deviations. Furthermore, metals showed to be more concentrated in the stabilised materials BSW4 comparing with BSW0 due to the mass loss occurred because of the degradation of organic matter (second influencing factor), with the exception of Cd, Na and Si.

Comparing BSW4 with BSW7, it can be noticed that most metals concentrations, unless Cr and Na, were lower in BSW7. This was presumably caused by the metal loss through percolation (third influencing factor), indicating that metals were transformed in more mobile forms during the last three weeks of biostabilisation.

Table 3.2 Results of heavy metal total content in BSW0, BSW4, BSW7
(values expressed in mg/kg DM)

	BSW samples			**Italian Decree 152/2006***		**EC doc 2001**	**ACO 2001**	**SEPA 2005**
Metals	**0**	**4**	**7**	**A**	**B**			
Al	9476.82 ± 1681.9	12375.5 ± 1389.4	10881.0 ± 593.2					
Ba	315.4 ± 21.1	396.1 ± 56.0	237.0 ± 19.5					
Ca	62895.8 ± 14207.8	68155.0 ± 13108.3	50467.3 ± 3992.6					
Cd	14.4 ± 6.0	1.7 ± 1.2	0.7 ± 0.1	2	15	5	3	3
Co	2.8 ± 0.1	7.9 ± 2.7	3.0 ± 0.5	20	250			
Cr	25.9 ± 2.6	53.3 ± 13.2	56.1 ± 6.6	150	800	600	250	400
Cu	66.5 ± 21.3	1221.9 ± 616.7	90.8 ± 15.1	120	600	600	500	200
Fe	5371.9 ± 821.8	12025.7 ± 1043.8	8149.8 ± 435.0					
K	5791.2 ± 1124.2	7904.5 ± 607.0	7068.2 ± 428.9					
Li	5.2 ± 0.7	6.6 ± 0.7	5.4 ± 0.2					
Mg	3468.0 ± 497.5	4459.6 ± 694.3	3268.7 ± 146.2					
Mn	158.5 ± 24.1	584.3 ± 283.1	159.2 ± 6.9					
Na	5381.6 ± 806.7	5074.8 ± 364.0	5530.8 ± 485.6					
Ni	36.8 ± 62.7	593.5 ± 201.1	62.7 ± 11.4	120	500	150	100	100
Pb	219.0 ± 159.3	359.5 ± 69.0	153.8 ± 18.4	100	1000	500	200	200
Si	117.6 ± 23.4	108.0 ± 62.8	89.1 ± 13.9					
V	17.1 ± 3.0	20.8 ± 2.0	17.3 ± 1.1	90	250			
Zn	272.0 ± 18.9	757.1 ± 204.2	382.9 ± 51.8	150	1500	1500	1800	1000

*Column A – soil contaminant thresholds for use in residential sites; Column B - soil contaminant thresholds for use in coomercial and industrial sites

Furthermore, comparing HM total content of BSW4 and BSW7 with limit values (Table 3.2), it can be seen that both materials did not fulfil thresholds of Italian Decree - column A. Furthermore, unlike BSW7, heavy metals content in BSW4 showed to exceed also all other limits. Therefore, from this point of view (HM total content), biostabilised waste after 7 weeks of biological process could be potentially utilised in environmental applications restricted to commercial and industrial sites. Again, in order to overcome the influence of carbon loss on metals content, HM concentrations were recalculated according to the equation 2.4 (see **Chapter 2**, page 30). Results are shown in Figure 3.3 and the same trend of non-corrected content was found, i.e. a higher concentration in BSW4 comparing with BSW0 and a decreased content in BSW7.

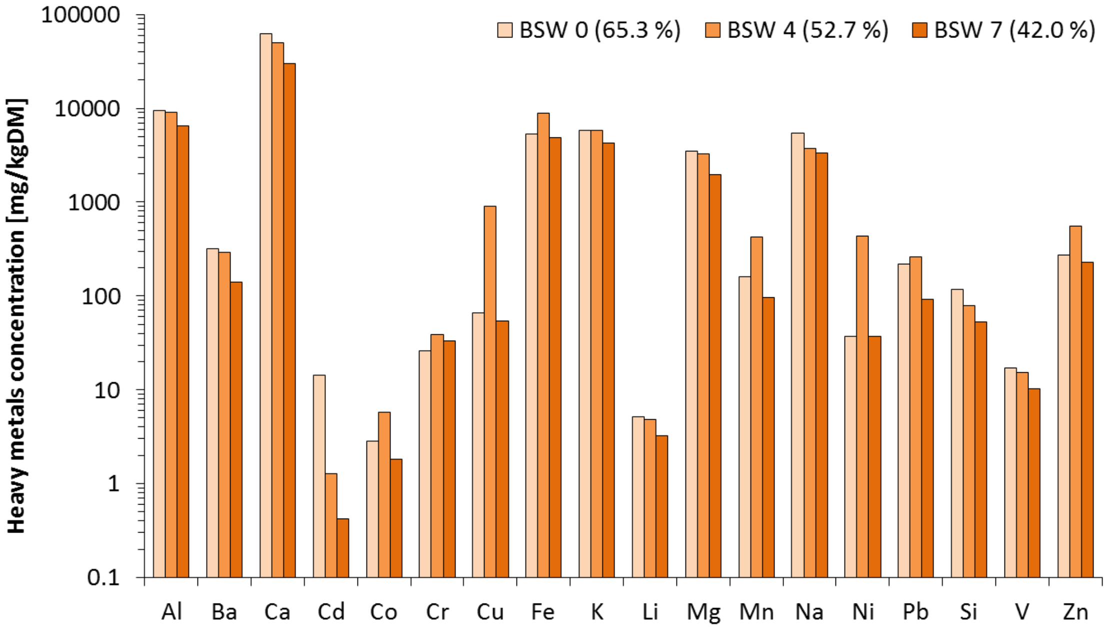

Figure 3.3 Metals corrected concentrations on the basis of VS content in BSW4 and BSW7 and comparison with metals content in BSW0

Leaching behaviour

Table 3.3 shows the results of pH, DOC and chlorides (mean ± standard deviation for 2 repetition per each sample) measured in the eluates obtained by the leaching test performed for the 8 BSW samples and limit values of MD 186/2006 (described in **Chapter 2**, page 20) are reported.

Table 3.3 Results of pH, DOC and chlorides measured in the eluates of the 8 BSW samples

BSW samples	pH	DOC (mg/l)	Cl^- (mg/l)
0	5.9 ± 0.01	2816.8 ± 294.8	1317.9 ± 119.2
1	6.5 ± 0.04	2123.6 ± 14.6	508.6 ± 18.7
2	6.6 ± 0.015	2147.5 ± 278.0	763.0 ± 71.8
3	6.6 ± 0.02	1589.0 ± 29.0	536.7 ± 32.5
4	6.6 ± 0.025	2400.8 ± 191.8	687.1 ± 77.2
5	6.7 ± 0.0	2394.0 ± 114.5	853.8 ± 8.1
6	6.7 ± 0.01	1736.8 ± 79.8	628.5 ± 16.1
7	6.8 ± 0.005	1835.5 ± 226.5	724.2 ± 49.3
Limit values	5.5 — 12	-	100

The pH values did not vary significantly, unlike what expected, during the biostabilisation process. However pH showed to follow approximately the characteristic trend of an aerobic biodegradation (Sirini et al., 2009), ranging from 5.9, at the beginning, to 6.8, at the end of the process. DOC and chlorides globally reduced after 7 weeks of aerobic biodegradation comparing with untreated waste. Nevertheless they did not showed a progressive decreasing trend (as found for TOC and VS) likely because of the heterogeneity of the tested material. Furthermore Cl^- concentrations were much higher than the limit value set by MD 186/2006.

Table 3.4 shows the results of metal concentrations (mean ± standard deviation for 2 repetitions per each sample) measured in the eluates of each BSW sample, as well as limit values set by MD 186/2006. Firstly, it has to be noticed that in most cases the standard deviations were relatively high and this again can be related to the heterogeneity of the waste. Cadmium was lower than the limit of quantification, therefore it was not reported. Concentrations in water phase of Ba, Ca, Co, Cr, Li, Mg, Mn, Ni, and Si was lower for BSW7 comparing with BSW0 whereas Cu, Fe and Pb concentrations were higher. Moreover Al, K, Na, V and Zn concentrations in the eluates of the weekly samples did not significantly vary. Comparing HM concentrations with limit values, only Co and V fulfilled the limit values set by MD 186/2006, hence, according to this regulation, biostabilised waste could not be subjected to material recovery.

The release of contaminants in water phase is generally governed by the variation in pH and heavy metals mobility, depending on each element, tends to be high at basic (pH > 9) and/or acidic (pH < 4) conditions (Whittle & Dyson, 2002; van der Sloot et al., 2004). Furthermore, in the organic matter rich matrices, as in the case of biostabilised waste, the role of solid organic matter and dissolved organic matter (DOC), is a key factor in the transfer of inorganic contaminants to the water phase (van der Sloot et al., 2004; van Praagh et al., 2009). Since the pH of BSW eluates were found to be around neutral values (see Table 3.3), the release of metals was assumed to be minimally influenced by this parameter (Whittle and Dyson, 2002), therefore DOC was likely the most dominant factor controlling it (van der Sloot et al., 2004) by means of complexation reactions with metals (van Praagh et al., 2009). Such metals affinity with DOC was verified by comparing metal concentrations found in the digested eluates (namely subjected to acid digestion procedure, as described above, in order to oxidise the dissolved organic matter) and not-digested eluates

Table 3.4 Results of metal concentrations measured in the eluates of the 8 BSW samples

Values expressed in mg/l

BSW samples	Al	Ba	Ca	Cr	Cu	Fe	K
0	2.11 ± 0.07	2.6 ± 0.13	991.5 ± 109.1	0.18 ± 0.02	0.15 ± 0.01	2.53 ± 0.38	300.2 ± 23.0
1	2.10 ± 0.02	2.15 ± 0.06	606.5 ± 14.6	0.08 ± 0.005	0.37 ± 0.02	2.39 ± 0.14	295.4 ± 72.7
2	2.28 ± 0.12	2.2 ± 0.15	482.4 ± 84.4	0.11 ± 0.005	0.31 ± 0.06	2.35 ± 0.1	285.8 ± 27.3
3	1.47 ± 0.09	1.88 ± 0.09	400.9 ± 24.3	0.30 ± 0.24	0.6 ± 0.03	2.87 ± 1.2	220.0 ± 10.4
4	2.52 ± 0.2	0.99 ± 0.001	489.9 ± 92.9	0.11 ± 0.03	0.73 ± 0.08	3.21 ± 0.39	322.9 ± 21.4
5	3.24 ± 0.17	0.92 ± 0.12	626.7 ± 64.8	0.15 ± 0.02	0.65 ± 0.03	5.04 ± 0.07	340.6 ± 9.8
6	3.24 ± 0.94	1.75 ± 0.16	486.9 ± 71.1	0.10 ± 0.007	0.65 ± 0.06	5.73 ± 0.16	282.2 ± 2.0
7	2.21 ± 0.137	1.42 ± 0.22	434.7 ± 32.4	0.08 ± 0.006	0.58 ± 0.002	4.4 ± 0.45	338.7 ± 0.6
Limit values	-	1	-	0.05	0.05	-	-

BSW samples	Mg	Mn	Na	Ni	Pb	Si	Zn
0	85.8 ± 3.9	3.08 ± 0.05	401.7 ± 32.9	0.28 ± 0.04	0.04 ± 0.003	8.53 ± 0.88	4.63 ±0.07
1	55.3 ± 15.1	1.04 ± 0.001	308.9 ± 14.9	0.31 ± 0.02	0.1 ± 0.008	5.9 ± 0.1	3.47 ± 0.15
2	46.4 ± 5.8	0.99 ± 0.17	299.4 ± 33.4	0.14 ± 0.001	0.12 ± 0.01	5.25 ± 0.65	3.65 ± 0.48
3	43.3 ± 5.0	0.83 ± 0.1	246.1 ± 24.5	0.28 ± 0.15	0.23 ± 0.009	4.31 ± 0.55	6.62 ± 0.19
4	52.9 ± 7.1	1.12 ± 0.13	428.9 ± 122.6	0.29 ± 0.07	0.21 ± 0.03	3.41 ± 0.01	4.19 ± 0.03
5	66.7 ± 3.0	1.16 ± 0.03	419.8 ± 19.1	0.35 ± 0.006	0.29 ± 0.006	2.81 ± 0.02	4.01 ± 0.18
6	57.3 ± 3.3	0.84 ± 0.05	341.5 ± 9.4	0.31 ± 0.02	0.22 ± 0.03	4.5 ± 1.6	3.14 ± 0.23
7	50.2 ± 4.5	0.87 ± 0.08	395.2 ± 47.3	0.20 ± 0.02	0.24 ± 0.015	3.42 ± 0.44	4.38 ± 0.04
Limit values	-	-	-	0.01	0.05	-	3

Values expressed in µg/l

BSW samples	Co	Li	V
0	41.8 ± 20.4	31.11 ± 12.74	18.50 ± 2.36
1	16.5 ± 1.2	15.2 ± 0.14	16.02 ± 1.67
2	17.4 ± 2.7	14.13 ± 1.43	19.75 ± 2.89
3	16.8 ± 3.2	12.84 ± 2.03	17.19 ± 2.92
4	18.4 ± 2.7	15.28 ± 0.05	27.14 ± 0.96
5	26.2 ± 1.4	19.14 ± 0.65	28.93 ± 0.63
6	16.7 ± 0.3	15.83 ± 0.78	23.55 ± 1.32
7	20.3 ± 1.5	12.46 ± 0.72	23.89 ± 1.90
Limit values	250	-	250

Specifically, in Figure 3.4 the comparison between metal concentrations of digested and not-digested eluates of BSW0, which showed to have the highest DOC concentration (see Table 3.3), is shown. It can be noticed that in the pre-digested eluate, for which a DOC breakdown of roughly 80 % was obtained, higher metal concentrations, especially for Co, Cr, Cu, Li, Ni, Pb and V, were measured. This demonstrated the high affinity of such metals with DOC and the consequent interference of the high concentration of the latter during ICP-AES running by causing a "blinding" of the optical reading.

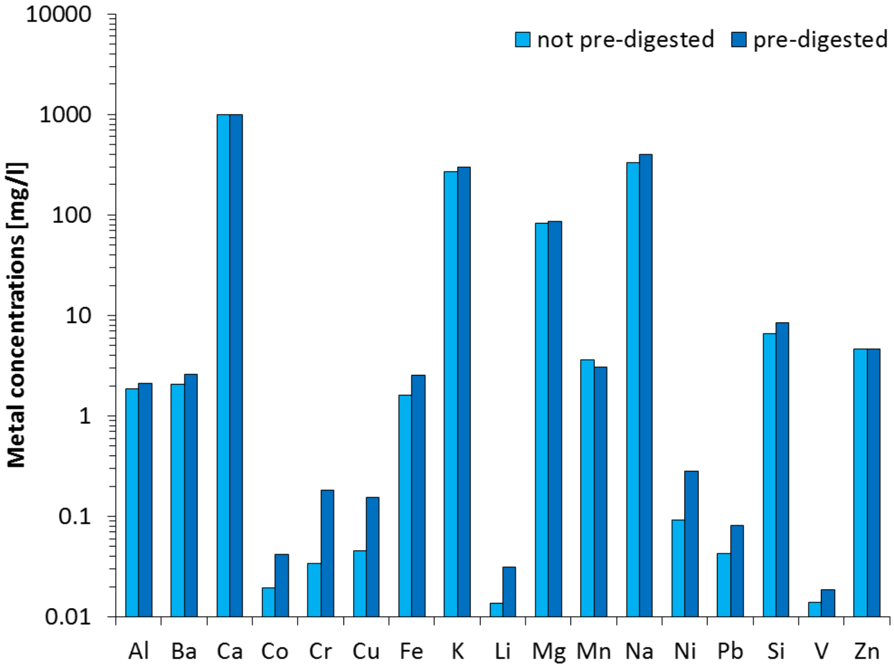

Figure 3.4 Comparison between metal concentrations in digested and not-digested eluates of BSW0

Also in this case, in order to evaluate how release of contaminants changed during the aerobic biodegradation process, the heavy metals and organic carbon percentage release was calculated by means of the equation 2.5 (see **Chapter 2**, page 31) and results are shown in Figure 3.5. It can be observed that Cr percentage release decreased during the 7 weeks of stabilisation as it tends to be bound to organic solid matter and to insolubilise (Ciavatta et al., 1993; Greenway and Song, 2002). For the same reason at the 4th week of stabilisation all other metals percentage release was lower comparing with the beginning. The exceptions were Al, Na and V, whose percentage release did not vary significantly, as well as Pb and organic carbon. Both Pb and organic carbon percentage release progressively increased from the beginning till the end of the process. Castaldi et al. (2006) and Christensen et al. (1999) reported, indeed, that changes in the water-soluble fractions of Pb were reflected in the water-soluble organic C concentrations as it is bound in DOC complexes. Then at the 7th week of aerobic biodegradation, the release of most metals increased likely because they were transformed in more mobile forms (as demonstrated also by the lower total content found at the 7th week of the process). The higher release of Co, Cu, Ni and Zn was also influenced by their affinity with the dissolved organic carbon (Amir et al., 2005; Castaldi et al., 2006; Christensen et al., 1999; Greenway and Song, 2002; van Praagh et al., 2009) which showed a progressive increasing release. Ultimately, it has to be noticed that copper showed a higher release at the end of the process also comparing to the beginning.

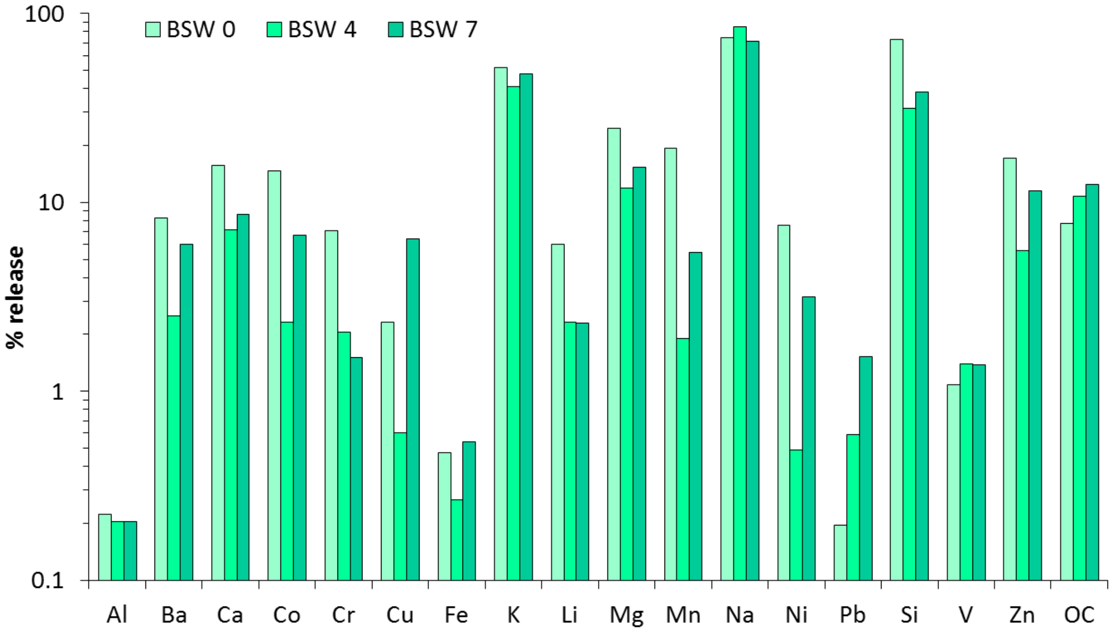

Figure 3.5 Comparison of heavy metals and organic carbon (OC) percentage release between BSW0, BSW4 and BSW7

QUALITY EVALUATION OF THE BIOSTABILISED WASTE SUBJECTED TO LAB RIPENING PHASE

Lab test for ripening phase and sampling procedure

The biostabilised waste was sampled, according to Italian standard UNI 10802 (2004), at the outlet of the biodegradation process lasting 4 weeks after the sieving unit at 20 mm in the MBT plant A (as described in **Chapter 2**, page 12). After coning and quartering, an amount of roughly 30 kg was collected and sent to the laboratory at the Institute of Waste Management of the University of Natural Resources and Life Sciences in Vienna (ABF-BOKU).

The sampled amount of BSW was then subjected to a ripening phase by placing it in a vertical cells system simulating open windrow configuration (Figure 3.6).

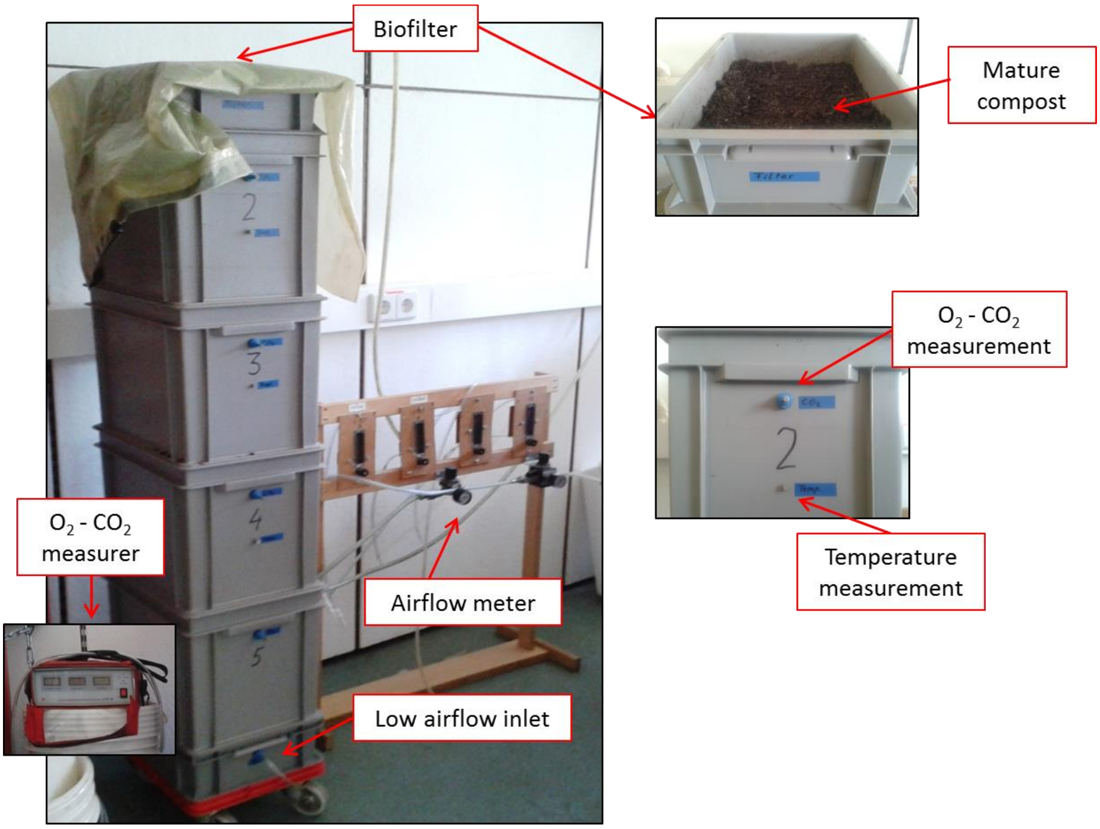

Figure 3.6 Lab ripening phase: vertical cells system simulating open windrow configuration

At the top of the system, a biofilter composed of mature compost was placed in order to reduce odour emissions. A low air flow rate was fed to the bottom of the system in order to simulate natural aeration conditions. Temperature of the room and of the rotting material, oxygen and carbon dioxide in the waste air were measured daily during the lab ripening phase in order to monitor the process. Mixing, adjusting in water content and turning over of the material were carried out once per week in order to keep optimised conditions for the ripening. During mixing of the material, samples were taken in order to analyse the biological reactivity and evaluate the changing in reactivity over time. Physical-chemical investigations were carried out as well on the collected samples during the ripening process, in order to evaluate the changing of the investigated characteristics.

Analytical methods

The biological reactivity was analysed by means of respiration test and gas generation test. Specifically, the respiration activity was determined by measuring the oxygen uptake during 4 days (RA_4) using two respirometric systems, i.e. Sapromat and OxiTop (Binner et al., 2012). The biogas production was determined by incubation test (Binner, 2002) measuring the gas generation sum during 21 days (GS_{21}). Such tests, including sample preparation, were carried out according to Austrian Standards OE NORM S 2027-4 (2012) and OE NORM S 2027-2 (2004), respectively. Furthermore, Fourier Transform Infrared (FTIR) spectroscopy was determined since this method enables assessing the potential reactivity of MBT waste directly via the chemical composition reflected by the FTIR spectrum (Böhm et al., 2010). Infrared spectroscopic investigation was carried out using the attenuated total reflection (ATR) technique (Bohm et al., 2010) by means of Bruker Optics ALPHA FTIR Spectrometer. Prior to the FTIR analysis, samples were air dried, grinded by means of agate mill and screened through a 0.63 mm sieve in order to obtain pulverised and homogeneous materials.

Both respiration test and FTIR spectroscopy were performed for BSW as-received (R0), and for BSW after 2 (R2), 3 (R3), 4 (R4) and 5 (R5) weeks of ripening phase. Incubation test was performed for BSW as-received (R0) and for BSW after 3 (R3) and 5 (R5) weeks of ripening phase. Respiration and incubation tests were conducted in duplicates. Differently, FTIR-spectroscopy was determined five times since the sample quantity to analyse was quite low (roughly 10 mg). Then the 5 spectra obtained were averaged for data analysis.

The 5 collected samples prior to and during the ripening phase (R0, R2, R3, R4, R5), after grinding to 0.63 mm, were also analysed to determine the organic matter content, the heavy metals total content and the contaminants release in water phase (leaching behaviour) by using the same analytical methods described in the previous section (page 37).

Results and discussion

Ripening phase monitoring

Figure 3.7 shows the setting of the air flow rate and the trends of temperature measured in the room and in the rotting material, as well as the CO_2 and O_2 concentrations measured in waste air during the lab ripening phase.

The highest temperatures, 10-15 °C higher than the room temperature, were measured in the first week of ripening with the maximum value equal to 41.5 °C registered in the 3rd day. During the 2nd week and half of the 3rd week, temperature decreased and kept around 35 °C, being 5 °C higher than the room temperature. In the last 10 days, a further decrease of temperature was observed by approaching to the room temperature and this was a first indication of the biological stabilisation of the material.

The maximum oxygen consumption and corresponding carbon dioxide release were registered at the beginning and in the 2nd week of the process, proving the high reactivity of the BSW as-received. It has to be noticed that between the 3rd and the 5th day, O_2 concentration in waste air significantly increased. This was due to the increase of the air flow rate from 20 l/h (set in the first day) to 60 l/h in order to keep O_2 concentration higher than 10 % (v/v) below which microbial activity may be strongly hampered or inhibited because of oxygen starvation. From the day 12 on, O_2 concentration kept at 10-11 % (v/v) and CO_2 at 8-9 % (v/v), increasing to 14 % (v/v) and decreasing to 6 % (v/v), respectively, in the last three days. This indicated again the achievement of biologically stable conditions.

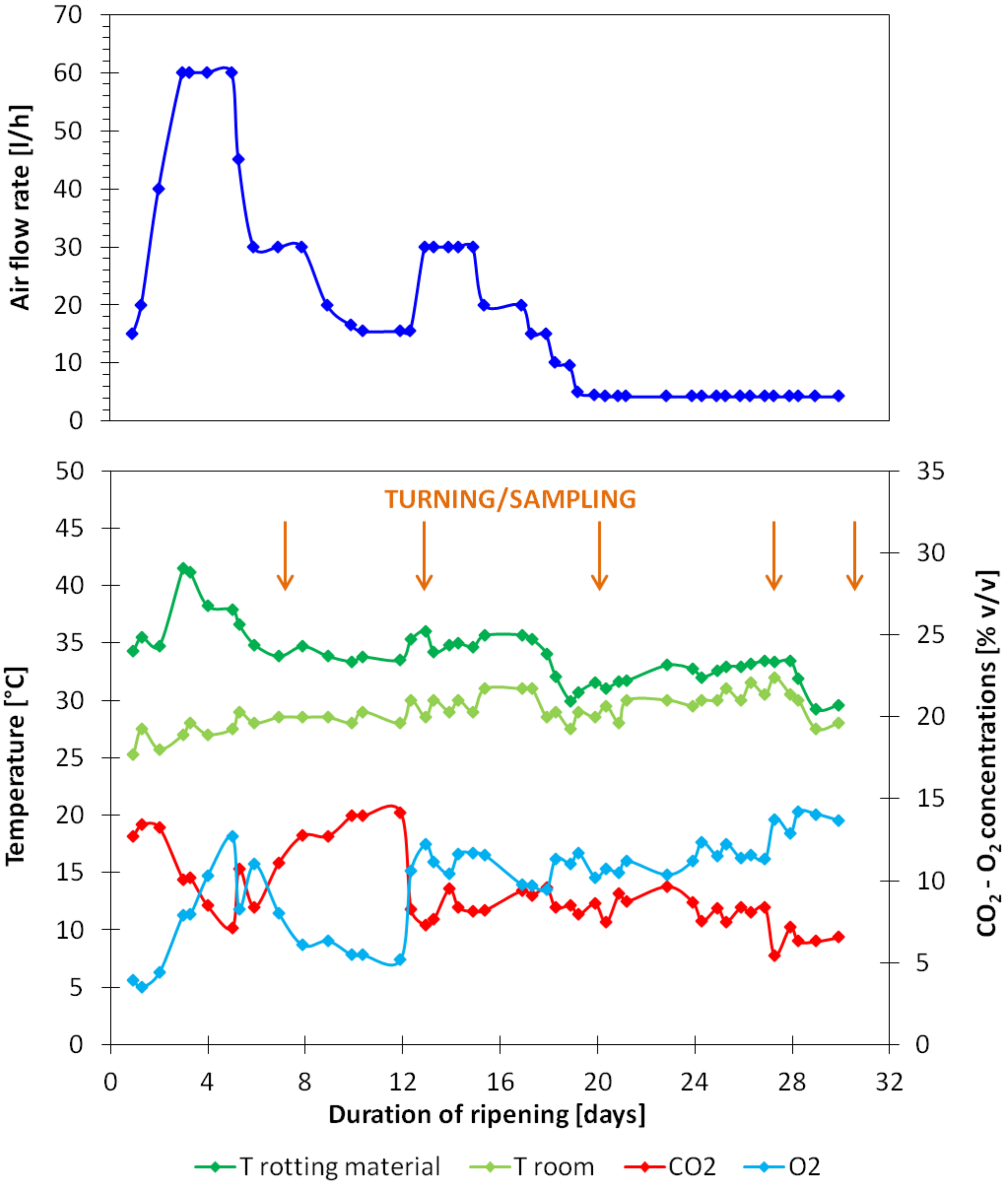

Figure 3.7 Setting of air flow rate and trends of temperature (rotting material and room), CO_2 and O_2 concentrations in waste air during the lab ripening treatment

Organic matter content and carbon mass balance

A slight reduction of organic matter content, in terms of TOC and VS, during the ripening phase was obtained, as showed in Table 3.5, where mean values along with standard deviations (of 3 repetitions) are highlighted. However TOC and VS showed to follow roughly the same linear decreasing trend (Figure 3.8a) during the ripening phase since, as also observed previously, such organic matter indices are well correlated.

Table 3.5 Results of organic matter content measured as VS and TOC

Sample	VS (% DM)	TOC (% DM)
R0	45.8 ± 0.1	21.7 ± 0.1
R2	40.9 ± 0.7	18.3 ± 0.04
R3	38.2 ± 0.2	19.0 ± 0.06
R4	37.2 ± 0.2	17.5 ± 0.08
R5	37.5 ± 0.1	16.6 ± 0.1
% reduction	18.1	23.5

In order to assess the amount of carbon lost and transformed in carbon dioxide, a mass balance in terms of C and CO_2 was determined. Specifically, the cumulative CO_2 and C mass were calculated by means of the following equations:

$$m_{CO_2,t} = \frac{V_{CO_2,t} \cdot Q \cdot \Delta t \cdot 24 \cdot MW_{CO_2}}{MV} \tag{3.1}$$

$$m_{C,t} = \frac{V_{CO_2,t} \cdot Q \cdot \Delta t \cdot 24 \cdot AW_C}{MV} \tag{3.2}$$

$$m_{CO_2,cum} = \Sigma\, m_{CO_2,t} \tag{3.3}$$

$$m_{C,cum} = \Sigma\, m_{C,t} \tag{3.4}$$

where

$m_{CO2,t}$ and $m_{C,t}$ are the weights in grams of carbon dioxide and carbon at time t, respectively;

$V_{CO2,t}$ is the volume (% v/v) measured at time t during the lab ripening phase (see Figure 3.7);

Q is the air flow rate (l/h) set during the ripening phase (see Figure 3.7);

Δt is the time interval between two CO_2 measures (days) and 24 is the conversion factor days – hours (h/d);

MW_{CO2} is molecular weight of carbon dioxide (g/mol);

AW_C is the atomic weight of carbon (g/mol);

MV is the molar volume (l/mol), i.e. $MV = MV_{st}\frac{T_t}{T_{st}}$, where MV_{st} = 22.4 l/h is the molar volume at standard temperature T_{st} = 273.15 K and standard pressure p_{st} = 1 atm (by assuming that CO_2 is a perfect gas) and T_t is the measured temperature at time t during the ripening phase (see Figure 3.7);

$m_{CO2,cum}$ and $m_{C,cum}$ are the cumulative mass in grams of carbon dioxide, equal to 2417.9 g and the cumulative mass of carbon, equal to 659.4 g.

Figure 3.8b shows the trend of the calculated cumulative carbon dioxide and carbon released during the ripening.

Then, the carbon percentage by weight was calculated as follow:

$$\%\,\mathrm{C} = 100 \cdot \frac{m_{c,cum}}{TOC_{in}} \qquad (3.5)$$

where TOC_{ini} is the initial TOC content (measured in the sample R0), expressed in grams. The resulting percentage carbon was found equal to 24.2 %, approximately corresponding to the TOC percentage reduction equal to 23.5 % (Table 3.5), indicating that the carbon mass loss was mainly due to transformation in CO_2 and no loss as DOC occurred.

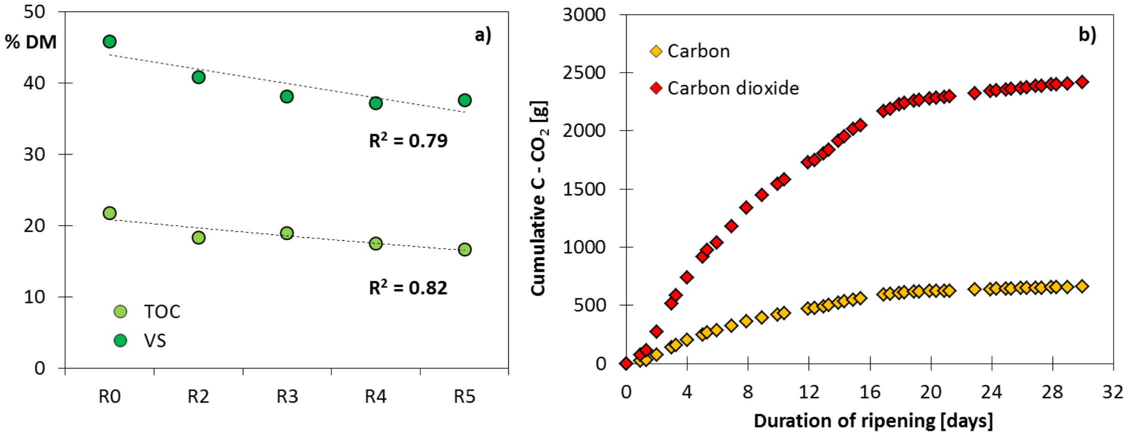

Figure 3.8 a) Decreasing trend of VS and TOC during the ripening phase and b) Cumulative amount of C-CO_2 released during the ripening phase

Biological tests

Table 3.6 shows the results of RA_4 (mean ± standard deviation for 2 repetitions per each sample) measured by Sapromat and OxiTop for the different samples. It can be noticed that BSW as-received (R0) was characterised by significant respiration activity, much higher than the limit value equal to 7 mgO_2/gDM set by the Austrian Landfill Ordinance (Binner et al., 2012). During the ripening treatment a reduction in respiration activity was observed by reaching RA_4 lower than the limit after 4 weeks. Furthermore, it has to be noticed that values found by OxiTop were a little bit lower than results from Sapromat. This is because Sapromat, based on a dynamic oxygen supply system, is less influenced by the possible deficit of oxygen than OxiTop which needs the periodically opening of the reaction vessels to replace consumed oxygen (Binner et al., 2012).

Table 3.6 Results of RA_4 (mgO_2/gDM) in Sapromat and OxiTop

Samples	Sapromat	OxiTop
R0	21.0 ± 0.05	17.0 ± 1.1
R2	12.3 ± 0.25	11.7 ± 0.05
R3	9.1 ± 0.45	7.9 ± 0.8
R4	6.1 ± 0.3	5.0 ± 0.05
R5	7.0 ± 0.25	6.8 ± 0.01

As showed in Figure 3.9, the average cumulative trend of oxygen consumption was found to be steep for sample R0 and then progressively less slope, reaching a certain stability showed by very similar trends of R4 and R5.

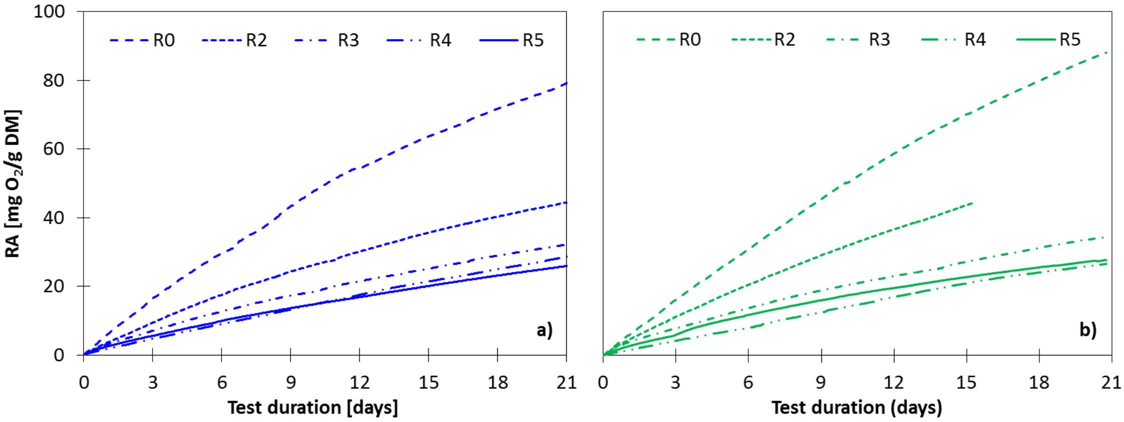

Figure 3.9 Cumulative trends of respiration activity in a) Sapromat and b) OxiTop

Table 3.7 shows the results of the incubation test. The average gas generation sum in 21 days was found to be high for R0 (BSW as-received) exceeding the limit of 20 Nl/kgDM set by the Austrian Landfill Ordinance (Binner et al., 2012). Values lower than the limit were obtained at the end of the process (5 weeks), when a significant reduction occurred.

It has to be observed that GS_{21} for repetition 1 of R0 was found to be quite low. This was due to the high reactivity of the material which caused the formation of acidification conditions, verified by the relatively low pH (< 7) measured in the leachate.

Table 3.7 Results of GS_{21} (Nl/kg DM)
(Nl indicates liters normalised to 0 °C and 1013 mbar)

Sample	Rep. 1	Rep. 2	Mean ± SD
R0	16.6*	45.5	45.5
R3	22.3	19.9	21.1 ± 1.2
R5	11.2	10.0	10.6 ± 0.6

* Outlier (lower finding due to acidification)

Differently, in order to reach methanogenic conditions more quickly and to promote biogas generation, for the 2nd repetition NaOH coins were added step by step (starting on day 13) to the pumped out leachate. The latter was then recirculated several times until pH reached a value ≥ 7. As a result, comparing the trends of gas generation sum of the two repetitions (Figure 3.10), it can be observed that repetition 2 reached a plateau after 60 days of incubation test whereas repetition 1 presented a much slower increasing trend. Furthermore, looking to the gas generation rate (Figure 3.10), it can be noticed that repetition 1 reached a peak 28 days later than repetition 2 and the maximum gas release was much lower. Regarding R3 and R5, maximum gas generation rates were registered in the days 27 and 19, respectively, being roughly 66 % and 82 % lower than the maximum gas generation rate found for R0 repetition 2.

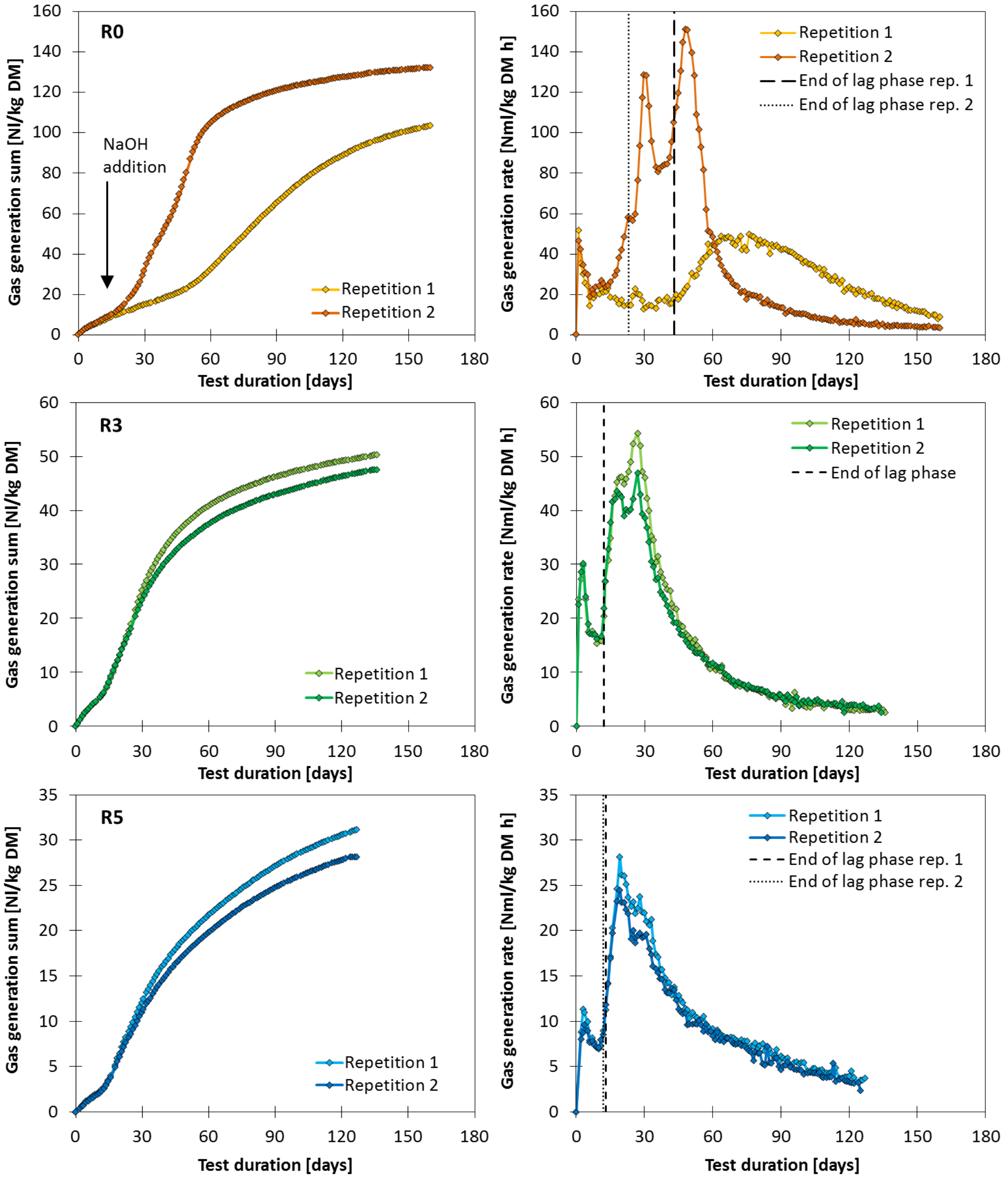

Figure 3.10 Trends of gas generation sum and gas generation rate during incubation test (attention to different scaling of y-axis)

FTIR-spectroscopic investigation

Figure 3.11 shows the FTIR-spectra of BSW investigated during the lab ripening phase. The most relevant indicator bands for MBT waste and the associated functional groups (Smidt and Meissl, 2006) are specified in Table 3.8 and highlighted in the graph (van Praagh et al., 2009; Böhm et al., 2010).

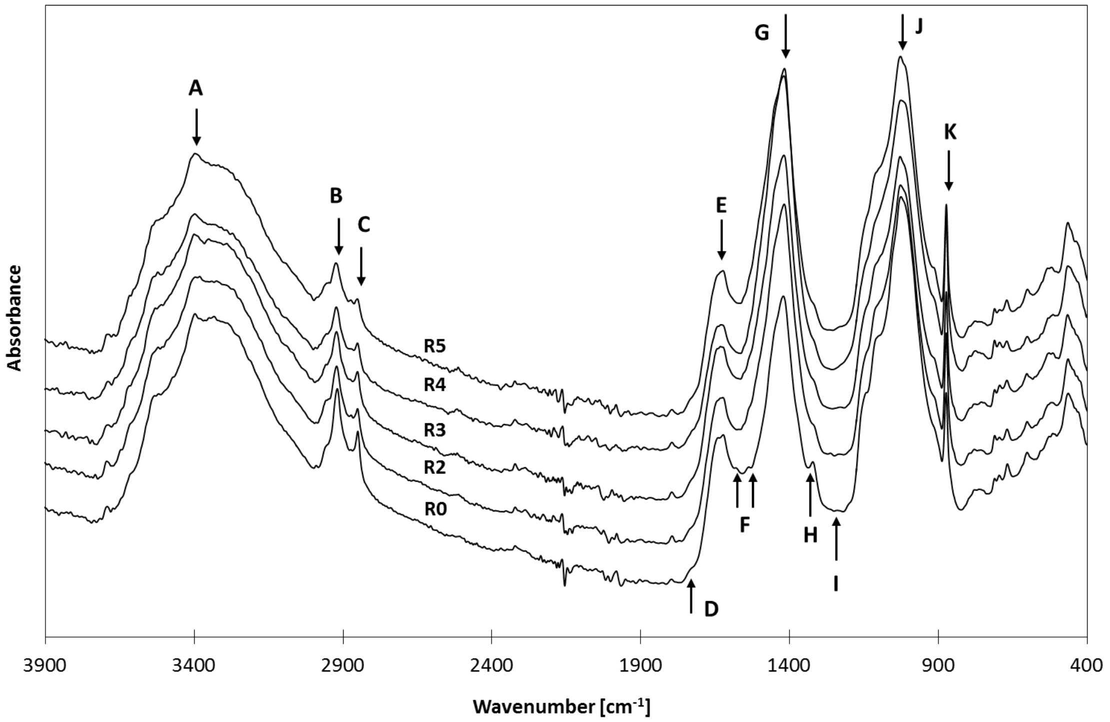

Figure 3.11 FTIR-spectra of BSW recorded during the ripening process

Bands, representing both organic and inorganic functional groups, undergo changes during a biodegradation process (Smidt et al., 2005). During the ripening process, it was observed that peak heights at 2920 cm^{-1} and 2850 cm^{-1} (aliphatic methylene, representing the skeleton of many biomolecules; Böhm et al., 2010), at 1740–1720 cm^{-1} (ketones, aldehydes, esters and the carboxylic group), and at 1640–1620 cm^{-1} (primary amide, carboxylates), tended to decrease due to decomposition of organic matter. Peaks at 1570–1540 cm^{-1} (secondary amides), at 1320 cm^{-1} (aromatic primary and secondary amines) and at 1260–1240 cm^{-1} (carboxylic acids, tertiary amides) disappeared after 2-3 weeks of ripening, indicating the biological stabilisation of the material (Smidt and Schwanninger, 2005). Bands at 1420 cm^{-1} and at 875 cm^{-1}, representing carbonates, and at 1030 cm^{-1}, attributed to clay minerals and silica, presented a relative increase due to the mineralisation. The band at 3400 cm^{-1}, associated to hydroxyl groups and absorbed water, showed a peak height roughly constant over time.

Table 3.8 Relevant indicator bands for BSW and associated functional groups

Functional group or component	Wavenumber (cm^{-1})	Assigned letter
Bonded and non-bonded hydroxyl groups and water	3400	A
Aliphatic methylene	2920	B
Aliphatic methylene	2850	C
Aldehyde, ketone, carboxylic acids, esters	1740 - 1720	D
Amide I, carboxylates	1640-1620	E
Amides II	1570-1540	F
Carbonate	1420	G
Aromatic primary and secondary amines	1320	H
Carboxylic acids - Amide III	1260-1240	I
Clay minerals - Silica	1030	J
Carbonate	875	K

Heavy metals total content and leaching behaviour

Table 3.9 shows the results of heavy metals (HM) total content (mean ± standard deviation for 3 repetitions per each sample) measured in the biostabilised waste as-received (R0) and in the BSW at the end of the ripening phase lasting 5 weeks (R5). Cadmium content was not reported since it was found lower than the limit of quantification. The results are compared with limit values reported by the Italian Decree (2006), the European Commission document (European Commission, 2001), the Austrian Compost Ordinance (ACO, 2001), as well as by the Scottish Environmental Protection Agency (SEPA) standard (Baird et al., 2005). It can be observed that soil contamination thresholds for use in residential sites (column A) were not fulfilled for both R0 and R5, and Ni content in R0 exceeded limits set by the Austrian Compost Ordinance and the Scottish EPA. Therefore, biostabilised waste after 5 weeks of ripening phase showed to be potentially utilised in environmental applications in commercial and industrial sites.

As previously discussed, HM total content changing during a biodegradation process is mainly influenced by three factors. In this case the heterogeneity of the material did not play a key role since BSW had a small particle size (< 20 mm) therefore it was quite homogeneous.

Table 3.9 Results of heavy metal total content in R0 and R5 and limit values (all values expressed in mg/kg DM)

Metals	R0	R5	Italian Decree 152/2006* A	Italian Decree 152/2006* B	EC doc 2001	ACO 2001	SEPA 2005
Al	11146.8 ± 1012.3	14130.2 ± 1664.1					
Ba	276.2 ± 24.1	331.5 ± 26.2					
Ca	70112.7 ± 4787.7	84043.1 ± 9204.1					
Co	4.0 ± 2.7	3.0 ± 0.3	20	250			
Cr	166.6 ± 181.8	33.9 ± 7.9	150	800	600	250	400
Cu	92.7 ± 20.8	150.6 ± 57.5	120	600	600	500	200
Fe	10640.8 ± 1453.9	11142.4 ± 1033.2					
K	7270.5 ± 521.2	8436.5 ± 860.3					
Li	8.1 ± 0.6	8.1 ± 0.8					
Mg	4328.0 ± 268.3	5186.3 ± 649.5					
Mn	217.5 ± 37.4	220.3 ± 32.7					
Na	129607.7 ± 12161.6	141679.0 ± 17078.4					
Ni	143.1 ± 150.6	54.4 ± 5.9	120	500	150	100	100
Pb	118.1 ± 13.9	147.6 ± 46.6	100	1000	500	200	200
Si	255.1 ± 28.8	277.6 ± 8.2					
V	22.9 ± 1.7	27.8 ± 3.3	90	250			
Zn	347.9 ± 104.8	375.3 ± 20.6	150	1500	1500	1800	1000

*Column A – soil contaminant thresholds for use in residential sites; Column B - soil contaminant thresholds for use in commercial and industrial sites

Furthermore the ripening phase was investigated at lab scale, unlike the previous investigation on the biostabilisation process which was conducted at real scale in the MBT plant, therefore higher quantities of material were involved by increasing much more the heterogeneity of the representative samples. As a result no big differences were found between the heavy metals total content in R0 and R5. However, heavy metals showed to be slightly more concentrated in R5 comparing with R0 likely due to mass loss during the ripening. In fact, by normalising the HM concentrations on the basis of VS content by means of the equation 2.4 (see **Chapter 2**, page 30), roughly the same values in R0 and R5 were found, as shown in Figure 3.12. The exceptions were Co, Cr and Ni which were lower in R5 than in R0.

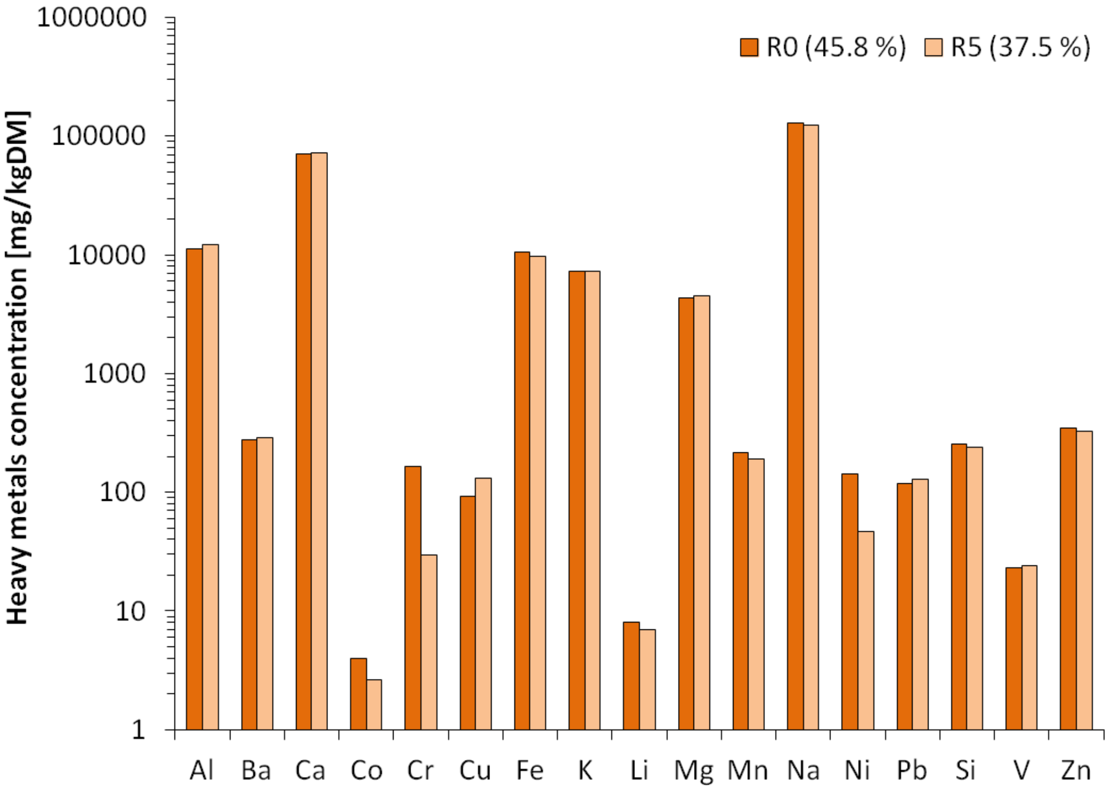

Figure 3.12 Metals corrected concentrations on the basis of VS content in R5 and comparison with metals content in R0

Table 3.10 shows the results of pH, DOC and chlorides (mean ± standard deviation for 2 repetitions per each sample) measured in the eluates obtained by the leaching test performed for the 5 BSW samples collected during the lab ripening phase and limit values of MD 186/2006 are also reported.

Table 3.10 Results of pH, DOC and chlorides measured in the eluates of the 5 BSW samples

Samples	**pH**	**DOC (mg/l)**	**Cl^- (mg/l)**
R0	6.8 ± 0.01	2065 ± 40.3	515.05 ± 12.0
R2	6.9 ± 0.01	1095.8 ± 30.0	544.35 ± 9.3
R3	7.2 ± 0.01	992.2 ± 17.7	764. ± 34.8
R4	7.2 ± 0.01	821.6 ± 7.2	708.2 ± 47.8
R5	7.4 ± 0.02	926.9 ± 58.1	838.5 ± 30.4
Limit	5.5-12	-	100

The pH values showed to slightly increase during the ripening phase from 6.9 to 7.4 which is the typical value of a biologically mature waste (Sirini et al., 2009). The dissolved organic carbon progressively reduced during 4 weeks of ripening, whereas at the end of the process DOC was higher. Unlike the intensive biodegradation phase in the biostabilisation basin (both the 4 weeks and the 7 weeks process), in this case chlorides showed to gradually raise during the ripening.

Table 3.11 shows the results of metal concentrations (mean ± standard deviation calculated for 2 repetitions per each sample) measured in the eluates of each BSW sample, as well as limit values set by MD 186/2006.

Table 3.11 Results of metal concentrations measured in the eluates of the 5 BSW samples

Values expressed in mg/l

Samples	Al	Ba	Ca	Cr	Cu	Fe	K
R0	1.3 ± 0.06	0.8 ± 0.01	540.5 ± 49.7	0.1 ± 0.02	0.4 ± 0.005	4.1 ± 0.1	283.3 ± 8.5
R2	1.1 ± 0.1	0.6 ± 0.07	603.9 ± 21.2	0.1 ± 0.0002	0.09 ± 0.009	6.1 ± 0.4	334.9 ± 6.1
R3	0.9 ± 0.004	0.7 ± 0.07	553.3 ± 1.5	0.09 ± 0.04	0.1 ± 0.04	4.7 ± 0.5	372.7 ± 2.5
R4	0.7 ± 0.07	0.7 ± 0.1	607.3 ± 113.3	0.08 ± 0.01	0.1 ± 0.01	4.8 ± 0.3	408.3 ± 30.8
R5	0.8 ± 0.2	0.7 ± 0.05	582.9 ± 120.4	0.06 ± 0.004	0.1 ± 0.03	5.2 ± 0.7	397.5 ± 25.3
Limit	-	1	-	0.05	0.05	-	-

Samples	Mg	Mn	Na	Ni	Pb	Si	Zn
R0	54.6 ± 1.9	0.8 ± 0.02	332.5 ± 17.5	0.2 ± 0.01	0.08 ± 0.003	5.6 ± 0.2	1.8 ± 0.02
R2	60.7 ± 0.9	0.4 ± 0.06	391.4 ± 5.6	0.1 ± 0.0002	0.03 ± 0.004	9.4 ± 0.4	1.0 ± 0.09
R3	60.5 ± 0.5	0.4 ± 0.004	435.6 ± 2.6	0.1 ± 0.04	0.1 ± 0.008	4.9 ± 0.04	1.1 ± 0.03
R4	64.7 ± 0.3	0.4 ± 0.04	483.7 ± 39.3	0.1 ± 0.003	0.04 ± 0.008	4.2 ± 0.4	1.1 ± 0.04
R5	63.0 ± 1.1	0.4 ± 0.01	467.8 ± 31.7	0.1 ± 0.03	0.03 ± 0.005	4.4 ± 0.3	0.9 ± 0.04
Limit	-	-	-	0.01	0.05	-	3

Values expressed in µg/l

Samples	Co	Li	V
R0	17.0 ± 0.6	11.8 ± 0.02	30.0 ± 0.7
R2	9.7 ± 1.5	11.7 ± 0.05	27.6 ± 2.3
R3	7.3 ± 0.2	8.3 ± 0.08	22.5 ± 0.1
R4	6.5 ± 0.3	9.2 ± 0.4	20.3 ± 3.0
R5	6.4 ± 0.5	9.2 ± 0.4	20.5 ± 2.7
Limit	250	-	250

For most metals, the concentrations in water phase slightly reduced during the ripening phase. The exceptions were the major elements, i.e. Ca, Fe, K, Mg, Na, whose concentrations slightly increased in the eluates. Comparing HM concentrations with limit values, again only Co and V fulfilled the limit values set by MD 186/2006, hence, according to this regulation, also biostabilised waste subjected to ripening phase could not be recovered.

The heavy metals and organic carbon percentage release was then calculated by means of the equation 2.5 (see **Chapter 2**, page 31), as shown in Figure 3.13. Results confirmed that most metals and organic carbon percentage release reduced at the end of the ripening. Differently, chromium, potassium, sodium and nickel release increased comparing with non-ripened BSW. Cr was probably oxidised to the hexavalent form (Cr^{VI}), which is more soluble than the trivalent form (Cr^{III}) (US EPA, 1999). Furthermore Cr^{VI} forms compounds with K and Na which can be very soluble at relatively high pH (7–8) (US EPA, 1999), as it is in this case. The higher sodium release after 5 weeks of ripening was assumed to be also influenced by the binding with chlorides whose leaching increased during the process, as previously discussed. Lastly, the higher nickel percentage release was likely due to the increase of pH (van der Sloot et al., 2004).

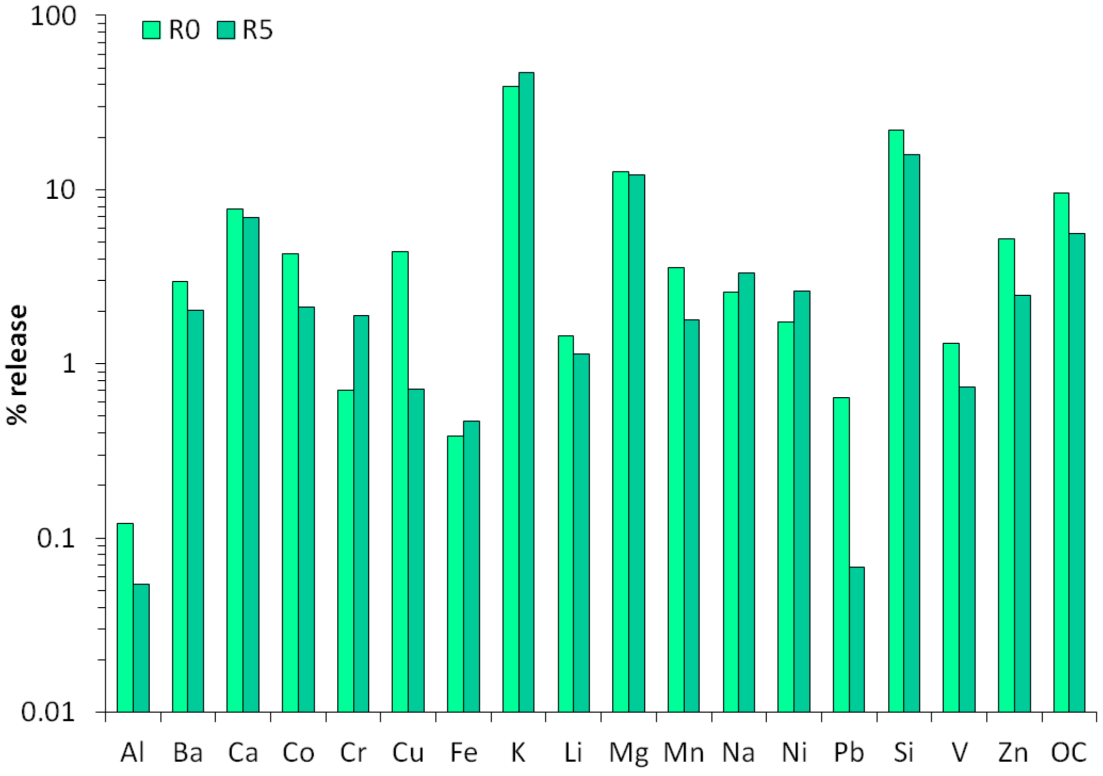

Figure 3.13 Comparison of heavy metals and organic carbon (OC) percentage release between R0 and R5

COMPARISON BETWEEN BSW OUTPUTS FROM THE LONGER BIOSTABILISATION PROCESS AND FROM THE RIPENING PHASE

Figures 3.14 and 3.15 show the trends of the dynamic respiration index (DRI) and respiration activity (RA_4) during the 7 weeks of biostabilisation process and during the ripening phase, respectively. It has to be pointed out that DRI for samples from the ripening phase, as well as RA_4 for samples from the intensive biostabilisation, were calculated by means of the correlation equation 3.1 (page 40).

A progressive and significant reduction of the biological reactivity was observed by following an exponential decreasing trends for both respiration indices, as highlighted by the high correlation coefficients (DRI: $R^2 = 0.93$ for longer biostabilisation and $R^2 = 0.86$ for ripening phase; RA_4: $R^2 = 0.99$ for longer biostabilisation and $R^2 = 0.86$ for ripening phase).

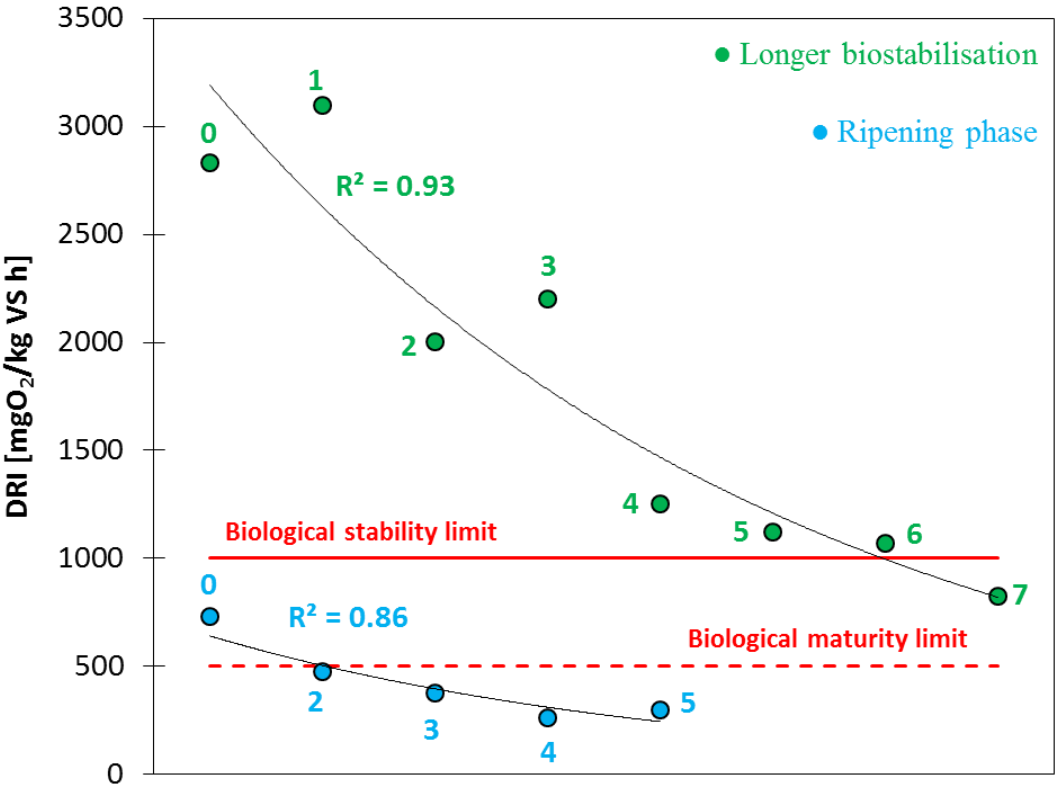

Figure 3.14 Trends of DRI during the 7 weeks of biostabilisation process and during the ripening phase

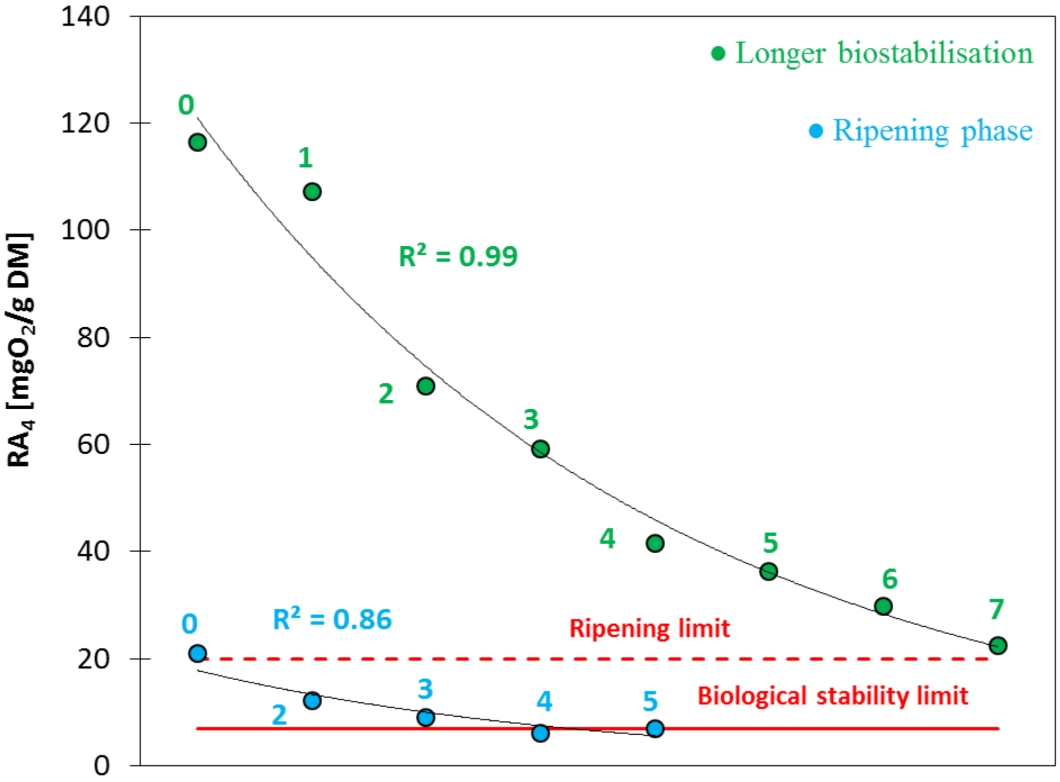

Figure 3.15 Trends of RA_4 during the 7 weeks of biostabilisation process and during the ripening phase

A high biological stability was obtained after 4 weeks of additional ripening phase when DRI was lower than the limit equal to 500 $mgO_2/kgVS·h$,, below which the material is considered biologically mature (Adani et al., 2004), and RA_4 was lower than 7 mgO_2/gDM, namely the limit set by the Austrian Landfill Ordinance. Furthermore, it can be noticed that BSW7 and R0 approached the RA_4 limit equal to 20 $mgO_2/kgDM$ set in order to evaluate the change of the treatment configuration, in MBT plants, from closed system (intensive biodegradation phase) to opened system (ripening phase). Therefore the two outputs from the biostabilisation at forced aeration conditions (lasting 7 weeks, BSW7, and 4 weeks, R0, respectively) showed to have the characteristic suitable for being subjected to a ripening phase.

Regarding heavy metals, chromium, copper, lead, nickel and zinc were taken into account for the comparison between BSW outputs from the two biodegradation phase (intensive biostabilisation, BSW7, and ripening, R5) since they are considered of greatest concern for a possible downstream environmental application. In fact, they are readily leachable and tend to bio-accumulate, causing short or long-term toxic effects to organisms in the environment and, therefore, they are the most commonly regulated in the field of organic waste (Richard & Woodbury, 1992; Whittle & Dyson, 2002; Castaldi et al., 2006). Furthermore, such metals are known to have a high affinity with organic carbon (Greenway & Song, 2002; Amir et al., 2005; Castaldi et al., 2006; van Praagh et al., 2009), by influencing their repartition solid/water phase.

Figure 3.16 shows the heavy metals total content comparison between BSW7 and R5. It can be observed that Ni, Pb and Zn had roughly the same concentrations in the two samples. Cu content was higher in R5 than in BSW7 likely because it tended to be bound to solid organic matter, unlike Cr content which was lower in R5.

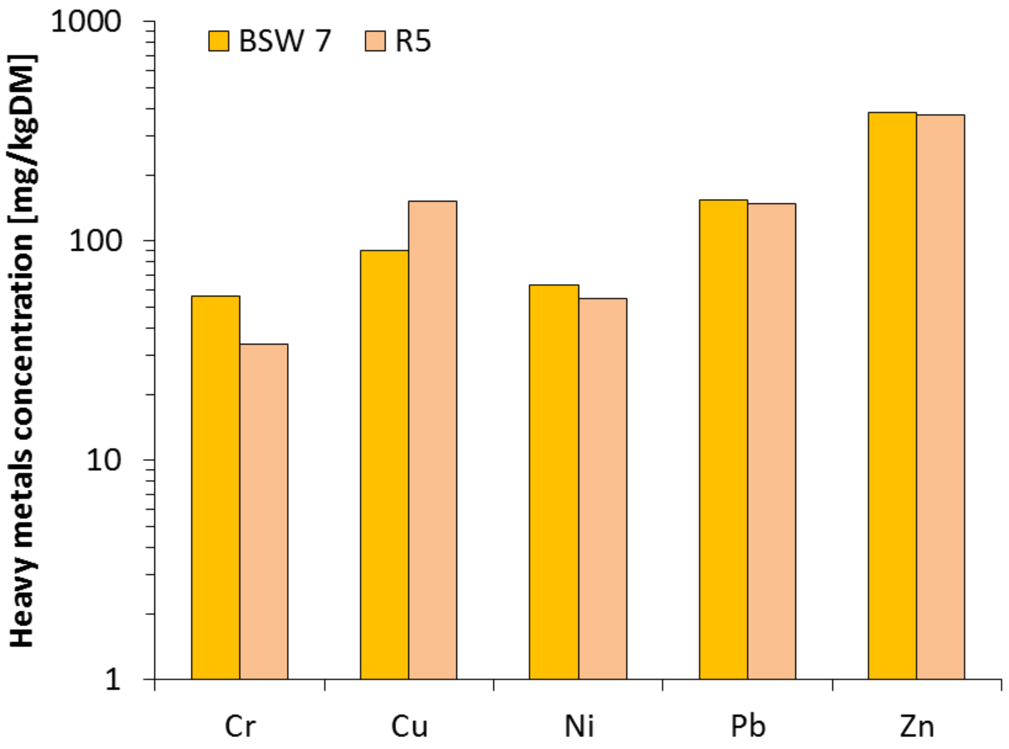

Figure 3.16 HM total content comparison between BSW7 and R5

Such consideration on chromium was confirmed by the release behaviour, as shown in Figure 3.17. Indeed, Cr had a higher release for R5, comparing with BSW7, probably because at the final stage of ripening it was in the more soluble Cr^{VI} form (as previously discussed). Differently, the release of the other metals, as well as of the organic carbon, showed be lower at the end of the ripening phase, indicating that metals were held on the solid organic matter, probably adsorbed to humic substances (Grimes et al., 1999;

Greenway and Song, 2002), since, as observed previously, BSW after 4 weeks of ripening phase showed to be biologically mature. Therefore, the degree of biostabilisation reached by the organic matter appears to be essential in determining the potential mobility of heavy metals (Castaldi et al., 2006).

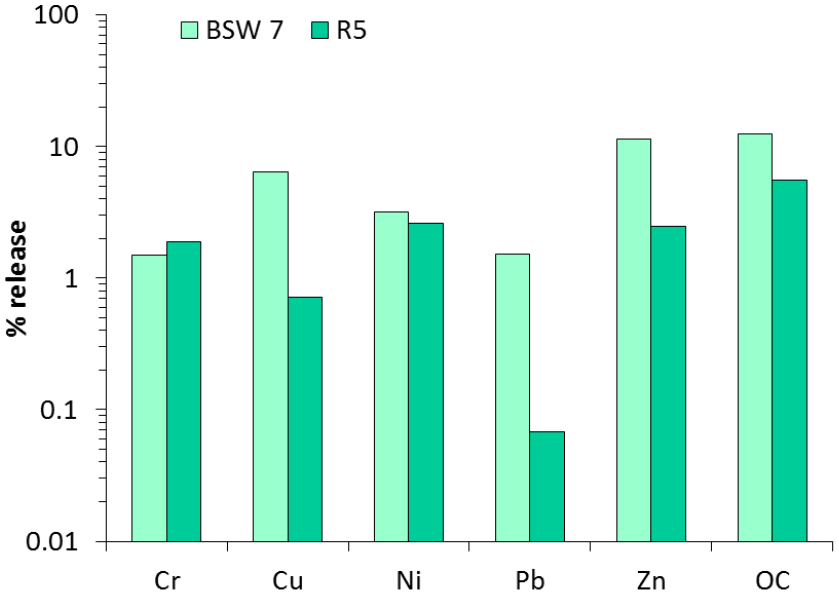

Figure 3.17 Comparison of heavy metals and organic carbon (OC) percentage release between BSW7 and R5

CONCLUSIONS AND PERSPECTIVES

The present research study aimed to assess the possible biostabilised waste recovery/utilisation, in alternative to landfilling, by evaluating different operating conditions and retaining times.

A first evaluation on the quality of the biostabilised waste (BSW) as currently treated by two MBT plants of Rome was carried out. Results on the biological and physical-chemical characteristics led to conclude that the BSW did not have a suitable quality for waste recovery. More specifically, the biostabilised waste was found still highly reactive after 4 weeks of intensive biodegradation process. Furthermore heavy metals total content was quite high and, in some cases, showed to exceed limit values set by some European regulations for waste recovery. A possible solution is to separate from biostabilised waste the fraction having particle size higher than 10 mm (which was found composed of high content of impurities and heavy metals) by obtaining a reduction in chemical-physical contamination without great losses in terms of mass and organic matter. The “refined” BSW (< 10 mm) could be used in environmental remediation applications (in commercial and industrial sites) whereas fraction higher than 10 mm could be sent to thermal treatment coupled to energy recovery rather than landfilling, given the great content of high calorific value materials.

Considering the unsuitability for recovery of the biostabilised waste as currently treated, second step of the research was to evaluate the influence on BSW characteristics of longer duration of the aerobic biological process. Specifically, an extension from 4 weeks, which is the duration in normal operating conditions of the plant, to 7 weeks of the biodegradation process at forced aeration condition, occurring in one of the two MBT plants of Rome considered in this work, was evaluated. Furthermore, a good biostabilised output, coming from the intensive biodegradation lasting 4 weeks, was subjected to a ripening treatment in slightly aerated lab test cells in order to analyse and evaluate a possible further increase of the biological stability and the related changing in physical-chemical characteristics. Regarding the biological reactivity, for both investigated stages (i.e. intensive biostabilisation for 7 weeks and ripening phase for 5 weeks), results confirmed that the biostabilised waste was highly reactive after 4 weeks of intensive biodegradation treatment. In the case of use as landfill cover, this would lead to acidification conditions and to high emissions of methane (as shown by the results of the incubation tests measuring the biogas generation), which is known to have a high green-house effect. By extending the process duration to 7 weeks, a good biological stability degree was reached. Furthermore it was observed that an additional ripening phase lasting at least 4 weeks (as indicated by lab-tests, possibly longer duration will be necessary in-situ) should be carried out in order to obtain a highly biostabilised waste, acquiring the characteristics of a biologically mature material.

The metals total content in the BSW outputs, both from the intensive biostabilisation process and from the lab ripening phase, was found to fulfil the requirements for a potential utilisation in environmental remediation applications but the latter have to be restricted to commercial and industrial sites (as indicated by the Italian regulatory regime).

Contaminants release in water phase showed to increase for some metals (i.e. Cu and Pb) during the biostabilisation of 7 weeks comparing with the untreated waste, due to the significant affinity with the dissolved organic carbon (by forming leaching complexes) which showed to be higher at the end of such process. Differently, most metals release was lower for ripened waste comparing with the output of the intensive biostabilisation process because they were bound to solid organic matter, probably adsorbed to humic substances. Only the release of chromium during the ripening phase showed to increase since it was probably in the Cr^{VI} status which forms very soluble compounds with K and Na (which showed a higher release at the of the ripening phase, as well), at pH in the range 7–8.

Furthermore the results of the leaching tests showed that heavy metals concentrations in the eluates of all BSW outputs (from 4 weeks and 7 weeks of biostabilisation process as well as from the lab ripening phase) did not fulfil the limits set by the Italian Ministerial Decree 186/2006 on non-hazardous waste recovery. Therefore from this point of view the biostabilised waste showed to not have a suitable quality for a possible recovery and this was in contrast with what was found for the heavy metals total content.

In conclusion, the only feasible utilisation for the biostabilised waste showed to be in monitored environments, such as in landfill sites as cover material, where the release of contaminants is controlled through the collection of the percolate and its subsequent treatment. However, it is important to remark that, even in the use as landfill cover, the biostablised waste need to be subjected to a longer duration of the biological process, including a ripening phase, otherwise strong pollutant loading may occur, such as high long-term biogas emissions.

Other uses of the biostabilised waste, such as in soil applications for landscape restoration, may be considered under the constraint to apply a risk assessment procedure on a site-specific level in order to evaluate the potential risk for receptors (groundwater and surface water, plants, animals and humans) and to establish at which acceptable levels of pollutants, taking also into account the migration routes, such land application is not harmful to the environment and the human health. Therefore, the observations and evaluations highlighted in the present research thesis could be useful in the development of such risk assessment.

In view of this, further surveys on the quality of the biostabilised waste coming from the MBT plants of Rome will be performed by considering the use of fresh water to add to the rotting material in the biostabilisation basin, rather than recirculating the percolate produced during the biodegradation process (current operating condition of the MBT plants of Rome). Moreover, additional investigations and evaluations on the biostabilised waste behaviour during a ripening phase and its final quality (in terms of biological stability degree and heavy metals content and release) need to be conducted by subjecting it to a real scale process.

Lastly, deeper investigations on leaching of contaminants, e.g. by means of pH dependence test and percolation test, has to be carried out as well in order to better understand release controlling mechanisms (e.g. by analysing the humic substances content in BSW and their release in water phase since they are known to strongly influence the mobility of some heavy metals) and to assess long term leaching behaviour.

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