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Assessment of management strategies for different types of waste thermal treatment bottom ash based on modelling of experimental leaching data

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ABSTRACT

Thermal treatment of waste materials such as commingled municipal solid waste, selected fractions of municipal solid waste (e.g. refuse derived fuel, RDF or Solid Recovered Fuel, SRF) or special waste (e.g. hospital waste), in Waste to Energy (WtE) plants (e.g. combustion or gasification facilities), generates different types of solid residues, among which the most abundant are bottom ash (BA), which generally account for 10-20 wt.% of the input waste mass. This slag-like material is produced worldwide in large quantities. Over the past few decades, in some European countries (e.g. Denmark and The Nederland), BA from incineration of Municipal Solid Waste (MSWI) is increasingly being recycled in construction applications (e.g. in road foundations, as aggregate in concrete or embankments) due its suitable physical (e.g. bulk density, particle size) and mechanical properties (e.g. compressive strength). However, the main concern regarding the utilization of BA is related to possible contamination of the environment due to potential release of harmful compounds upon contact with water (i.e. its leaching behaviour). In fact, compared to natural aggregates, BA generally exhibits higher concentrations of contaminants (e.g. metals, metalloids and salts) that, depending on its specific characteristics and the environmental conditions to which it can be subjected to, may be more or less mobile. Thus, to ensure that the utilization or disposal of this type of residue is environmentally safe, its leaching behaviour in terms of the release of salts and toxic metals needs to be thoroughly investigated. Standardized laboratory leaching tests are frequently used tools to assess the potential release of contaminants from BA. Results from leaching tests alone might not be sufficient to predict the overall environmental impacts resulting from the reuse/disposal of BA; however, these may be used as input data for evaluation tools, such as risk assessment and life cycle assessment (LCA), which allow to quantify potential impacts on the environment and human health.

The main objective of this doctoral thesis was to evaluate management strategies for bottom ash (BA) produced by three different types of waste thermal treatment plants, paying particular attention on the environmental consequences associated with the release of contaminants from these residues in the specific disposal/reuse scenarios selected. This evaluation was achieved by combining the most significant results obtained applying different types of leaching test (i.e. column percolation tests, batch tests as a function of L/S ratio, compliance leaching tests and pH-dependent leaching tests), with assessment methods such as LCA and risk assessment. Particularly, two different management scenarios, namely landfill disposal and reuse as unbound filler material in a road sub-base construction, were evaluated. BA samples generated from (i) a refuse derived fuel incineration plant (RDF-I BA), (ii) a refuse derived fuel gasification facility (RDF-G BA) and (iii) a hospital waste incineration plant (HW-I BA), were considered. These specific types of BA were selected since their leaching behaviour and potential alternative management options have been significantly less investigated up to now compared to MSWI BA.

The results of the experimental activity indicated a fairly lower release of contaminants, as a function of both the L/S ratio and pH, for the RDF-G BA, which showed to comply with acceptance criteria for inert waste landfilling. While HW-I BA and RDF-I BA only met the limit values set for disposal in non-hazardous waste landfills. However, the latter type of BA (i.e. RDF-I BA) displayed a generally higher release of amphoteric metals (i.e. Pb, Zn and Cu) and chlorides. Moreover, a remarkable difference in the acid neutralization capacity (ANC) of the RDF-I BA compared to the other two types of BA, was observed. Indeed, while RDF-G BA and HW-I BA showed an almost negligible ANC, which was associated to their mineralogy mainly made up by amorphous phases, RDF-I BA displayed a significant ANC for pH values between 11 and 12, due to the abundance of hydrated phases detected in its solid matrix.

In order to decrease the leaching of contaminants from the RDF-I BA the effect of (i) the removal of the fine particle size fraction ($d<0.425$mm), which showed a rapid and high release of contaminants, from the bulk sample of RDF-I BA and (ii) a natural weathering treatment, carried out at laboratory scale for a time period of 12 months, were also investigated. While the first treatment showed not to be effective, since the fine particle size fraction represented only 10% by weight of the total sample of the

RDF-I BA; the weathering process has led on the one hand to a relevant decrease of the release of Ba, Cu and to a lower extent of Pb, but on the other hand showed to favour the mobilization of oxyanion-forming metalloids such as Cr and Mo.

From the comparison between batch and column percolation tests as a function of the L/S ratio, carried out on each type of BA, a generally higher release (of up to two orders of magnitude) was observed for the batch tests. This finding was mainly attributed to the fact that, differently from the batch experiments, in the column tests the continuous renewal of the leachant solution can lead to non-equilibrium release conditions. This was also confirmed by the interpretation of the column test results with an analytical model that showed that most of the observed leaching trends could be described quite well assuming the contaminants release to be limited by mass-transfer.

Finally, the results of the LCA indicated that when assessing possible management strategies for BA, its environmental properties should be surely included, since the leaching behaviour showed to significantly affect environmental impacts, especially with respect to toxicity-related categories, proving to vary case by case depending on the type of BA considered. This finding may have important implications for the management of the analysed types of BA, since up to now at least in Italy the same strategies (i.e. mainly disposal in landfills for non-hazardous waste) were applied for all kinds of bottom ash. However, it appears that, depending on the specific origin of the BA, alternative management options such as reuse in road as unbound material may also be viable. In particular, from an environmental perspective, the residues that showed the lowest impacts and hence may potentially be the most fit for reuse applications are the RDF-G BA, although as also found by LCA its negligible ANC could represent a limiting factor. Anyhow, from the risk assessment study, the obtained results highlighted that reuse in road may be a suitable alternative to landfilling also for the other two types of BA (i.e. RDF-I BA and HW-I BA). In fact, when the contaminants attenuation factors (i.e. LDF and SAM) were considered, the concentration values of metals and inorganic compounds estimated in the groundwater table, for a time period of 100 years, have shown not to exceed the limit values for groundwater protection set by the Italian legislation.

SOMMARIO

Il processi di trattamento termico dei rifiuti, come ad esempio i rifiuti solidi urbani indifferenziati, frazioni pre-trattate di rifiuti (quali ad es. combustibile derivato da rifiuti, CDR o combustibile solido secondario, CSS) o rifiuti speciali (per es. rifiuti ospedalieri), in appositi impianti di termovalorizzazione (quali inceneritori e gassificatori), generano diverse tipologie di residui solidi, tra cui il più abbondante, pari circa al 10-20 % in peso dei rifiuti trattati, è rappresentato dalle scorie di fondo (bottom ash, BA).

Il crescente impiego della termovalorizzazione dei rifiuti ha suscitato, negli ultimi anni, un forte interesse nell'individuazione di adeguate strategie gestionali per le BA, che grazie alle loro caratteristiche fisiche (es. densità e granulometria) e proprietà tecniche (es. resistenza a compressione) molto simili a quelle degli aggregati naturali, si prestano ad essere riutilizzati come materiale da costruzione. Per tali ragioni, il recupero delle BA in vari settori dell'ingegneria civile (principalmente nella costruzione di sottofondi stradali e come aggregati nel calcestruzzo) è sempre più praticato in diversi Paesi Europei, come ad esempio l'Olanda e la Danimarca. Tuttavia, rispetto agli inerti naturali comunemente impiegati nell'edilizia, le BA generalmente presentano una maggiore concentrazione di componenti potenzialmente tossici per l'ambiente, quali metalli (es. Pb, Cu e Zn), metalloidi (es. Cr, Mo e Sb) e sali (es. cloruri e solfati), che a seconda delle specifiche caratteristiche delle BA e delle condizioni ambientali a cui esse vengono sottoposte, se a contatto con acqua, possono essere più o meno rilasciati (o lisciviati) nell'ambiente. Pertanto, una corretta valutazione di possibili opzioni di gestione per le BA, richiede uno studio approfondito del comportamento a lisciviazione di questi residui e un'appropriata analisi dell'impatto ambientale derivante dal rilascio di composti tossici nello specifico scenario di smaltimento/riutilizzo ipotizzato. I test di cessione su scala di laboratorio sono gli strumenti più utilizzati per la determinazione del potenziale rilascio di contaminanti dalle BA e più in generale da materiali granulari. Tuttavia, i risultati ottenuti dai test di cessione non sono sufficienti a prevedere i complessivi impatti ambientali relativi a specifici scenari di smaltimento/riutilizzo per le BA; di conseguenza, essi dovrebbero essere utilizzati come dati di input per strumenti di valutazione quali l'analisi del ciclo di vita (LCA) e l'analisi di rischio che permettono di esaminare in maniera più ampia e anche di quantificare le conseguenze ambientali e sulla salute umana associate al rilascio di contaminanti da questi materiali.

Il principale obiettivo della presente tesi di dottorato è stato quello di valutare le strategie di gestione applicabili per tre tipologie di BA prodotte da diversi impianti di trattamento termico dei rifiuti, ponendo particolare attenzione alle conseguenze ambientali connesse con il rilascio di contaminanti da questi residui in specifici scenari di smaltimento/riutilizzo. Per esaminare i diversi scenari selezionati, i risultati ottenuti applicando diverse tipologie di test di cessione (test di percolazione in colonna, prove in modalità batch in funzione del rapporto liquido solido (L/S), test di conformità e test in batch in funzione del pH) sono stati utilizzati come parametri di input in strumenti di valutazione quali l'LCA e l'analisi di rischio.

In particolare, per ciascuna tipologia di BA considerata, sono state valutate due differenti opzioni di gestione, ossia lo smaltimento in discarica e il riutilizzo come materiale di riempimento non legato per la costruzione di un sottofondo stradale. Le tre tipologie di BA analizzate in questo studio sono state prodotte da: (i) un impianto di incenerimento di CDR (refuse derived fuel incineration, RDF-I BA); (ii) un impianto di gassificazione di CDR (refuse derived fuel gasification, RDF-G BA); (iii) un impianto di incenerimento di rifiuti ospedalieri (hospital waste incineration, HW-I BA). Queste specifiche tipologie di BA sono state selezionate in quanto, a causa del recente impiego di tecnologie quali l'incenerimento e la gassificazione per la valorizzazione energetica del CDR, così come del piuttosto limitato numero di impianti esclusivamente dedicati al trattamento termico dei rifiuti ospedalieri, c'è una carenza di studi riguardanti il loro comportamento ambientale e possibili opzioni gestionali alternative allo smaltimento in discarica.

I risultati dell'attività sperimentale hanno mostrato un rilascio piuttosto limitato di contaminanti, sia in funzione del L/S che del pH, per le RDF-G BA, che sono risultate conformi ai criteri di accettazione in discariche per rifiuti inerti. Mentre le HW-I BA e

le RDF-I BA hanno dimostrato di rispettare i valori limite fissati per lo smaltimento in discarica per rifiuti non pericolosi. Tuttavia, in generale per le scorie da incenerimento del CDR (RDF-I BA) è stato osservato un rilascio maggiore di contaminanti (es. Ba, Cloruri, Cu, Pb e Zn). Inoltre, questa tipologia di BA ha mostrato una capacità di neutralizzazione acida (ANC) notevolmente differente rispetto a quella osservata per le altre due tipologie di BA. Infatti, mentre le RDF-G BA e HW-I BA hanno presentato un’ANC quasi trascurabile, che è stata associata alla loro mineralogia principalmente costituita da fasi amorfe, le RDF-I BA hanno mostrato una significativa ANC per valori di pH compresi tra 11 e 12, dovuta all'abbondanza di fasi idrate identificate nella sua matrice solida tramite analisi XRD.

Al fine di ridurre la lisciviazione di contaminanti dalle RDF-I BA sono stati inoltre valutati gli effetti (i) della rimozione della frazione granulometrica più fine (d <0.425 mm) dal campione totale di RDF-I BA, che aveva presentato un rilascio molto rapido e più elevato di contaminanti e (ii) di un trattamento di invecchiamento naturale, effettuato su scala di laboratorio per un periodo di 12 mesi. Mentre il primo trattamento ha dimostrato di non essere efficace, in quanto la frazione fine rappresenta solo il 10% in peso del campione totale della RDF-I BA; il processo di invecchiamento naturale ha portato da un lato ad una rilevante diminuzione del rilascio di elementi quali Ba, Cu e in misura minore Pb, dall'altro ha invece mostrato di favorire la mobilitazione degli ossianioni (ad es. Cr e Mo).

Dal confronto tra i risultati ottenuti dai test di lisciviazione in batch e in colonna in funzione del L/S, per la maggior parte degli elementi analizzati e per tutte e tre le tipologie di scorie, i test in batch hanno generalmente mostrato valori di concentrazione maggiori (fino a due ordini di grandezza). Questo risultato è stato principalmente attribuito al fatto che nei test in colonna, diversamente dagli esperimenti in batch, il continuo rinnovo della soluzione lisciviante può portare ad un rilascio governato da condizioni di non equilibrio. Ciò è stato anche confermato dall'interpretazione dei risultati dei test in colonna con un modello analitico tramite il quale si è potuto appurare che la maggior parte degli andamenti di lisciviazione osservati può essere ben descritta assumendo che il rilascio dei contaminanti sia limitato dal trasferimento di massa.

Infine, i risultati ottenuti dall'LCA hanno indicato che nella valutazione di possibili strategie di gestione per le BA, le proprietà ambientali di questi materiali devono essere sicuramente tenute in conto, in quanto il comportamento a lisciviazione ha dimostrato di influenzare in modo significativo gli impatti ambientali, in particolare per quanto riguarda le categorie di impatto legate alla tossicità, mostrando di variare caso per caso a seconda della specifica tipologia di BA considerata. Questo risultato può avere importanti implicazioni per la gestione delle BA considerate in questo studio, in quanto fino ad ora almeno in Italia per tutte le tipologie di BA generate da trattamento termico dei rifiuti vengono applicate le stesse modalità di gestione, ovvero prevalentemente lo smaltimento in discariche per rifiuti non pericolosi. Tuttavia, i risultati di questo studio suggeriscono che, a seconda dell'origine specifica delle BA, queste potrebbero essere adottate anche per opzioni di gestione alternative come ad esempio nella realizzazione di sottofondi stradali. In particolare, da un punto di vista ambientale, i residui che hanno mostrato di essere potenzialmente i più idonei all'utilizzo sono le RDF-G-BA anche se, come rilevato anche nello studio di LCA la sua bassa capacità di neutralizzazione acida potrebbe rappresentare un fattore limitante. Comunque, i risultati ottenuti applicando l'analisi di rischio hanno evidenziato che il riutilizzo nella costruzione di sottofondi stradali può essere una valida alternativa alla discarica anche per le altre due tipologie di BA (cioè RDF-I BA e HW-I BA). Infatti, nei casi in cui sono stati considerati i fattori di attenuazione della lisciviazione di contaminanti, i valori di concentrazioni di metalli e composti inorganici stimati nella falda, per un periodo di tempo di 100 anni, hanno dimostrato di non superare i valori limite stabiliti dalla normativa Italiana per la protezione delle acque sotterranee.

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INTRODUCTION AND OVERVIEW

BACKGROUND

Thermal treatment of Municipal solid waste (MSW) with energy recovery is one of the most established and applied technologies (Eurostat, 2011) within the integrated waste management systems employed in developed countries. The main advantages of waste thermal treatment are on the one hand the significant reduction in weight (by 70-80 %) and volume (by 80-90 %) of the treated waste, and on the other hand, the possibility of utilizing the energy content of the waste to convert it to heat and electricity (Chandler et al., 1997; Consonni et al., 2005; Münster and Lund, 2010; Arena, 2012). However, the main problem related to this technology is that it generates various types of solid residues and gaseous emissions. Nevertheless, while the latter are limited by increasingly advanced flue gas cleaning technologies with high removal efficiencies, the majority of incombustible components and the products resulting from the treatment of the stack gases ends up in the solid residues. The most common solid waste streams from waste thermal treatment are: bottom ash (BA), grate siftings, boiler ash, economizer ash and air pollution control (APC) residues, i.e. fly ash and/or residues from cleaning of acid stack gasses (Hjelmar et al., 2010). Bottom ash by far represents the most abundant solid residue, accounting for 10-30% of the input waste mass (Chandler et al., 1997; Sabbas et al., 2003). As BA exhibits similar technical properties to those of natural aggregates, in recent years, several efforts have been made in order to encourage the recycling of BA as a secondary material in construction applications (Crillesen and Skaarup, 2006). This may result in two main beneficial effects: (1) a decrease in waste landfilling, which presents significant environmental impacts including land use and (2) a reduction in the consumption of virgin raw materials. The main recycling options proposed for BA are either as filling material in road sub-base construction (Åberg et al., 2006; Lidelöw and Lagerkvist, 2007; Hjelmar et al., 2007) or as an aggregate in concrete manufacturing (Ferraris et al., 2009; Cioffi et al., 2011; van der Wegen et al., 2013). Although technical properties are the first requirement to be fulfilled, the main concern related to the reuse of such materials is the possible contamination of the environment due to the release of toxic compounds upon contact with water (i.e. leaching). In fact, compared to natural aggregates, BA generally exhibits a higher content of contaminants (such as metals, metalloids and salts) that depending on the environmental conditions to which the material may be subjected to and the specific characteristics of the BA itself, may be more or less mobile (Chimenos et al., 2000; van der Sloot et al., 2001). In the last decades many studies have analysed the environmental behaviour of municipal solid waste incineration (MSWI) BA (e.g. van der Sloot, 1996; Meima and Comans, 1999; Sabbas et al., 2003; Polettini and Pomi, 2004; Dijkstra et al., 2006; Hykš et al., 2009). In these studies it has been reported that the leaching behaviour of BA is influenced by both the field conditions to which the material can be subjected to in the specific application/disposal scenario (pH, the amount of water in contact with the waste solid matrix, i.e. the liquid to solid ratio L/S, and temperature) and the intrinsic characteristics of the material itself (particle size distribution, chemical composition and the solubility of the mineral phases constituting the residues). Over recent years, several experimental methods have been developed to evaluate the release of contaminants from waste materials and many efforts have been made in order to harmonize leaching test procedures (e.g. Kosson et al., 2002; Van der Sloot et al., 2003; van der Sloot and Dijkstra, 2004; Van der Sloot and Kosson, 2012). However, as highlighted by Grathwohl and Susset (2009) there is still a debate on the one hand on which is the most suitable leaching test method for characterisation and regulatory purposes, and on the other hand on how to interpret and use the results obtained by the different standardized leaching test methods. Moreover, evaluations focused exclusively on the quantification of leaching fail to consider important aspects such as risk for the environment associated with the release of contaminants as well as potential environmental impacts on a regional or global scale, such as resource use, toxicity for humans or water resources and climate change (Roth and Eklund, 2003; Toller, 2008). Hence, in order to establish the viability of specific management options for a particular type of BA, a wider evaluation based on the combined use of specific leaching data obtained applying a test method relevant for the hypothesized management scenario with evaluation methods such as life cycle assessment (LCA) and risk assessment is required.

Bottom ash characteristics and management options

Bottom ash (BA) is the most abundant solid residue produced by waste thermal treatment processes (for 85 to 95%) and accounts for 15-30% by weight of input waste (Chandler et al., 1997; Hjelmar et al., 2010). BA is generated and collected on the bottom part of the thermal treatment furnace and could be described as a heterogeneous slag-like mixture which primarily consists of coarse non-combustible materials (such as ash, ceramics, glass and scrap metals) which has similar physical and technical properties to those of natural aggregates. Regarding its composition, over the last decades, both mineralogical and chemical characteristics have been extensively described for many different incineration plants and countries (e.g. Hjelmar, 1996; Wiles, 1996; Chandler et al., 1997; Chimenos et al., 1999; Izquierdo et al., 2002; Forteza et al., 2004; Rocca et al., 2012). Particularly, regarding mineralogy it has been found that BA is mainly made up of glassy constituents (roughly 75 wt. %) and minerals that are metastable under atmospheric conditions (Zevenbergen et al., 1994). This principally depends to the fact that BA is formed at high temperature in the combustion chamber and then rapidly quenched in water. Minerals such as quartz (SiO_2), calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), ettringite ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 26H_2O$), portlandite ($Ca(OH_2)$) and haematite ($\alpha$-$Fe_2O_3$) are the most commonly found in BA. Between 15 and 45% (w/w) of BA consists of non-combusted materials. It includes: glass, soil residues such as pyroxene ($Ca(Mg,Fe)Si_2O_6$), quartz (SiO_2), feldspars ($(K,Ca,Na)(Al,Si)_4O_8$), metals, alloys and some residual organic material. The remaining part (55-85% w/w) is represented by melt products constituted by both large glassy melted components and ash that may contain glass (Hjelmar et al., 2010). Minerals that are commonly formed within melts are glass, spinel-group minerals (e.g. magnetite: Fe_3O_4), and melitite-group minerals (e.g. gehlenite: $Ca_2Al_2SiO_7$ and akermanite: $Ca_2(Mg,Fe)Si_2O_7$) (Eighmy et al., 1994; Meima and Comans, 1999; Piantone et al., 2004; Hjelmar et al., 2010). The significant amount of metastable minerals contained in BA makes this residue highly reactive under atmospheric conditions (pressure and temperature) leading to important changes in its mineralogical composition when the material is exposed to air and rainwater

(Meima and Comans, 1999; Chimenos et al., 2000; Polettini and Pomi 2004). The most relevant natural weathering process for BA is represented by carbonation, which involves the reaction of CO_2 present in the atmosphere with the metastable minerals contained in BA leading to oxidation of some metals, precipitation/dissolution of hydroxides phases and relatively soluble minerals and neo-formation of reactive sorptive solid substrates. Looking at the chemical composition of this type of residue, it was found that Si, Al, Fe, Ca, Na and K represent the major constituents (concentrations above 10 g/kg of BA), making up around 80–90% of its total mass. However, relatively high concentrations of toxic compounds such as metals, e.g. Pb, Cu, Zn and Ni (1–10 g/kg of BA), soluble salts e.g. sulphates and chlorides (1–10 g/kg of BA) and oxyanions, e.g. Cr, Mo, Sb (less than 1 g/kg of BA) have been also reported (Chandler et al., 1997; Bayuseno and Schmahl, 2010, Hjelmar et al., 2010). In a study on the content of trace elements conducted on different waste fractions (Riber and Christensen, 2006) it was found that As, Cu and Pb generally come from metal items, whereas Cr derives from leather or textile and Cd, Ni and Zn from batteries. Nevertheless, as shown in some studies (e.g. Rendek et al., 2007; Rocca, 2011) BA characteristics may vary depending on both the type of thermal treatment process employed (e.g. incineration, gasification and pyrolysis) and the characteristics of the input waste (e.g. commingled waste, Refuse Derived Fuel (RDF) or Solid Recovered Fuel (SRF) and hazardous waste such as Hospital waste). Up to now, at least in Italy, no distinction is made on the basis of BA origin and due to the significant amount of trace contaminants in BA, the most adopted management strategy is disposal in landfills for non-hazardous waste. On the contrary, in some European countries such as Denmark, The Netherlands and Germany, recycling of MSWI BA in replacement of natural aggregates is a well-established practice. The most widely used reuse option is as unbound material in construction works such as in road sub-bases and embankments (Astrup and Christensen, 2005; Åberg et al., 2006; Hjelmar et al., 2007; Lidelöw and Lagerkvist, 2007), while recycling as aggregates in concrete production is becoming increasingly applied (Crillesen and Skaarup, 2006; Van der Wegen et al., 2013). However, the main concern of reusing such materials is related to the possible contamination of the environment due to the higher content of contaminants contained in BA compared to natural aggregates. Nevertheless, for a proper assessment of the environmental impacts related to the beneficial utilization of bottom ash, information is needed not only on the total content of contaminants in the material, but especially on the potential release of such contaminants upon contact with water (i.e. leaching process). Indeed, numerous studies on MSWI bottom ash demonstrated that for most compounds a direct correlation not necessarily exists between their total content in the bottom ash and the amounts leached, as several other additional factors have been indicated to affect leaching (e.g. van der Sloot, 1996; Dijkstra et al., 2002; Kosson et al., 2002; Sabbas et al., 2003; Ecke and Aberg, 2006). Thus, the quantification of the leaching of salts and metals from this type of material is required prior to utilization. In this regard, during the last decades, different experimental procedures have been standardized to quantify leaching from waste materials at a European level (CEN/TC 292, European Committee for Standardisation, Technical Committee ‘Characterisation of Waste’) and many efforts have been done for their harmonization (Kosson et al, 2002; van der Sloot et al., 2003; van der Sloot and Kosson, 2012). Leaching tests are generally used for both compliance purposes such as to obtain values to compare to landfill acceptance criteria (EC/33/2003), as well, in some countries such as the Netherlands, to evaluate the utilization of materials in construction works (e.g. Dutch Building materials Decree, 1995; Dutch Soil Quality Decree, 2007) and for characterization purposes in order to assess the release behaviour of waste materials (van der Sloot and Dijkstra, 2004).

In the following paragraph, the most used standardized leaching test procedures and the main factors affecting leaching from BA are discussed in detail.

Characterization of leaching from BA and standardized leaching test methods for granular materials

As mentioned in the previous section leaching is a complex process in which several factors are involved. Different parameters related to both (i) the intrinsic characteristics of the material, i.e. particle size, chemical composition and speciation, leaching-available fractions and the solubility of the mineral phases making up the solid matrix and (ii) the specific field conditions, i.e.: pH, the amount of water in contact with the material (i.e. liquid-to-solid ratio, L/S) and weathering processes, were found to significantly affect the release of pollutants from BA and more generally from granular waste materials (van der Sloot, 1996; Sabbas et al., 2003). Moreover, the leaching of contaminants (i.e. metals and metalloids) and salts has been indicated to be characterised by very long time horizons, thousands of years and decades, respectively (Sundquist, 1999; Hellweg, 2000). As reported by Hykš (2008), to obtain a proper quantification of the leaching process in specific scenarios, field data would be required. However, the long-term leaching emissions (i.e. centuries) cannot be estimated by field measurements, thus these necessarily provide information only on the initial stage of the leaching process. Laboratory leaching experiments are then a valuable option for obtaining data regarding long-term emissions. However, the type of leaching test to perform should try to reflect as closely as possible the scenario it describes. Nevertheless, due to the overall complexity of the leaching process, it is generally believed that a single leaching test cannot provide an adequate description of the phenomena. Consequently, to obtain a better assessment of the leaching behaviour of a material in a specific scenario, a combination of different types of leaching tests should be performed. In order to explain more in detail the above mentioned concepts, in the following a brief overview of both the main factors affecting leaching processes and the different types of existing leaching test procedures, also applied in this study to characterize the leaching behaviour of the considered types of bottom ash, is provided.

Main factors affecting leaching processes

The main parameters and processes which were recognized to most affect the release of contaminants from BA include:

- Chemical speciation of metals: it refers to the different chemical species into which the elements may be present in solution. The speciation of an element is mainly controlled by pH, which depends in turn on the dissolution/precipitation of mineral phases making up the solid matrix of the BA to which the component is chemically bound;

- Availability of metals: that refers to the maximum leachable concentration of the metal. Availability mainly depends on the chemical and mineralogical characteristics of the material, which are affected by both the operational conditions of the thermal treatment applied and, to a lower extent, by the type of the waste input (Rendek et al., 2007);
- Weathering reactions (i.e. carbonation process): that refer to the reaction of the metastable minerals contained in the BA with atmospheric CO_2 that leads to the oxidation of some metals, precipitation/dissolution of hydroxides phases and relatively soluble minerals, and neo-formation of reactive sorptive solid substrates, influencing the rate of the mass transfer of the contaminants from the solid matrix of the BA to the liquid phase (Zevenbergen et al., 2000; Chimenos et al., 2003);
- Particle size: that was shown to influence the chemical and morphological characteristics of BA, and hence leaching (Stegemann et al., 1995; Chimenos et al., 1999). In general the finest particle size fractions of BA have shown to be characterized by a higher content of toxic metals and soluble salts with respect to the other fractions (Baciocchi et al., 2010). In addition, leaching processes are directly affected by particle size, since a reduction of particle size corresponds to an increase of the specific surface area and hence to an enhancement of the release of the different elements from the solid matrix of the material.

As reported by Hykš et al. (2009) and Allegrini (2014), inorganic elements can be divided into three groups, depending on their predominant “leaching-control” mechanism:

- Availability-controlled elements (e.g. Na, Cl^- and K), which are present in the material in the form of readily soluble species and thus the availability of the source mineral is the limiting factor. Their release is basically unaffected by changes in pH. Moreover, the release is generally the highest during the initial steps of the percolation test, then a fast decrease in concentration occurs as a consequence of the depletion the total content of the element in the BA;

- Solubility-controlled elements (e.g. Ca, and Si), whose release is limited by the solubility of the mineral phases in which the element is bound. In this case, since the solubility of the mineral phases generally varies considerably as a function of pH, also leaching concentrations are pH-dependent and may vary of several orders of magnitude in a pH interval spanning from 4 to 12; release as a function of the L/S, instead in this case, is generally rather constant also for high L/S values;
- Sorption/complexation-controlled elements (e.g. Cd, Cu, and Pb), whose release is mainly governed by different mechanisms from the two mentioned above (availability/solubility). Generally, oxyanion-forming metals (e.g. CrO_4^{2-}) and metal cations (e.g. Cu_2^{+}) belong to this group. The main mechanisms controlling the leaching process are complexation with dissolved organic carbon (Van Zomeren and Comans, 2004), sorption on the surface of hydrous ferric(hydr)oxides (HFO) and hydrous aluminium (hydr)oxides (AlO) (Meima and Comans, 1998; Dzombak, 1990) or on other mineral phases, and solid solution formation with minerals containing Ca, e.g. ettringite ($Ca_6(Al(OH)_6)_2(SO_4)_3 \cdot 26H2O$) (Cornelis et al., 2008).

Standardized leaching test methods for granular materials

Leaching tests are experimental procedures in which a liquid (i.e. leachant) is put into contact with the tested material under specific conditions, after which the resulting leachate (also called eluate) is collected and analysed allowing to quantify the release of the contaminants. Laboratory leaching tests can be divided into two main categories:

- “Compliance” tests that are used to determine whether the material complies with a specific behaviour or with specific reference values established by EU, National or local regulations;
- “Characterization” tests that are used to obtain information on the short and long term leaching behaviour and properties of materials. The influence of the Liquid/solid (L/S) ratio, leachant composition, factors controlling leachability such

as pH, redox potential, complexing capacity, ageing of materials and physical parameters are addressed in these tests.

Compliance leaching tests

Compliance leaching tests usually consist of a one stage batch test, in which the material, generally ground (d<4 mm), is put into contact with deionized water (DI) and stirred for a set time period (24 h) and at a fixed L/S ratio (e.g. 2 or 10 l/kg). These tests are generally employed at European level for compliance purposes to determine the acceptance of a waste in one of the different types of landfills (EC/33/2003), or in some countries such as Denmark for regulating the utilization of waste materials (e.g. bottom ash) in construction (Ministry of Environment and Energy, 2000). In Italy, the batch test with a liquid to solid ratio of 10 l/kg (UNI/EN 12457-2) is by far the most used for predicting the leaching properties of the residues. This test is employed either for compliance with landfill acceptance criteria (Ministerial decree 27/09/2010) or for assessing the possibility of reusing a non-hazardous waste for specific applications (Ministerial decree 186/2006). It is important to point out that the latter norm currently does not specifically refer to BA from waste thermal treatment.

Characterization leaching tests

Characterization leaching tests are commonly applied to assess the leaching behaviour of the tested material as a function of pH and the L/S ratio. The CEN/TS 14429 batch test is generally used for the evaluation of the pH-dependent leaching process. This test allows to evaluate the base/acid neutralization capacity (BNC/ANC) of the material, as well as the release of major and trace elements as a function of pH. The test, carried out on particle size reduced samples (d<1 mm), consists of different parallel batch experiments in which the tested material is put into contact with DI water containing different aliquots of acid or base in order to obtain eluates with pH values spanning within a wide pH range (3.5-12.5). Each suspension is equilibrated and stirred for 48 h and a fixed L/S ratio of 10 l/kg is employed.

As far as the L/S ratio is concerned, the influence of this parameter on the leaching process can be achieved by performing both batch (static) or column (dynamic) leaching tests. Batch tests typically involve different parallel batch experiments in which the amount of leachant (i.e. DI water) put into contact with the material is varied in order to obtain different L/S ratios. Currently a standardized procedure for this type of test does not exist, however Kosson et al. (2002) developed a method (i.e. SR 003.1) which consists of five parallel batch extractions with DI water employing the following L/S ratios: 0.5, 1, 2, 5 and 10 l/kg, applying a contact time of 48 h, on particle size reduced material (d<2 mm). Conversely in column percolation tests (CEN/TS 14405) the material is compacted into a column (5-10-cm inner diameter) in which new leachant (i.e. DI water) is continuously pumped with an upward flow through the column until the desired L/S value is reached. Moreover, the L/S ratio can be related to the time-scale by knowing the height of the material filling the column and the water infiltration rate (van der Sloot, 1996). It has to be pointed out, that in some cases, column leaching tests are also used for compliance purposes such as for example in The Netherlands, where the column test procedure NEN 7343 (1995) is employed for assessing the compliance of granular materials with the criteria established for use in construction (Verschoor et al., 2008). It is worth noting that the L/S ratio is a key parameter for any of the different leaching test procedures described above. In fact, since the L/S ratio represents the volume of liquid [l] in contact with the dry mass of the tested material [kg], for a given leaching test, by multiplying the concentrations [mg/l] measured in the eluate for the applied L/S ratio, the results can be expressed in terms of released mass [mg of contaminant/kg of dry material]. In this way, the results obtained from different leaching test methods and for different types of materials can be easily compared (Hykš, 2008; Grathwohl and Susset, 2009). Characterization leaching tests (both as a function of pH and the L/S ratio) provide more information than a simple batch test, allowing to better assess solubility of contaminants and major components, material geochemistry and mechanisms controlling release. Indeed, the pH dependence tests address changes in exposure conditions and can be used to assess chemical speciation issues (van der Sloot and Kosson, 2012). The results of pH dependence tests have been widely used in mechanistic geochemical speciation modelling to quantify the chemical phases (minerals and sorptive phases) controlling release (Astrup et al., 2006; Dijkstra et al., 2008; Hykš et al., 2009; Rocca et al., 2012). Whereas, column leaching tests have been recognized as the most suitable lab-scale method for assessing the release kinetics of contaminants from granular materials, since they more realistically resemble field conditions than the other available test methods (Cappuyns and Swennen, 2008; Kalbe et al., 2008; López Meza et al., 2008; Grathwohl and Susset, 2009). However, evaluations focused exclusively on the quantification of leaching fail to consider important aspects such as risk for the environment associated with the release of contaminants, as well as potential environmental impacts on a regional or global scale, such as resource use, toxicity for humans or water resources and climate change (Roth and Eklund, 2003; Toller, 2008). Hence, in order to assess the viability of specific management options for a particular type of BA, a wider approach based on the combined use of relevant leaching data with evaluation tools such as life cycle assessment (LCA) and risk assessment is required.

In the following paragraph a general overview of LCA and risk assessment based approaches, that are the decision tools employed in this study for evaluating environmental impacts related to different management options for the considered types of BA, is provided.

Environmental impact assessment tools

Given the wide range of possible reuse strategies for waste materials, and because of the substantial lack of regulations and standards, environmental impact and risk assessment through life cycle assessment (LCA) and environmental risk assessment methods are being currently increasingly applied. Through risk assessment, practitioners can evaluate local scale impacts and by life cycle assessment, one can evaluate global scale issues such as avoided production of raw materials (e.g. sand, aggregates) thanks to their substitution with waste materials. LCA and risk assessment might effectively support decision-making regarding which management options are to be preferred for a specific waste material (Tiruta-Barna et al., 2007).

Life cycle assessment

Within the last decades, the life cycle assessment (LCA) methodology has been increasingly applied in the field of waste management as a valuable decision-support tool to identify environmentally-sound solutions (Manfredi and Christensen, 2009; Turconi et al., 2011; Laurent et al., 2014a). Life cycle assessment, also known as “cradle-to-grave assessment”, is a standardized methodology (EN ISO 14044 and 14040:2006) that allows to estimate environmental burdens and potential impacts that a product or a system can generate during all the stages of its whole life cycle, from raw material extraction, through production and utilization to final disposal (Wenzel et al., 1997). An LCA study includes inputs of energy and resources as well as outputs of waste and emissions to air, water and soil and consists of the following sequential four phases:

- goal definition and scoping: that consists in the definition of the objective of the study and of the expected outcomes; the system boundaries system (what is and is not included in the study); the main assumptions and the methodological choices made; the functional unit (FU) which yields a quantitative measurement of the functions provided by the system and is the reference to which all inputs and outputs are related to, thus ensuring comparability of the LCA results;
- life-cycle inventory (LCI): that regards the definition and quantification of all of the inputs (resources and energy consumption) and the outputs (emissions, material or energy recovery) of each stage of the system over its life-cycle referred to the functional unit;
- life cycle impact assessment (LCIA): that is aimed at the identification and evaluation of the potential environmental impacts of the studied system. In this phase, LCI results are characterized with respect to selected relevant impact categories (e.g. global warming, acidification, human toxicity) and the emissions are converted to potential environmental impacts. The impact assessment results can be further normalized adopting different criteria, such as for example relating all impacts to those resulting from one person per year, yielding units for both

resources and environmental impacts in Person Equivalents (PE), and finally weighted according to political goals;

- interpretation: that concerns the interpretation of the results of the previous phases (i.e. LCI and LCIA) in relation to the goal and scope of the study in order to draw conclusions and provide recommendations.

LCA is an iterative process, so the results of one of the four phases could require the revision of the other phases. This is a consequence of the complexity of any systems' life cycles, whose assessment involves a substantial learning process for the LCA practitioner.

Risk assessment

The management and clean-up strategies adopted for contaminated sites in Italy relies on a risk-based approach, where for the definition of remediation goals the actual pollution of the site is evaluated depending on the effective risk posed to human health or the environment (Verginelli, 2011). Several technical standards for risk assessment to contaminated sites are available at the US and EU level. One of the most widely adopted procedures is the ASTM standard (E1739-95, E2081-00) which implements the Risk-Based Corrective Action (RBCA) at chemical release sites. In Italy the methodological criteria developed by the national environmental agency (ISPRA, 2008) is the reference document for the application of human health and environment risk assessment. This document is based on the partial application of the ASTM-RBCA (2000) procedure. The procedure outlined in this document is based on the information collected during the contaminated site investigation, which is used to evaluate the potential effects on the health of exposed receptors and on the environment, allowing to assess whether a particular site requires remedial action and eventually the specific risk-based remediation goals. Namely, the risk is defined by using site-specific data concerning receptors, exposure potential, site hydrogeology and the type, amount, and toxicity of the chemicals of concern. The ASTM RBCA is based on a "tiered" approach to risk and exposure assessment, where each tier refers to a different level of complexity. Namely in Tier 1, aimed at the definition of the contamination screening values, only on-site receptors are considered. Transport of contaminants is described through simple analytical models and conservative default values are used for all hydrogeological, geometrical and exposure data, without requiring any site characterization. In Tier 2, aimed at the evaluation of site-specific target levels, off-site receptors are included in the conceptual model; all input data should possibly be site-specific, whereas models used to describe contaminants transport are still analytical. Usually, the risk analysis procedure is performed using Tier 2 conditions that represent a reasonable compromise between the need for a detailed site assessment and the advantages of handling a rather simple and easy-to-use management tool. Therefore, only in very specific situations, where a more detailed description of the contaminant transport through numerical models is required, risk analysis is performed following the Tier 3 approach. Several software packages are available for carrying out Tier 1 and Tier 2 RBCA assessments. The most commonly used in Italy, which have been validated in the ISPRA guidelines (2008), are: RBCA Tool Kit, BP-RISC and Giuditta.

AIMS AND CONTENT OF THE THESIS

The main objective of this thesis was to evaluate management options for bottom ash (BA) produced by different types of waste thermal treatment plants. To improve the basis for making decisions regarding BA management, firstly an in depth analysis of the leaching behaviour of the types of BA considered, was conducted. Specifically, in order to identify the influence of different parameters (e.g. pH and L/S ratio) on the release of contaminants from these residues, various laboratory leaching tests were performed paying particular attention to the interpretation of the obtained results (Section1). Secondarily, the most significant experimental leaching data were selected and employed in evaluation tools such as LCA and risk assessment in order to gain insight on the environmental consequences associated to the release of contaminants in the specific disposal/reuse scenarios considered (Section 2).

Specifically, the evaluation was focused on the following three types of bottom ash: BA produced by both incineration and gasification of refuse derived fuel (RDF-I BA and RDF-G BA, respectively) and BA generated at a dedicated hospital waste incineration facility (HW-I BA). These specific types of BA were selected since their leaching behaviour and potential management options have been significantly less investigated up to now (Baciocchi et al., 2010; Gori et al., 2011; Rocca et al., 2012; Rocca et al., 2014) compared to MSWI BA (e.g. Meima and Comans, 1999; Dijkstra et al., 2006; Dijkstra et al., 2008; Hykš et al., 2009) as a result, on the one hand of the relatively recent development of RDF thermal treatment technologies and on the other hand of the particular nature of hospital waste. However, in recent years, thermal treatment of RDF is increasingly applied in some EU regions, such as Central Italy, with the target of enhancing the energy recovery of conventional waste incineration plants (Rotter, 2010). In fact, RDF, which consists of the dry light fractions of residual MSW produced by mechanical biological treatment plants, presents a higher calorific value and homogeneity compared to commingled residual MSW. Typically, thermal treatment of RDF is carried out in grate-fired incineration plants; however, owing to its characteristics, this type of waste, differently from residual MSW, is also suitable to be treated in gasification plants. The potential advantages of this thermal process versus incineration are associated with both the higher electrical conversion efficiencies that may be attained and the lower emissions of contaminants associated to both gaseous emissions and solid residues. Hence, although waste gasification is a quite recent technology in Europe, it is expected that its use will increase in the future for the energetic valorization of RDF (or SRF). Moreover, incineration is by far the most applied treatment for the destruction of infectious and toxic organic/inorganic substances contained in hospital waste. Hence, it can be expected that the production of BA from these types of thermal treatment processes will increase in future years, thus the evaluation of the leaching behaviour and of appropriate management strategies for these specific types of BA will become more and more important.

The thesis was structured into two main sections, in the first (Section 1), which includes Chapter 1 and Chapter 2, the results obtained from the experimental analysis performed for the evaluation of the leaching behaviour of the three types of considered BA are provided. Specifically, in Chapter 1 the influence of the liquid-to-solid ratio (L/S) on the release of major components and potential contaminants for the three types of BA was examined. In order to evaluate different leaching test procedures, both batch (static) and column (dynamic) tests were performed and compared for each type of material and the main mechanisms controlling the leaching of each constituent were identified by interpreting the results obtained from the column tests with an analytical model. A step forward for the evaluation of the leaching properties of the three types of considered BA was addressed in Chapter 2. In particular, acid neutralization capacity (ANC) and the release of major compounds and trace contaminants as a function of pH was evaluated in order to derive a suitable description of the leaching behaviour of the BA under the pH conditions that may occur in disposal/reuse scenarios. In addition, due to the higher heterogeneity and release of contaminants observed for the RDF-I BA compared to the other two types of BA, only for this material, the leaching behaviour (as a function of both the L/S and pH) was evaluated separately for two different particle size fractions, i.e. coarse (0.425-12 mm) and fine (<0.425 mm), and the influence of a weathering treatment (carried out at laboratory scale for 12 months) was also investigated.

In Section 2, in which Chapter 3 and Chapter 4 are included, the most significant experimental leaching data, obtained in Section 1, were selected and employed in LCA and risk assessment in order to evaluate the potential environmental consequences associated with release of contaminants from these materials in specific disposal/reuse scenarios. In Chapter 3 potential environmental impacts associated with landfilling and reuse in road sub-base construction for the RDF-I and RDF-G BA were evaluated and compared by life-cycle assessment (LCA). Both non-toxicity related impact categories (i.e. global warming and mineral abiotic resource depletion) and toxic impact categories (i.e. toxicity to humans and ecotoxicity to freshwater) were assessed. To provide a quantitative assessment of the leaching properties of the two types of BA, some of the experimental leaching data obtained in Section 1, were used as input to the LCA model in order to estimate the cumulative release of potentially toxic metals from these waste materials in each considered scenario. Particular attention was paid on the sensitivity of the results of the assessment in terms of leaching properties and the determination of emissions by leaching. In particular, the sensitivity analysis regarded the following issues: leaching data selection, material properties and assumptions related to emissions modelling. In Chapter 4 a further step towards the evaluation of the environmental impacts related to the two different management options considered in the LCA study (i.e. landfilling and recycling in road sub-base construction) for the three types of considered BA, was addressed. Specifically, potential risks for groundwater due to the emission of contaminants from the considered types of BA were investigated. A different approach compared to standard risk assessment methodologies was proposed. Specifically, the developed method was based on the results obtained by the column leaching tests, which allowed to estimate the main mechanisms controlling the leaching behaviour of the three types of BA, i.e. the prevailing of equilibrium or non-equilibrium conditions during contaminant release (Chapter 1). Specific field conditions expected in the two scenarios (e.g. the infiltration rate and prevailing release mechanisms) were evaluated. Using the equations employed for the modelling of column test results and relevant estimated parameters (e.g. contaminants diffusion coefficients and maximum available leaching concentrations) the amounts of contaminants expected to be released from the BA in the specific scenario and to reach the groundwater table were calculated as a function of time for a framework of concern of 100 years.

Finally, in the Conclusions section the most interesting findings obtained in this study are summarized, compared and discussed, highlighting some critical issues and suggesting future developments regarding the evaluation of management options for the types of BA investigated in this study.

SECTION 1

EVALUATION OF THE LEACHING BEHAVIOUR OF WASTE THERMAL TREATMENT BOTTOM ASH AS A FUNCTION OF DIFFERENT PARAMETERS: EXPERIMENTAL LEACHING DATA

*This section reports the results of a lab-scale investigation carried out to assess the leaching behaviour as a function of different parameters (i.e. L/S ratio, pH and particle size distribution) of BA produced by three different types of waste thermal treatment plants. Namely, BA generated at a dedicated hospital waste incineration plant (HW-I BA) and BA produced by both incineration and gasification of refuse derived fuel (RDF-I BA and RDF-G BA, respectively) were considered. The first part of the experimental activity (Chapter 1) focused on the influence of the liquid-to-solid ratio (L/S) on the release of major components and potential contaminants for the three types of analysed BA. In order to evaluate different leaching tests procedures, both batch (static) and column (dynamic) tests were performed and compared for each type of material. The results indicated a generally lower release of contaminants for the RDF-G BA, which showed to comply with acceptance criteria for inert waste landfilling. Whereas HW-I BA and RDF-I BA only met limit values set for disposal in non-hazardous waste landfills. However, RDF-I BA displayed a generally higher release especially of amphoteric metals (i.e. Pb, Zn and Cu) and chlorides. In addition, the different tests carried out highlighted that the release obtained from batch tests was for some elements of up to two orders of magnitude higher than the one observed in column tests. This finding was mainly attributed to the fact that, differently from the batch experiments, in the column tests the continuous renewal of the leachant solution can lead to non-equilibrium release conditions. This hypothesis was also supported by the interpretation of the column test results with an analytical model that showed that most of the observed leaching trends could be described quite well assuming contaminants release to be limited by mass-transfer.

In order to provide a description of the leaching behaviour of the BA samples under environmental conditions that may occur in specific disposal/reuse scenarios, the second part of the experimental activity (Chapter 2) was focused on the evaluation of the release of major and trace elements as a function of pH. Results indicated a remarkable difference in the acid neutralization capacity (ANC) of RDF-I BA compared to the other two types of BA. Indeed, RDF-G BA and HW-I BA displayed an almost negligible and low ANC, respectively, which was mainly associated to their mineralogy, principally made up by amorphous phases. On the contrary, due to the abundance of hydrated phases detected in the RDF-I BA, a significant ANC, for pH values between 11 and 12, was found for this type of material, meaning that for modifications in environmental conditions corresponding to up to 2 meqH^+/g d.m., a quite stable leaching process could be expected. However, this type of BA showed a fairly high release of contaminants at its strongly alkaline native pH (12.4). Indeed, a generally higher leaching of contaminants (e.g. Ba, Chlorides, Cr, Cu, Pb and Zn), both as a function of the L/S ratio and pH, was observed for the RDF-I BA sample compared to the other two types of analysed BA. Hence, in order to improve the leaching behaviour of this type of BA (i.e. RDF-I BA) the effect of (i) the removal of the fine particle size fraction (d<0.425mm), which showed a fast and high release of contaminants, from the bulk sample and (ii) a natural weathering treatment, carried out at laboratory scale for 12 months, were also investigated. While the first treatment was shown not to be effective, since the fine particle size fraction only represented 10% by weight of the total sample of the RDF-I BA; the weathering process led on the one hand to a relevant immobilization of Ba, Cu and to a lower extent of Pb, and on the other hand showed to favour the mobilization of oxyanion-forming metalloids such as Cr and Mo.

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CHAPTER 1

ANALYSIS AND INTERPRETATION OF THE LEACHING BEHAVIOUR OF BOTTOM ASH BY BATCH AND COLUMN TESTS

1.1 INTRODUCTION

As mentioned in the Introduction Section, in the last decades, several studies have focused on the potential utilisation of waste materials (e.g. steel slag, construction and demolition waste and bottom ash from waste thermal treatment) as useful products for replacing natural aggregates in civil engineering applications (Forteza et al., 2004; Petkovic et al., 2004; Das et al., 2007; Huang et al., 2007). However, compared to natural aggregates, these materials generally contain higher concentrations of harmful compounds (e.g. metals and metalloids) that may be released upon contact with water (i.e. leached) posing a potential risk for the environment and ultimately human health. The leaching behaviour of BA has been reported to be influenced by both the field conditions to which the material can be subjected to in specific application/disposal scenarios (pH, the amount of water in contact with the waste solid matrix, i.e. the liquid to solid ratio L/S, and temperature) and the intrinsic characteristics of the material itself (particle size distribution, chemical composition and the solubility of the mineral phases constituting the residues) (van der Sloot, 1996; Sabbas et al., 2003). Over recent years, in order to evaluate the release of contaminants from waste materials under specific conditions, different types of standardized leaching tests, making use of both static (batch) and dynamic (column) procedures, were developed (e.g. van der Sloot et al., 1997; Kosson et al., 2002; Hage and Mulder, 2004). Typically, in batch tests, a sub-sample of the studied material is placed in contact with a liquid phase for a fixed time (generally 24h-48h) during which pseudo-equilibrium conditions are assumed to be established (López Meza et al., 2008). However, batch tests only allow to assess the leaching of contaminants at the specific experimental conditions tested (e.g. fixed L/S ratio or pH) without providing any information on the release kinetics (Kalbe et al., 2008). Conversely, in dynamic tests (i.e. column tests) water is flowed through the material and then collected at set L/S ratios that have been related to the time-scale by knowing the height of the material in the column and the water infiltration rate (van der Sloot, 1996). As highlighted by Grathwohl and Susset (2009) there is still a debate both on which is the most suitable leaching test method for characterisation and regulatory purposes and on how to interpret and use the results obtained by the different standardized procedures. For instance, column tests are recognised as the most suitable lab-scale method for assessing the release of contaminants from granular materials since they more realistically resemble field conditions (Cappuyns and Swennen, 2008; Kalbe et al., 2008; López Meza et al., 2008; Grathwohl and Susset, 2009). However, there is some discussion on how to use the results obtained from these dynamic tests. On the contrary, batch tests are less complicated and time-consuming compared to column tests, although they provide results under conditions that may not necessarily be representative of field conditions. So far, only a few studies comparing batch and column tests were found in the literature and depending on the types of analysed material different results were observed. For example, López Meza et al. (2008) conducted a comprehensive experimental study comparing leaching data obtained by column and batch tests as a function of the L/S ratio on five different types of granular materials (i.e. concrete, construction debris, aluminium recycling residue, coal fly ash and bottom ash) concluding that overall the two types of tests provide comparable results. Al-Abed et al. (2008) and Quina et al. (2011) reached the same conclusions by analysing mineral processing waste and air pollution control (APC) residues from municipal solid waste incineration (MSWI), respectively. On the contrary, Kalbe et al. (2008), which focused on contaminated soil, demolition waste and waste incinerator bottom ash, found a good agreement between the two types of tests only with regard to the release of sulphates and chlorides, while for the leaching of metals (e.g. Cu and Cr) they observed significant discrepancies.

In this Chapter, the results obtained applying different batch and column leaching test procedures for the three types of considered bottom ash (BA) are compared and discussed. Namely, BA generated at a dedicated HW incineration plant and BA produced by either incineration or gasification of refuse derived fuel (RDF) were analysed. As previously mentioned, these types of BA were selected since their leaching behaviour has been significantly less investigated up to now compared to MSWI BA (e.g. Meima and Comans, 1999; Dijkstra et al., 2006; Dijkstra et al., 2008; Hykš et al., 2009). The previous studies performed on these specific types of BA, that mainly focused on the analysis of the physical-chemical and mineralogical characteristics as well as leaching as a function of pH of these residues, indicated that even though these

BA present a similar chemical composition, owing to the differences in the type of thermal treatment applied, their mineralogy and leaching behaviour may differ considerably (Baciocchi et al., 2010; Gori et al., 2011; Rocca et al., 2012; 2015). However, there is still a lack of information regarding the release of potentially harmful compounds as a function of the L/S ratio, which, as previously mentioned, is recognised to be one of the key parameters influencing the leaching behaviour of a solid residue. Therefore, in this study different leaching test methods making use of both batch and column test procedures were applied to assess the release behaviour of the three types of BA as a function of the L/S ratio. Another aim of this work was to gain some insight on what kind of information may be attained by column leaching tests and how the results may be interpreted in view of assessing potential management options for the analysed waste materials. Hence, for each type of BA, the experimental results were also compared to evaluate the differences of the leaching concentrations of the different elements obtained from batch and column test methods. In addition, the data achieved from the different test methods were compared to current EU and Italian regulatory criteria to analyse if the type of test employed may affect the disposal/reuse options resulting for each type of residue. Furthermore, two analytical models based on equilibrium and non-equilibrium mass release were employed and compared to the leaching trends resulting from the column experiments in order to allow to identify the key mechanisms controlling leaching and to provide some insight on how to assess the long-term behaviour of the residues in a field scenario.

1.2 MATERIALS AND METHODS

1.2.1 BA sampling and characterization

The three types of BA examined in this study are produced by: i) a dedicated hospital waste incineration plant (HW-I BA) equipped with a rotary kiln combustion chamber with operational temperatures of 1000-1200 °C; ii) a fluidised bed gasifier treating RDF (RDF-G BA) and operating at temperature 1200-1400 °C which results in the direct melting of the slag; iii) a RDF incineration plant (RDF-I BA) employing a water-cooled grate combustion chamber and an operating temperature of 850-1000 °C. Regarding the RDF incineration and gasification facilities it has to be specified that both plants are fed by the dry light weight fraction of residual MSW (i.e. the flow formerly termed as RDF) obtained from mechanical biological treatment (MBT) plants located in the same region in central Italy (Lazio region). It should be noted that although the definition and classification methods for RDF were replaced with those regarding SRF by the issuing of Italian Legislative Decree 205 (2010), both the above mentioned MBT plants and thermal treatment facilities are still currently authorized respectively to produce and treat RDF; for this reason in this work the term RDF is used instead of SRF.

It is worth noting that the experimental activities were performed on fresh samples of the same types of BA analysed by Rocca et al. (2012, 2015).

The BA collected at each plant was firstly homogenised through quartering (UNI 10802:2013) and then the grain size fraction ≥12 mm (which for all three materials was < 5% by weight) was removed and not analysed. Furthermore, coarse metallic, ceramic and glass fragments larger than 5 mm were manually removed from the RDF-I BA sample. For each type of BA, the particle size distribution (ASTM D422-63, 2007), the total organic carbon (TOC) and carbonate ($CaCO_3$) content as well as the chemical and mineralogical composition were determined. The total carbon (TC), total inorganic carbon (TIC) and total organic carbon (TOC) was determined with a Shimadzu solid sample module (SSM-5000A) analyser. Approximately 250 mg of grinded sample (<0.2 mm) was weighed and TC was measured by catalytic combustion at 900 °C. Next, TIC was determined after H_3PO_4 addition at 200 °C for carbonate ($CaCO_3$) decomposition and TOC was quantified by subtraction of TC and TIC (UNI 13137, 2002). The total content of major (Al, Ca, Fe, K, Mg, Na and Si) and trace elements (Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, V, Zn) was measured by analysing the solutions obtained from an alkaline digestion of the samples, with an Agilent 710-ES inductively coupled plasma optical emission spectrometer (ICP-OES). All analyses were carried out in triplicate. The mineralogy of the materials was determined by X-ray diffraction (XRD) analysis, employing the same instrument and operating parameters reported in previous works (Rocca et al., 2012).

1.2.2 Leaching test methods

1.2.2.1 Column set-up and procedure

The column tests were performed with 37-cm high Plexiglas columns with a 10-cm inner diameter according to the standard method CEN/TS 14405 (2004). To avoid preferential flows of water into the material, the bottom section of each column was equipped with a perforated plate. The columns were closed with flanges sealed with polypropylene O-rings, stainless steel nuts and bolts. Depending on the type of analysed material, 2.5-4.5 kg of wet BA was packed into the columns. To ensure proper water flow over the width of the column and as a support for the pre-filter (glass fiber pre-filter of 2.7 μm pore size), a thin layer (2.5 cm) of non-reactive quartz sand was placed in the top and bottom sections of the column. The columns were then slowly saturated with an upward flow of deionized (DI) water by using a peristaltic pump, then the pump was stopped for a period of three days in order to equilibrate the system. After the equilibration phase, the pump was started again setting a flow rate of around 48 ml/h ± 5 ml/h. In each experiment, seven distinct leachates were collected at different cumulative L/S ratios (0.1, 0.2, 0.5, 1, 2, 5, and 10 l/kg of dry BA). Column tests were carried out in duplicate.

1.2.2.2 Batch set-up and procedure

To assess the differences in the release of major and trace components between column and batch testing, different types of batch tests were also performed.

First, the batch test SR 003.1 at different L/S ratio reported by Kosson et al. (2002) was carried out. This test consists of five parallel batch extractions with DI water employing the following L/S ratios: 0.5, 1, 2, 5 and 10 l/kg and applying a contact time of 48 h. In short, 40 ml of DI water were used in each test and the amount of BA was varied in order to achieve the set L/S ratio. This type of test requires a particle size reduction of the sample below 2 mm. However, since the column tests were conducted on unground BA, to evaluate the effect of the grain size of the material on the results achieved in batch mode, the SR 003.1 test was carried out on both ground (<2 mm) and unground samples. Furthermore, in order to obtain values that could be directly compared to the acceptance criteria reported in Annex II of the European Landfill Directive (2003/33/EC) both the compliance batch leaching tests UNI/EN 12457 part 1 (L/S= 2 l/kg) and part 2 (L/S= 10 l/kg) were performed. In these two types of tests, BA samples were ground to obtain a particle size lower than 4 mm and leached with DI water for 24 h applying a L/S of 2 l/kg and 10 l/kg, respectively. Moreover, leachate concentration obtained from the batch test at L/S of 10 l/kg were also compared to the requirements set by the Italian legislation for the reuse of non-hazardous waste (M.D. 186/2006), although these limits currently do not specifically apply to BA from waste thermal treatment. Leaching tests at L/S of 10 l/kg were performed in triplicate whereas the ones at L/S of 2 l/kg were carried out in duplicate.

1.2.2.3 Chemical analyses

The pH values of all eluates were measured (Hanna Instrument pH-meter) and the leachate solutions were filtered through 0.45 μm pore size filters before performing the chemical analyses. The samples collected were separated in two sub-samples: one acidified with nitric acid for metal and metalloid analysis and the other directly analysed to determine chlorides and Dissolved Organic Carbon (DOC) contents. Concentrations of major compounds and trace elements were measured with an Agilent 710-ES inductively coupled plasma optical emission spectrometer (ICP-OES). The leaching of soluble chlorides were evaluated by titration with $AgNO_3$ (ISO 9297:1989) and the concentration of dissolved organic carbon (DOC) was determined with a Shimadzu TOC–V CPH/CPN analyser.

1.2.3 Modelling of column test results

As previously mentioned, in order to allow to identify the key mechanisms controlling leaching and to provide some insight on how to assess the long-term behaviour of the considered types of BA in a field scenario, two analytical models based on equilibrium and non-equilibrium mass release were employed and compared to the leaching trends resulting from the column experiments. Specifically, the equilibrium model, on the basis of the solid-water partition coefficient (K_d) and the total concentration of a specific element in the waste, allows to estimate the concentration in the pore water surrounding the material at equilibrium conditions as a result of leaching. However, while the K_d model has been applied successfully for organic contaminants, as also recently reported by Grathwohl (2014), it has substantial limitations when applied to inorganic compounds; e.g. solubility controlled substances like Al and Si can be limited by slow dissolution kinetics. Hence, such chemical processes cannot be adequately modelled employing the K_d approach. For these reasons, also a non-equilibrium model assuming leaching to be limited by mass-transfer was applied to the results obtained from the column tests. In the present paragraph, the two analytical models employed in this study and the main assumptions are briefly reported and discussed.

As described in Paragraph 1.2.2.1, before performing each test, the columns were saturated and maintained disconnected from the pump for 3 days. This procedure was performed in order that during the early stages of the test the concentration of each contaminant in solution (C_{sol}) could be assumed to be equal to the corresponding concentrations in equilibrium with the solid material, C_{mat}^{eq} (mg/l) (Eq. 1.1):

$$C_{mat}^{eq} = C_{sol} = \frac{C_s}{K_d} \tag{1.1}$$

where C_s (mg/kg) is the total concentration of the element in the BA and K_d the solid-water partition coefficient (l/kg). Assuming that the column set up may be described as a continuous piston flow system, after a leachate replacement of approximately 1 pore volume, non-equilibrium conditions governed by mass transfer can be expected. In these cases, a reduction of pore water concentrations below the equilibrium values is typically observed (Kosson et al., 2002; Grathwohl, 2014). For non-equilibrium conditions, to describe the outlet contaminant concentration from the material, the analytical solution proposed by Brouwers (1997) and later extended by Ogunro and Inyang (2003) can be used (Eq. 1.2).

$$C_{mat}^{no-eq} = \left[(1-\theta) \cdot \frac{\pi}{4} \cdot d_{col}{}^{2} \cdot h_{col} \right] \cdot \frac{M_{s,0}}{V_{sc}} \cdot \frac{6}{q \cdot d_{eq}} \sqrt{\frac{D_a}{\pi \cdot t}} \tag{1.2}$$

where θ (-) is the porosity of the tested BA, d_{col} (cm) the inner diameter of the column, h_{col} (cm) the height of the column packed with the material, $M_{s,0}$ (mg) the initial content of the target contaminant in the material, V_{sc} (cm^3) the volume of BA in the column, d_{eq} (cm) the equivalent particle size of the bulk slag (which can be estimated as reported by Brouwers, 1997), q (l/s) the flow-rate of leachant through the column, D_a (cm^2/s) the apparent diffusion coefficient of the element and t (s) the time of percolation.

Eq. (1.2) can be rewritten in a more compact form as reported in Eq. 1.3:

$$C_{mat}^{no-eq} = C_s \cdot \rho \cdot (1-\theta) \cdot V_{col,mat} \cdot \frac{S}{q} \sqrt{\frac{D_a}{\pi \cdot t}} \tag{1.3}$$

where $V_{col,mat}$ is the volume of the column packed with the BA (cm^3), ρ the dry bulk density of the material (kg/cm^3) and S (1/cm) the volumetric specific surface area of BA in the column (Ogunro and Inyang, 2003):

$$S = \frac{6}{d_{eq}} \tag{1.4}$$

To elute from the column, the element present in the liquid solution must also flow through the sand layer placed above the material. Hence, to assess the expected outlet concentration eluting from the column Eq. 1.5 was used:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} \tag{1.5}$$

where R is the retardation factor, D (cm^2/s) the diffusion coefficient and v the Darcian flow velocity through the sand layer (cm/s). It is important to point out that in the column apparatus the influence of the sand layer on leaching is most probably negligible, since the thickness of the sand layer placed above the slag was of only 2.5 cm. However, as this model was developed not only to describe the results of lab-scale tests but also leaching processes occurring in field conditions (see Chapter 4) it was decided to maintain this term. In fact, this aspect may be relevant for the assessment of the leaching concentrations in specific disposal/reuse scenarios, since generally the slag is not located directly above the aquifer, but in a landfill or construction application typically placed on top of a soil layer of a certain thickness.

An analytical solution of Eq. 1.5 can be derived assuming the boundary conditions reported in Eq. 1.6-1.8:

$$C(h_{sand},0) = 0 \tag{1.6}$$

$$C(0,t) = C_0 \tag{1.7}$$

$$\frac{\partial C}{\partial z}(\infty,t) = 0 \tag{1.8}$$

where h_{sand} (cm) represents the thickness of the sand layer in the column above the material and C_0 (mg/l) the concentration of the element eluting from the material. Note that in Eq. 1.6 the assumption that the concentration in the sand layer is null ($C=0$) at $t=0$ is only a boundary condition to solve Eq. 1.5; indeed after the saturation of the column, at the beginning of the experiment the concentration of the different constituents in the sand layer is most probably already relevant. In Eq. 1.7 z = 0 refers to the interface between the material and the sand layer. Using the boundary conditions reported in Eq. 1.6-1.8, the following expression (Eq. 1.9), to calculate the concentration expected in the solution sampled at the outlet of the column, C_{col} (mg/l), was obtained (Van Genuchten and Alves 1982):

$$C_{col}(h_{sand},t) = \frac{C_0}{2} \cdot \left[erfc\left(\frac{h_{sand} - \frac{v}{R} \cdot t}{2 \cdot \left(\alpha \cdot \frac{v}{R} \cdot t \right)^{1/2}} \right) + \exp\left(\frac{h_{sand}}{2 \cdot \alpha} \right) \cdot erfc\left(\frac{h_{sand} + \frac{v}{R} \cdot t}{2 \cdot \left(\alpha \cdot \frac{v}{R} \cdot t \right)^{1/2}} \right) \right] \tag{1.9}$$

with:

$$\begin{cases} C_0 = C_{mat}^{eq} & \text{for t<t*} \\ C_0 = C_{mat}^{no-eq} & \text{for t} \geq \text{t*} \end{cases} \tag{1.10}$$

where *α* (cm) denotes the longitudinal dispersivity (which can be estimated as 0.1 of h_{sand}) and *R* (-) the retardation factor through the sand layer that, assuming a linear equilibrium partitioning, can be calculated as reported in Eq. 1.11:

$$R = 1 + \frac{\rho_{sand} \cdot K_d}{\theta_{sand}} \tag{1.11}$$

where θ_{sand} is the sand porosity, ρ_{sand} the bulk density of the sand layer and K_d (l/kg) the soil-water partition coefficient.

t* reported in Eq. 1.10 represents the time required to achieve a mass transfer-controlled release condition that can be fixed equal to approximately 1 pore volume of replaced leaching solution and calculated as shown in Eq. 1.12:

$$t^* = \frac{V_{sat}}{q} \tag{1.12}$$

where V_{sat} is the water volume needed to saturate the pore volume of the column (l) and *q* (l/s) the applied flow-rate.

For small values of *α*, Eq. 1.9 can be reduced to (Eq. 1.13):

$$C_{col}(h_{sand}, t) = \frac{C_0}{2} \cdot erfc\left(\frac{h_{sand} - \frac{v}{R} \cdot t}{2 \cdot \left(\frac{v}{R} \cdot \alpha \cdot t \right)^{1/2}} \right) \tag{1.13}$$

Hence substituting Eq. 1.1 and Eq. 1.3 in Eq. 1.13, the concentration expected in the solution at the outlet of the column, C_{col} (mg/l), can be calculated as reported in Eq. 1.14:

$$C_{col}(t) = \frac{C_s}{K_d} \cdot \frac{1}{2} \cdot erfc\left(\frac{h_{sand} - \frac{v}{R} \cdot t}{2 \cdot \left(\frac{v}{R} \cdot \alpha \cdot t \right)^{1/2}} \right) \qquad \text{for } t<t^* \qquad (1.14a)$$

$$C_{col}(t) = \left(C_s \cdot \rho \cdot (1-\theta) \cdot V_{col,mat} \cdot \frac{S}{q} \sqrt{\frac{D_a}{\pi \cdot t}} \right) \cdot \frac{1}{2} \cdot erfc\left(\frac{h_{sand} - \frac{v}{R} \cdot t}{2 \cdot \left(\frac{v}{R} \cdot \alpha \cdot t \right)^{1/2}} \right) \qquad \text{for } t \geq t^* \qquad (1.14b)$$

Note that Eq. (1.14) is similar but not exactly the same as the solution reported by Grathwohl and Susset (2009), since Eq. 1.14a describes the flow of the contaminant through the sand layer, where it was assumed that the concentration of the contaminants at $t=0$ can be considered to be negligible. The other key difference is that in the solution proposed by Grathwohl and Susset (2009) it was assumed that local equilibrium conditions are fulfilled both initially and during the whole percolation process, whereas in this study, as shown in Eq. 1.14b, leaching was considered to be limited by mass transfer for t≥t*. In addition, in order to account for the depletion of the source of the contaminant over time (t) due to the progressive release from the BA, C_s in Eq. 1.14 can be calculated as shown in Eq. (1.15) assuming a flux-controlled release (Verginelli and Baciocchi, 2013):

$$C_s(t) = C_{s,0} \cdot \exp(-\mu t) \qquad (1.15)$$

with:

$$\mu = \frac{v}{R_{BA} \cdot (h_{col} - h_{sand}) \cdot \rho \cdot K_d} \qquad (1.16)$$

where $C_{s,0}$ is the initial concentration of the element in the BA, R_{BA} (-) is the retardation factor through the BA packed in the column and K_d is the solid-water partition coefficient (l/kg).

1.3 RESULTS AND DISCUSSION

1.3.1 Bottom ash characterization

The grain size distribution of the three types of analysed BA is reported in Figure 1.1. From the graph, it can be observed how the gasification BA presented a higher homogeneity compared to the other two types of BA as indicated by the lower gradation of the curve.

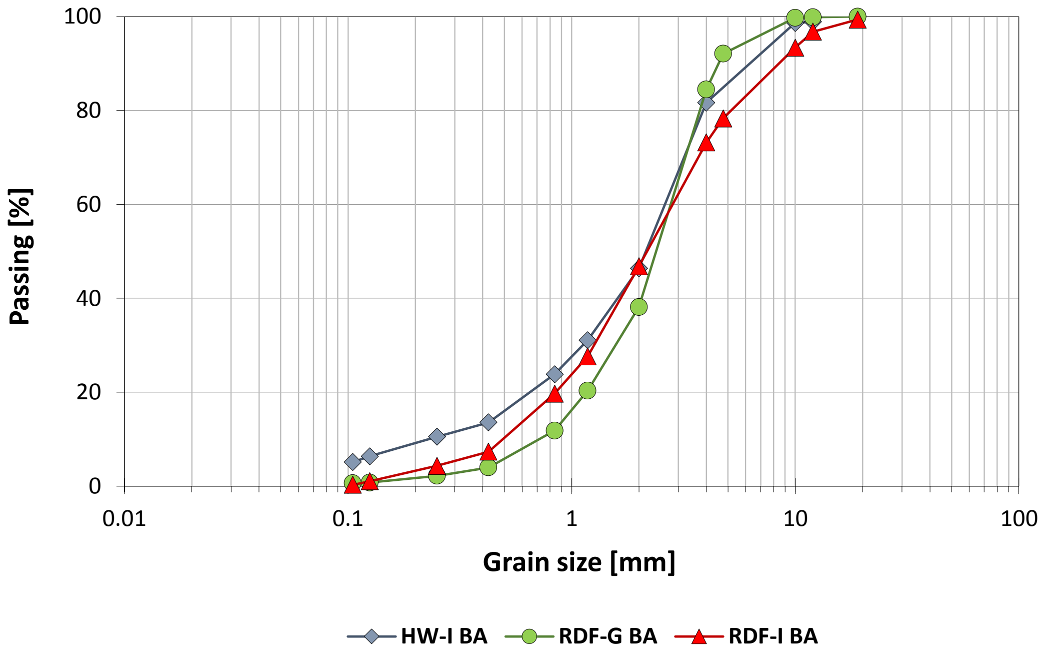

Figure 1.1 Particle size distribution of the three types of analysed BA: hospital waste incineration BA (HW-I BA), RDF gasification BA (RDF-G BA) and RDF incineration BA (RDF-I BA).

Table 1.1 reports the chemical composition, TOC and calcite content of the three types of analysed BA. Overall the results showed to be in line with the ones reported in our previous studies regarding these specific types of residues, i.e. (Lategano et al., 2007; Rocca et al., 2013; Rocca et al., 2015) for the HW-I BA, (Baciocchi et al., 2010; Rocca et al., 2012; Rocca et al., 2013) for the RDF-I BA and (Rocca et al., 2012) for the RDF-G BA. In addition, all the measured elements for the HW-I BA showed to be in the range of values typically observed for this type of BA (Idris and Saed, 2002; Filipponi et al., 2003; Kougemitrou et al., 2011). As can be noted comparing the concentration values reported in Table 1.1, the three types of BA presented a quite similar content of macro-constituents, with the exception of the higher Fe amount retrieved in the RDF-G BA and the lower Ca and K concentrations of the HW-I BA. As for trace constituents, the HW-I BA showed to be enriched in Ba and Cr with respect to the other two types of residues, while the RDF-I BA presented a significantly higher concentration of Pb and Zn; Ni and Cu resulted more abundant in the RDF-G BA and actually the measured content of the latter element was significantly higher than the concentrations reported for this type of BA in previous studies (Rocca et al., 2012; Gori et al., 2011).

Table 1.1 Chemical composition, total organic carbon (TOC) and carbonate ($CaCO_3$) content of HW-I BA, RDF-G BA and RDF-I BA.

	HW-I BA	**RDF-G BA**	**RDF-I BA**
Macro-constituents (g/kg dry matter)			
Al	63	56	81
Ca	152	223	243
Fe	15	82	19
K	4	13	11
Mg	11	14	14
Na	25	16	22
Si	126	89	80
Trace elements (mg/kg dry matter)			
Ba	2788	866	1187
Cd	<30	<30	<30
Co	<40	43	123
Cr	2854	2419	813
Cu	2896	23720	2810
Mn	510	1132	1197
Mo	50	30	<20
Ni	545	656	258
Pb	<20	62	573
V	30	75	38
Zn	774	204	2377
TOC (wt.% dry)	6.5	< 0.2	0.27
$CaCO_3$ (wt.% dry)	1.7	< 0.2	5.4

As for the organic and inorganic carbon content of the slag, as shown in Table 1.1, the HW-I BA presented a significantly higher TOC than the other two types of residues. Actually, as discussed in Rocca et al., 2013, the high TOC measured for this type of BA is to be related to elemental black carbon that is generated through a pyrolytic-like process taking place in the rotary kiln combustion system due to an oxygen-deficient atmosphere that limits the complete combustion of the HW feedstock. The incineration slag instead exhibited a low TOC content but a noteworthy calcite content probably related to the significant amount of paper in the treated RDF, while, owing to the high operating temperature of the gasification process, neither organic or inorganic carbon was detected in the RDF-G BA.

The mineralogy of the three types of BA determined by X-ray diffraction (see Fig. A.1 in the Annex A) also proved to be very similar to that observed in previous studies (Rocca et al. 2012; 2015). In particular, the HW-I and RDF-G BA showed to be mainly made up by an amorphous matrix and only few crystalline phases were detected. Namely, for the HW-I BA the identified mineral phases were calcite ($CaCO_3$), hematite (Fe_2O_3), Fe-silica ($Fe\text{-}SiO_2$) and gehlenite ($Ca_2Al_2SiO_7$). For the RDF-G BA, only akermanite ($CaMgSi_2O_7$), magnetite (Fe_3O_4) and gehlenite ($Ca_2Al_2SiO_7$) were detected. On the contrary, RDF-I BA showed to contain a wide variety of crystalline phases such as gehlenite ($Ca_2Al_2SiO_7$), calcite ($CaCO_3$), hydrocalumite ($Ca_4Al_2Cl_2O_6 \cdot 10H_2O$), portlandite ($Ca(OH)_2$), quartz ($SiO_2$), anorthite ($CaAl_2Si_2O_8$), akermanite ($Ca_2MgSiO_7$) and hematite ($Fe_2O_3$).

1.3.2 Release as a function of the L/S ratio

Figure 1.2, Figure 1.3 and Figure 1.4 report, for the tested HW-I BA, RDF-G-BA and RDF-I BA, the release of constituents and pH values as a function of the liquid to solid ratio obtained from the different types of performed leaching tests. Namely, the average concentration values leached per kg of dry slag obtained from the column test (CEN/TS 14405), batch test (SR 003.1) on ground and unground BA and the two compliance leaching tests at L/S = 2 l/kg (UNI/EN 12457-1) and L/S = 10 l/kg (UNI/EN 12457-2) are shown as a function of the applied L/S ratio. It should be noted that the results of the column test are expressed in terms of the cumulative amount of constituent released up to the specific overall L/S ratio applied from the beginning of the experiment. For each type of BA, it was decided to exhibit the leaching concentrations of 8 constituents that include regulated trace elements, macro-constituents and DOC. The selection of the constituents to report in Figures 1.2-1.4 was made on the basis of the relevance of the concentration values retrieved for each BA, and also in order to allow to report and discuss different leaching profiles.

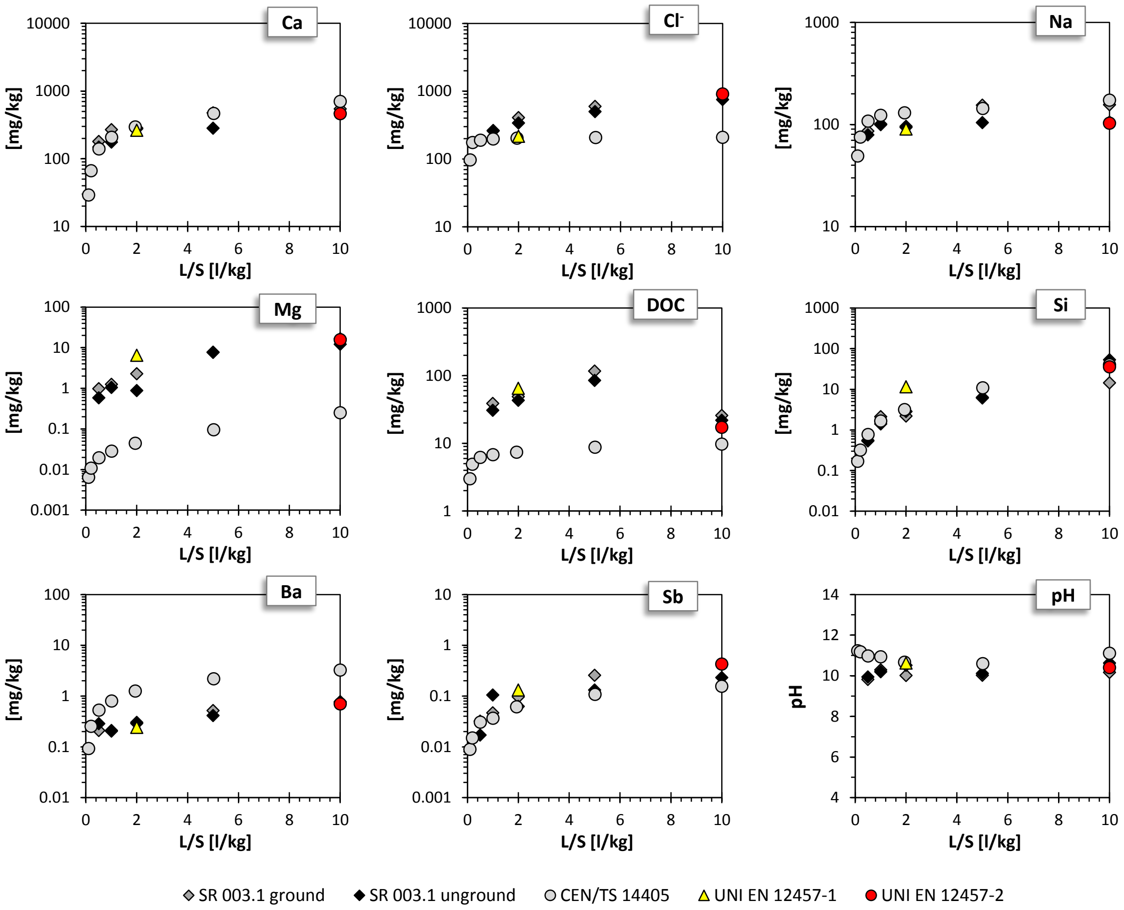

Figure 1.2 Release of Ca, Na, Cl$^-$, DOC, Si, Ba, Sb and Mg (mg/kg dry wt.), and pH as a function of the applied L/S ratio (l/kg) for the HW-I BA.

The complete results of all the different types of leaching tests performed on the HW-I, RDF-G and RDF-I BA are reported respectively in Tables A.1, A.2 and A.3 of the Annex A. As far as HW-I BA are concerned (Fig. 1.2), among the regulated constituents, Cl$^-$, DOC, Ba and Sb were detected in the eluates of all the leaching tests performed. On the contrary, differently from what could be expected from the chemical composition of this type of BA (see Table 1.1), Cu concentrations in all the analysed eluates proved lower than the instrumental quantification limit (0.03 mg/l), suggesting that this element is in a poorly available form for leaching.

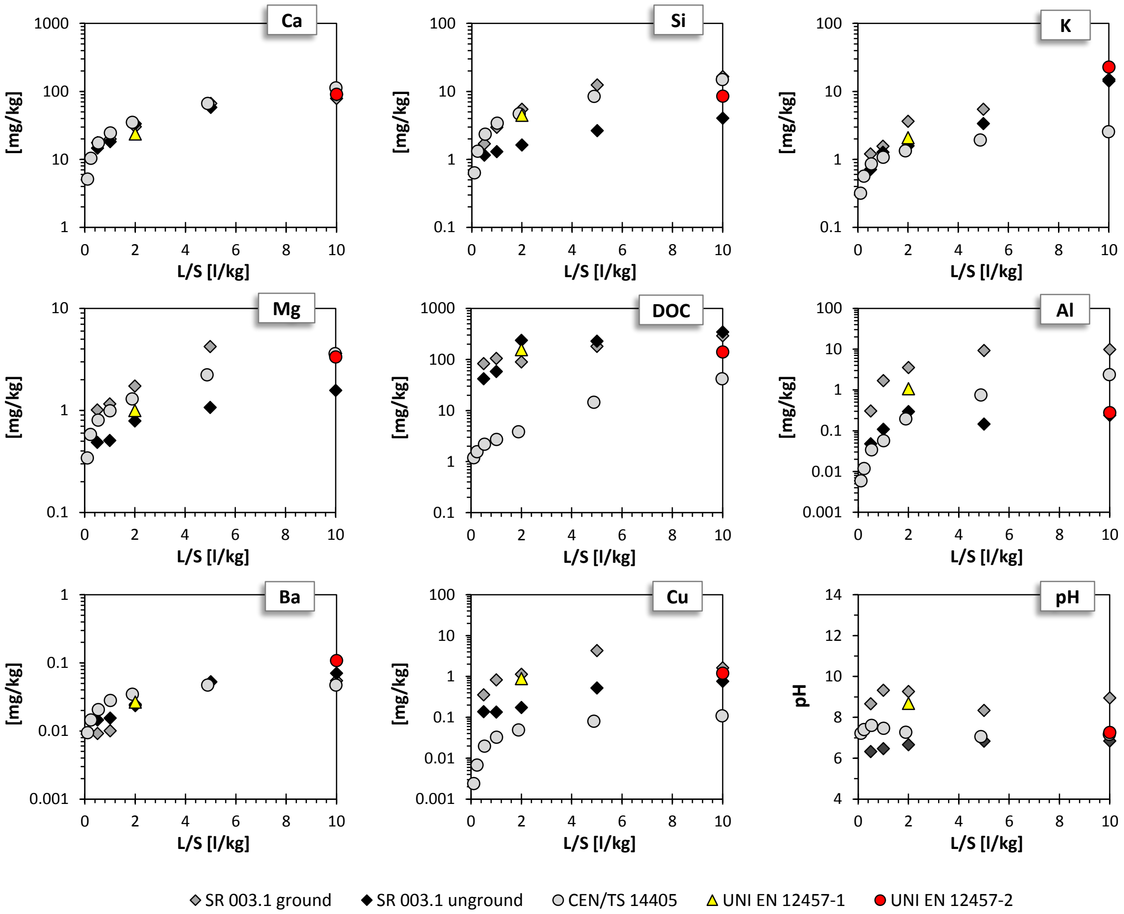

Figure 1.3 Release of Ca, Si, K, Mg, Al, Cu, DOC and Ba (mg/kg dry wt.), and pH as a function of the applied L/S ratio (l/kg) for RDF-G BA.

Similarly Cr, that together with Cu and Ba exhibited the highest total content among trace elements (see Table 1.1), was only detected in the eluates of the batch tests, with concentrations of approximately 0.1 mg/l at a L/S of 10 l/kg (see Table A.1 in the Annex A). The different results observed for Cr in the two types of tests, may be mainly ascribed to the different pH values (see Fig. 1.2) measured for the batch tests (ranging from 9.8 to 10.6) compared to those observed in the leachate of the column test (ranging from 10.6 to 11.3). In fact, pH dependence leaching tests carried out on this type of slag indicated that the solubility of Cr is higher in the pH range resulting for the batch tests respect to the one observed for the column tests (Rocca et al., 2015). Similarly to what observed for the HW-I BA, the results obtained for RDF-G BA (Fig. 1.3) reveal that the release of contaminants is quite limited with respect to their total content. In fact, although for this type of BA, pH values (see Fig. 1.3) showed to vary significantly depending on the type of leaching test applied (ranging from 7 to 7.6 in the column test, from 6.3 to 6.9 in the batch test on the unground BA and from 8.3 to 9.3 in the batch test conducted on the particle size-reduced sample) the only regulated constituents presenting concentration values above the instrumental quantification limits in all the leaching tests performed were Cu, Ba and DOC (see Table A.2 in the Annex A).

For the RDF-I BA, as shown in Fig. 1.4, a generally higher release of contaminants as a function of the L/S ratio compared to the other two types of BA was observed. Namely, significant concentrations of amphoteric metals such as Pb and Zn were only detected in the eluates of this type of BA (see Table A.3 in the Annex A). Since the solubility of these elements greatly depends upon pH, exhibiting an increase under both strongly acidic and alkaline conditions (Sabbas et al., 2003), this finding may be in part ascribed to the higher content of these elements in this material compared to the other two types of analysed BA (Table 1.1), but also can be due to the differences in their native pH. In fact, the pH values derived from the batch and column tests for RDF-I BA, proved to be highly alkaline, ranging from 12.4 to 12.9 (see Fig. 1.4). Moreover, differently from what observed for the other two tested materials, for this type of BA pH values did not differ appreciably from batch and column tests. These differences between the native pHs of the three types of BA could be mainly related to their different mineralogical composition (see Fig. A.1 in the Annex A). In fact, the high pH value measured for the RDF-I BA can be principally ascribed to the abundance of alkaline soluble phases observed for this type of material (Rocca et al., 2012) compared to HW-I BA and RDF-G BA, that conversely exhibited a high content of amorphous phases.

Overall, the obtained results showed that despite all the three types of examined BA contained a relatively high total content of contaminants (see Table 1.1) only a small amount of these elements, also at the highest L/S ratio tested (10 l/kg), was actually leachable and thus environmentally available. Namely, the percentage release was less than 1% for RDF-G BA and HW-I BA and lower than 5% for RDF-I BA. However, it is important to point out that, depending on the specific environmental scenario, these relatively low leaching concentrations might still cause concern.

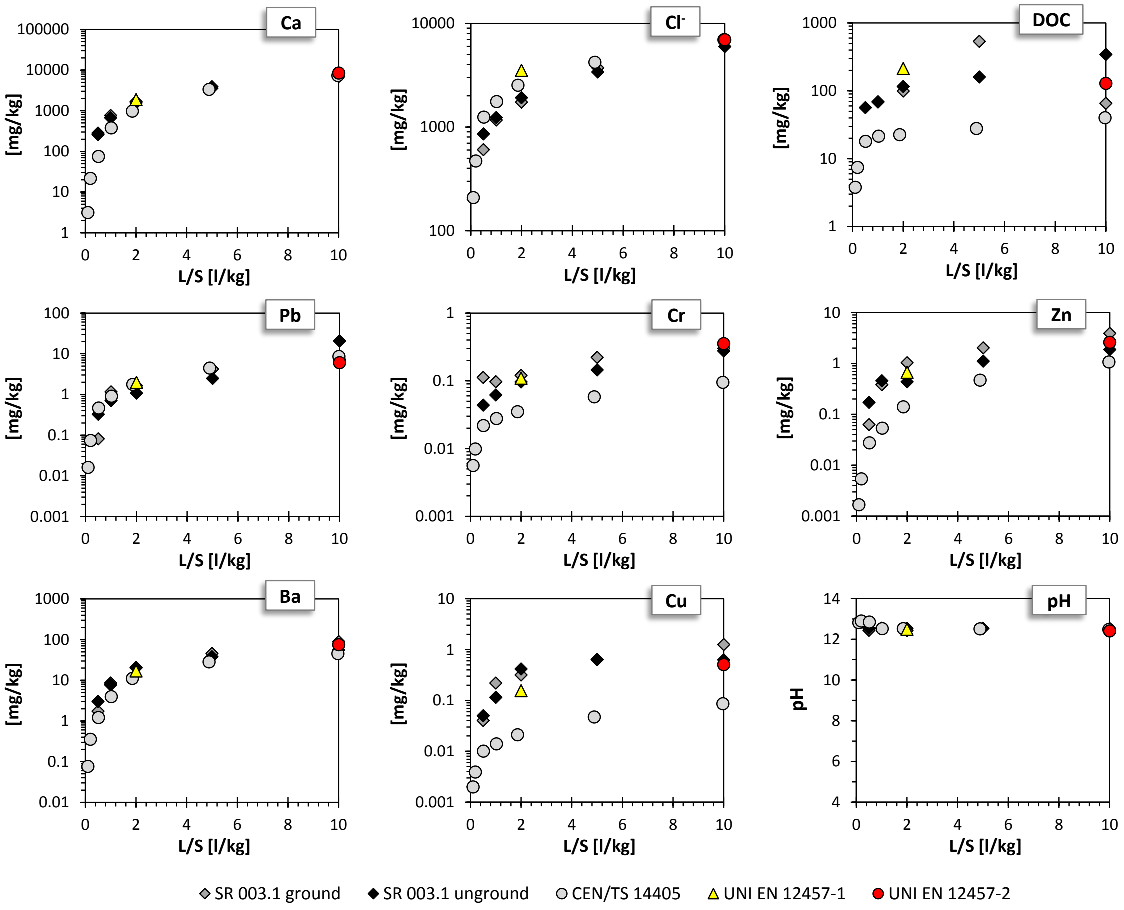

Figure 1.4 Release of Ca, Cl$^-$, DOC, Ba, Cu, Pb, Cr and Zn (mg/kg dry wt.), and pH as a function of the applied L/S ratio (l/kg) for RDF-I BA.

Moreover, the higher release of Cu was observed for BA exhibiting an increased leaching of DOC (i.e. RDF-I BA and RDF-G BA) confirming that for waste thermal treatment BA leaching of Cu could be related to its complexation with DOC, as also indicated by Dijkstra et al. (2006), Meima et al. (1999) and van Zomeren and Comans, (2004). On the contrary, for HW-I BA, despite the significant content of TOC, a lower release of DOC was noticed and concentrations of Cu in the eluates were always below the instrumental quantification limit. These results may be explained by the fact that, as shown by Rocca et al. 2013 through TG_DTA coupled with MS analysis of the carbon fraction of BA samples, the relevant concentration measured by TOC analysis for this type of BA is actually related to elemental carbon instead of organic carbon.

1.3.3 Comparison of column and batch tests

Fig. 1.2, Fig. 1.3 and Fig. 1.4 allow to observe that in general for all three types of analysed BA the results achieved from column and batch tests followed, from a qualitative point of view, similar trends. Compliance leaching tests results as well were in good agreement, at both L/S = 2 l/kg and at L/S = 10 l/kg, with those obtained by SR 003.1 batch test at the same L/S ratios, despite the different grinding degree of the samples (d< 4mm and d< 2mm, respectively) and the duration of the tests (24 h for compliance tests and 48 h for SR 003.1). However, the range of concentrations represented in these figures is quite wide since it is plotted on a logarithmic scale, thus does not allow for a quantitative comparison between the results obtained from the different leaching tests. To better assess this point, Figure 1.5 reports for the three types of analysed BA, the correlation between the element release (expressed as mg/kg of dry matter) obtained by batch tests (SR 003.1) on both ground and unground material and column tests as a function of the applied L/S ratio. Furthermore, in order to assess the influence of the particle size reduction on the obtained results, for each type of BA, the compounds release from the batch tests on the ground samples was compared to the one attained from batch tests conducted on unground BA. Referring to Fig. 1.5, it can be noticed that for some elements differences of up to two orders of magnitude between the release obtained from column and batch tests can be identified. For instance, for HW-I BA (Fig. 1.5a and Fig. 1.5b), the concentration values of Mg measured in batch tests, on both ground and unground samples, showed to be higher of up to two orders of magnitude than those obtained from the column test. For the other elements, the release from HW-I BA obtained from the two types of test fell within an average factor of 10, although a general tendency of the batch tests of providing higher concentrations can be noticed.

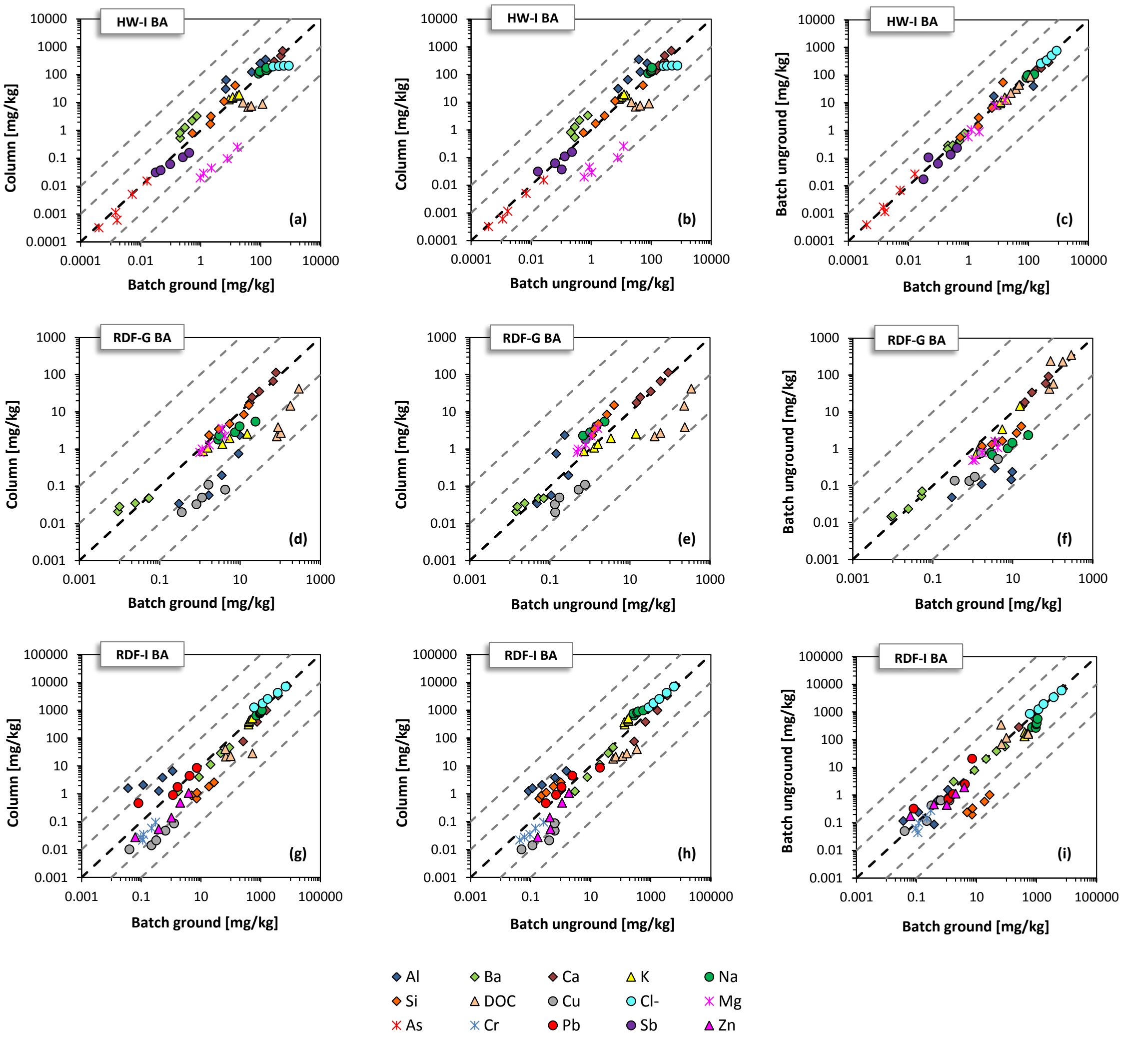

Figure 1.5 Correlations between column and batch tests results on ground and unground BA and between batch tests performed on unground and ground material for HW-I BA (a, b and c), RDF-G BA (d, e and f) and RDF-I BA (g, h and i). The diagonal black line denotes a linear correlation ratio of 1:1.

Regarding RDF-G BA (Fig. 1.5d and Fig. 1.5e), the release of both K and DOC as determined from batch and column tests proved to be poorly correlated. Moreover, the concentration values of the latter element and Cu were in both types of batch tests higher of up to two orders of magnitude than the ones observed in the column test, thus confirming again the correlation between the release of DOC and Cu. Although to a lower extent (within one order of magnitude), the same results for Cu and DOC were also observed for the RDF-I BA (Fig. 1.5g and Fig. 1.5h), in agreement with the results reported by van der Sloot et al. (2003) that found that batch tests often lead to a greater mobilisation of DOC compared to column tests. Moreover, the results reported in Fig. 1.5 reveal that the type of leaching test method applied (batch or column) affected the results more than the particle size reduction of the material. In fact, batch tests carried on ground samples generally gave comparable results to those performed on the unground ones (see Fig. 1.5c, Fig. 1.5f and Fig. 1.5i). However, for the RDF-G BA, the leaching of some elements (e.g. Si, Al, Na and Mg) proved higher from the batch tests carried out on the ground BA, see Fig. 1.5f. The higher release observed for the ground samples can be mainly ascribed to the greater surface area available for the leaching process (Chimenos et al., 2003). As to the higher effect of grinding observed in the RDF-G BA with respect to the other tested material, this could be in part explained by the initial mean particle size of RDF-G BA that was greater than the one observed for the other two types of BA (see Fig. 1.1) thus making the effect of grinding more important for this type of BA. Moreover, the specific characteristics of the material may have played an important role in increasing the release on the ground sample of the RDF-G BA. In fact, the vitrified solid matrix of this material, in which the contaminants are incorporated in a more stable form compared to the other two types of BA, may have been more significantly affected by the grinding process, leading to a higher release of contaminants compared to the test performed on the unground BA.

1.3.4 Comparison with regulatory limits

The European Landfill Directive (2003/33/EC, EU LFD) provides limit values for three different types of leaching tests, i.e.: UNI/EN 12457 part 1 at L/S of 2 l/kg, UNI/EN 12457 part 2 at L/S of 10 l/kg and the first eluate C_0 (L/S= 0.1 l/kg) of the column leaching test CEN/TS 14405, specifying that the tests used for compliance purposes should consist of at least a batch leaching test. Table 1.2 reports for the three types of analysed BA the release values (mg/kg) obtained from each type of leaching test highlighting the values that exceeded the EU LFD criteria for inert waste (for the limit values refer to Table A.4 in the Annex A). Note that the comparison was focused only on inert waste since no value exceeded the EU LFD criteria for disposal in non-hazardous waste landfills. Moreover, the results obtained from the batch test at L/S of 10 l/kg were also compared to the limit values set from the Italian legislation for the reuse of non-hazardous waste (M.D. 186/2006).

Table 1.2 Comparison of the release obtained by compliance leaching tests UNI/EN 12457 part 1 (L/S= 2 l/kg), UNI/EN 12457 part 2 (L/S= 10 l/kg) and the first eluate C_0 (L/S= 0.1 l/kg) of the column leaching test CEN/TS 14405 for the analysed BA with the limits set by European Landfill Directive (2003/33/EC, EU LFD) and the Italian legislation for reuse of waste materials (M.D. 186/2006). Results are reported in mg/kg. Bold values: concentrations > EU LFD criteria for inert waste landfilling; underlined values: concentrations > Italian reuse limits. LOQ: Limit of Quantification (reported below the Table).

	HW-I BA			**RDF-G BA**			**RDF-I BA**		
	C_0	**L/S = 2 l/kg**	**L/S = 10 l/kg**	**C_0**	**L/S = 2 l/kg**	**L/S = 10 l/kg**	**C_0**	**L/S = 2 l/kg**	**L/S = 10 l/kg**
pH	11.23	10.62	10.40	7.22	8.68	7.26	12.81	12.49	12.41
As	0.00005	0.02	0.025	0.0002	0.001	<LOQ	0.0002	<LOQ	<LOQ
Ba	0.09	0.24	0.7	0.01	0.03	0.1	0.08	**17**	**75**
Cr	0.004	0.09	**1.2**	<LOQ	<LOQ	<LOQ	0.006	0.1	0.35
Cu	<LOQ	<LOQ	<LOQ	0.002	0.9	1.2	0.002	0.16	**0.51**
Mo	0.017	0.1	<LOQ	<LOQ	<LOQ	<LOQ	0.002	0.04	0.12
Pb	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**0.02**	**2**	**6**
Sb	0.009	**0.13**	**0.43**	0.0009	0.006	0.006	**0.03**	0.004	0.026
Se	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.0007	<LOQ	<LOQ
V	<LOQ	0.02	0.12	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Zn	0.003	0.04	<LOQ	<LOQ	<LOQ	<LOQ	0.002	0.7	2.6
DOC	3	65	17	1	154	140	4	215	129
Cl^-	**100**	215	**909**	<LOQ	<LOQ	<LOQ	**209**	**3528**	**6957**

Limit of quantifications (LOQ) in mg/l: As (0.001), Be (0.001), Cd (0.005), Co (0.005), Cr (0.007), Cu (0.005), Hg (0.001), Mo (0.01), Ni (0.009), Pb (0.03), Se (0.002), V (0.005), Zn (0.01), Cl^- (20)

For the HW-I BA, by referring to the results obtained from the batch test at L/S of 10 l/kg, the elements which exceeded the EU LFD criteria for inert waste but complied with the limit values set for non-hazardous waste landfilling were Cr, Sb and Cl^-. As to the Italian legislation, only Cr showed to be above the limit for reuse. Considering the other two types of leaching test methods, the same classification was obtained but, only Sb for the batch test at L/S of 2 l/kg and Cl^- for the first eluate of column test, showed to exceed the criteria for inert waste landfilling. Moreover, for this type of BA also the TOC content (6.5%) was above the limit value set for disposal in inert waste landfills (3%). For RDF-I BA, leaching concentrations of Ba, Pb and Cl^- showed to exceed the limit values for inert waste landfilling for both batch types of leaching tests. Besides these elements, also Cu and the pH value were higher than the Italian limit values for reuse. Concerning column test results, the elements that showed to be critical for the disposal of this type of BA in inert waste landfills were Pb, Sb and Cl^-.

Regarding RDF-G BA, the concentration values of all the contaminants detected in the eluates of the three compliance leaching tests showed to comply with the EU LFD criteria for inert waste landfilling and only the release of Cu was slightly higher than the limit value for reuse.

1.3.5 Modelling of column test results and implications for long-term leaching

The higher release observed for the batch experiments compared to the column tests can be mainly related to the different mode of execution of the two types of leaching tests. In fact, while in the batch test the material is assumed to be in a pseudo-equilibrium condition with the water phase, in the column test the continuous renewal of the leachant solution may possibly hinder the establishment of equilibrium conditions. Hence, as described in Paragraph 1.2.3, to better analyse and interpret the results of the column tests, two models were employed and compared to the experimental data, one assuming equilibrium conditions, i.e. percolation-controlled release, and the other hypothesizing non equilibrium conditions, i.e. mass transfer-controlled release. Specifically, for percolation-controlled release Eq. 1.14a was employed, while to simulate mass-transfer release Eq 1.14b was used. The parameters employed for modelling the results of the column tests, derived from the characteristics of the BA and the specific test conditions applied, are reported in Table 1.3. The retardation factor due to the presence of the sand layer was considered to be negligible, i.e. in Eq. 1.14 a,b R was assumed equal to 1. In the modelling of percolation controlled-release, the gradual decrease of the total content of the contaminant over time was taken into account and C_s was calculated according to Eq. 1.15 and 1.16; the K_d values assumed for the various constituents for each type of BA, calculated as the ratio between the total content of the element in the BA, C_s, and its maximum concentration in the leachate of the column test (C_{sol}), are reported in Table 1.4.

Table 1.3 Parameters employed in Eq. 1.14a,b to model the leaching concentrations as a function of the L/S ratio for each type of BA.

Parameters	**Symbol**	**Unit**	**HW-I BA**	**RDF-G BA**	**RDF-I BA**
Average flow-rate	q	l/s	1.52E-05	1.36E-05	1.44E-05
BA dry bulk density	ρ	kg/cm^3	1.21E-03	1.7E-03	1.1E-03
BA porosity	θ	-	0.3	0.34	0.47
BA equivalent particle size	d_{eq}	cm	0.1	0.15	0.11
BA moisture content	u	% w/w	24.9	1.8	19.2
Water needed to saturate the pore volume	V_{sat}	l	0.27	0.94	0.85
Total test duration	t_{tot}	s	1.98E+06	3.30E+06	2E+06

For the modelling of mass transfer controlled-release instead, C_s was assumed to be equal to the total content of the element in the BA. The apparent diffusion coefficients resulting for the different major and trace constituents for each type of BA were derived from the fitting of Eq. 1.14b with the experimental data and are exhibited in Table 1.4.

In Figure 1.6, Figure 1.7 and Figure 1.8 the average concentrations (mg/l) of selected major and trace constituents measured in the eluates of the column leaching tests carried out respectively for the HW-I BA, RDF-G BA and RDF-I BA are reported, along with the results obtained by the application of the model assuming either equilibrium i.e. percolation-controlled release (solid red line) or non-equilibrium conditions i.e. mass-transfer-governed release (dotted blue line). Referring to Fig. 1.6, 1.7 and 1.8, it can be noticed that in the very early stages of the test, for some elements (such as Cu, Pb and Al), a slight increase of the concentration in the eluate was observed. This trend can be ascribed to the adsorption of these elements to the sand placed on top of the slag leading to a retardation of the release of these elements from the column (i.e. R> 1).

At higher liquid to solid ratios (approximately after the displacement of one pore volume), a decrease of effluent concentrations, that can be ascribed to the occurrence of mass release under non-equilibrium conditions, was observed. This result is also confirmed by the fact that at high L/S ratios the pseudo-equilibrium model predicts effluent concentrations that are significantly higher than the ones observed in the effluent of the column tests.

Table 1.4 Solid-water partition coefficients (K_d) assumed for modelling percolation-controlled release and apparent diffusion coefficients (D_a) used for modelling mass transfer controlled release. n.a. stands for "not applicable", meaning that the mass-transfer controlled model (eq. 1.14b) did not fit the concentration trend of the specific element.

	HW-I BA		**RDF-G BA**		**RDF-I BA**	
	K_d [l/kg]	**D_a [cm^2/s]**	**K_d [l/kg]**	**D_a [cm^2/s]**	**K_d [l/kg]**	**D_a [cm^2/s]**
Al	$7.8x10^{+02}$	$9x10^{-15}$	$1.8x10^{+05}$	n.a	$1.4x10^{+04}$	$2x10^{-18}$
Ba	$1.8x10^{+03}$	$3x10^{-16}$	$9.3x10^{+03}$	$3x10^{-18}$	$1.4x10^{+02}$	n.a.
Ca	$4.2x10^{+02}$	$5x10^{-15}$	$4.6x10^{+03}$	$9x10^{-17}$	$3x10^{+02}$	n.a.
Cr	-	-	-	-	$1.5x10^{+04}$	$6x10^{-18}$
Cu	-	-	$5.7x10^{+05}$	$1x10^{-20}$	$1.4x10^{+05}$	$6x10^{-19}$
K	$6.5x10^{+01}$	$9x10^{-16}$	$4.5x10^{+03}$	$1x10^{-17}$	$1.8x10^{+01}$	$3x10^{-13}$
Mg	$1.6x10^{+05}$	$4x10^{-20}$	$4.4x10^{+03}$	$1.5x10^{-17}$	-	-
Na	$4.9x10^{+01}$	$1x10^{-15}$	$2.4x10^{+03}$	$3.5x10^{-17}$	$1.6x10^{+01}$	$2x10^{-13}$.
Pb	-	-	-	-	$4.7x10^{+02}$	n.a.
Si	$2.2x10^{+04}$	n.a.	$1.5x10^{+04}$	$1x10^{-17}$	$3.2x10^{+04}$	$4x10^{-19}$
Zn	-	-	-	-	$2x10^{+04}$	n.a.

On the contrary, for most constituents the observed trends could be quite well described using the mass-transfer controlled model defined in Eq. (1.14b). Although, as previously stated the apparent diffusion coefficients, D_a, were fitted with the experimental leaching data, the resulting values (see Table 1.4) for most contaminants proved of the same order of magnitude of those derived from aqueous diffusion coefficients (typically in the range of 10^{-5} - 10^{-6} cm^2/s), applying the equation reported by Grathwohl (2014) with an intraparticle porosity (ε) of 0.0005-0.001. These ε values are in line with the ones considered for fine soil by Beyer et al. (2009) and for quartz and limestone by Rugner et al. (1999).

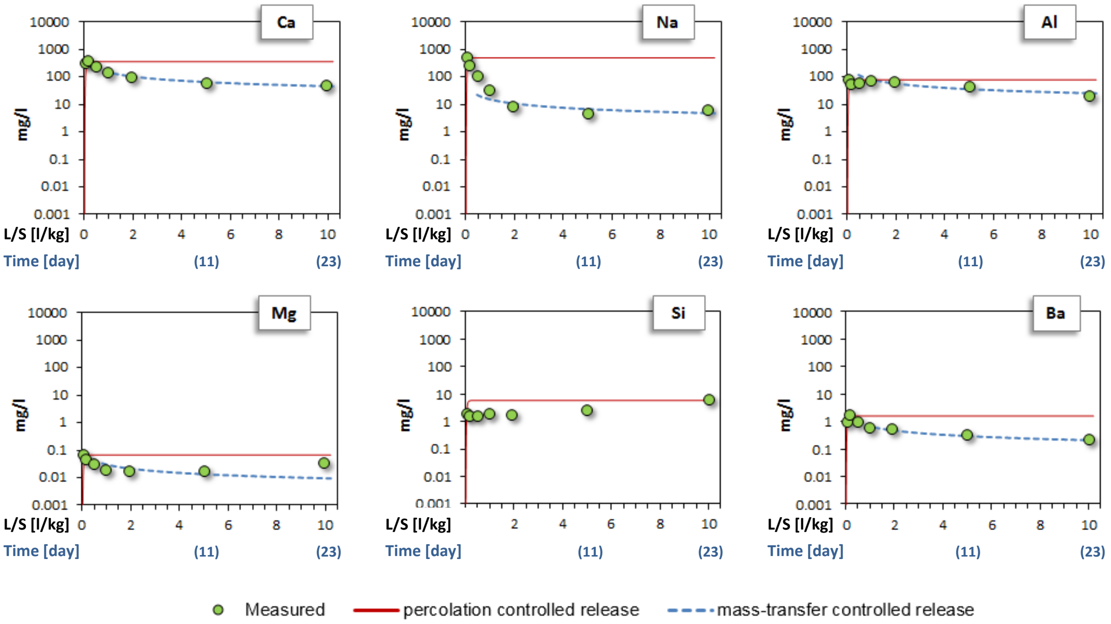

Figure 1.6 Average leaching concentrations (mg/l) obtained from the column tests as a function of the L/S ratio for the HW-I BA: comparison of measured data (green dots) with model predictions. Percolation-controlled release (solid red line) calculated with Eq. 1.14a, mass transfer controlled release (dotted blue line) calculated with Eq. 1.14b. On the x-axis, the time scale used in the model is also reported as a reference.

Hence, the obtained results suggest that for the three types of analysed BA, the release of most of the considered constituents was governed by the mass transfer rate. This is a key aspect to consider when making long-term field evaluations, since contaminant release governed by mass-transfer implies that the results obtained from the column test cannot be directly used to predict the leaching behaviour expected in the field. In fact, differently from a flux-controlled release, in a leaching scenario limited by the mass desorption rate, the switch from the L/S ratio to time is not applicable (Pantini et al., 2015). This means that for a mass-transfer controlled scenario, column tests resemble the contaminant release expected in the field for leaching times in the order of the duration of the experiment (20-40 days depending on the type of BA, see Fig. 1.6-1.8).

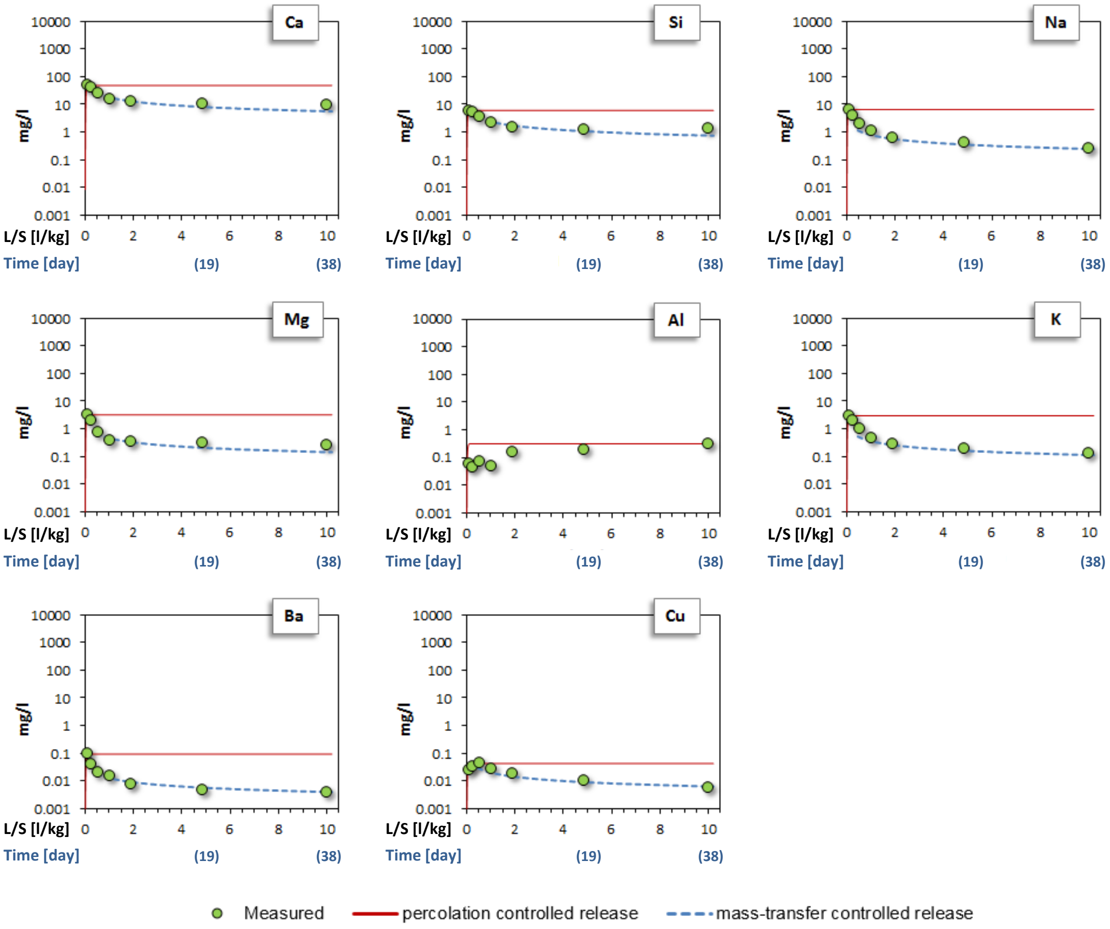

Figure 1.7 Average leaching concentrations (mg/l) obtained from the column tests as a function of the L/S ratio for the RDF-G BA: comparison of measured data (green dots) with model predictions. Percolation-controlled release (solid red line) calculated with Eq. 1.14a, mass transfer controlled release (dotted blue line) calculated with Eq. 1.14b. On the x-axis, the time scale used in the model is also reported as a reference.

In this view, the results obtained from column tests can be used to estimate the apparent diffusion coefficients for each element of concern. These coefficients can then be employed in a screening model such as the one used for the modelling of column test results (Eq. 1.14) using as flow rate the infiltration rate expected in the considered disposal scenario for the time framework of concern.

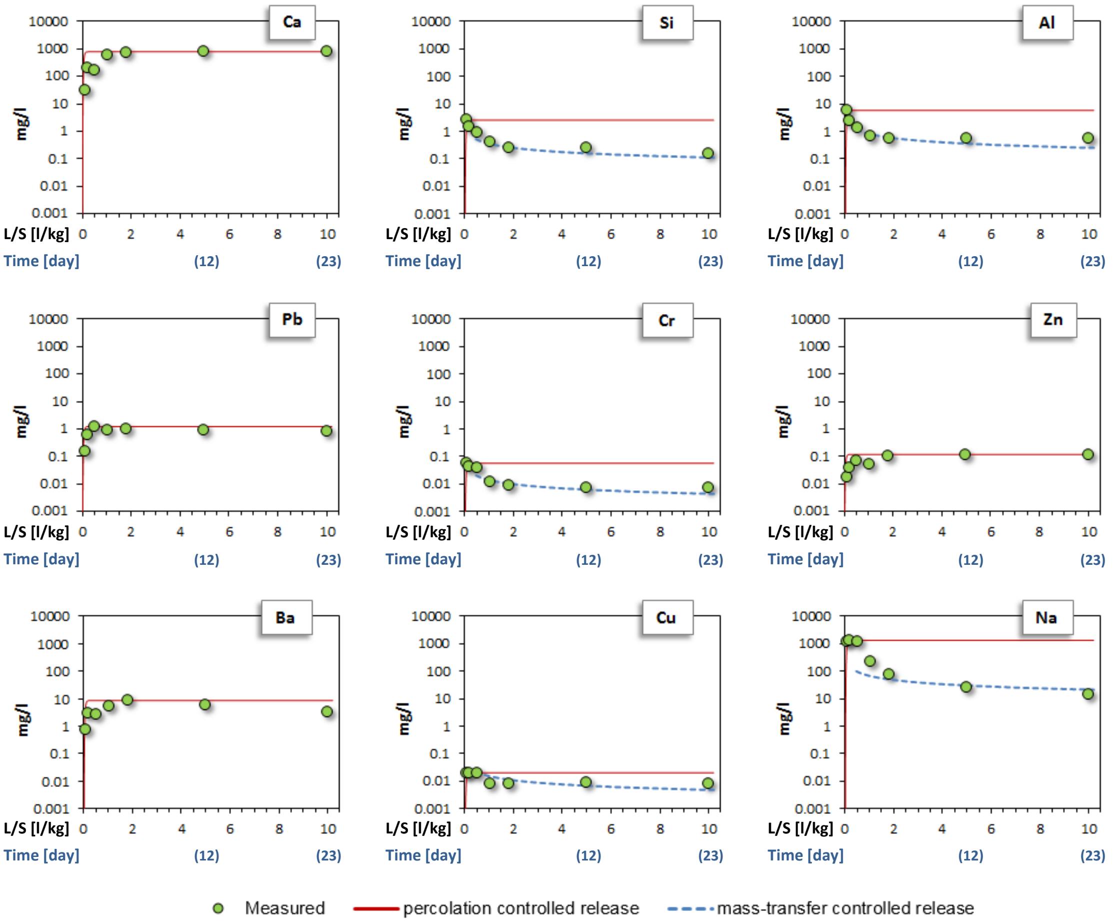

Figure 1.8 Average leaching concentrations (mg/l) obtained from the column test as a function of the L/S ratio for the RDF-I BA: comparison of measured data (green dots) with model predictions. Percolation-controlled release (solid red line) calculated with Eq. 1.14a, mass transfer controlled release (dotted blue line) calculated with Eq. 1.14b. On the x-axis, the time scale used in the model is also reported as a reference.

However, for a reliable assessment of the contaminant release expected in the field, particular caution should also be paid in correctly combining the equilibrium and non-equilibrium models. Indeed, as also observed in the first eluates of the column experiments, at the beginning of a rainfall event, the contaminant present in the water porosity of the disposed material is expected to be near the equilibrium values and only after a renewal of a pore volume, the switch to a mass transfer is expected to occur.

It should also be noted that the release of the different constituents may also be influenced by the frequency and average duration of each rainfall event. In fact, it is likely that the leaching behaviour of the disposed material may be significantly different if the site of concern is characterised by short-term and frequent rainfall events with respect to sites where rainfall events are less frequent but present a longer duration. On the other hand, particular attention should also be paid to the apparent diffusion coefficients required in the model. In fact, as highlighted in this work, depending on the considered material, the same element may exhibit a different leaching behaviour. For instance, making reference to Fig. 1.6-1.8, it can be noticed that Ca and Ba for RDF-I BA showed different trends compared to the ones observed for HW-I BA and RDF-G BA. Furthermore, for RDF-G BA, that as described above are characterised by a vitrified solid matrix, the derived apparent diffusion coefficients (see Table 1.4) of most of elements were of up to two orders of magnitude lower than the ones obtained for the other two types of BA considered in this work. This hence suggests that, as expected, the mass release of each element strictly depends not only on the contaminant’s properties but also on the composition and characteristics of the considered material, such as its mineralogy. Hence, in order to gain more insight on the potential mineralogical phases and mechanisms controlling the release of the different components for each type of BA, it could be interesting to couple the model developed in this study with the results of geochemical modelling.

In addition, it should also be taken into account that the diffusion coefficients were calculated on the basis of the results of the column tests carried out on fresh BA with deionized water. Hence, in order to more realistically assess the long-term leaching behaviour of the BA in field conditions, the effects of weathering and of a variation in the pH of the eluant should also be considered. The effects of weathering could be particularly relevant for the leaching behaviour of RDF-I BA, which are characterized by a significant content of hydroxide and oxide phases (see e.g. Baciocchi et al., 2010); whereas, since the RDF-G BA and HW-I BA displayed respectively an almost negligible or low acid neutralization capacity, variations in the pH of the eluant may play an especially important role for these materials (see Rocca et al., 2012; Rocca et al., 2015). Some of these aspects will be discussed in the Chapter 2.

1.4 CONCLUSIONS

In this Chapter the leaching behaviour as a function of L/S of the considered types of BA i.e. hospital waste incineration (HW-I), RDF gasification (RDF-G) and RDF incineration (RDF-I) BA, was investigated. The experimental results showed that despite the relatively high content of contaminants measured in the solid matrix of the three types of BA, only a small amount of these elements was actually available for the leaching process. A generally lower release of contaminants was observed for the RDF-G BA, which showed to comply with acceptance criteria for inert waste landfilling. HW-I BA and RDF-I BA instead showed to meet the limit values established for landfilling of non-hazardous waste. Hence, these findings show that the environmental behaviour of BA generated from different waste to energy plants may vary significantly depending on the characteristics of the feed waste, but especially of the thermal treatment process applied. Currently up to now, at least in Italy, no distinction is made for BA management based on the type of feed waste or thermal treatment that originated it, and the only option adopted besides non-hazardous waste landfilling is as additive in cement production. However, it appears that for certain types of BA such as the RDF gasification slag tested in this work alternative management options may be viable.

As to the different leaching test methods applied, the obtained results showed that although for most of the elements considered a relatively good correlation between batch and column leaching tests results was observed, the release obtained from batch tests was generally higher (for some elements of up to two orders of magnitude) than the one obtained from column tests. This finding was mainly attributed to the different mode of execution of the two types of tests. In fact, while at the end of the batch tests the material can be assumed to be in a pseudo-equilibrium condition with the water phase solution, in the column tests the continuous renewal of the leachant solution can lead to non-equilibrium release conditions. This hypothesis was also supported by the application of an analytical model, that highlighted that most of the leaching trends observed in the different column experiments could be described quite well assuming the release to be limited by mass-transfer that lead to concentrations in the eluates below equilibrium values. This is a crucial aspect to be considered for the interpretation and application of the lab-scale results to assess the management options and long-term leaching behaviour of the material in field conditions. In fact, although in this specific case the type of leaching test applied showed not to affect the final result in terms of compliance with the limits set for landfill disposal or reuse, the critical contaminants and the leaching trends showed to vary depending on the type of test considered. Furthermore, the fact that for most contaminants release showed to be limited by the mass desorption rate, implies that the frequently adopted switch from L/S ratios to time in order to asses long term release is not applicable for these materials and hence the column tests results can be directly employed only to describe the release expected in the field for relatively short timeframes (i.e. in the order of the duration of the experiment). However, from the results of the column tests, mass-transfer rate coefficients for each contaminant and type of BA may be derived and hence employed in a model to assess the leaching behaviour of the specific type of BA in a disposal or reuse scenario as a function of field conditions and scenario assumptions. This approach, eventually coupled with the results of geochemical modelling, may be useful to derive data that can be employed in a risk-based or life cycle assessment framework for evaluating potential environmental impacts deriving from the specific disposal/reuse option considered.

CHAPTER 2

EFFECT OF PH, PARTICLE SIZE AND WEATHERING ON THE LEACHING BEHAVIOUR OF BOTTOM ASH

2.1 INTRODUCTION

Besides the L/S ratio, of which the influence on the leaching behaviour of the three types of BA was extensively analysed in Chapter 1, also other aspects should be investigated in order to carry out a complete evaluation of the leaching characteristics of these materials. For instance, evaluations about the acid neutralization capacity (ANC) and leaching behaviour as a function of pH should be surely included in order to take into account the geochemical processes that can occur in disposal/reuse scenarios. Indeed, solubility and release of trace metals is primarily governed by pH and ANC, which is the capacity of the material of buffering pH variations that generally occur when the material is exposed to water and the atmosphere (Bendz et al., 2007). The most important alteration processes for MSWI bottom ash include oxidation of metals (e.g. aluminium, iron, copper), precipitation/dissolution of oxide phases and relatively soluble minerals (e.g. calcite; ettringite) and neo-formation of reactive sorptive solid substrates such as Fe/Al (hydro)oxides (Meima and Comans, 1997, 1998; Chandler et al., 1997; Dijkstra et al., 2002, 2006; Cornelis et al., 2008; Arickx et al., 2010). The native alkaline pH of MSWI bottom ash (around 11.5-12.5) is mainly controlled by the relatively fast dissolution of $Ca(OH)_2$. At these pH values the release into the environment of amphoteric metals (e.g. Cu, Pb and Zn), which exhibit increased solubility under both strongly acidic and alkaline conditions resulting in a V-shaped solubility curve (Sabbas et al., 2003), represents the major concern. In addition, as mentioned in the Introduction Section the significant amount of metastable minerals contained in BA makes this residue highly reactive under atmospheric conditions. Thus, when this material is exposed to atmospheric agents, in disposal/reuse scenarios, natural weathering reactions may occur leading to important changes in the mineralogical characteristics of the material, as well as in its leaching behaviour (Meima and Comans, 1999; Chimenos et al., 2000). Indeed, due to carbonation reactions, pH drops and this, together with the neo-formation of secondary minerals, affects the release of trace metals. In particular, a decrease in the leaching of amphoteric metals and an increase in the mobility of oxyanion forming species, such as Cr and Mo, have been indicated to occur upon weathering for MSWI BA (e.g. Meima and Comans, 1999; Chimenos et al., 2003; Polettini and Pomi, 2004).

Furthermore, another aspect which showed to influence both the chemical and mineralogical characteristics of BA, consequently affecting its leaching behaviour (both as a function of pH and the L/S ratio) is represented by the particle size of the material (Chimenos et al., 1999). For example, the finest particle size fractions of samples collected from several incineration plants have shown to present a higher content of contaminants compared to the coarser ones (Chimenos et al., 1999; Stegemann et al., 1995; Chimenos et al., 2003). Based on the above considerations, the primary focus of this study was to assess the release of major components and trace contaminants as a function of pH for the three types of BA considered (i.e. RDF incineration and gasification BA and hospital waste incineration BA) in order to derive a suitable description of the leaching behaviour of BAs under possible pH environmental conditions that may be achieved in disposal/reuse scenarios. In addition, due to the higher heterogeneity and release of contaminants observed for RDF-I BA compared to the other two types of BA (see Chapter 1), only for this material the effect of particle size and the influence of natural weathering on the leaching behaviour (as a function of both L/S and pH) was also evaluated.

2.2 MATERIALS AND METHODS

2.2.1 Materials

The same BA samples analysed in Chapter 1 were used for the assessment of the leaching behaviour of the three types of BA as a function of pH (refer to Paragraph 1.2.1 for BA sampling and preparation).

For the evaluation of the effect of particle size on the leaching behaviour of the RDF-I BA, this sample was further divided into two different grain size classes, namely the coarse (0.425-12 mm) and the fine (<0.425 mm) fractions that were separately analysed to determine their main characteristics, as well as release of contaminants both as a function of pH and L/S ratio. The coarse fraction (approximately 92% wt. of the BA) was by far quantitatively more abundant than the fine one (around 8% wt. of the BA).

For the assessment of the effect of the weathering process on the leaching behaviour of the RDF-I BA a new sample of around 50 kg was collected at the RDF incineration plant. The sample was firstly homogenised through quartering (UNI 10802:2013). The grain size fraction ≥12 mm, constituting less than 5% by weight, was discarded and was not considered for the analysis; furthermore, coarse metallic, ceramics and glass fragments larger than 5 mm were manually removed. Afterwards, without initial particle size separation, the BA sample was naturally weathered for 1 year in the laboratory upon contact with air at controlled temperature and humidity and at atmospheric pressure. After this period of laboratory scale weathering, the BA was characterised and the leaching behaviour as a function of pH and the L/S ratio was analysed. For both particle size fractions and the weathered sample of RDF-I BA the total organic carbon (TOC) and carbonate ($CaCO_3$) content as well as the chemical composition were determined following the same procedures reported in Paragraph 1.2.1.

Results of the chemical composition of the above mentioned RDF-I BA samples (i.e. coarse fraction, fine fraction and weathered sample) are reported in Table 2.1 along with that of the mixed/fresh sample of the RDF-I BA, reported and discussed in Chapter 1. As can be noted in Table 2.1, the two particle size fractions and the weathered sample presented a quite similar content of macro-constituents compared to the mixed/fresh RDF-I BA sample.

As for trace constituents, the mixed/fresh sample showed to be more enriched in Cr, Mn, Ni, Sn and Pb with respect to both the other two particle size fractions and the weathered sample. The coarse fraction of RDF-I BA presented a higher concentration of Ba, Cu and Zn compared to the fine and the mixed ones. While, Ni and Cu resulted more abundant in the weathered BA with respect to the fresh sample. However, the concentration of each detected compound resulted of the same order of magnitude in all of the analysed samples. Moreover, no significant differences were observed regarding the TOC content, which ranged from a minimum value of 0.14% for the coarse fraction to a maximum of 0.48% for the aged sample. While the $CaCO_3$ content of both the fine fraction and the weathered sample proved 1% higher than the value measured for the mixed/fresh sample. These findings agree, for the fine fraction, with the XRD analysis, which showed a higher intensity of the peaks associated with calcite for this particle size fraction compared to the coarse and mixed ones (see Fig. A.2 in Annex A), and for the aged sample, with the fact that calcite formation was identified as one of the most relevant effects of weathering with regard to changes in BA mineralogy (e.g. Meima and Comans, 1997; Chimenos et al., 2003; Piantone et al., 2004).

Table 2.1 Comparison of the chemical composition, total organic carbon (TOC) and carbonate ($CaCO_3$) content of the fine fraction, the coarse fraction and the weathered sample of RDF-I BA with the ones obtained for the RDF-I BA mixed/fresh sample.

	RDF-I BA fine	**RDF-I BA coarse**	**RDF-I BA mixed/fresh**	**RDF-I BA weath.**
Macro-constituents (g/kg dry matter)				
Al	46	90	81	78
Ca	283	205	243	193
Fe	14	17	19	16
K	9	11	11	12
Mg	13	14	14	14
Na	12	25	22	13
Si	59	89	80	49
Trace elements (mg/kg dry matter)				
Ba	1113	1261	1187	1116
Cr	745	675	813	371
Cu	3760	7940	2810	4116
Mn	348	563	1197	494
Mo	<20	<20	<20	<20
Ni	73	65	258	75
Pb	492	212	573	550
Sn	182	70	231	145
V	34	39	38	44
Zn	2285	3789	2377	3884
TOC (wt. % dry)	0.34	0.14	0.27	0.48
$CaCO_3$ (wt. % dry)	6.64	4.51	5.4	6.68

2.2.2 Methods

The standardized CEN/TS 14429 leaching test procedure was carried out to evaluate the base/acid neutralization capacity (BNC/ANC) of the BA samples as well as the release of major and trace elements as a function of pH. In short, the procedure, consisting of different parallel batch tests with a fixed L/S ratio of 10 l/kg, was carried out using 4 g of ground samples (d< 1mm) of BA, adding 40 ml of solution containing different aliquots of deionized water (DI) and sodium hydroxide (NaOH) or nitric acid (HNO_3) in order to obtain eluates with pH values spanning within a wide pH range (3.5-12.5). Each suspension was equilibrated and stirred on a tumbler for 48 h. The pH value of each eluate was then measured (Hanna Instrument pH-meter) and the leachate solutions were filtered through 0.45 μm pore size filters and acidified with nitric acid, before performing the chemical analyses. Concentrations of major compounds and trace elements in the obtained eluates were measured with an Agilent 710-ES inductively coupled plasma optical emission spectrometer (ICP-OES).

Besides the pH dependence leaching test, for the assessment of the effects of particle size and weathering on the leaching behaviour of the RDF-I BA, the same leaching test procedures reported in Paragraphs 1.2.2 were employed. Namely, release of contaminants as a function of L/S ratio was assessed by performing both batch and column leaching tests (i.e. UNI/EN 12457 part 1 and part 2, SR 003.1 on ground and unground samples and CEN/TS 14405).

To assess if particle size and weathering have any effects on the classification of the RDF-I BA, also in this case, the data resulting from the different test methods were compared to current EU landfill acceptance criteria (2003/33/EC) and Italian regulatory criteria for the reuse of non-hazardous waste (M.D. 186/2006).

In the following paragraph, the most significant results obtained from this experimental study are presented and discussed.

2.3 RESULTS AND DISCUSSIONS

2.3.1 ANC and leaching behaviour as a function of pH

As previously mentioned, the acid neutralization behaviour is an important parameter for the evaluation of reuse or disposal options for BA. Indeed, based on the ANC results, an estimation can be made on the amount of acid required to significantly modify the pH of the BA leachate and, subsequently pH dependent leaching processes. This is important to estimate the effects that ageing and local environmental conditions may exert on pH and hence on the leaching behaviour of the BA. The acid/base neutralization capacity (ANC/BNC) curves obtained for the three types of analysed BA are reported in Figure 2.1.

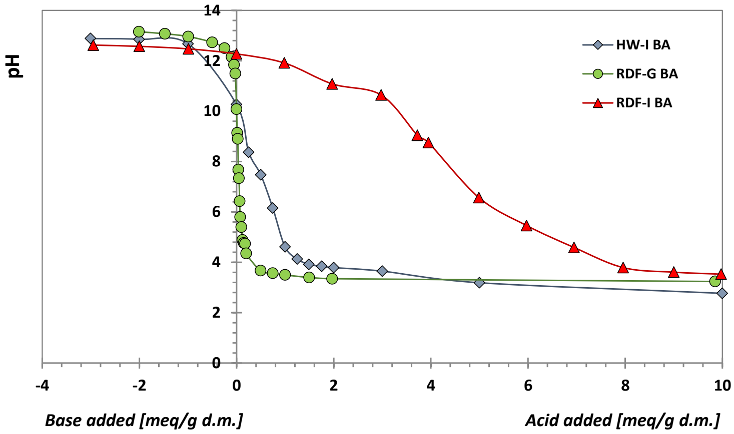

Figure 2.1 Acid/base neutralization capacity (ANC/BNC) curves for the HW-I BA, RDF-G BA and RDF-I BA samples.

As may be noted in Fig. 2.1, the results highlight a remarkable difference in the acid neutralization capacity of RDF-I BA compared to the other two types of analysed BA, which may be mainly attributed to their different mineralogical composition, as confirmed by the results of XRD analysis (refer to Fig. A.1 in Annex 1). In fact, RDF-I BA exhibited a high buffering capacity for pH values between 11 and 12, related to the significant content of hydrated phases, such as calcium hydroxide and hydrocalumite, calcium silicate-containing phases as well as of carbonates observed for this types of

BA. While RDF-G BA and HW-I BA displayed respectively an almost negligible and low ANC, since a rapid drop in pH was registered after the addition of a few meq of H^+/g of dry BA. This behaviour was mainly associated to the limited quantity of rapidly soluble Ca based hydroxides/silicates species and carbonates detected in the RDF-G BA and HW-I BA, that primarily control the ANC of typical MSWI BA (e.g. Johnson et al., 1995). On the other hand, a relatively extensive plateau of the ANC at a pH interval between 5 and 3 was found for these types of BA. This might be related to the presence of amorphous glassy phases that are generally characterized by a buffering capacity at pH 4. A similar ANC behaviour for the three types of BA was also found by Rocca, 2011. These findings are highly significant especially for the evaluation of the leaching behaviour of the RDF-G BA and HW-I BA in specific disposal or application scenarios. In fact, considering the negligible and low acid buffering capacity exhibited respectively by these two types of BA, the external environmental conditions to which the materials may be subjected to, e.g. contact with acidic rainwater (pH 5-6), could lead to a rapid drop of the native pH of the eluates resulting in an increase of the mobility of some contaminants, such as Cu, Pb and Zn. Hence, particularly for these types of residues, the evaluation of the concentrations of contaminants released at low pH values is of crucial importance.

The pH dependent leaching curves of some selected major (Al, Ca, Si, K and Mg) and trace elements (Ba, Cr, Cu, and Zn) for the three types of BA are shown and compared in Figure 2.2. These graphs also report the total content of each element in the bottom ash solid matrix (refer to Table 1.1) and, for the elements whose concentrations resulted lower than the instrumental quantification limit, the corresponding limit of quantification (LOQ). Regarding major components, Ca, K and Mg release as a function of pH for RDF-I BA was found to be around one and two order of magnitude higher than those observed for HW-I BA and RDF-G BA, respectively. Moreover, while the K solubility curves were quite similar for the three types of BA, the Ca and Mg ones differed. In particular, the Ca and Mg solubility curves of RDF-I BA resulted similar to those typically observed for MSWI BA (e.g. Dijkstra et al., 2008). Instead, the Ca and Mg curves for the gasification BA presented a very significant decrease in leaching concentrations for pH values above 3, probably in relation to the amorphous characteristics of this type of slag. The HW-I BA exhibited Ca and Mg leaching curves with an intermediate trend with respect to that of the other two types of slag, although more similar to that of the RDF-I BA.

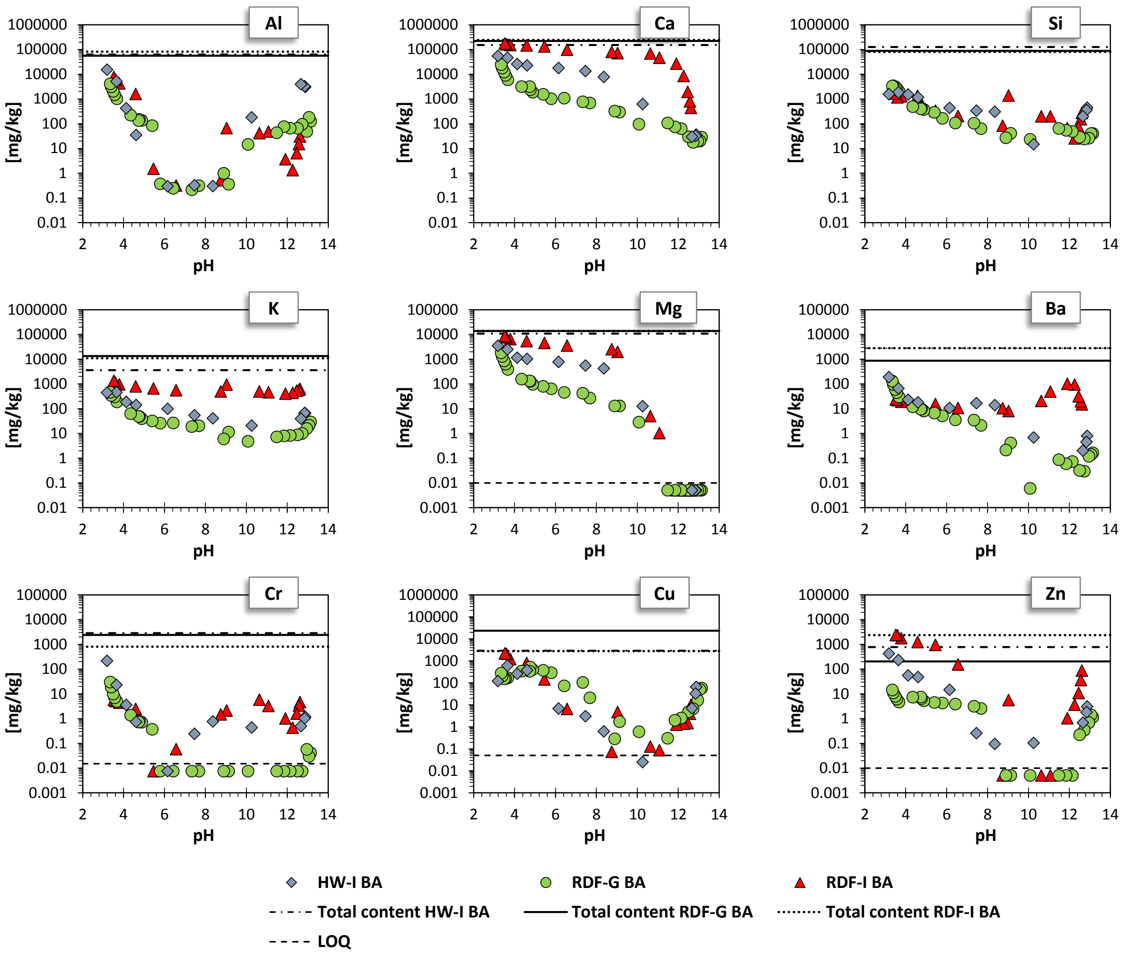

Figure 2.2 Mass release (mg/kg dry wt.) of Al, Ca, Si, K, Mg, Ba, Cr, Cu, and Zn as a function of pH for HW-I BA, RDF-G BA and RDF-I BA samples. Total content (lines) and element release (dots). HW-I BA (blue), RDF-G BA (green) and RDF-I BA (red). As a convention, data resulting below the LOQ are reported as half of the LOQ value.

Among the trace contaminants again Ba and Zn showed to display the highest release for the RDF-I BA, which can be mainly related to the higher total content of these elements observed for this type of BA, especially for Zn. Also in this case the shape of the leaching curves with pH differed on the basis of the type of BA considered.

However, the release of Cu showed to present quite similar values and pH trends for the three types of BA, although the initial concentration of this element in the RDF-G BA solid matrix was significantly higher than the one observed for the other two types of residues. In addition, also the Cr leaching curves for the three materials appeared to be similar, except for pH values above 6, for which leaching from the RDF-G BA showed to be negligible. The leaching behaviour of the RDF-G BA can be related to the specific characteristics of this residue that, as discussed in Chapter 1, presents a vitrified solid matrix in which the contaminants are probably incorporated in a more stable form compared to the other two types of BA. In addition, for the RDF-I BA it can be noticed that at the most acidic pH values the Ca, Mg, Cu and Zn leaching concentrations were quite similar to the total contents of these elements in the slag solid matrix.

2.3.2 Effects of particle size and weathering on the leaching behaviour of RDF-I BA

In this Paragraph the main effects of the particle size and the weathering process on the leaching behaviour, as a function of both pH and L/S ratio, of RDF-I BA are discussed.

2.3.2.1 Effects of particle size

ANC and leaching behaviour as a function of pH

The comparison of the acid/base neutralization capacity curves (ANC/BNC) obtained for the two particle size fractions (i.e. fine and coarse) with the one of the mixed fraction is reported in Figure 2.3.

As may be noted from the graph, the fine fraction displayed a significantly higher buffering capacity for pH values between 12 and 9 compared to the other two types of BA fractions. This can be mainly attributed to the differences in the mineralogy of the samples, the fine fraction presenting a higher portlandite content with respect to the coarse and mixed ones, as indicated by XRD analysis (see Fig. A.2 in Annex A).

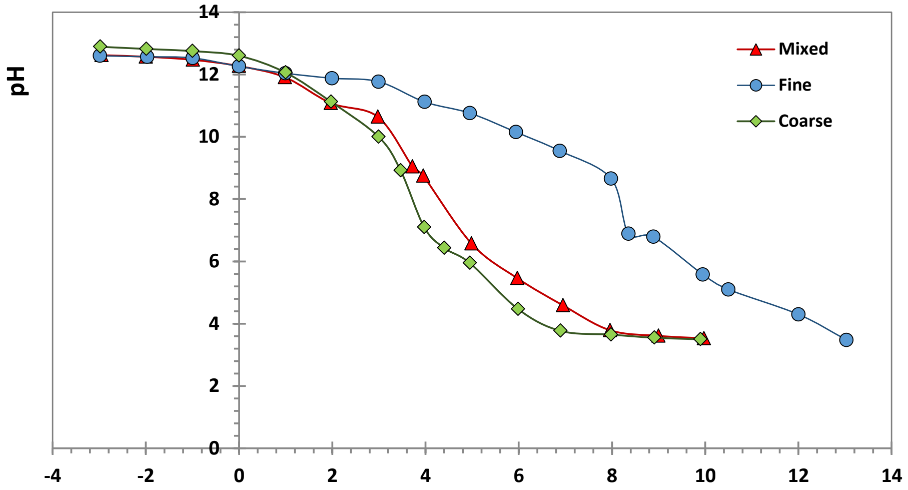

Figure 2.3 Acid/base neutralization capacity (ANC/BNC) curves for the fine, coarse and mixed fractions of RDF-I BA.

The ANC and mineralogical composition of the coarse and the mixed fractions instead showed to be fairly similar, in agreement with the fact that the mixed fraction was prevalently made up by the coarse fraction (92%).

The release curves of major components (Al, Ca, Si, K and Mg) and trace elements (Ba, Pb, Cu, Zn, Cr, Mo and Ni) as a function of pH for the three particle size fractions of the RDF-I BA are reported in Figure 2.4. Also in this case, the graphs include both the total content of each element in the bottom ash solid matrix (see Table 2.1) and for the elements whose concentrations resulted lower than the instrumental quantification limit, the corresponding limit of quantification (LOQ). As it can be noticed in Fig. 2.4, despite the different ANC observed for the finest fraction compared to the other two particle size fractions, with regard to the release of contaminants as a function of pH, no significant differences were found among the three samples. Indeed, for all the elements analysed, the solubility curves of the three particle size fractions, displayed very similar trends with respect to both the shape and released amount over the whole pH range investigated. Hence, it is likely that the minerals controlling the release of such components from the three particle size fractions were the same.

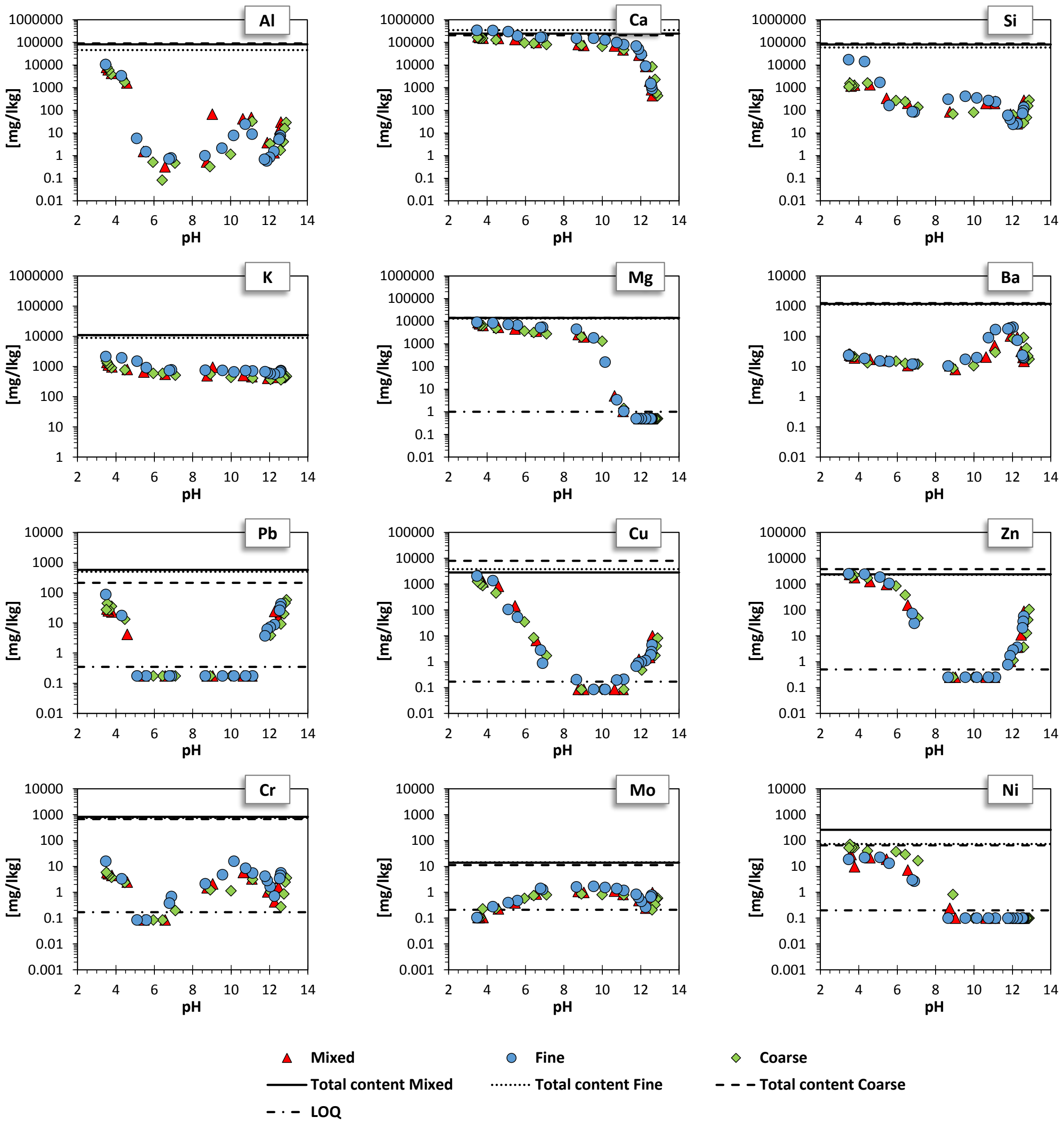

Figure 2.4 Mass release (mg/kg dry wt.) of Al, Ca, Si, K, Mg, Ba, Pb, Cu, Zn, Cr, Mo and Ni as a function of pH for the three particle size fractions of RDF-I BA. Total content (lines) and element release (dots). Mixed sample (red), Fine fraction (blue) and Coarse fraction (green). As a convention, data resulting below the LOQ are reported as half of the LOQ value.

Leaching behaviour as a function of the L/S ratio

Since the main purpose of this section is to analyse the influence of particle size on the leaching behaviour as a function of the L/S ratio of the RDF-I BA, hereinafter, only the results obtained by the column leaching tests for the three particle size fractions are reported and compared. However, as previously mentioned, for these materials also the batch test as a function of the L/S (SR 003.1) was conducted, and by the comparison of the results obtained from this test with the ones of the column test, as also found in Paragraph 1.3.2 a general good correlation was noticed for both the coarse and the fine sample. Nevertheless, as also noticed for the mixed fraction (see Fig. 1.4), for most of the elements analysed, the batch test generally provided leaching concentrations higher than those observed in the column test (see graphs d, e, f and g reported in Fig. A.3 and Fig. A.4, Fig. A.5 in Annex A).

Figure 2.5, reports the comparison between the cumulative mass release of constituents (mg/kg of dry matter) and pH values of the leachate as a function of the liquid to solid ratio, obtained from column leaching tests, performed on each type of particle size fraction of the RDF-I BA. It is worth noting that for the mixed and the coarse fractions the results shown refer to the average concentration values calculated by duplicate tests, whereas for the fine fraction, due to the limited amount of material available, only one test was carried out. In Fig. 2.5, when available, the total content (lines) of each element in the BA (Table 2.1) is also reported as a reference. Although many different elements were measured, for sake of conciseness, only the trends obtained for selected elements are shown as an example.

From the obtained results, a generally higher release of contaminants was observed for the fine particle size fraction, while the coarse and the mixed one showed a quite similar release (note that 92% of the mixed fraction is composed of the coarse one). This finding may be likely ascribed to the higher surface area available for the leaching process for the finest fraction that may have led to a greater mobilization of some contaminants (Chimenos et al., 2003). Moreover, for most of the analysed elements (i.e. K, Cu, Zn, Cl^-, DOC and Pb to a lower extent) a generally fast release was observed for all the three types of particle size fractions, but especially for the fine one (see the leaching curves of Cu, Cl^-, Pb, Zn and DOC). Indeed, as it can be noticed in Fig. 2.5

these elements reached maximum release values already at low L/S ratios after which the release curves showed an almost constant trend.

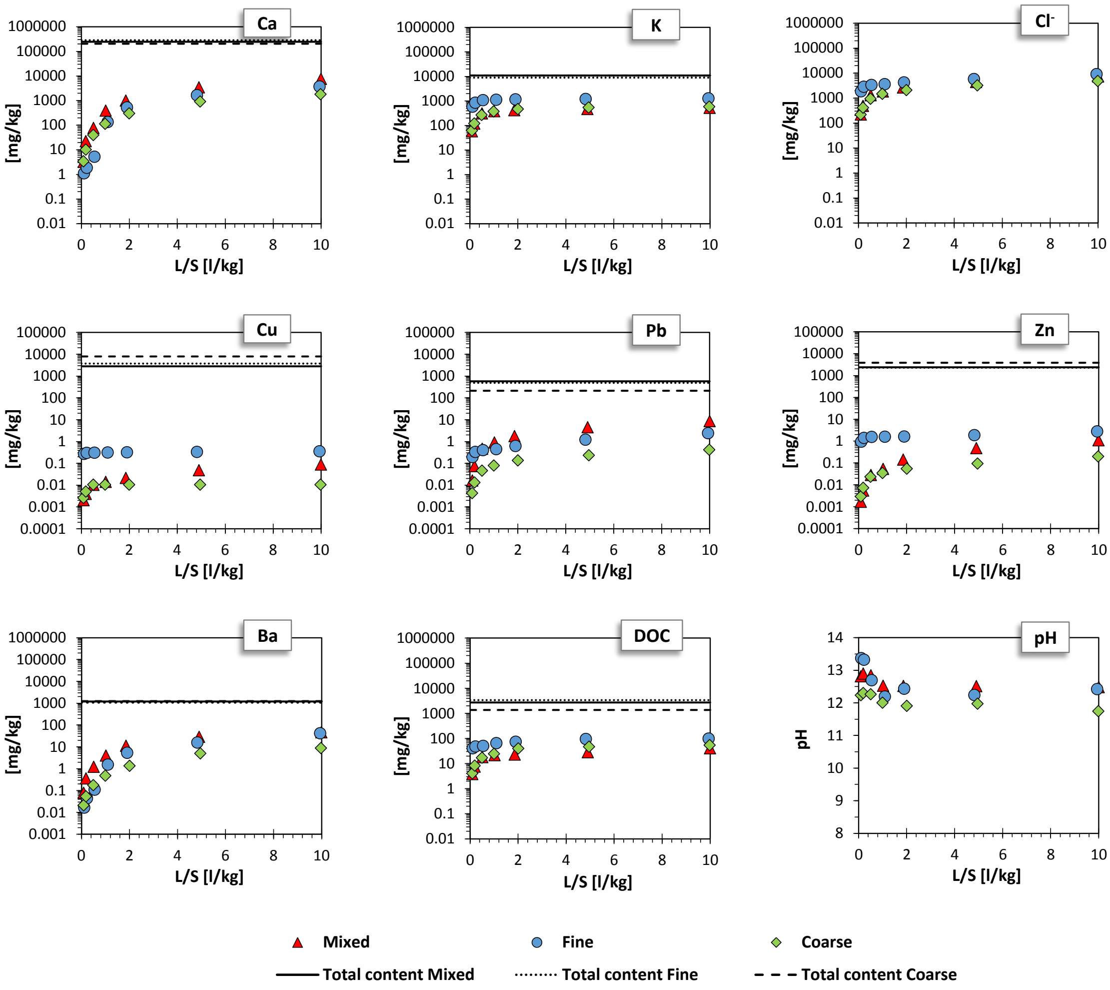

Figure 2.5 Cumulative mass release (mg/kg dry wt.) of Ca, K, Cl$^-$,Cu, Pb, Zn, Ba and DOC and pH values as a function of the applied L/S ratio (l/kg) for the three particle size fractions of RDF-I BA. Total content (lines) and cumulative element release measured in the column tests (dots). Mixed sample (red), Fine fraction (blue) and Coarse fraction (green).

These trends can be ascribed to the fact that in the early stages of the test, due to the pre-equilibration of the columns at the beginning of the experiment, it is likely that the leaching mechanism was controlled by equilibrium conditions, i.e. a wash out or percolation controlled mechanism prevailed leading to the maximum leachable concentrations. While for higher L/S ratios (after a leachate replacement of approximately 1 pore volume), the occurrence of non-equilibrium conditions, regulated by a mass-transfer controlled release led to a decrease of the concentrations in the effluent. The switch from equilibrium to non-equilibrium conditions showed to be faster for the fine particle size fraction, for which constant release trends were observed at lower L/S ratios (around L/S = 0.1-0.5 l/kg) compared to the coarse and the mixed fractions (around L/S = 0.5-2 l/kg). This is likely due to the greater pore volume of the coarse and mixed fractions in the column, because of a larger average particle size, that implies that a longer time is required to achieve a complete renewal of the pore volume. For the elements which instead showed a much wider variability as a function of the L/S ratio (e.g. Ca and Ba) a release, mechanism under equilibrium conditions can be assumed to take place during the whole duration of the column test. As far as pH is concerned, for all the three particle size fractions of the RDF-I BA, pH values in the column showed to decrease with increasing L/S ratios until a L/S = 2 l/kg, after which a rather constant trend was observed. Moreover, for low L/S ratios, the pH of the eluates of the fine fraction exhibited higher values (13.4-12.7) compared to the ones displayed by the mixed (12.8-12.6) and the coarse (12.2-12) ones. This can be related to the higher portlandite content observed by XRD analysis for the fine fraction with respect to the coarse and mixed ones (see Fig. A.3 in the Appendix A).

2.3.2.2 Effects of weathering

ANC and leaching behaviour as a function of pH

Figure 2.6 shows the comparison between the ANC/BNC curves derived from the pH dependence leaching test for the weathered and fresh BA samples.

From Fig. 2.6 it can be observed that the buffering capacity of the fresh and aged BA samples showed a similar trend. However, for the same amounts of acid additions, included in the range 0-5 meq H^+/g dry matter, for the weathered BA lower pH values compared to the fresh sample were observed.

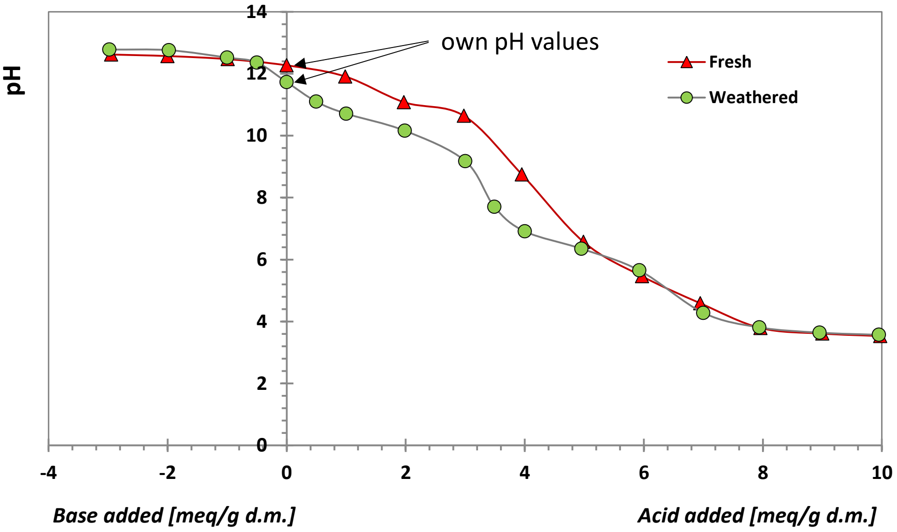

Figure 2.6 Acid/base neutralization capacity (ANC/BNC) curves for the fresh and weathered sample of RDF-I BA.

These results suggest that a lower amount of alkalinity, probably due to the dissolution of hydroxides and silicates phases, was available for buffering acid additions in the weathered material compared to the fresh one, since part of it had likely reacted with CO_2 during aging process. This was also confirmed by the lower native pH value observed for the weathered sample compared to the fresh one, 11.7 and 12.3 respectively. In addition, the acid titration curve obtained for the weathered BA revealed the presence of a slight plateau around pH 7 that may be related to the buffering of carbonate phases (Johnson et al., 1995). Indeed, such a behaviour suggested an increased amount of carbonates in the BA sample after weathering. Nevertheless, the effect of the weathering process on the analysed sample appeared to be less relevant than the one observed for the same type of BA in a previous study. In fact, Rocca (2011) found more marked differences in the ANC behaviour of fresh and aged BA samples, also for lower weathering periods (e.g. 3, 6 and 9 months) than the one employed in this study (i.e. 12 months), thus suggesting that most likely the BA sample analysed in this study, for unclear reasons, underwent only a partial aging process. This result is also confirmed by the low increase in the carbonate content (see Table 2.1) and the still high native pH of the BA sample after the aging process (see Table 2.2).

The release of major (Al, Ca, Si, K and Mg) and trace (Ba, Pb, Cu, Zn, Cr, Mo and Ni) components measured in the eluates of the pH dependence leaching test, for the fresh and weathered BA samples, are reported and compared in Figure 2.7.

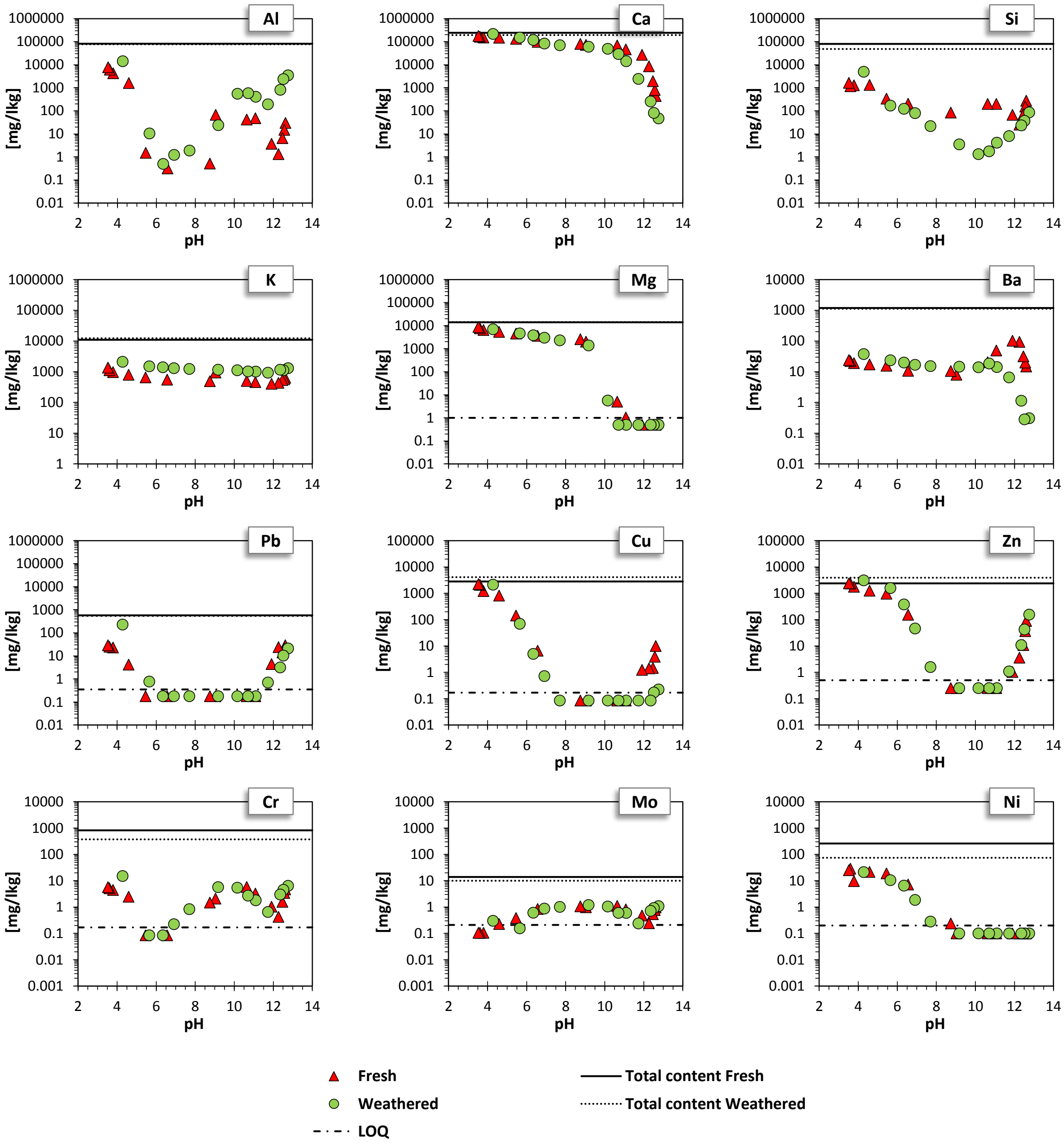

Figure 2.7 Mass release (mg/kg dry wt.) of Al, Ca, Si, K, Mg, Ba, Pb, Cu, Zn, Cr, Mo and Ni as a function of pH for the fresh and weathered RDF-I BA samples. Total content (lines) and element release (dots). Fresh sample (red) and weathered sample (green). As a convention, data resulting below the LOQ are reported as half of the LOQ value.

As it can be noticed from the graphs, in agreement with Rocca (2011), the fresh and weathered BA samples showed rather similar pH dependent leaching trends with respect to the shape of the curves and leachate amounts of both major and trace compounds over the whole pH range investigated. However, the release curves of some elements (i.e. Al, Ca, Si, Ba and Cu) for pH values higher than 10 (or between 8 and 10 in the case of Si) showed differences between the two samples. For instance, a slight decrease in the mobility of Ca for the weathered sample was observed. This may be likely due to a partial conversion of the reactive phases such as portlandite into calcite as a result of the reaction with CO_2 and, subsequently, a change in the solubility-controlling phases compared to the fresh sample. This finding was also consistent with the results obtained from the compliance leaching test EN 12457-2 (L/S = 10 l/kg), for which Ca release for the fresh BA was higher than for the aged sample, 8455 mg/kg and 2993 mg/kg, respectively (results of EN 12457-2 batch test for the weathered sample are reported in Fig. A.6 in Appendix A). As for the differences in the leaching curves of Si and Al observed upon weathering, while this process appeared to exert a mobilization effect for the latter at a pH above 10, the opposite was found for Si for pH values ranging from 8 to 12. The same result found for Ca was also observed for Ba. However, as it can be noticed in Fig. 2.7, for this element the release value obtained for the weathered sample dropped by several orders of magnitude compared to the fresh one for pH values above 11. A similar result was also found in previous studies carried out on carbonated alkaline residues (i.e. steal slag) in which this behaviour was attributed to the possible formation of a Ba-Ca carbonate solid solution, resulting in the incorporation of Ba in a calcite structure and leading to a reduction of Ba release (Huijgen and Comans, 2006; Capobianco et al., 2014). Also Cu leaching showed to decrease after weathering for pH values above 11.5. Overall, apart from the above discussed exceptions, in general, the fresh and weathered BA samples showed rather similar pH dependent leaching trends with respect to the shape of the curves and release amounts of both major and trace compounds over the whole pH range investigated. Given these similarities, it seems that the mineralogical and chemical changes occurring in the BA upon the analysed weathering period did not significantly affect the solubility of the minerals which mainly controlled the release of such components from this type of residue.

Leaching behaviour as a function of the L/S ratio

The comparison between the cumulative mass release of constituents (mg/kg of dry matter) and pH values as a function of the liquid to solid ratio (L/S), obtained from column leaching tests performed on the weathered and fresh sample of the RDF-I BA, is reported in Figure 2.8. Results refer to the average concentration values calculated by column tests conducted in duplicate. In the same figure, when available, the total content (lines) of each element in the BA (refer to Table 2.1) is also reported as a reference. Note that in Fig. 2.8, for illustration purposes only, the values lower than the limit of quantification (LOQ) were also reported (dashed light symbols). Moreover, it is important to point out that for the weathered BA, in the second replication of the column test, Pb showed leaching concentrations below the limit of quantification (0.008 mg/l) during the entire duration of the test. Hence, the release curve reported in Fig. 2.8 for this element, is the average of the cumulative release values obtained from the first replica, with the ones calculated from the second one assuming that, for each considered L/S ratio, the leaching concentration value was equal to the limit of quantification. Despite the quite similar release as a function of pH displayed by the fresh and weathered samples (see Fig. 2.7), significant differences were instead observed with the respect to their leaching behaviour as a function of L/S ratio, especially for the trace elements (i.e. Cu, Pb, Zn, Ba, Cr and Mo). Indeed, on the one hand natural weathering proved to be effective in reducing the release of amphoteric metals (i.e. Cu, Pb and Zn), which showed to be lower (by one to two orders of magnitude) for the aged sample compared to the fresh one. In fact, as can be noticed from Fig. 2.8, Cu and Zn showed to be completely depleted after a L/S ratio of 2 l/kg was reached, moreover as mentioned before, in one of the column tests Pb was not even detected. On the other hand, natural weathering led to an increase (of up to one order of magnitude) of the release of oxyanion-forming metalloids, i.e. Cr and Mo from the BA. These findings may be mainly related to the different pH values measured in the column tests of the weathered and fresh BA samples. Indeed, while the trend of pH showed to be similar (decreasing with an increase of the L/S ratios, reaching a constant value for L/S > 2 l/kg) for the weathered BA around 1 point lower pH values were measured (ranging from 12.4 to 11.6) compared to the fresh sample (ranging from 12.8 to12.5).

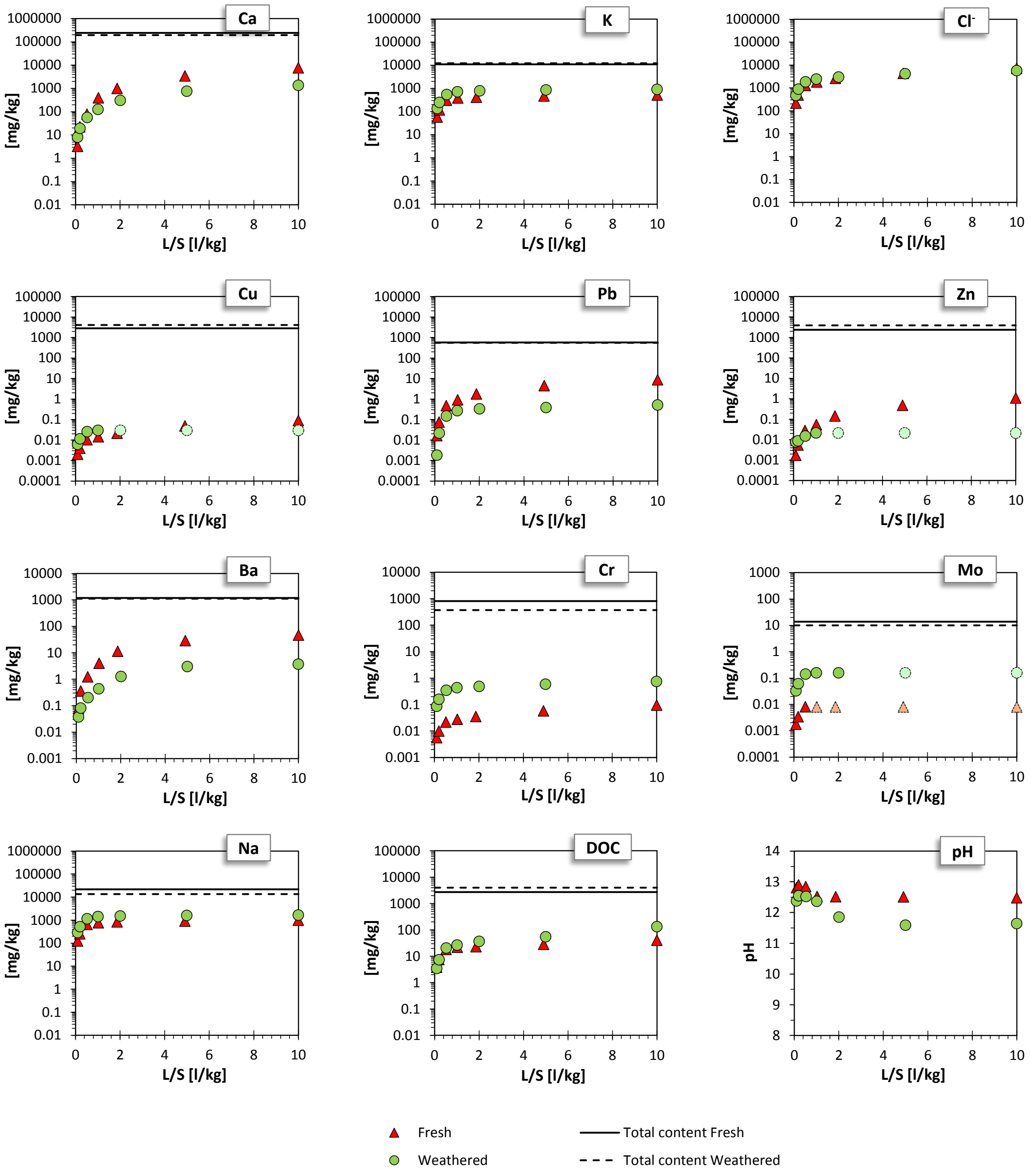

Figure 2.8 Cumulative mass release (mg/kg dry wt.) of Ca, K, Cl^-,Cu, Pb, Zn, Ba, Cr, Mo, Na and DOC and pH values as a function of the applied L/S ratio (l/kg) for the fresh and weathered RDF-I BA samples. Total content (lines) and cumulative element release measured in the column tests (dots). Fresh sample (red) and weathered sample (green). For illustration purposes only, the values lower than the limit of quantification (LOQ) were also reported (dashed light symbols).

Referring to Fig. 2.7 it can be noticed how in the pH range resulting for the weathered sample in the column tests, the release of amphoteric metals and oxyanion-forming metalloids decrease and increase, respectively; the opposite behaviour can be instead observed for the pH range measured for the fresh sample. Another interesting aspect to note is that the release of Ca and Ba proved to be in line with the results obtained by the pH-dependent leaching test, showing higher concentration values in the eluates of the fresh sample.

Overall, the results attained applying the different types of leaching tests proved to be in good agreement with the results of prior investigations regarding weathered RDF-I BA (Baciocchi et al., 2010; Rocca, 2011) and MSWI BA (e.g. Meima and Comans 1999; Chimenos et al., 2003; Polettini and Pomi, 2004).

In order to assess if the weathering process influenced the mechanisms controlling the leaching behaviour of the RDF-I BA, the model described in Paragraph 1.2.3 was also applied to the results of the column tests obtained for the weathered BA sample. In Figure 2.9 the average concentrations (mg/l) of selected major and trace constituents measured in the eluates of the column leaching tests carried out on the weathered RDF-I BA are reported, along with the results obtained by the application of the model assuming either equilibrium i.e. percolation-controlled release (solid red line) or non-equilibrium conditions i.e. mass-transfer governed release (dotted blue line). Comparing the results reported in Fig. 2.9 with the ones obtained for the fresh sample (see Fig. 1.7), it was noticed that for most of the elements analysed (e.g. Ca, Si, Al, Cr and Ba) release is likely controlled by the same leaching mechanisms for both BA samples. However, Pb and Zn release, which for the fresh sample showed to be governed by a percolation-controlled mechanism, for the weathered sample displayed leaching trends that, as can be noticed in Fig. 2.9, were well described by the equation representing non-equilibrium conditions (i.e. mass-transfer controlled release). This result indicates that, upon weathering, leaching of these elements may be governed by sorption on hardly soluble phases such as carbonates.

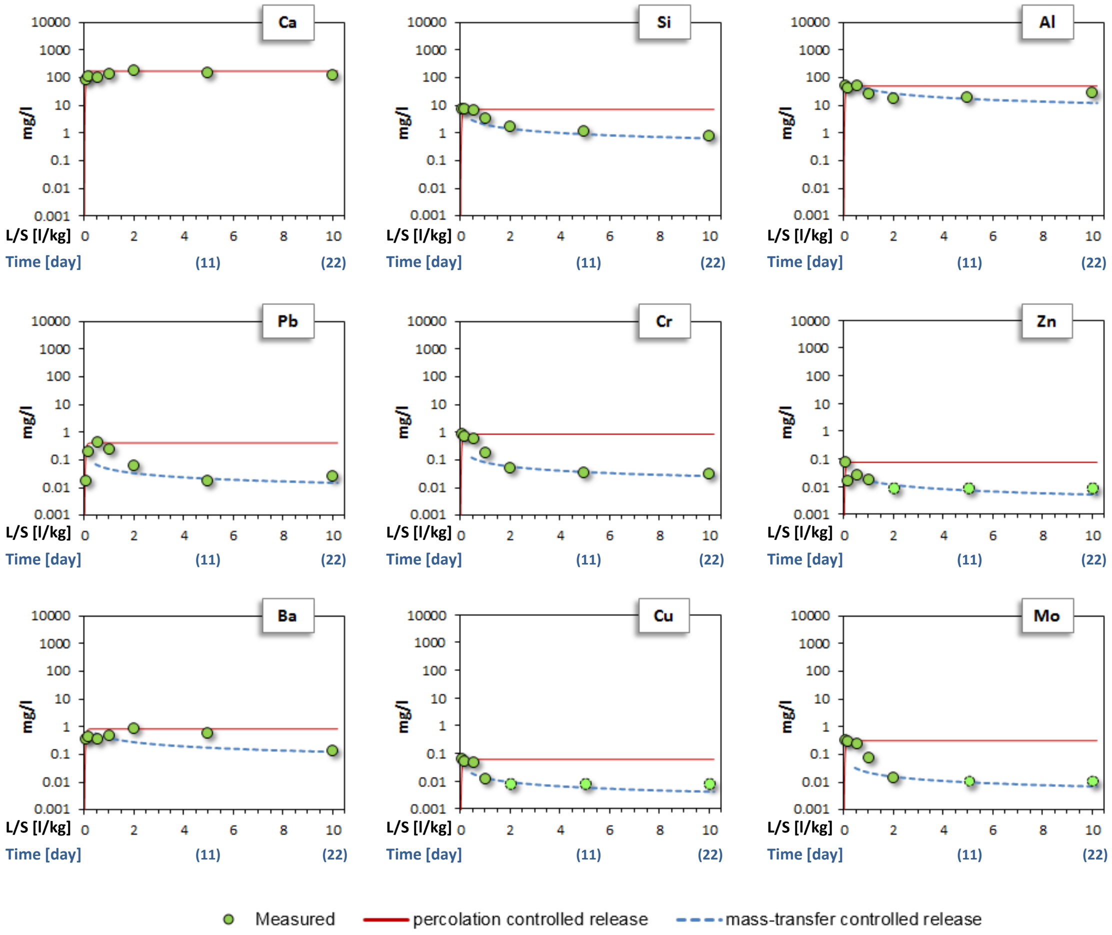

Figure 2.9 Average leaching concentrations (mg/l) obtained from the column tests as a function of the L/S ratio for the weathered sample of the RDF-I BA: comparison of measured data (green dots) with model predictions. Percolation-controlled release (solid red line) calculated with Eq. 1.14a, mass transfer controlled release (dotted blue line) calculated with Eq. 1.14b. On the x-axis, the time scale used in the model is also reported as a reference. For illustration purposes only, the values lower than the limit of quantification (LOQ) were also reported (dashed light dots).

It is worth noting that also for the weathered BA, the batch test as a function of the L/S was carried out on both ground and unground samples. The results attained from the column and batch tests were quite comparable. However, as expected, for some elements, the batch test performed on the ground sample provided release values higher than those observed both in the column test and the batch test conducted on the unground material, which instead were quite similar (see graphs a, b and c of Fig. A.3 and Fig. A.6 in the Appendix A).

2.3.2.3 Comparison with regulatory limits

In order to assess the effect of particle size and weathering on the classification of RDF-I BA, results obtained from the leaching tests performed on the fine and coarse fractions, as well as on the weathered sample, were compared to European landfill acceptance criteria (2003/33/EC) and with the limit values set by the Italian legislation for reuse of waste materials (M.D. 186/2006). Table 2.2 reports, for the three types of analysed RDF-I BA samples, the release values (mg/kg) obtained from the UNI/EN 12457 part 1 at L/S of 2 l/kg, UNI/EN 12457 part 2 at L/S of 10 l/kg and the first eluate C_0 (L/S= 0.1 l/kg) of the column leaching test (CEN/TS 14405). For each type of leaching test, values exceeding acceptance criteria for inert, non-hazardous and hazardous waste landfilling are indicated. Moreover, the results obtained from the batch test at L/S of 10 l/kg were also compared to the Italian regulatory limits for reuse (limit values reported in Table A.4 in Appendix A).

For the fine particle size fraction of the RDF-I BA, the same classification was obtained considering both types of batch leaching tests. Specifically, Cr, Pb, and Cl^- release values exceeded the EU LFD criteria for inert waste landfilling but complied with those for non-hazardous waste disposal for both types of tests; Ba leaching however was higher than the limit for inert waste landfilling only for the test carried out at L/S= 10 l/kg. Besides these elements, also the concentration of Cu and pH were higher than the Italian limit values for reuse. Interestingly, considering the results of the column test, some elements showed to even exceed the limit values for hazardous waste landfilling (i.e. Cr, DOC and Cl^-), confirming the fast and high release observed for this fraction in the column test experiments compared to the coarse and mixed ones (see Fig. 2.5). As for the coarse fraction, in Table 2.2 it can be noticed that, for the three leaching tests considered, leaching complied with landfill criteria for non-hazardous waste. The elements which exceeded limit values for disposal in inert waste landfills were Cr and Cl^- for the column test and Ba, Pb and Cl^- for both batch tests. Besides these elements also the pH value was higher than the Italian limit values for reuse.

For the weathered sample the elements that showed to be critical, exceeding the acceptance criteria for inert waste landfilling but complying with those established for non-hazardous waste disposal, were Cr, Mo and Cl^- for the column test and Cr, Pb and Cl^- for both batch tests. In addition to the latter elements, with regard to the Italian legislation, also pH was still above the limit value for reuse and very similar to that obtained for the fresh sample (see Table 1.2), confirming again that the BA sample analysed in this study was limitedly carbonated.

Table 2.2 Comparison of release obtained by compliance leaching tests UNI/EN 12457 part 1 (L/S= 2 l/kg), part 2 (L/S= 10 l/kg) and the first eluate C_0 (L/S= 0.1 l/kg) of the column leaching test CEN/TS 14405, for the analysed BA sample, with the limits by the European Landfill Directive (2003/33/EC, EU LFD) and the Italian legislation for reuse of waste materials (M.D. 186/2006). Results are reported in mg/kg. Bold black values: concentrations > EU LFD criteria for inert waste landfilling; bold red values: concentrations > EU LFD criteria for non-hazardous waste landfilling; bold red underlined values: concentrations > EU LFD criteria for hazardous waste landfilling; underlined black values: concentrations > Italian reuse limits. LOQ: Limit of Quantification (reported below the Table).

	RDF-I BA fine			**RDF-I BA coarse**			**RDF-I BA weath.**		
	C_0	**L/S = 2 l/kg**	**L/S = 10 l/kg**	**C_0**	**L/S = 2 l/kg**	**L/S = 10 l/kg**	**C_0**	**L/S = 2 l/kg**	**L/S = 10 l/kg**
pH	13.37	13.02	12.41	12.24	12.9	12.37	12.38	12.62	12.5
Ba	0.02	4.4	**71.72**	0.02	**14.3**	**74.62**	0.04	2.67	9.7
Cr	**2.48**	**0.3**	**0.64**	**0.08**	0.12	0.2	**0.09**	**0.27**	**0.5**
Cu	**0.3**	0.13	0.57	0.003	0.15	0.45	0.006	0.07	0.1
Mo	**0.4**	0.07	0.2	0.013	0.035	<LOQ	**0.03**	0.11	0.12
Pb	**0.2**	**1.9**	**7.15**	0.004	**3**	**6.6**	0.002	**0.28**	**0.85**
Zn	**0.9**	0.47	2.1	0.003	0.56	1.7	0.008	0.3	0.77
DOC	**41**	128	218	4	53	133	4	7	79
Cl^-	**1853**	**4389**	**8196**	**209**	**2954**	**6099**	**460**	**2490**	**4035**

Limit of quantifications (LOQ) in mg/l: As (n.a.), Be (0.001), Cd (0.005), Co (0.005), Hg (n.a.), Mo (0.01), Ni (0.009), Se (n.a.), V (0.005)

From the comparison of the results of the leaching tests with current legislation regarding waste management, it can be concluded that, for the coarse fraction and the weathered sample, the choice of the compliance leaching test does not seem to affect the final conclusions regarding the classification of both materials. Moreover, in most cases, the critical contaminants identified from each type of leaching test were in good accordance. However, significant differences also in terms of compliance with landfill acceptance criteria were obtained in the results of the batch and column tests for the fine fraction of the RDF-I BA.

2.4 CONCLUSIONS

In order to provide a description of the leaching behaviour of BA under pH conditions that may occur in specific disposal/reuse scenarios, in this study, the release of major and trace elements as a function of pH for the three types of considered BA (i.e. RDF incineration and gasification BA and hospital waste incineration BA), was assessed. In addition, due to the higher heterogeneity and release of contaminants observed for the RDF-I BA compared to the other two types of BA, for this material the effect of particle size and the influence of a weathering process on the leaching behaviour (as a function of both L/S and pH) was also evaluated.

The experimental results indicated a remarkable difference in the acid neutralization capacity (ANC) of RDF-I BA compared to the other two types of analysed BA. Indeed, RDF-G BA and HW-I BA displayed an almost negligible and low ANC, respectively. This was mainly associated to their mineralogy, which showed to be principally made up by amorphous phases. In light of this, the low ANC observed could be a parameter that may prove critical for the reuse of these two types of BA. In fact, the external environmental conditions to which the materials may be subjected to in specific application scenarios e.g. when in contact with acidic rainwater (pH 5-6), could lead to a rapid drop of the pH of the leachate, resulting in an increase of the mobility of some contaminants, such as Pb and Zn, which instead were not detected or found in very low concentrations at their native pH (10.4 for the HW-I BA and 7.3 for the RDF-G BA, Table 1.2). On the contrary, due to the abundance of hydrated phases, a significant ANC, for pH values between 11 and 12, was found for the RDF-I BA, meaning that for modifications in environmental conditions corresponding to up to 2 meqH^+/g d.m., the pH of the eluates should not change significantly. However this type of BA showed fairly high release values related to its strongly alkaline native pH (12.4).

Regarding the effects of particle size on the leaching behaviour of RDF-I BA, while the release of contaminants as a function of pH was shown not to be affected by the particle size distribution of the tested material, significant differences were instead found for the release as a function of the L/S ratio. Indeed, the obtained results showed a generally higher and faster release of contaminants (e.g. Cr, DOC and Cl^-) for the fine particle size fraction, which showed to exceed the limit values for hazardous waste landfilling when the results of the first eluate of the column test were considered. This was mainly related to the higher surface area available for the leaching process for this particle size fraction compared to the coarse and the mixed ones. However, the removal of the finest particle size fraction from the bulk sample of RDF-I BA was shown not to significantly improve the leaching of contaminants. Indeed, the coarse particle size fraction exhibited a quite similar release to the mixed one, exceeding landfill criteria for inert waste for the same contaminants also observed for the mixed fraction. This was principally related to the fact that the coarse fraction represents 92% by weight of the bulk sample of RDF-I BA (i.e. mixed fraction).

As to the effects of natural weathering of the RDF-I BA, the findings of this study evidenced that this treatment, carried out at laboratory scale for a period of 12 months, was able to modify some important properties of the RDF-I BA, especially the release of several metals as a function of L/S ratio, likely due to the reaction with CO_2 of the reactive mineral phases present in this type of residue. In particular, although the native pH of the weathered sample showed not to differ significantly from that of the fresh sample, weathering resulted in a relevant immobilization effect for Ba and Cu, which, contrarily to what observed for the fresh sample, showed to comply with limit values for both inert waste landfilling and Italian limits for reuse. In addition a significant decrease (of up to one order of magnitude) was also observed for Pb release, which however, for both batch compliance leaching tests, still demonstrated to exceed the acceptance criteria for inert waste landfilling and reuse. On the other hand, the weathering process favoured the mobilization of oxyanion-forming metalloids such as Cr and Mo. However, while Cr exceeded the limit values for inert waste landfilling for all the three types of leaching tests considered, for Mo only the release value detected in the first eluate of column test was above those limits.

Finally, the main phases controlling the leaching behaviour of the slag did not appear to change significantly upon the investigated weathering period, since the pH dependent leaching curves of each constituent of the fresh and aged BA samples were rather similar. However, for a few elements (i.e. Pb and Zn) the main mechanisms governing leaching as a function of the L/S ratio, identified on the basis of the interpretation of the results of the column leaching tests, showed to differ for the fresh and weathered samples. In particular, leaching of Pb and Zn for the fresh sample showed to be governed by a percolation-controlled mechanism, while after weathering, a mass-transfer controlled release was found, which could be related to sorption on hardly soluble phases such as carbonates.

SECTION 2

ASSESSMENT OF MANAGEMENT OPTIONS FOR BOTTOM ASH BASED ON MODELLING OF EXPERIMENTAL LEACHING DATA

*In this section the most significant leaching data obtained from the experimental activities described in Section 1 were selected and employed in LCA and risk assessment studies in order to gain insight on the environmental consequences associated with the release of contaminants resulting for two different management options (i.e. landfilling and reuse as filling material in road sub-base construction) of the considered types of BA. Specifically, in Chapter 3 potential environmental impacts associated with the two hypothesized scenarios for the RDF-I and RDF-G BA were evaluated and compared by life-cycle assessment (LCA). Both non-toxicity related impact categories (i.e. global warming and mineral abiotic resource depletion) and toxic impact categories (i.e. human toxicity and ecotoxicity) were assessed. Specific attention was paid on the sensitivity of leaching properties and the determination of emissions by leaching, including: leaching data selection, material properties and assumptions related to emission modelling. The LCA results showed that for both types of BA, landfilling was associated with the highest environmental impacts in the non-toxicity related categories. For the toxicity related categories, the two types of residues behaved differently. For incineration BA the contribution of metal leaching to the total impacts had a dominant role, with the highest environmental loads resulting for the road scenario. For the gasification BA, the opposite result was obtained, due to the lower release of contaminants observed for this material compared to incineration BA.

A further step towards the evaluation of the environmental impacts related to the two different management options assumed (i.e. landfilling and recycling in road sub-base construction) for the three types of analysed BA, was made by employing a risk-based approach (Chapter 4). Potential risks for the groundwater associated to the release of contaminants from the considered BA in the management scenarios hypothesized for the LCA study were investigated. A different approach compared to the standard risk assessment methodologies was proposed. Specifically, the developed method was based on the results obtained by the column leaching tests which allowed to estimate the main mechanisms controlling the leaching behaviour of the three types of BA, i.e. the prevailing of equilibrium or non-equilibrium conditions during contaminant release (see Chapter 1). The specific field conditions expected in the two scenarios (e.g. the infiltration rate and prevailing release mechanisms) were evaluated and using the equations employed for the modelling of column test results and estimated parameters, i.e. contaminants diffusion coefficients, D_a (cm^2/s) and maximum available leaching concentrations, C_{sol} (mg/l), the amounts of contaminants expected to be released from the BA and to reach the groundwater table, were calculated as a function of time considering a timeframe of 100 years. The risk for the groundwater resource $R_{GW}(t)$ was finally assessed by comparing the calculated concentrations of contaminants at the point of compliance with the reference values (CSC_{GW}) set by the Italian legislation for groundwater protection. Results showed that, for both of the considered scenarios the leaching of metals and inorganic constituents from the three types of BA, in nearly all cases seemed to not pose a risk for the groundwater resource. This was particularly true when contaminant attenuation due to sorption of the leachate constituents onto clean soils underlying the affected soil zone (LDF) and concentration dilution owing to the transfer of the contaminant from the leachate to groundwater (SAM) were considered. However, making reference to the worst cases for both the landfill and road scenarios (e.g. no soil attenuation, no dilution in groundwater, no geomembrane in the bottom liner of the landfill), some contaminants, such as Al, Ba, Cr and Pb for the RDF-I BA and Al for both RDF-G BA and HW-I BA, showed to potentially pose a risk for the groundwater resource, particularly for the road scenario.

**Part of this section was published as*

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

CHAPTER 3

LCA OF MANAGEMENT STRATEGIES FOR RDF INCINERATION AND GASIFICATION BOTTOM ASH

3.1 INTRODUCTION

As it has been mentioned in the Introduction Chapter, in order to establish the viability of specific management options for a particular type of BA, evaluations focused exclusively on the quantification of leaching, through the utilization of laboratory leaching tests, fail to consider other important aspects such as risks for the environment associated to the release of contaminants as well as potential environmental impacts on a regional or global scale, such as resource use, toxicity for humans or water resources and climate change (Roth and Eklund, 2003; Toller, 2008). Hence, for a wider assessment of the potential environmental impacts deriving from a specific management strategy for BA, leaching test results should be used in broader evaluations which allow the quantification of the impacts on the environment and human health.

By far the most applied methodology for assessing the potential environmental impacts associated to waste management systems is life cycle assessment (LCA) (Astrup et al., 2014; Laurent et al., 2014a, 2014b). Specifically, several studies addressed the importance of considering the release of toxic substances resulting from the landfilling of different types of waste, including bottom ash, focusing either on long-term emissions (e.g. Hellweg, 2000; Doka and Hischier, 2005; Doka, 2009), or on short-term ones (within 100 years) estimated mainly on the basis of field or literature data (e.g. Obersteiner et al., 2007; Manfredi, 2009; Damgaard et al., 2011). It should be considered that the specific properties of the waste and field conditions may significantly affect the leaching behaviour of the material. In addition, field data regarding the emissions originating from the landfilling of specific types of waste (such as bottom ash from RDF thermal treatment) may not be available. Hence, in order to improve the description of the environmental behaviour of a specific waste material in a disposal/reuse scenario, it is important to make reference to data representative of both the properties of the material and real site conditions. This may be achieved by employing the results of laboratory leaching tests. A few studies have focused in particular on the environmental aspects associated to the recycling of MSW incineration residues in a LCA perspective using the results of laboratory and/or field leaching tests (Olsson et al., 2006; Birgisdóttir et al., 2007; Allegrini et al., 2015). Specifically, while

Olsson et al. (2006) evaluated the potential environmental impacts of the use of bottom ash in road construction making reference to field tests, Birgisdóttir et al. (2007) compared landfilling and reuse in road by employing laboratory leaching tests. Allegrini et al. (2015) assessed the importance of including impacts related to leaching and data quality in LCA when evaluating management strategies for solid residues. In particular, in this study the results of several laboratory leaching tests as well as their analysis by geochemical modelling were employed for the assessment of MSWI BA reuse in road sub bases. Nevertheless, no specific studies regarding analysis of management options for RDF thermal treatment BA were found.

This study focuses in particular on the RDF gasification and incineration bottom ash and aims at identifying and comparing by LCA the potential environmental impacts associated with two different management options for these specific types of BA, i.e. landfilling and reuse as filling material in road sub-bases. The study was performed employing the EASETECH LCA model (Clavreul et al., 2014) and the results of the leaching tests applied to each type of BA (see Section 1) were used to estimate the potential release of contaminants under environmental conditions relevant to the disposal/utilization scenario considered. Moreover, in order to evaluate the robustness of the conclusions of the LCA, a sensitivity analysis was performed to evaluate the influence of the type of leaching test employed to estimate the potential release of contaminants, the pH value of the leachant and important scenario modelling assumptions.

3.2 MATERIALS AND METHODS

3.2.1 Bottom ash data

This study focuses on the RDF-I BA and RDF-G BA analysed in Section 1. Hence, for characterisation data regarding the main physical, chemical, mineralogical and environmental properties of the two types of BA refer to Chapter 1 and Chapter 2. To estimate the potential release of contaminants in each management scenario the results of the following types of standardized leaching tests were employed in this work:

percolation column test (CEN/TS 14405), batch compliance tests at a L/S of 2 l/kg (EN 12457-1) and at a L/S of 10 l/kg (EN 12457-2), and pH-dependence leaching test (CEN/TS 14429).

3.2.2 LCA methodology

3.2.2.1 Goal, scope and model

The goal of the present LCA was to evaluate and compare the environmental impacts related to two different management options (landfilling and use as road sub-base filling material) for the RDF incineration and gasification BA. The functional unit (FU) selected was 1 Mg of humid BA produced at a RDF thermal treatment plant. The LCA was conducted according to the consequential approach (ILCD, 2010), thus marginal processes were selected for electricity production. System expansion was applied for solving multifunctionality issues. Upstream impacts related to waste and residues generation were neglected following the zero burden assumption. The study was performed according to EN ISO 14040:2006 and 14044:2006 standards. A time horizon of 100 years was considered, and Italian conditions were assumed concerning climate and precipitation rates. The life cycle impact assessment (LCIA) was carried out following the recommended methodologies reported in Hauschild et al. (2013). The impact categories included in the assessment were: global warming (GW), stratospheric ozone depletion (OD), photochemical oxidant formation (POF), terrestrial acidification (TA), eutrophication in terrestrial environments (EP), eutrophication in freshwater environments (EF), eutrophication in marine environments (EM), abiotic depletion of fossil resources (AD fossil), abiotic depletion of mineral resources (AD mineral), toxicity to humans in relation to carcinogenic substances (HTc), toxicity to humans in relation to non-carcinogenic substances (HTnc) and ecotoxicity to freshwater (ET). The results were reported in terms of characterized potential impacts and the characterization methods applied for each impact category are shown in Table B.1 in Annex B. The study was performed using the LCA modelling tool EASETECH specifically developed by the Technical University of Denmark for the assessment of solid waste management systems and technologies.

3.2.2.2 Scenario description, system boundaries and assumptions

For the two types of BA the following scenarios were considered:

- Landfill scenario: disposal of BA in a landfill for non-hazardous waste in central Italy;
- Road scenario: utilization of BA as unbound filling material in a secondary road sub-base in central Italy.

It should be noted that the second scenario is only hypothetical since the reuse of BA for such an application is not currently allowed by the Italian legislation (Ministerial decree 186/2006). However, in many European countries, the utilization of bottom ash in road construction is a well-established practice (e.g.: Crillesen and Skaarup, 2006; Astrup, 2007); for this reason it was considered relevant to include this scenario in the assessment as a potential future management option.

The system boundaries, of which a schematization is provided in Figure 3.1, included: BA transport from the incineration/gasification plant to the landfill or the road construction site; leaching of potentially toxic metals from the BA; the avoided extraction, crushing, transport and leaching of virgin material (which was assumed to be gravel) for the road scenario; materials and energy consumption for the construction of the landfill (capital goods) and energy consumption for the treatment of the wastewater. The impacts related to the construction of the road using BA were neglected because they were assumed to be the same as those deriving from the construction of a road employing only natural gravel. Furthermore, differently from the landfill, which would be constructed for the purpose of disposing of the BA, the construction of the road was considered to occur independently from BA generation and management, therefore it was not included in the system boundaries. The transport distance was assumed to be 70 km in both cases and was assumed to take place on a 28-32 ton Euro 4 truck. Specifically, the EASETECH process “Truck, 28t-32t, Euro4, highway” in which emissions and energy consumption are modelled using the software TEMA 2010 (Transportministeriet, 2010) was employed. Due to the consequential approach adopted in the present LCA study, the data on electricity consumption used for the modelling were based on Italian marginal electricity production data. Particularly, the

ECOINVENT database process “electricity production, natural gas, at conventional Italian power plant” was chosen. As reported by Turconi et al. (2011), in fact, during the past few decades, natural gas was the most important energy resource employed for electricity production in Italy, thus it is the most likely energy source that may be influenced by a change in the electricity demand related to changes in the assumed system.

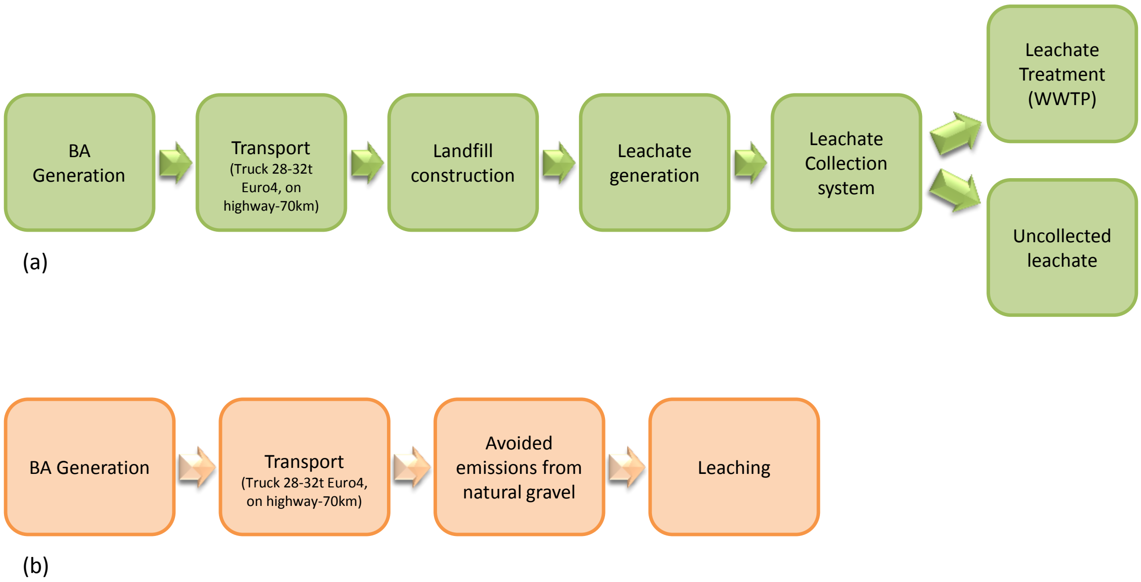

Figure 3.1 Scheme of the landfill (a) and road construction (b) scenarios, as modelled in EASETECH.

Landfill Scenario

The two types of BA were assumed to be disposed of in two different cells of a typical excavated-type of landfill for non-hazardous waste in central Italy. To estimate the size of the two cells, the total annual amount of each type of BA produced and disposed of in the landfill was estimated based on the capacities of the thermal treatment plants of the Lazio region (ARPA LAZIO, 2013; ISPRA, 2013). The BA characteristics and landfill geometry assumed for the calculation of the leachate production are summarized in Table 3.1. The BA moisture content was measured according to the UNI EN 14346 standard procedure. The minimum compacted dry bulk densities of the materials, corresponding to 1.1 Mg/m^3 for the RDF-I and 1.7 Mg/m^3 for the RDF-G BA, were estimated on the basis of column leaching tests data, in particular from the dry weight of the BA employed in the tests and the filling volume. These values were then adjusted on the basis of literature data (Hjelmar et al., 2010) to take into account compaction at the landfill site; hence the final dry bulk density values of 1.4 and 1.75 Mg/m^3 were assumed respectively, for the landfilled of RDF-I and RDF-G BA.

Table 3.1 Landfill parameters.

Parameters	RDF-I BA	RDF-G BA	Unit
Time of disposal	10	10	y
Total landfill height	10	10	m
Trench height	6	6	m
Hill height	4	4	m
Slope of the hill*	14	14	°
Slope of the trench*	30	30	°
Amount of BA landfilled (wet weight)	7.6E+07	2.4E+07	kg/y
BA dry bulk density	1.4	1.75	Mg/m^3
Moisture content	19.2	1.8	% w/w
Landfill cell volume	4.39E+05	1.35E+05	m^3
Landfill cell main area	4.92E+04	1.65E+04	m^2

* angle formed with the horizontal axis.

For the sake of simplicity the cross section of the landfill was schematized as a double trapezoid. According to the Italian landfill legislation (Legislative decree 36/2003), the following characteristics of the capping system layer were considered (where k represents the hydraulic conductivity of each considered layer):

- Low permeability barrier: 1 m clay (k = 10^{-7} m/s);
- Drain: 0.5 m gravel (k = 10^{-3} m/s);
- Top cover: 1 m loamy sand (k = 10^{-6} m/s).

The hydraulic conductivity of the clay barrier was increased of one order of magnitude (from 10^{-8} m/s to 10^{-7} m/s) in order to take into account of desiccation and cracking processes, which are typically observed after the construction of the capping system (see e.g.: Albright et al., 2006; Sadek et al., 2006). Four time periods were considered in the simulation of the landfill scenario as assumed by Birgisdóttir et al. (2007).

Specifically, the BA was assumed to be disposed of in a landfill during a 10-year period (active phase), followed by a two-year period in which the capping system is put in place but vegetation (mostly shrubs) is not well established. The third period in which the vegetation is established (after-care period) was assumed to last 45 years. During the first three periods (57 years in total), 80% of the produced leachate is assumed to be collected and treated in a wastewater treatment plant (WWTP), while the remaining 20% of the leachate is hypothesized to reach the surrounding environment due to some defects in the liner and the collection system. For the fourth period (43 years long), in which a passive state of the landfill was assumed, no leachate collection system was considered. Based on the above assumptions and considering an average rainfall of 800 mm/year (data of the “Meteorological Service of the Italian Air Force”, 2014), the net water infiltration into the landfill and the corresponding cumulative L/S ratio for each of the four time periods considered were calculated for each type of BA. Both parameters (i.e. net infiltration and L/S ratio) were estimated using the Landfill Water Balance (LWB) model for predicting leachate production in landfills (Pantini et al., 2013). The calculated values are reported in Table 3.2.

Table 3.2. Estimation of net water infiltration and resulting cumulative L/S ratios in the landfill for each time period and both types of BA (RDF-I BA and RDF-G BA).

		RDF-I BA		**RDF-G BA**	
Time Period	year	Net Infiltration [%]	Cumulative L/S [l/kg]	Net Infiltration [%]	Cumulative L/S [l/kg]
I°	10	60.9	0.39	72.2	0.40
II°	2	21.4	0.69	21.6	0.59
III°	45	22.8	1.34	22.9	1.16
IV°	43	22.8	1.97	22.9	1.71

For each obtained cumulative L/S ratio value, the corresponding release of potentially hazardous inorganic compounds from the two types of BA were extrapolated from the results of column percolation tests (see Paragraph 1.3.1) and used as input to the model for the baseline scenario. In particular, for both types of BA, the average leaching values obtained by a duplicate test were used. The total emissions for the landfill scenario related to the leaching process for each type of BA are reported in Table B.2 in Annex B. It should be noted that the release of the elements for which measured leaching concentrations resulted lower than instrumental quantification limits were not considered in the assessment. Moreover, it has to be specified that all the Cr measured in the leaching experiments was assumed to be Cr(VI) as a conservative assumption, since Cr(VI) was not specifically analysed, and also because the speciation of this metal in BA leachate was found to be dominated by Cr(VI) rather than Cr(III) (Kersten et al., 1998). The percolation leaching test was selected to derive the data employed in the baseline scenario, since its methodology, described in Paragraph 1.2.2.1, is considered to be more representative of the behaviour of the material in a field application and also because it allows to attain the trend of cumulative release as a function of the L/S ratio from which the leaching at a specific L/S may be extrapolated.

The distribution of metals, metalloids and salts leached out from the landfill body was hypothesized to be partitioned using some of the conservative assumptions applied by Birgisdóttir et al. (2007) and Butera et al. (2013). Specifically, 85% of metals and metalloids (i.e. As, Ba, Cr, Cu, Mo, Pb, Sb, Se and Zn) was assumed to be discharged to industrial soil and 15% to surface water, whereas the total amount (100%) of chlorides (Cl^-) and dissolved organic carbon (DOC) was hypothesized to be emitted to surface water. The removal efficiencies assumed for the contaminants in WWTP (see Table B.3 in Annex B) were taken from Manfredi and Christensen (2009) and from the EASETECH database module "Leachate treatment WWTP". The treated wastewater was assumed to be discharged to surface water bodies. Only the energy requirements for the treatment of the collected leachate was included in the assessment, while the capital goods for the construction of the WWTP were neglected.

The quantification of the capital goods for the construction of the landfill was included applying the approach and relevant assumptions reported in Brogaard et al. (2013) (i.e. the type of machinery used, transport distances from production sites of the materials and goods to the landfill, lifetime of materials and components). The data on materials and energy consumption refer to the same landfill described in the previous paragraph (excavated type). For the sake of simplicity, no distinction was made on the basis of the type of landfilled BA; thus, the capital goods required for the construction of the landfill for the two types of BA were assumed to be equal. The calculation was made considering the disposal of a total amount of 1 million Mg of BA with an average dry bulk density of 1.6 Mg/m^3 and average moisture content of 15% w/w. The time of disposal and the characteristics of the landfill (i.e. trench and hill heights and slopes) considered were the same as those reported in Table 3.2. A total volume of $5.3E^{+05}$ m^3 and a main surface area of $5.9E^{+04}$ m^2 were estimated and used for the evaluation of the capital goods. Moreover, since BA is mainly composed of inorganic matter, no biogas emissions were considered from the landfill site; therefore, biogas collection and utilization systems were not included in the assessment. The quantification of materials and energy needed for the construction of the considered landfill is presented in Table B.4. Furthermore, the aggregated data per Mg of humid BA landfilled (FU) and the material processes used to model capital goods are shown in Table B.5; both tables are reported in Annex B.

Road Scenario

In this scenario, it was assumed that RDF-I and RDF-G BA are employed as unbound material in a sub-base of a typical secondary road in central Italy. The chosen substituted virgin material was gravel and for both types of BA a substitution ratio of 1:1 on a weight basis was assumed. This assumption was based on the consideration that the particle size of both types of BA (see Fig. 1.1), in particular their reduced content (<10%) of fines (d<0.425 mm), is quite similar to that of the gravel typically employed for these applications.

The avoided emissions related to the extraction, crushing, transport and leaching of the substituted gravel were taken into account. Specifically, the ECOINVENT v.3. database process “gravel, crushed at mine, CH” was used for modelling the extraction and crushing of the gravel. The transport distance from the quarry of the gravel to the road construction site was assumed to be of 100 km and the same type of vehicles hypothesized for the transport of the BA were selected (Truck, 28t-32t, Euro4, highway).

In this scenario the L/S ratio (l/kg) was estimated using the simplified equation shown in Equation 3.1, assuming a percolation-controlled scenario as reported by Kosson et al.

(1996) and the same average annual precipitation considered in the landfill scenario (800 mm/y).

$$\frac{L}{S} = \frac{I_{eff} \cdot t}{\rho_{mat} \cdot h} \tag{3.1}$$

where:

- I_{eff} is the average net infiltration of the water through the road (mm/year), taken as 10% of annual precipitation (Birgisdóttir et al., 2007);
- t is the considered temporal horizon (i.e. 100 years);
- ρ_{mat} represents the dry bulk density of BA in the road, which was assumed equal to the one considered for the landfill scenario (see Table 3.1);
- h is the thickness of the BA layer assumed equal to 0.35 m (CNR, 1993);

The final L/S ratio values obtained after 100 years were 16.3 l/kg for the RDF-I BA and 13 l/kg for the RDF-G BA. As in the landfill scenario, the leaching data for the potentially hazardous inorganic compounds were extrapolated from the results of column tests. The total emissions for the road scenario related to the leaching process for each type of BA are reported in Table B.6 in Annex B. The leaching data employed to estimate the release of contaminants from the substituted gravel was taken from experimental results of leaching tests reported in Birgisdóttir (2005). Specifically, the results obtained from two-stage batch leaching test (UNI/EN 12457-3) at a L/S of 10 l/kg were used, since in this case it was not possible to extrapolate the leaching concentrations at L/S ratios higher than 10 l/kg. The use of leaching data derived at a lower L/S ratio for the substituted gravel compared to the values employed for the two types of BA was anyhow considered to be a conservative assumption, since for higher L/S ratios generally higher leaching concentration values are retrieved. Moreover, also in this case, for the estimation of the potential release from both BA samples and gravel, the elements with measured concentrations lower than instrumental quantification limits were not considered in the assessment. As for the transfer of the released contaminants to the environment, it was assumed that 100% of the water percolating into the road reaches the surrounding area and that the repartition of the contaminants is the same as assumed for the landfill scenario (85% to industrial soil and 15% to surface water). The BA layer was assumed to stay in place for 100 years.

3.2.2.3 Sensitivity analysis

Since several important assumptions were made in this study, especially with regard to the estimation of the release of contaminants from the two types of BA in each scenario, in relation to both the selection of the experimental method used to assess the leaching behavior of the materials and to the parameters assumed for modelling the scenarios, a sensitivity analysis was performed to analyze the influence of both aspects. Some of these assumptions also influenced the calculation of the L/S ratios and consequentially the estimation of the leaching concentrations.

Regarding the type of test selected, the data resulting from batch leaching tests performed on RDF-I and RDF-G BA (reported in Chapter 1) were used and compared to the results obtained using column test leaching data in the baseline scenario. Specifically, the results of the standard batch test UNI/EN 12457 part 1 (L/S= 2 l/kg) and part 2 (L/S= 10 l/kg) were employed for assessing the release of the two types of BA in the landfill and road scenario, respectively. In addition, results obtained from the pH-dependence batch leaching test (in Chapter 2) carried out at a L/S ratio of 10 l/kg (CEN/TS 14429) were used to estimate the effect of a variation of the pH of the eluate on the potential release of contaminants resulting for the road scenario; this could not be done for the landfill scenario since the L/S ratio employed in the pH-dependence test did not fit the conditions assumed for the landfill scenario, i.e. L/S =2 l/kg.

Relatively to the landfill and road scenarios, the following parameters were varied:

- Distribution of contaminants in the environment after leaching from the BA;
- Net infiltration;
- BA dry bulk density;
- Transport distance;
- Height of the landfill;

It should be noted that these parameters, except for the distribution of contaminants and the transport distance, affect the calculation of the L/S ratio which consequently modifies the resulting leaching data. In order to estimate the range of the variation of the environmental impacts resulting from the modification of the above mentioned parameters, a best case and worst case value for each parameter were tested in the sensitivity analysis. Best case indicates that the change of that parameter results in a lower potential environmental impact compared to the baseline scenario. Worst case means the opposite.

For the bulk densities only best case values were assigned to each type of BA as the values calculated from the column test were assumed to be the minimum degree of compaction that can be obtained for these materials. Therefore, the dry bulk density sensitivity was performed by increasing of 15 percentage points the values used in the baseline scenarios. Moreover, in the landfill scenario, the effect of varying the net infiltration was evaluated by modifying the hydraulic conductivity of the clay layer in the capping system which was shown to be the most affecting parameter. Table 3.3 shows the variations of the parameters assumed in the two considered scenarios for each type of BA.

Table 3.3 Parameters considered in the sensitivity analysis.

Parameter	Unit	Baseline Scenario	Best case	Worst case
Landfill scenario				
Contaminants distribution (CD)	%	85% soil_15% water	100% soil	100% water
Net infiltration (k clay)	m/s	10^{-7}	10^{-8}	10^{-6}
RDF-I BA Bulk density (ρ)	Mg/m^3	1.4	1.6	-
RDF-G BA Bulk density (ρ)	Mg/m^3	1.75	2	-
Transport distance (TD)	km	70	50	100
Thickness (H)	m	10	15	8
Road scenario				
Contaminants distribution (CD)	%	85% soil_15% water	100% soil	100% water
Net infiltration (i)	%	10	5	15
RDF-I BA Bulk density (ρ)	Mg/m^3	1.4	1.6	-
RDF-G BA Bulk density (ρ)	Mg/m^3	1.75	2	-
Transport distance (TD)	km	70	50	100

3.3 RESULTS AND DISCUSSION

3.3.1 Inventory

The life cycle inventory (LCI) of the main contaminants that contribute to the emissions in the two considered environmental compartments (i.e. surface water and industrial soil) for both types of BA and for the two scenarios are reported in Table 3.4.

Specifically, Table 3.4 shows the total amount of each compound expressed as kg per Mg of humid BA (FU) and the relatively contribution (in percentage) of each sub-process considered in the scenario modelling. Transport of the BA from the thermal treatment plants to the landfill/road and the construction of the landfill were not reported since their contributions were negligible (0% and less than 0.2%, respectively). It should be noted that the sub-process “Avoided emissions” in the road scenario includes the avoided emissions related to the extraction, crushing, transport and leaching of the substituted gravel. From the results obtained, it can be noticed how for the emissions to the surface water in the landfill scenario, for both types of BA, the WWTP was in general the main contributor. This was mainly related to the fact that for the first 57 years 80% of the leachate collected from the landfill was assumed to be sent to the WWTP that discharges its effluents in a superficial water body. Regarding the emissions to industrial soil in the landfill scenario, the only contributor was leaching from the disposed BA. In the road scenario both the emissions to surface water and industrial soil for the RDF-I BA were generally dominated by the leaching process, apart from the emissions of As, Cr(VI) and Mo to the surface water in which the contribution of the avoided emissions from natural gravel was comparable to the one of the leaching process.

For the RDF-G BA, different results were obtained depending on the type of compound and the environmental compartment considered, but in general compared to the RDF-I BA, the contribution of the avoided emissions from natural gravel was found to be more significant.

Table 3.4. Life cycle inventory (LCI) of the main contaminants in the two considered environmental compartments (i.e. surface water and industrial soil) for both types of BA (RDF-I BA and RDF-G BA) and for the two scenarios (Landfill and Road). The total amount (kg/FU) and the main processes contributing (%) to each emission are reported.

		Landfill			**Road**		
Compartment	**Compound**	**Total [kg/FU]**	**WWTP [%]**	**Leaching [%]**	**Total [kg/FU]**	**Avoided emissions [%]**	**Leaching [%]**
					RDF Incineration BA		
Emissions to surface water	**As**	3.20E-07	75	24	4.55E-07	45	55
	Ba	1.43E-03	52	48	5.93E-03	1	99
	Cl^-	9.08E-01	19	81	1.24E+02	0	100
	Cr(VI)	1.18E-05	87	13	7.34E-08	50	50
	Cu	6.33E-06	82	18	1.37E-05	2	98
	DOC	1.03E-02	43	57	3.07E-02	6	94
	Mo	9.74E-07	80	20	-6.90E-07	63	37
	Pb	2.21E-04	54	46	1.53E-03	0	100
	Sb	2.60E-05	59	41	1.63E-04	0	100
	Se	2.01E-06	54	46	1.12E-05	2	98
	Zn	2.94E-05	67	33	2.39E-04	2	98
Emissions to industrial soil	**As**	4.44E-07	0	100	1.32E-05	0.06	99.94
	Ba	3.86E-03	0	100	3.38E-02	0.49	99.51
	Cr(VI)	8.48E-06	0	100	7.42E-05	0	100
	Cu	6.33E-06	0	100	7.97E-05	0	100
	Mo	1.10E-06	0	100	5.52E-06	0	100
	Pb	5.77E-04	0	100	8.72E-03	0	100
	Sb	6.07E-05	0	100	9.21E-04	0	100
	Se	5.18E-06	0	100	6.50E-05	0	100
	Zn	5.46E-05	0	100	1.38E-03	0.02	99.98
					RDF Gasification BA		
Emissions to surface water	**As**	3.84E-07	89	11	-1.69E-06	90	10
	Ba	4.43E-06	69	31	-5.21E-05	89	11
	Cu	2.07E-05	87	13	1.57E-05	2	98
	DOC	2.44E-03	29	71	6.24E-02	3	97
	Sb	7.39E-07	62	38	3.05E-06	12	88
Emissions to industrial soil	**As**	2.41E-07	0	100	2.41E-07	1	99
	Ba	7.69E-06	0	100	7.69E-06	84	16
	Cu	1.54E-05	0	100	1.54E-05	0	100
	Sb	1.58E-06	0	100	1.58E-06	0	100

This could be mainly attributed to the generally lower release of contaminants observed from this type of material. In fact, the leachate concentrations of only a few compounds (i.e. As, Ba, Cu, DOC and Sb) were found to be higher than instrumental quantification limits (Table A.2 in Annex A), see Tables B.2 and B.6 in Annex B.

Moreover, it has to be specified that all the contributions of the avoided emissions from natural gravel were mainly due to the extraction and crushing processes rather than to leaching and transport. Summarizing, it may be concluded that for RDF-I BA, the emissions of Ba, chlorides (Cl^-), DOC and Pb proved to be the most significant; whereas, for the RDF-G BA, the emission of DOC to surface water was found to be significantly higher than that of the other contaminants.

3.3.2 Potential environmental impacts

In Figure 3.2 the potential environmental impacts resulting for the landfill (L) and road (R) scenarios for both types of BA are shown and compared. The results are presented as characterized potential impacts, where positive values represent the environmental loads, while negative values indicate savings. For each impact category, both the total net impact and the contribution of the sub-processes included in each scenario (e.g. transport, construction of the landfill and leaching) are shown. In the landfill scenario, impacts related to leaching are given by the sum of the contribution of the uncollected leachate emitted from the landfill and the emissions of the contaminants to the surface water after leachate treatment in the WWTP. The potential impacts for all the three toxicity-related categories considered (i.e. toxicity to humans related to carcinogenic substances, toxicity to humans related to non-carcinogenic substances and freshwater ecotoxicity) are shown in the graphs. Whereas, among the non toxicity-related impact categories Global Warming (GW) and Mineral Abiotic Resource Depletion (AD Mineral) were chosen as appropriate representatives also for the remaining non toxic categories.

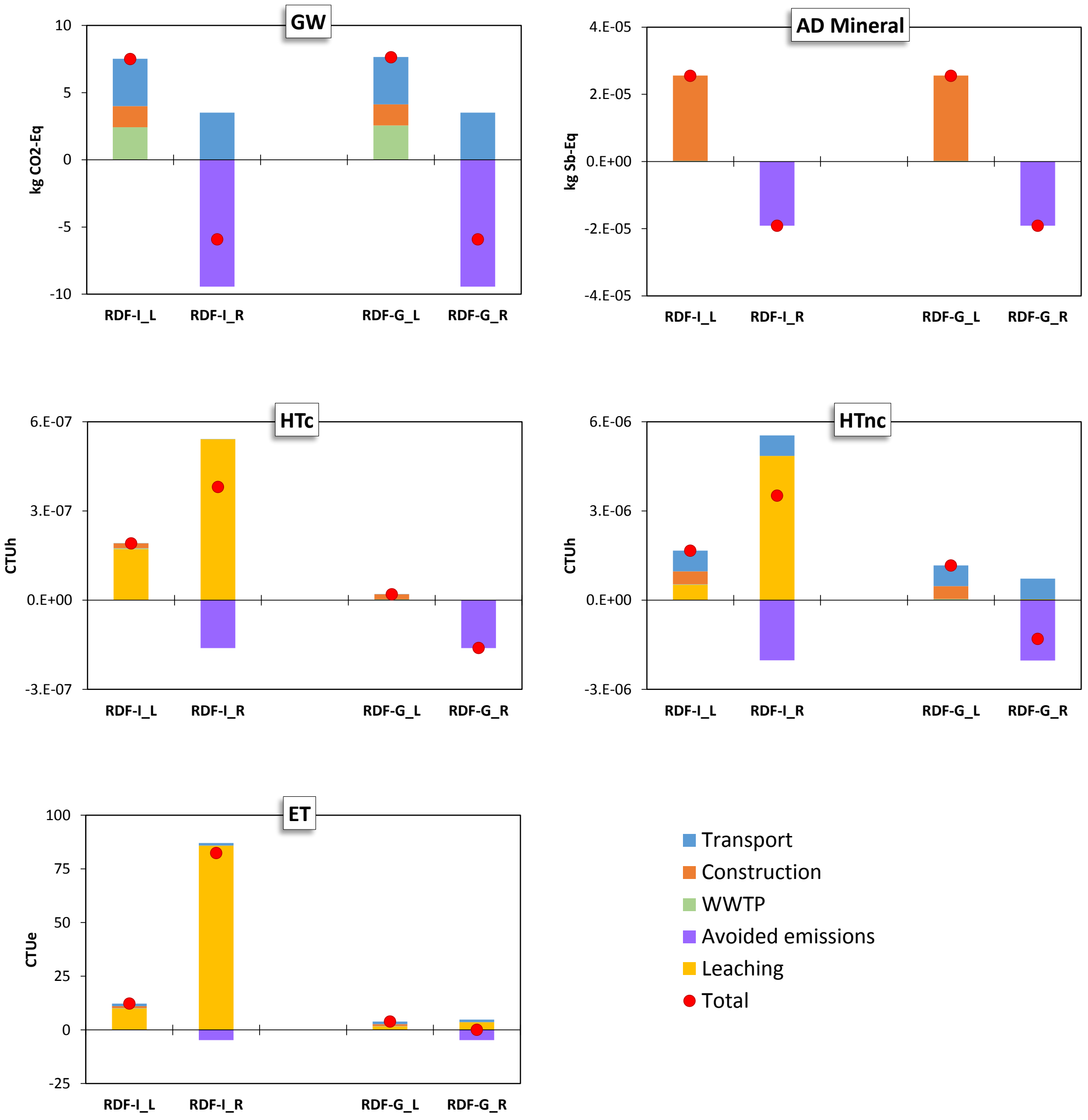

Figure 3.2 Characterized potential environmental impacts for the baseline scenarios (RDF-I: Refuse Derived Fuel incineration bottom ash; RDF-G: Refuse Derived Fuel gasification bottom ash; L: landfill; R: road).

In both scenarios and for both types of BA, the results obtained for POF, TA, EM, AD Fossil and EP impact categories were very similar to those observed for the GWP category, while EF and OD presented the same trend shown by AD Mineral. The results attained for the impact categories not shown in Fig. 3.2 are anyhow provided in Figure B.1 in Annex B.

3.3.2.1 Non-toxicity related impact categories

Large differences depending on the type of management option considered were found for both types of BA with regard to global warming and mineral abiotic resource depletion. These differences were mainly related to the savings obtained from the avoided emissions of natural gravel in the road scenario. In fact, the net potential impacts on GWP and AD Mineral in the road scenario, for both types of BA, were negative, representing potential savings. For the landfill scenario, instead, positive impacts were observed for both impact categories. Environmental loads to the GWP category were associated to the transport of the BA from the production facility to the landfill site (approximately 46%), the energy requirements for leachate treatment (around 33%) and the capital goods related to the landfill construction (21%). Whereas, the positive contribution to AD Mineral is fully related to the consumption of raw materials such as Cu (50%), Cd (15%), Pb (10%) and Mo (8%), mainly used for the construction of the office (28%) and garage (68%) buildings in the landfill site. Although only a few studies have addressed the importance of including capital goods in LCA studies (Ecobalance 1999; Ménard et al., 2004; Frischknercht et al., 2007; Brogaard et al., 2013), from the obtained results it is clear that the environmental impacts associated to these processes in the non-toxicity related impact categories are not negligible and they should hence be taken into account when assessing such a scenario. Finally, it should be highlighted that, due to the same assumptions made regarding the transport distance, capital goods and avoided emissions from natural gravel use, and because of the negligible contribution of leaching on the non toxicity-related impact categories, the total environmental impacts for the two types of BA in both scenarios showed to be very similar. The only minor difference found for the landfill scenario is related to the energy consumption of the WWTP because of the slightly different amounts of leachate generated from the two types of BA.

3.3.2.2 Toxicity related impact categories

Regarding the toxicity related impact categories (i.e. HTc, HTnc and ET), the results showed that for the RDF-I BA in both scenarios the leaching of hazardous compounds, taking into account both emissions to surface water and industrial soil, played a dominant role on potential environmental impacts, with a contribution greater than 75% to HTc and ET. In particular, comparing the two management options for this type of BA, the highest potential impacts were observed for the road scenario due to the higher L/S ratio considered. As can be noted in Table 3.5, for HTc, in both scenarios, the leaching impacts were almost completely related to Cr(VI) primarily due to the high characterization factor (CF) associated with this element in this impact category and secondarily because of the lack of CFs for other compounds detected in the eluates (e.g.: Ba, Cu, Sb and Zn). However, in the landfill scenario, the main contribution (73.4%) to HTc was due to Cr(VI) emissions to the surface water, whereas in the road scenario Cr (VI) emissions to industrial soil provided the highest impacts (73.2%). Regarding ET, the main contributors to the leaching impacts were Ba and Zn in both scenarios, while for the HTnc category also Pb was important, besides Ba and Zn. Also for ET and HTnc, the landfill scenario appeared to be impacted more by the emissions to surface water, while the emissions to industrial soil gave higher contributions in the road scenario. This may be related to the assumptions made for the modelling of the scenarios regarding the distribution of contaminants. In fact in the landfill scenario it was assumed that most of the landfill leachate is treated in a WWTP and then the treated wastewater is discharged in surface water bodies, while in the road scenario most of the water percolating through the material is assumed to come directly in contact with the surrounding soil. The results obtained for the RDF-G BA do not follow the same trend observed for RDF-I BA, due to the significantly lower release of contaminants compared to the incineration BA (see Table 3.4). In fact for the RDF-G BA, for all the three toxicity-related impact categories, the landfill scenario presented higher potential impacts compared to reuse in road construction. This was related to the low contribution of the leaching from RDF-G BA in road (less than 2% for both human toxicity impact categories) with respect to the avoided emissions from natural gravel.

Moreover, the leachate concentrations of most of the elements detected for the RDF-G BA, such as As, Ba and Cu, showed to reach maximum values for low L/S ratios (i.e. 1-2 l/kg) and then to remain quite constant for higher L/S ratios (see Paragraph 1.3.1).

Table 3.5 Contribution of contaminants to the total leaching-related impacts for HTc, HTnc and ET for both types of BA (RDF-I BA and RDF-G BA) and each scenario (landfill and road). n.CF: characterization factor not available.

		Landfill			**Road**		
	Compound	**HTc [%]**	**Htnc [%]**	**ET [%]**	**HTc [%]**	**Htnc [%]**	**ET [%]**
				RDF Incineration BA			
Emissions to surface water	**As**	0.07	1.69	0.13	0.16	1.30	0.11
	Ba	n.CF	27.40	21.83	n.CF	12.11	10.64
	Cr(VI)	73.38	0.06	12.42	25.71	<0.01	1.59
	Cu	n.CF	<0.01	3.49	n.CF	<0.01	0.90
	Mo	n.CF	<0.01	<0.01	n.CF	<0.01	<0.1
	Pb	0.04	5.17	0.83	0.10	3.79	0.67
	Sb	n.CF	1.85	0.32	n.CF	1.23	0.23
	Se	n.CF	n.CF	0.15	n.CF	n.CF	0.10
	Zn	n.CF	7.48	11.50	n.CF	6.52	11.04
Emissions to industrial soil	**As**	0.05	1.25	0.04	0.48	3.95	0.12
	Ba	n.CF	37.09	29.55	n.CF	34.35	30.15
	Cr(VI)	26.38	0.02	4.47	73.23	<0.01	4.54
	Cu	n.CF	<0.01	1.85	n.CF	<0.01	2.71
	Mo	n.CF	<0.01	<0.01	n.CF	<0.01	<0.1
	Pb	0.07	8.00	1.28	0.33	12.74	2.25
	Sb	n.CF	2.48	0.37	n.CF	3.98	0.66
	Se	n.CF	n.CF	0.19	n.CF	n.CF	0.28
	Zn	n.CF	7.50	11.58	n.CF	19.99	34.00
Total Impact [CTU]		**1.72E-07**	**5.12E-07**	**9.98**	**5.42E-07**	**4.85E-06**	**85.88**
				RDF Gasification BA			
Emissions to surface water	**As**	75.07	67.76	0.95	25.07	18.15	0.23
	Ba	n.CF	2.85	0.42	n.CF	2.25	0.29
	Cu	n.CF	0.12	70.36	n.CF	0.05	24.45
	Sb	n.CF	1.76	0.06	n.CF	4.22	0.12
Emissions to industrial soil	**As**	24.93	22.84	0.12	74.93	55.05	0.26
	Ba	n.CF	2.47	0.36	n.CF	6.39	0.83
	Cu	n.CF	0.05	27.68	n.CF	0.14	73.48
	Sb	n.CF	2.16	0.06	n.CF	13.76	0.34
Total Impact [CTU]		**1.89E-10**	**1.53E-08**	**1.62**	**3.00E-10**	**3.03E-08**	**3.62**

Hence, although the L/S ratios calculated for the landfill and road scenario were significantly different, no remarkable differences were observed in the leaching behavior of this type of BA in the two scenarios. As can be noted in Table 3.5, in fact, in both scenarios As emissions gave the highest contributions in terms of HTc and HTnc impact categories, while Cu was the major contributor for ET impacts.

Similarly to RDF-I BA, the landfill scenario appeared to be impacted more by the emissions to surface water, while the emissions to industrial soil gave higher contributions in the road scenario. As previously stated, elements with measured concentrations in the eluates below instrumental quantification limits (i.e. Cr, Mo, Pb, Se and Zn) were not included in the assessment. However, if the instrumental quantification limits were assumed as the concentration values leached from the RDF-G BA and therefore employed to calculate the potential release of these elements, the overall results of the LCA may change considerably. In fact, as reported in Figure B.2 in the Annex B, in this case higher potential impacts were observed with regard to the HTc and the ET categories for the road rather than the landfill scenario.

In general, as also found in others studies (Birgisdóttir, 2005), the leaching of potentially hazardous compounds during a 100 years period was less than 1% of the total amount contained in the BA for both types of materials and scenarios, apart for Ba (< 4%) and Pb (< 3%) for the RDF-I BA. Hence, after a 100 years period, a significant amount of contaminants still remains in the residues and may be potentially leachable. Several studies regarding emissions from landfills (e.g.: Helleweg, 2000; Astrup et al., 2006; Hauschild et al., 2008) indicated that release of heavy metals occurs over very long time periods (thousands of years). Although several attempts (e.g. Christensen et al., 2007) have been made to include these long-term emissions in LCA, no common consensus or assessment principle has been reached. For this reason, these potential long-term emissions have been excluded from this study.

Finally, it is important to point out that, although the characterization method used for the toxic related impact categories (i.e. the USEtox model as reported in Table B.1 in the Annex B) represents the recommended life cycle assessment impact (LCIA) model for characterising the human and ecotoxicological impacts of chemicals (Rosenbaum et al., 2008), currently it provides interim CFs for only some inorganic contaminants and no CFs for emissions to the groundwater. Hence, the contribution of some pollutants such as dissolved organic carbon and chlorides that were found to yield significant emissions in the inventory phase (see Table 3.4), was not accounted for because of missing CFs in the current version of USEtox (see Table 3.5).

As can be noted in Fig. 3.2, for the landfill scenario, the contribution of other sub-processes besides leaching showed to be relevant only for the HTnc impact category, i.e. the transport of BA (42% for RDF-I and 60% for RDF-G BA) and the construction of the landfill (26% for RDF-I and 37% for RDF-G BA). For the road scenario, the contribution of the avoided emissions related to gravel substitution were not negligible for all impact categories; in particular for HTnc they accounted for 27% and 74% of total impacts for RDF-I and RDF-G BA, respectively. However, it should be highlighted that also for the toxicity-related categories this impact reduction was mainly due to the avoided emissions related to the excavation and the crushing of the natural gravel rather than to its avoided transport and leaching. It is noteworthy to observe that this result was achieved notwithstanding that batch tests results were used to describe the leaching behaviour of natural gravel (see Paragraph 3.2.2.2), which as discussed in Chapter 1 generally provide higher release values compared to column tests.

3.3.3 Sensitivity analysis

As previously mentioned, the main uncertainties of the present study can be related to the leaching data used for modelling the scenarios. In this regard, since the leaching process was shown not to affect the potential environmental impacts found for the non-toxicity related categories, the sensitivity analysis was performed only for toxicity impact categories.

3.3.3.1 Influence from the type of leaching test data

Figure 3.3 reports the comparison of the total potential environmental impacts obtained by using column (baseline scenarios) and batch leaching tests data. It has to be specified that for both types of tests average leaching values, obtained by duplicate tests, were used. However, the variability of the results obtained by the replicates was also assessed by using the data obtained from each single test and no significant differences were found, since for both types of slag, the leaching test results were quite reproducible. Results show that in general, and mainly for RDF-I BA, the potential environmental impacts estimated by using batch test data were higher than those obtained in the baseline scenarios in which the column test data were employed, especially for HTc and ET impact categories. In fact, in agreement with the total emissions related to the leaching process calculated for each types of BA and both scenarios (compare Table B.7 with Tables B.2 and B.6 in the Annex B), for most of the considered compounds, especially Cr, Ba, Zn for RDF-I BA and Cu for the RDF-G BA, the values resulting from the batch tests were greater than those obtained from the column test.

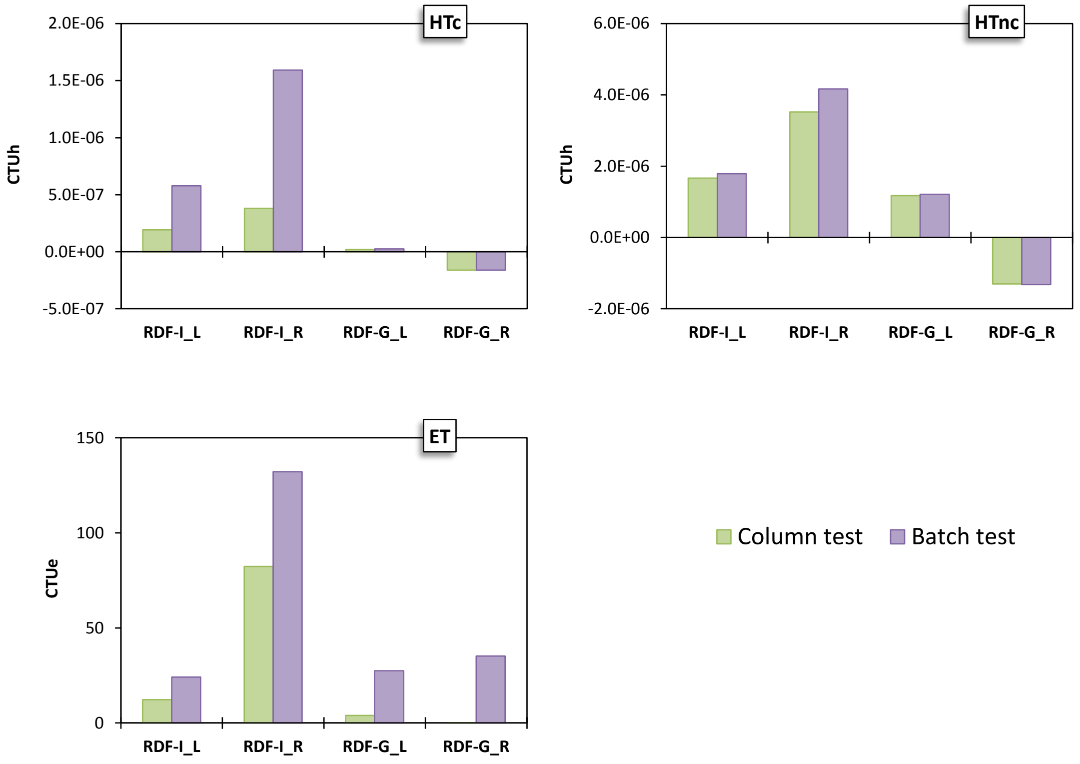

Figure 3.3 Comparison of the total potential environmental impacts resulting from column (baseline scenarios) and batch test data for the modelling of the leaching behavior of the two types of bottom ash.

These results can be related mainly to the different mode of execution of the two types of leaching tests. In fact, while in the batch tests the material is in a pseudo-equilibrium condition with the water phase; the column test is a dynamic test in which the leachant is continuously renewed. Moreover, the batch test was performed on size reduced material (d< 4mm) whereas the column test was carried out on the material as received, as reported in Section 2.1; thus, the major specific surface area available for the leaching in the batch tests may have favoured the increase of the release of contaminants observed for these type of tests (Chimenos et al., 2003; López Meza et al., 2008). From these results, it can be concluded that, although the potential environmental impacts obtained using batch tests data were found to be greater than those achieved in the baseline scenarios, the overall results of the LCA study do not change, since the landfill scenario still represents the management option that yields less impacts for RDF-I BA and more impacts for RDF-G BA, in terms of toxicity categories. For the gasification slag the only exception was observed for the ecotoxicity category, for which the use of batch test data results in higher impacts for the road scenario compared to the landfill one, due to a one order of magnitude higher Cu release in the batch test at L/S of 10 l/kg than the one obtained by the column leaching test at an L/S of 13 l/kg (compare Table B.7 with Table B.6 in the Annex B).

3.3.3.2 Influence of pH

As addressed in Chapter 2 leaching from BA, for most contaminants, is closely affected by changes in pH of the leaching system. Hence, pH is a very important parameter to evaluate when assessing the environmental behaviour of a waste material in specific reuse or disposal scenarios. As previously mentioned, variations in pH are related to the buffering capacity of the material in question, i.e. the acid/base neutralization capacity (ANC/BNC). As observed in Fig. 2.1, the ANC of RDF-I and RDF-G BA displayed remarkable difference below pH 12, which was mainly attributed to their different mineralogical composition. In particular, while RDF-I BA exhibited a high buffering capacity for pH values between 11 and 12, for the RDF-G BA after the addition of few micro equivalents of nitric acid, a rapid drop in pH was registered (from 12 to 5). These findings are highly significant especially for the evaluation of the leaching behavior of RDF-G BA in specific disposal or application scenarios. In fact, considering the negligible acid buffering capacity exhibited by this type of slag, the external environmental conditions to which the material may be subjected to, e.g. contact with acidic rainwater (pH 5-6), could lead to a rapid drop of the natural pH of the eluates (from above 11 to below 6), resulting in an increase of the mobility of some contaminants, such as Cr, Cu, Pb and Zn. For this reason, the variation of the leaching-related environmental impacts associated to the potential changes in the pH of this type of BA was evaluated.

Figure 3.4 shows, for the three toxicity-related impact categories, the variation of the potential environmental impacts related to leaching from gasification BA in road as a consequence of change in the pH of the material (where 10 represents the native pH of the RDF-G BA). In the graphs the main contaminants (i.e.: Ba, Cr (VI), Cu, and Zn) contributing to the total leaching-related impacts for each considered impact category are also shown for pH values spanning from the native pH of the BA to the most acidic value tested in the lab leaching experiments. However, it should be pointed out that most probably in a field application scenario the realistic end pH value may be close to neutrality, so strongly acidic pHs may be rarely reached.

Results indicate that for both human toxicity categories, a pH decrease may lead to a significant increase of the potential environmental impacts. The main contributors to the impacts were Zn and Ba for HTnc and Cr(VI) for HTc. The contribution to ET was mainly related to the leaching of Cu, in accordance with the relation between Cu solubility and pH observed for RDF-G BA (Rocca et al., 2012; Paragraph 2.3.1). The relevance of these contaminants in terms of their contribution to toxicity impacts is related to both the high CFs employed in the considered impact methodology and the significant leachate concentrations obtained from the pH dependent leaching test (Paragraph 2.3.1).

The pH values for which the total impacts (including also the other sub-processes besides leaching) become higher than those associated to the landfill scenario, thus changing the overall results of the assessment, were: 5.4 for the HTc, 7.34 for HTnc and 9.14 for ET (red circles in Fig. 3.4).

Despite the significantly higher buffering capacity of the RDF-I BA, pH changes showed to affect the overall leaching-related environmental impacts also for this type of slag (see Figure B.3 in Annex B). For HTnc and ET, a pH decrease from the native value of 12.3 to 8.8 showed to have no effect on the total leaching-related environmental impacts, whereas, moving from a neutral pH value of 6.6 to the strongly acidic pH of 3.5, a significant increase of the potential environmental impacts, mainly related to leaching of Cu and Zn for ET and Zn for HTnc, was observed. The impacts of the HTc category instead, showed to be dominated by the leaching of Cr(VI) following the solubility curve observed for this element.

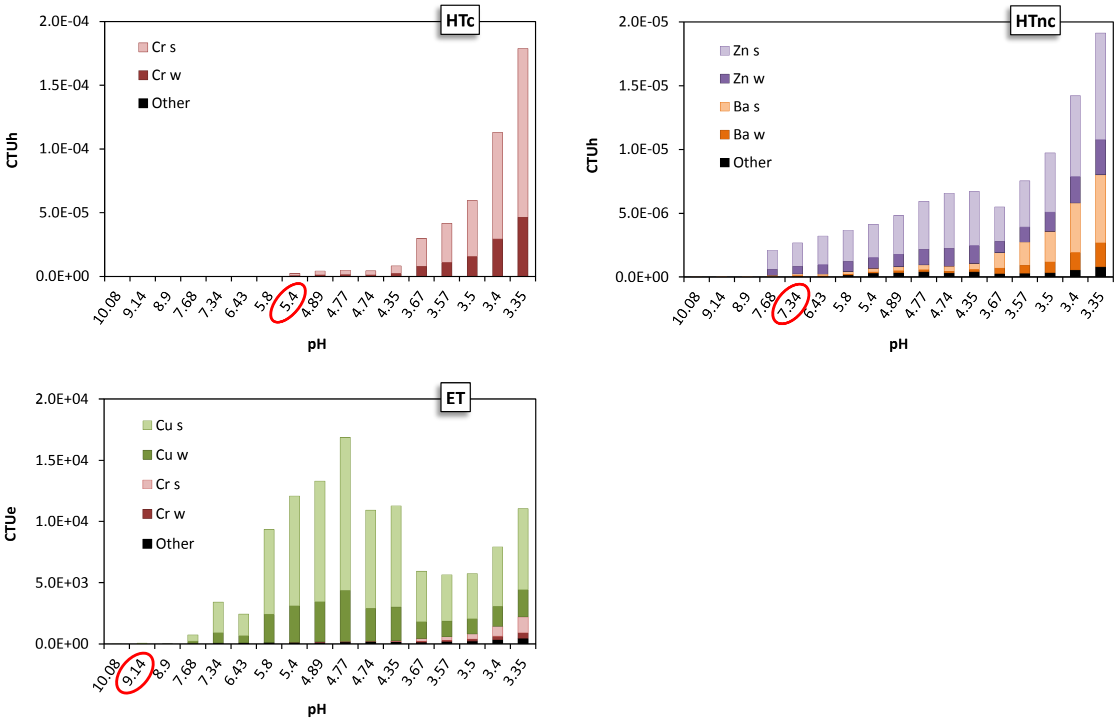

Figure 3.4. Characterized potential environmental impacts related to leaching from gasification bottom ash for the road scenario as a function of pH, with s: emission to industrial soil; w: emission to surface water. Red circles represent the pH values for which the total impacts (including also the other sub-processes besides leaching) become higher than those associated to the landfill scenario.

Due to the generally higher release of contaminants as a function of pH found for the RDF-I BA (Paragraph 2.3.1), the total leaching-related environmental impacts for this type of material were also in this case higher than those obtained for the RDF-G BA. However, as previously mentioned, this type of material exhibited a high buffering capacity reaching a pH value of 6.6 only after the addition of 5 meq H^+/g dry matter. Hence, while for ET and HTnc, the pH changes that can occur in a disposal or reuse scenario may be expected not to represent a problem for the RDF-I BA, for HTc, due the trend of Cr(VI) mobilization with pH, higher impacts may result even for low pH variations.

3.3.3.3 Influence of the parameters assumed for scenario modelling

Figure 3.5 reports the results obtained by changing the parameters assumed for the modelling of the two scenarios (refer to Table 3.3). The bars in the graphs represent the percentage of variation of the results with respect to the impacts obtained for the baseline scenario (zero axis). Table B.8 and Table B.9, in the Annex B, also report the net values of the potential environmental impacts estimated for both scenarios and for each type of BA. In general, in both scenarios, the largest variations of the results were found for the RDF-I BA due to the higher variability of the leaching concentrations observed for this type of material. The only exception was noticed for the impacts related to the ET category in the road scenario for the RDF-G BA. In fact, as clearly shown in the right bottom graph of Fig. 3.5, for this impact category, the variation percentages of the results for three of the four considered parameters (i.e. distribution of contaminants, net infiltration, transport distance) were very high, reaching for example a value of 3000% when 100% of the emitted pollutants were assumed to be discharged in the surface water compartment.

However, this was due more to the small absolute value of the ET impacts of RDF-G BA in the road scenario, rather than to the differences between the total impacts observed for the baseline scenario and the ones obtained varying the parameters. For the RDF-I BA, in both scenarios the distribution of contaminants and the net infiltration of rain water were the parameters that most influenced the results for all three impact categories. To a lower extent, also the change of the height of the BA layer in the landfill scenario affected the results. In general, the values assumed for the dry bulk density of the slag showed to exert a less relevant effect compared to the other parameters. For the RDF-G BA, as already mentioned, except for the ET impact category, no significant variation of the results was observed. This is principally related to the low contribution of the leaching process to the human toxicity impact categories already observed in the baseline scenario. The influence of the variation of the transport distance was found to be negligible for the HTc category for both types of BA and scenarios, while the other two impact categories (HTnc and ET) were affected to a different extent depending on the type of residue and the scenario considered. Specifically, a higher percentage of variation (ranging from -16% to 25%) was observed with regard to HTnc for the RDF-G BA in the landfill scenario.

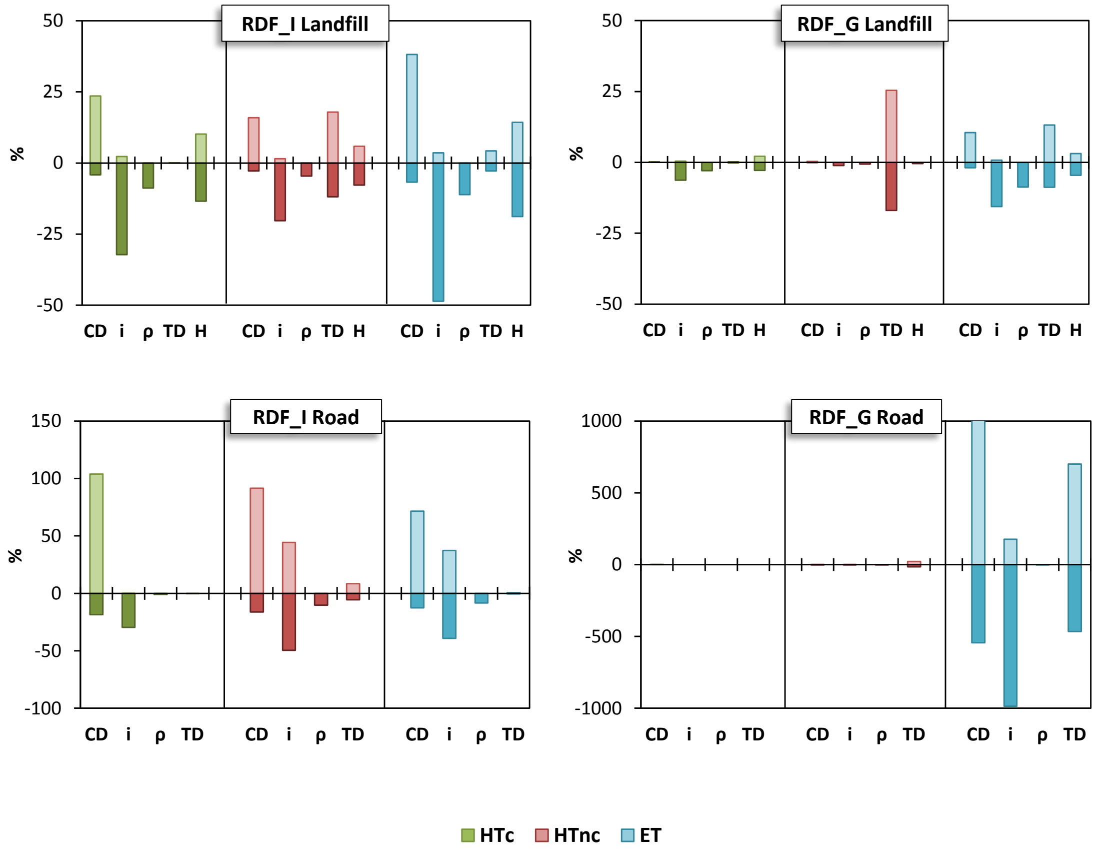

Figure 3.5 Percentage of variation of the total potential environmental impacts with respect to the results obtained for the baseline scenarios (zero axis). CD: contaminants distribution; i: net infiltration; ρ: dry bulk density; TD: transport distance; H: height of the landfill.

3.4 CONCLUSIONS

In this study the potential environmental impacts associated to landfilling and reuse in road sub-base construction of RDF incineration and gasification BA were evaluated by LCA. The data employed to estimate the cumulative release of potentially toxic metals from these waste materials in each scenario were extrapolated from experimental leaching tests (i.e. column percolation tests) and used as input data for the LCA model. For all non toxicity-related impact categories and both types of BA, reuse of BA as a filler in road sub-bases appeared to be beneficial with respect to landfilling. Whereas, toxicity-related impacts showed to differ significantly depending on both the type of BA and the management scenario considered, as a function of the leaching behaviour of the material. Specifically, for RDF-I BA leaching proved to be the major contributor to the total environmental impacts and reuse in road appeared to yield significant impacts in all the toxicity-related categories that were found to be higher than those obtained for the landfill scenario. For the RDF-G BA, instead, the contribution of leaching to the toxicity related impacts was negligible, making reuse in road particularly interesting. However, the low acid neutralization capacity observed for this type of BA may represent a limiting factor. Indeed, leaching impacts were significantly affected by pH conditions, and decreases in pH could lead to increased environmental impacts related to RDF gasification bottom ash.

The selection of type of leaching data used for determining the release of contaminants from the two types of BA (batch leaching test data instead of column leaching data) showed to significantly influence the quantified environmental impacts (batch data yielding higher emissions), however the overall ranking of scenarios was not affected. The most critical modeling assumptions made in this study were: the distribution of contaminants between environmental compartments (i.e. soil vs. surface water) and the net infiltration of rain water into the waste body. While the overall conclusions of the LCA in this study were robust with respect to consistent changes in the evaluated parameters, it is recommended that LCA studies involving residue leaching include careful evaluation of the importance of material properties and scenario assumptions. In this regard, there are additional factors that may be important to consider and that were not taken into account in this study; for example the use of field leaching tests instead of laboratory leaching tests results, the utilization of more sophisticated models to estimate the amount of water in contact with the material (especially for the road scenario) and the use of LCA together with other decision tools (i.e. site-specific risk assessment).

Finally, it should be considered that the two types of bottom ash analysed in this work presented quite different physical characteristics besides environmental properties.

Hence, also their technical performance should be specifically examined in order to identify the most suitable reuse applications and the maximum substitution ratios with respect to virgin raw materials applicable in each case.

CHAPTER 4

RISK ASSESSMENT WITH REGARD TO GROUNDWATER PROTECTION OF MANAGEMENT STRATEGIES FOR DIFFERENT TYPES OF BOTTOM ASH

4.1 INTRODUCTION

A further step towards the evaluation of the environmental impacts related to the two different management options hypothesized (i.e. landfilling and recycling in road sub-base construction) for the analysed types of BA, was carried out by employing a risk-based approach. Risk assessment generally takes into account both the risk for human health and the environment. However, given the nature of the contaminants of concern for this work (i.e. inorganic contaminants) that are hardly volatile and considering the potential scenarios identified for waste disposal/reuse, it was decided to focus only on the evaluation of risks for the groundwater resource related to the leaching pathway. As shown in the previous section, only a small fraction of pollutants is available for leaching from BA, having then the potential to migrate to the groundwater. As described by Townsend et al. (2006), in risk assessment based-studies, the evaluation of the leachable fractions from the material can be performed following basically two different types of approaches. The first one is based on the use of literature values for solid-water partition coefficients (K_d), specific to each contaminant, that on the basis of the total concentration of the pollutant in the waste allow to estimate the leachate concentration in the pore water. This is the approach commonly applied for soils contaminated by organic compounds, whereas for inorganic contaminants, it is widely recognised that the use of literature K_d values may lead to predictions that are not representative of the site-specific leaching scenario. To overcome this limitation, before performing the risk assessment, experimental studies aimed at assessing the waste-specific leaching behaviour can be carried out. This second type of approach is widely applied at a European level (e.g. in Denmark, Norway and Sweden) for the evaluation of recycling and reuse strategies for solid mineral waste (e.g. thermal process residues, mining and quarry waste, construction and demolition waste). Generally in these countries, before performing the risk assessment, the evaluation of the waste as a pollution source term (in any scenario) is assessed in depth according to the EN 12920 methodological standard (CEN, 1997) (Tiruta-Barna et al., 2007). This methodology consists of seven steps: (1) description/definition of the problem and the solution sought for, (2) description of the scenario, (3) material/waste description, (4) assessment of the parameters' influence on the leaching behaviour, (5) leaching behaviour modelling, (6) behavioural model validation, (7) conclusion. The standard recommends developing and applying complementary experimental (leaching tests) and modelling tools in order to assess the long-term leaching behaviour of the material in the application scenario. It should be anyhow highlighted that the results achieved employing this type of approach should be referred only to the specific material and scenario considered in the analysis.

An alternative approach to the ones described above was developed in the Netherlands to derive emission limit values for inorganic components in materials to employ in construction applications. In this approach two models are used to describe vertical reactive transport through the soil profile and the retardation of components in the soil profile. Specifically, a linear partitioning model employing lower-bound literature Kd values is adopted to describe sorption of the contaminants to soil. Then, a geochemical model accounting for speciation and surface complexation is applied for verification and validation of the results of the linear distribution approach (Verschoor et al., 2008).

In this work it was decided to follow an approach based on experimental leaching data in relation to a specific management scenario. In particular, the risk to the groundwater resource expected for the two management options described in Paragraph 3.2.2.2 (i.e. landfilling and recycling as a filler for road sub base construction) was evaluated based on the results obtained by column leaching tests (see Chapter 1) which were previously performed and modelled for the determination of the main mechanisms controlling the leaching process for the three types of analysed BA. As also found by Susset and Grathwohl (2002, 2008), depending on the properties of the contaminants and the characteristics of the material, equilibrium or non-equilibrium conditions can prevail during contaminant release. The occurrence of equilibrium or non-equilibrium conditions can significantly affect the leaching scenario. Indeed, equilibrium conditions lead to a flux-controlled release where the saturation concentration or the maximum concentration of the contaminant (C_{sol}) is observed in the effluent over extended periods of time (depending on the concentration of the contaminant in the material). On the contrary, for non-equilibrium conditions, the release is limited by mass-transfer as a consequence of a relatively slow diffusion of the contaminant in the intraparticle pore space. Under these conditions, the concentration in the effluent starts to decrease rapidly showing a subsequent extended tailing. Based on the above considerations it is hence evident that for a reliable assessment of the contaminant release expected in the two assumed management scenarios, particular caution should be paid to correctly identify the process governing the contaminant release from the considered material. For instance, as also observed in the first eluates of the column experiments, at the beginning of a rainfall event, the contaminant present in the water-filled porosity of the disposed material is expected to be near equilibrium values and only after a renewal of a pore volume, the switch to mass transfer control may be expected to occur. In the following, after a brief description of the applied methodology and of the modelled scenarios, the results of the risk assessment study performed for the different types of BA considered in this work are presented and discussed.

4.2 MATERIALS AND METHODS

The first step in a risk assessment procedure consists in the evaluation of the concentrations expected at the point of compliance (C_{poc}). The point of compliance (*POC*) is defined as the point in which the concentration values of the contaminants in the groundwater must comply with threshold values set for the target quality of the groundwater resource. Fate and Transport models are generally applied in a forward-calculation mode to predict the C_{poc} based on the concentration in the source of contamination (C_{source}), which in this case is represented by the BA layer:

$$C_{poc} = C_{source} \cdot FT \tag{4.1}$$

where *FT* is the Fate & Transport Factor that accounts for the attenuation of the contaminant along the migration pathway. Alternatively, analytical models can also be applied in a back-calculation mode to determine the source-area constituent concentration corresponding to an acceptable concentration at the point of compliance (ASTM, 2000).

In the case of risk assessment for groundwater the Transport Factor (*FT*) which can be used is the Leaching Factor, *LF*, which accounts for the contaminant's attenuation during the transport from the source, located in the vadose zone, to the groundwater table.

$$C_{poc} = C_{source} \cdot LF \tag{4.2}$$

The risk for the groundwater resource (R_{GW}) is then calculated by comparing the value of concentration of the contaminant in the water table at the point of compliance (C_{poc}), with threshold values defined for groundwater protection:

$$R_{GW} = \frac{C_{poc}}{CSC_{GW}} = \frac{C_{source} \cdot LF}{CSC_{GW}} \tag{4.3}$$

As threshold values in this study the ones set by the Italian Legislative Decree 152/2006 (Threshold Concentrations of Contamination, CSC_{GW}) were adopted. Furthermore, comparison with the threshold values was carried out assuming no attenuation or dispersion of the contaminants in the groundwater (i.e. the BA layer was assumed to be directly above the POC).

4.2.1 Model proposed in this study

One of the most widely adopted risk-assessment approaches is the ASTM Risk-Based Corrective Action (RBCA) method. The leachate model proposed in the RBCA standard is based on the following assumptions: (i) constant chemical source concentration (ii) linear equilibrium partitioning between the different phases, (iii) steady-state leaching from the vadose zone to ground water resulting from the constant leaching rate and (iv) well-mixed dispersion of the leachate within the groundwater "mixing zone" (ASTM, 2000). As discussed in Chapter 1, the release of most contaminants from the BA analysed in this work cannot be properly described assuming equilibrium partitioning based on the Kd approach. Therefore, in order to take into account of non-equilibrium leaching conditions, a modified version of the ASTM model was developed.

Specifically, the model developed in this work is based on the following assumptions (in bold the assumptions that differ from the ASTM ones are highlighted): (i) constant concentration of the contaminants in the material (i.e. bottom ash), **(ii)** non-linear equilibrium partitioning between the different phases, **(iii)** transient leaching from the vadose zone to the groundwater, (iv) well-mixed dispersion of the leachate within the groundwater "mixing zone". It should be noted that, in this case, since for all three types of tested BA, release as a function of the L/S ratio resulted always much lower than the total content of the various contaminants (see Chapter 1), it was decided not to account for the depletion of the source of the contaminant over time, but to make the same assumption as the ASTM model (constant concentration of the source over time). Based on these assumptions, the concentration at the point of compliance is a function of time, $C_{POC}(t)$, and can be estimated through Equation 4.4, in which $C_{leach}(t)$ is the leached concentration of the contaminant from the BA (mg/l), $\alpha(t)$ the attenuation factor (-), *SAM* the Soil Attenuation Model (-) and *LDF* is the Leachate Dilution Factor [(mg/l_{wat})/(mg/kg_{soil})], described here below.

$$C_{poc}(t) = \frac{C_{leach}(t)\cdot\alpha(t)\cdot SAM}{LDF} \tag{4.4}$$

LDF, which is included in the leaching factor (*LF*) considered by the ASTM model, accounts for the dilution of the concentration occurring when the contaminant is transferred from the leachate to the groundwater:

$$LDF = 1 + \frac{v_{gw}\cdot\delta_{gw}}{I_{eff}\cdot W} \tag{4.5}$$

where δ_{gw} is the groundwater mixing zone height (cm), v_{gw} the groundwater Darcy velocity (cm/s), *W* the width of the source-zone area longitudinal to the groundwater flow (cm) and I_{eff} the infiltration rate (cm/s).

The groundwater mixing zone thickness δ_{gw} can be calculated as follows*:*

$$\begin{cases} \delta_{gw} = (0.01 \cdot W^2)^{0.5} + d_a \cdot \left[1 - \exp\left(- \frac{W \cdot I_{eff}}{v_{gw} \cdot d_a} \right) \right] & \text{per } \delta_{gw} \le d_a \\ \delta_{gw} = d_a & \text{per } \delta_{gw} > d_a \end{cases} \tag{4.6}$$

where d_a (cm) is the groundwater thickness.

The groundwater Darcy velocity v_{gw} is calculated as follows:

$$v_{gw} = \frac{K_{sat} \cdot i}{\theta_e} \tag{4.7}$$

where K_{sat} is the soil hydraulic conductivity (cm/s), i the groundwater gradient (-) and θ_e the effective porosity in the vadose zone (-).

SAM in Eq. 4.4, also generally included in the ASTM model, is the Soil Attenuation Model, which takes into account depth effects by accounting for the sorption of constituents from the leachate onto clean soils underlying the affected soil zone (Connor et al., 1997). *SAM* (-) is calculated by the following equation:

$$SAM = \frac{d}{L_{gw}} \tag{4.8}$$

where d is the thickness of the source (cm) and L_{gw} the depth to groundwater from the bottom of the source of contamination (cm).

$C_{leach}(t)$ in Eq. 4.4 is the leaching concentration of the contaminant from the BA (mg/l), which depending on the prevailing release mechanism, can be calculated for equilibrium and non-equilibrium conditions as follows:

$$\begin{cases} C_{leach} = C_{sol} & \text{for equilibrium conditions} \\ C_{leach}(t) = C_s \cdot \rho_{mat} \cdot (1 - \theta_{mat}) \cdot V_{mat} \cdot \frac{S_{mat}}{q} \sqrt{\frac{D_a}{\pi \cdot t}} & \text{for non-equilibrium conditions} \end{cases} \tag{4.9}$$

where C_{sol} (mg/l) is the concentration of the contaminant under equilibrium conditions (i.e. the maximum leachable concentration measured from the column test), C_s (mg/kg) the total content of the contaminant in the BA solid matrix, ρ_{mat} (kg/cm^3), θ_{mat} (-), V_{mat} (cm^3) and S_{mat} (cm^{-1}) are respectively the bulk density, the porosity, the volume and the volumetric specific surface area of the BA in the considered scenario, q (l/s) the flow-rate of leachant through the source, D_a (cm^2/s) the apparent diffusion coefficient of the contaminant estimated by modelling the results of column test and t (s) time.

The leachate flowrate q (l/s) is calculated through the following equation:

$$q = I_{eff,source} \cdot A_{mat} \cdot 10^{-3} \tag{4.10}$$

where $I_{eff,souce}$ (cm/s) is the water infiltration rate through the source and A_{mat} (cm^2) is the surface area of BA that contributes to the leaching process in the considered scenario and 10^{-3} is a conversion factor (l/cm^3).

α(t) in Eq. 4.4 is the attenuation factor (-), that takes into account the fact that the contaminant contained in the leaching solution must also migrate through the soil layer placed below the material before reaching the groundwater table:

$$\alpha(t) = \frac{1}{2} \cdot erfc\left(\frac{L_f - \frac{I_{eff}}{R} \cdot t}{2 \cdot \left(\frac{I_{eff}}{R} \cdot \alpha_z \cdot t \right)^{1/2}} \right) \tag{4.11}$$

where R (-) is the retardation factor through the soil layer between the source term (i.e. BA layer) and the groundwater table, L_f (cm) the depth of the water table from the bottom of the source of the contamination and α_z (cm) the vertical dispersivity.

The retardation factor R, assuming a linear equilibrium partitioning, can be calculated as follows:

$$R = 1 + \frac{\rho_s \cdot K_{sw}}{\theta_s} \tag{4.12}$$

Where θ_e (-) is the effective soil porosity, ρ_s (kg/cm^3) the soil bulk density and K_{sw} (L/kg) the soil-water partition coefficient.

The depth of the water table from the bottom of the source L_f, can be derived as follows:

$$L_f = L_{gw} - d \tag{4.13}$$

The vertical dispersivity α_z, is calculated by the following equation (Vanderborght and Vereecken, 2007):

$$\alpha_z = 0.33 \cdot L_f^{0.62} \tag{4.14}$$

Hence substituting eq. (4.9) and eq. (4.11) in eq. (4.4), the concentration of contaminants expected at the point of compliance, $C_{POC}(t)$ can be calculated as follows:

$$C_{POC}(t) = \frac{C_{sol} \cdot \frac{1}{2} \cdot erfc\left(\frac{L_f - \frac{I_{eff}}{R} \cdot t}{2 \cdot \left(\frac{I_{eff}}{R} \cdot \alpha_z \cdot t \right)^{1/2}} \right)}{LDF} \cdot SAM \tag{4.15a}$$

$$C_{POC}(t) = \frac{\left(C_s \cdot \rho_{mat} \cdot (1 - \theta_{mat}) \cdot V_{mat} \cdot \frac{S_{mat}}{q} \sqrt{\frac{D_a}{\pi \cdot t}} \right) \cdot \frac{1}{2} \cdot erfc\left(\frac{L_f - \frac{I_{eff}}{R} \cdot t}{2 \cdot \left(\frac{I_{eff}}{R} \cdot \alpha_z \cdot t \right)^{1/2}} \right)}{LDF} \cdot SAM \tag{4.15b}$$

Note that Eq. 4.15a refers to equilibrium conditions (i.e. percolation controlled release) while Eq. 4.15b denotes concentration under non-equilibrium conditions, which means release governed by mass-transfer.

The risk for the groundwater resource, $R_{GW}(t)$ can be hence calculated as follows:

$$R_{GW}(t) = \frac{C_{poc}(t)}{CSC_{GW}} \tag{4.16}$$

4.2.2 Scenario modelling and input parameters

The same two types of scenarios assumed for the LCA study and described in Paragraph 3.2.2.2 (i.e. landfilling and recycling in road sub-base construction) were modelled for the three types of BA and the risk for groundwater as a function of time was calculated. Also in this case, a time framework of 100 years was considered. It is worth noting, that for risk calculation, as a conservative assumption, the point of compliance (*POC*) in the groundwater table was assumed to be positioned directly under the BA layer, meaning that the attenuation due to transport and dispersion in the groundwater was neglected (*POC=0*). The fixed input parameters assumed for both scenarios are reported in Table 4.1. The soil between the BA layer and the groundwater table was assumed to be sand, hence the Darcy velocity was calculated using the specific characteristic parameters (i.e. θ_e and K_{sat}) for this type of soil. Moreover, in all simulations the retardation factor R through the sand layer was assumed to be equal to 1 (i.e. negligible adsorption of the contaminant onto the soil layer).

Table 4.1 Fixed input Parameter

Parameter	**Symbol**	**Unit**	**Value**
Groundwater thickness	d_a	m	10
Groundwater gradient	i	m/m	0.01
Effective soil porosity$^{(*)}$	θ_e	-	0.38
Hydraulic conductivity$^{(*)}$	K_{sat}	m/s	8.3E-05

$^{(*)}$ *Values referring to a sand layer (ISPRA, 2008)*

The contaminants considered in this study, selected on the basis of the results of the column leaching tests are reported in Table 4.2. The table also shows, for each contaminant, the Italian reference values for groundwater protection (Threshold Concentrations of Contamination, CSC_{GW}) used for risk evaluation.

Table 4.2 Contaminants considered in this study and corresponding CSC_{GW} values (Italian Legislative Decree 152/2006). * For barium the value reported in the table refers to the maximum contaminant level for groundwater *(MCL)* established by the US EPA (EPA, 2012).

	Al	**Ba**	**Cr(VI)**	**Cu**	**Pb**	**Zn**
CSC_{GW} [mg/l]	0.2	2*	0.005	1	0.01.	3

4.2.2.1 Landfill Scenario

In the first scenario, the three types of BA were assumed to be disposed of in different cells of a typical excavated-type of landfill for non-hazardous waste in central Italy. The conceptual model of the leaching of contaminants to the groundwater for the landfill scenario is schematized in Figure 4.1.

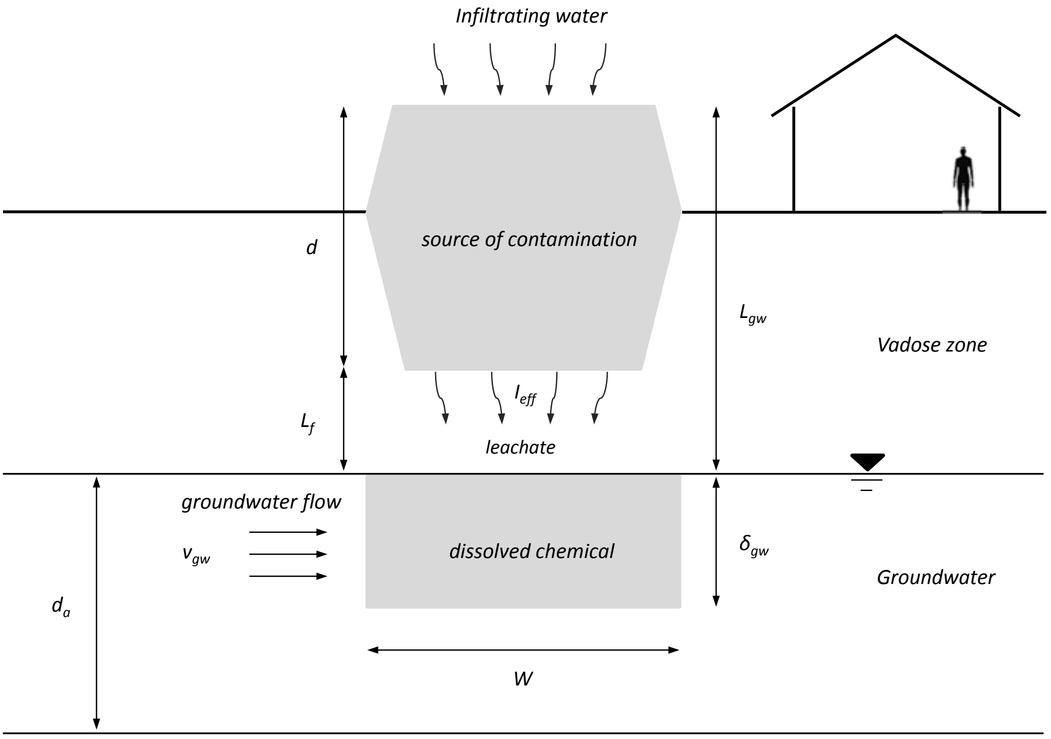

Figure 4.1 Conceptual model of the leaching process for the landfill scenario.

To assess the size of the three cells, the total annual amount of each type of BA produced and disposed of in the landfill was estimated based on the capacities of the thermal treatment plants of the Lazio region (ARPA LAZIO, 2013; ISPRA, 2013).

It is worth noting that, based on the results obtained for the RDF-I BA and RDF-G BA using the Landfill Water Balance (LWB) model (Pantini et al., 2014) for predicting leachate production in landfills (refer to Paragraph 3.2.2.2), as an assumption, for all three types of BA, the net infiltration rate of rain through the landfill body, $I_{eff,source}$ (m/s), was assumed to be equal to 65% of the annual precipitation of 800 mm/year (data of the Meteorological Service of the Italian Air Force, 2014) during the active phase of the landfill (i.e. the first 10 years) and equal to 20% for the remaining 90 years period (after-care period). The calculated values for $I_{eff,source}$ for the landfill scenario are $1.65 \cdot 10^{-08}$ m/s during the active phase of the landfill and $5.07 \cdot 10^{-09}$ m/s for the after-care period, respectively. The most significant parameters related to BA characteristics and landfill geometry assumed and used as input for the modelling of the landfill scenario are summarized in Table 4.3.

Table 4.3. Parameters assumed for the modelling of the landfill scenario for the three types of BA.

Parameters	**Symbol**	**Unit**	**RDF-I BA**	**RDF-G BA**	**HW-I BA**
Source thickness	d	m	10	10	10
Trench height	d_1	m	6	6	6
Hill height	d_2	m	4	4	4
Amount of landfilled BA (wet weight)	Q_{mat}	ton	7.6E+05	2.4E+05	7E+04
BA dry bulk density	ρ_{mat}	ton/m^3	1.4	1.75	1.6
Moisture content of BA	u_{mat}	% w/w	19.2	1.8	24.9
Landfill cell volume	V_{mat}	m^3	4.4E+05	1.4E+05	3.3E+04
Landfill bottom surface	A_{bottom}	m^2	4E+04	1.2E+04	2.4E+03
Landfill main surface	A_{mat}	m^2	4.9E+04	1.65E+04	4.8E+03
Porosity of BA	θ_{mat}	-	0.47	0.34	0.3
Width of source-zone area	W	m	222	128	69
Depth to groundwater	L_{gw}	m	15	15	15
Leachate infiltration rate (with geom.)	$I_{eff(g)}$	m/s	2.94E-10	2.94E-10	2.94E-10
Leachate infiltration rate (no geom.)	I_{eff}	m/s	2E-9	2E-9	2E-9
Volumetric surface area of BA	S_{mat}	m^{-1}	0.55	0.4	0.6

From Table 4.3 it can be noticed that two different leachate infiltration rates were calculated and used as input for the modelling of the landfill scenario. Specifically, the risk for the groundwater resource was evaluated both with and without the presence of a geomembrane in the liner system of the landfill.
The leachate infiltration rate I_{eff} was calculated as follows:

$$I_{eff} = L_L / A_{bottom} \tag{4.17}$$

where L_L (m^3/s) is the outgoing leachate flux from the landfill and A_{bottom} (m^2) the bottom surface of the landfill (see Table 4.3). Here below the equations used for the estimation of the output leachate flux from the landfill with or without the geombrane are briefly described. It should be noted that in both cases the L_L term is a function of the bottom surface of the landfill (A_{bottom}), therefore the resulting infiltration rate is independent of the amount of BA disposed and of the landfill's geometry, as evident from the values of the leachate infiltration rates reported in Table 4.3.

Leachate production in the presence of a geomembrane

The flux of leachate from the landfill (L_{Lg}) in the presence of a geomembrane is given by (ISPRA, 2005):

$$L_{Lg} = A_{bottom} \cdot \left[\left(\rho_p \cdot L'_{Lp} \right) + \left(\rho_h \cdot L'_{Lh} \right) + \left(\rho_f \cdot L'_{Lf} \right) \right] \tag{4.18}$$

where ρ_p, ρ_h and ρ_f (number/ha) are the defects density of pinholes, holes and flaws of the geomembrane, respectively and L'_{Lp}, L'_{Lh} and L'_{Lf} (m^3/s) the corresponding leachate fluxes. Leachate fluxes entering into pinholes, holes and flaws are derived by the following equations (Giroud et al., 1992):

$$\begin{cases} L'_{Lm} = C_d \cdot i_{av} \cdot h_{leach}^{0.9} \cdot a_p^{0.1} \cdot K_c^{0.74} & \text{pinholes} \\ L'_{Lh} = C_d \cdot i_{av} \cdot h_{leach}^{0.9} \cdot a_h^{0.1} \cdot K_c^{0.74} & \text{holes} \\ L'_{Lt} = C_d \cdot i_{av} \cdot h_{leach}^{0.9} \cdot a_f^{0.1} \cdot K_c^{0.74} & \text{flaws} \end{cases} \tag{4.19}$$

where:

- C_d (-):is the dimensionless constant that describes the quality of the contact between the geomembrane and the underlying layer. Giroud et al. (1992) proposed two values for this constant: 0.21 in the case of good contact and 1.15 in the case of bad contact. Specifically the latter value was employed in the calculations;
- h_{leach} (m): height of the level of leachate above the geomembrane, assumed to be equal to 1m;
- i_{av} (m/m): average vertical hydraulic gradient;
- $a_{p,h,f}$ (m^2): area of defects (pinholes, holes and flaws) in the geomembrane;
- K_c (m/s): hydraulic conductivity of the clay layer assumed under the geomembrane in the liner system of the landfill (K_c = 1E-09 m/s).

The average vertical hydraulic gradient in presence of the geomembrane is given by (ISPRA, 2005):

$$i_{av} = 1+0.1\cdot\left(\frac{h_{leach}}{d_{unsat}}\right)^{0.95} \tag{4.20}$$

where d_{unsat} (m) is the thickness of the clay layer, assumed equal to 1m.

The characteristics assumed for the geomembrane are reported in Table 4.4.

Table 4.4 Defects of the geomembrane (ISPRA, 2005).

Type of defect	*Symbol*	$\rho_{m,h,t}$ [number/ha]	$a_{m,h,t}$ [m^2]
pinholes	*p*	25	10
holes	*h*	5	6
flaws	*f*	2	4

Leachate production in the absence of a geomembrane

The flux of leachate from the landfill (L_L) in the case of the absence of a geomembrane is given by the following Darcy equation (ISPRA, 2005):

$$L_L = K_c \cdot i_f \cdot A_{bottom} \tag{4.21}$$

where i_f (m/m) is the vertical hydraulic gradient, calculated as follows:

$$i_f = \frac{h_{leach} + d_{unsat}}{d_{unsat}} \tag{4.22}$$

where h_{leach} (m) is the height of the level of leachate above the bottom part of the landfill and d_{unsat} (m) is the thickness of the clay layer representing the mineral barrier placed below the landfill; both parameters were assumed to be equal to 1 m.

Modelling of leaching for the landfill scenario

The leachate produced at any landfill site is usually pumped out and sent to the municipal wastewater treatment system. However, it is likely that a constant head of leachate permanently remains on the bottom part of the landfill. Hence, for the modelling of the landfill scenario, a constant head of leachate (h_{leach}) of 1 m on the bottom part of the landfill was assumed. Due to this assumption it is likely that the prevailing leaching mechanism controlling the release of contaminants in this scenario is mass-transfer (i.e. non-equilibrium conditions). Hence, for the modelling of the expected concentration of contaminants in the groundwater $C_{POC}(t)$ from the landfill, equation 4.17b was employed. However, as explained in Chapter 1, a certain time t* is required in order to achieve a mass transfer-controlled release condition, corresponding to approximately 1 pore volume renewal. Here, for sake of simplicity, to assess when the switch to a mass-transfer leaching mechanism is expected to occur, the concentrations obtained with equation 4.11b, i.e. $C_{leach}(t)$, were compared to the maximum dissolved concentrations, C_{sol}, observed in the first eluates of the lab-scale column tests that as discussed in Chapter 1 were considered as representative of equilibrium concentrations. When the calculated concentration $C_{leach}(t)$ was higher than the obtained C_{sol}, equilibrium conditions were assumed and the latter value was considered; conversely, for $C_{leach}(t)$ values below C_{sol} mass transfer-controlled release was hypothesized and the calculated value was considered. The total content of the contaminants in the BA solid matrix, C_s (mg/kg), and the apparent diffusion coefficients, D_a (cm^2/s), derived in Paragraph 1.3.5 from the results of the column tests, and used as input to the model are reported in Table 4.5. Note that for the elements (e.g. Pb and Zn for the RDF-I BA) that in lab-scale column tests exhibited a leaching mechanism release mainly dominated by wash out (indicated with n.a. in the table), the groundwater concentration was estimated using equation 4.17a.

Once the $C_{POC}(t)$ was calculated for each contaminant for the three types of BA, the risks for groundwater were evaluated using the Eq. 4.16. Specifically, for each type of BA three different cases were assessed, namely one with the geomembrane in the liner system of the landfill, one without the geomembrane and a worst case scenario in which the absence of the geomembrane was considered and both the SAM and LDF parameters were assumed to be equal to 1 (i.e. no sorption of constituents from the leachate onto clean soils underlying the affected soil zone and no dilution of the concentration occurring when the contaminant is transferred from the leachate to the groundwater).

Table 4.5 Total content and diffusion coefficients of contaminants for the three types of BA. n.a. stands for "not applicable", meaning that the mass-transfer controlled model (eq. 1.14b) did not fit the concentration trend of the specific element.

	RDF-I BA		**RDF-G BA**		**HW-I BA**	
	C_s [mg/kg]	**D_a [cm^2/s]**	**C_s [mg/kg]**	**D_a [cm^2/s]**	**C_s [mg/kg]**	**D_a [cm^2/s]**
Al	$1.8x10^{+04}$	$2x10^{-18}$	$5.6x10^{+04}$	n.a	$6.3x10^{+04}$	$9x10^{-15}$
Ba	$1.2x10^{+03}$	n.a.	$8.7x10^{+02}$	$3x10^{-18}$	$2.8x10^{+03}$	$3x10^{-16}$
Cr	$8.1x10^{+02}$	$6x10^{-18}$	-	-	-	-
Cu	$2.8x10^{+03}$	$6x10^{-19}$	$2.4x10^{+04}$	$1x10^{-20}$	-	-
Pb	$5.7x10^{+02}$	n.a.	-	-	-	-
Zn	$2.4x10^{+03}$	n.a.	-	-	-	-

4.2.2.2 Road Scenario

The conceptual model of the leaching process of chemicals to the groundwater for the road scenario is schematized in Figure 4.2. In this scenario, the three types of BA were assumed to be recycled as unbound material in a sub-base of a typical secondary road in Italy in replacement of natural aggregates (i.e. gravel). The most significant parameters employed as input for the modelling of the road scenario for the three types of BA are summarized in Table 4.6. It is worth noting that the BA characteristics, i.e. amount (Q_{mat}), dry bulk density (ρ_{mat}), moisture content (u_{mat}), porosity (θ_{mat}), volumetric specific surface area (S_{mat}) and the volume (V_{mat}) assumed for the modelling of the road scenario were the same as those used for the landfill scenario (see Table 4.3).

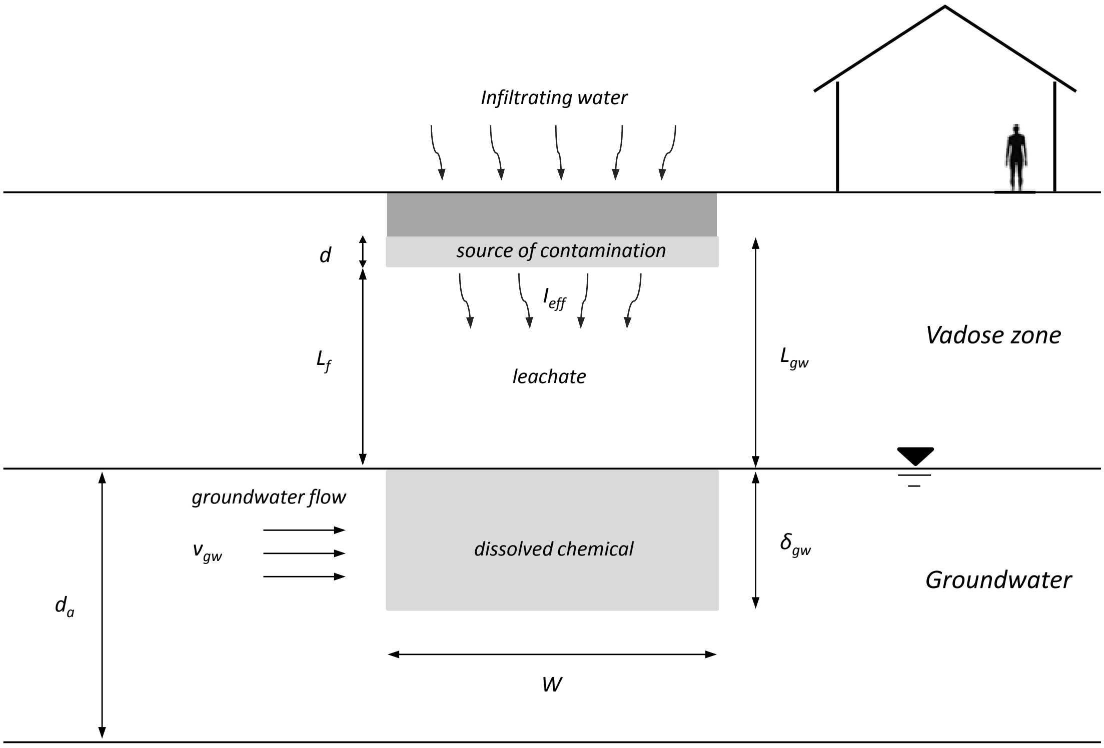

Figure 4.2 Conceptual model of the leaching process for the road scenario.

Due to the low thickness of the road, in this scenario, the leachate infiltration rate $I_{eff,source}$ (m/s) under the BA layer, was assumed to be equal to the average net infiltration of the water through the road, which was taken as 10% of the annual precipitation of 800 mm/year (i.e. $I_{eff,source}=I_{eff}$). The calculated value for $I_{eff,source}=I_{eff}$ for the road scenario is $2.54 \cdot 10^{-9}$ m/s. It should be noted that the distance from the bottom of the BA layer from the groundwater was assumed to be the same as that considered in the landfill scenario (5 m).

Table 4.6 Parameters assumed for the modelling of the road scenario for the three types of BA.

Parameters	**Symbol**	**Unit**	**RDF-I BA**	**RDF-G BA**	**HW-I BA**
Source thickness	d	m	0.35	0.35	0.35
Width of source-zone area	W	m	7	7	7
Depth to groundwater	L_{gw}	m	5.35	5.35	5.35
Road surface	A_{mat}	m^2	1.25E+06	3.85E+05	9.39E+04

Modelling of leaching for the road scenario

For the road scenario, differently from what assumed for the landfill one, it was considered that the prevailing mechanism controlling leaching was percolation (i.e. equilibrium conditions were assumed). Indeed in the column tests it was observed that in the first eluates of the column experiments the contaminant present in the water filled porosity of the material is near to equilibrium conditions. The switch to a mass transfer scenario was observed to occur only after approximately a pore volume renewal. Considering that in the simulated road scenario, the net water infiltration in the BA layer was quite limited (i.e. 8 cm/y) and discontinuous (as strictly linked to the single rainfall event) it is likely that a complete renewal of a pore volume is never reached during a single rainfall event. Hence, for the modelling of the expected concentration of contaminants in the groundwater $C_{POC}(t)$ from the road, equation 4.17a was employed.

The concentrations of the contaminants under equilibrium conditions C_{sol} (mg/l), used as input to the model and reported in Table 4.7, were the maximum leachable concentrations measured in the column test. For each type of BA two cases were considered for the risk assessment, one with the calculated LDF and SAM values and a worst case scenario in which, as in the landfill scenario, both SAM and LDF parameters were assumed to be equal to 1.

Table 4.7 Maximum concentrations of the contaminants in the leaching solution for the three types of BA. n.d. not detected.

	C_{sol} [mg/L]					
Material	**Al**	**Ba**	**Cr**	**Cu**	**Pb**	**Zn**
RDF-I BA	5.7	8.6	0.06	0.02	1.2	0.12
RDF-G BA	0.3	0.09	n.d.	0.04	n.d.	n.d.
HW-I BA	80	1.6	n.d.	n.d.	n.d.	n.d.

4.3 RESULTS AND DISCUSSION

4.3.1 Landfill Scenario

Table 4.8 reports the parameters calculated for the landfill scenario for the three types of BA used as input to the model for the estimation of the concentration in the groundwater at a generic time t, $C_{POC}(t)$.

Table 4.8 Calculated input parameters for the modelling of the landfill scenario.

Parameters	**Symbol**	**Unit**	**RDF-I BA**	**RDF-G BA**	**HW-I BA**
Darcy velocity	v_{gw}	m/s	2.1E-06	2.1E-06	2.1E-06
Height of the groundwater mixing zone*	$\delta_{gw(g)}$	m	10	10	6.95
Height of the groundwater mixing zone	δ_{gw}	m	10	10	7
Leachate dilution factor*	$LDF_{(g)}$	-	3.3E+02	5.7E+02	7.3E+02
Leachate dilution factor	LDF	-	4.9E+01	8.4E+01	1.1E+02
Soil attenuation model	SAM	-	0.67	0.67	0.67
Depth of the water table	L_f	m	5	5	5
Leachate flow rate active phase period	q	L/s	8.12E-01	2.72E-01	7.94E-02
Leachate flow rate after care period	q	L/s	2.5E-01	8.37E-02	2.44E-02
Vertical dispersivity	α_z	m	0.16	0.16	0.16

*note that the symbols with the subscript *(g)* refer to the parameters calculated in presence of the geomembrane.

The results obtained for the landfill scenario are shown in Figure 4.3. In these graphs the risk for the groundwater resource given by each contaminant as a function of selected time periods (i.e. 30, 50 and 100 years) are reported for the three cases considered (i.e. geomembrane in the liner system of the landfill, without the geomembrane and the worst case scenario in which no geomembrane was considered and both the SAM and the LDF factors were assumed to be equal to 1) and the different types of BA. In these graphs the calculated risks are compared to the reference value ($R_{GW}(t)$= 1); the elements for which the associated risk exceeds the reference value, denote a $C_{POC}(t)$ higher than the corresponding threshold value defined for groundwater protection CSC_{GW}.

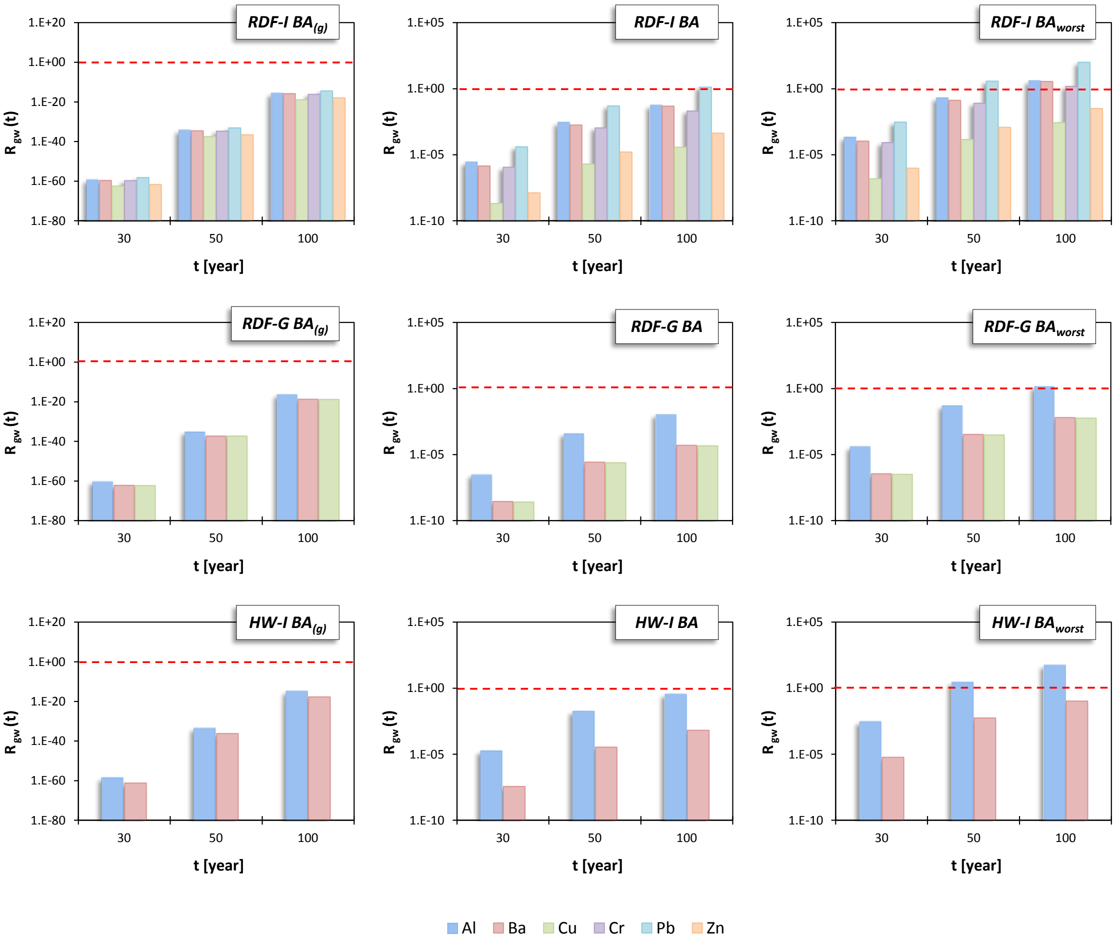

Figure 4.3 Results of the risk assessment for the landfill scenario. The graphs on the left side refer to the case with the geomembrane (g) for RDF-I BA, RDF-G BA and HW-I BA from the top to the bottom, respectively. The graphs in the middle represent the results obtained for the case without the geomembrane. The graphs on the right side refer to the worst case scenario (no geomembrane and SAM and LDF equal to 1). The red dashed line indicates the reference value ($R_{GW}(t)$= 1).

Making reference to the obtained results, it can be noticed that for the cases with and without the presence of geomembrane, the risks for the groundwater resource calculated for the three types of analysed BA, were in nearly all cases well below the threshold concentration values set by the Italian law for groundwater protection (i.e. $Rgw << 1$). The only exception was Pb for RDF-I BA in the case without the geomembrane, for which the concentration expected in the groundwater after 100 years of leaching, resulted slightly higher than the threshold CSC value. The same figure also highlights that the risks continued to increase with time, i.e. indicative of non-equilibrium conditions even after 100 years. This implies that the risks for the groundwater resource would continue to grow with time. As far as the worst-case scenario is concerned (i.e. no attenuation in the soil layer and no dilution in the groundwater), again the risks showed to increase with time and making reference to the risks calculated after 100 years, it can be noticed that the release of some contaminants, such as Al, Ba, Cr and Pb for the RDF-I BA and Al for both RDF-G BA and HW-I BA is expected to pose a potential risk for the groundwater resource. As expected, once again the RDF-I BA showed to be the most problematic type of residue among the three types of analysed BA. Among the contaminants leached out from this type of BA, Pb showed to be the one associated to the highest risk. This was mainly due on the one hand to the low CSC_{GW} set by the Italian legislation (i.e. 0.01 mg/l) for this contaminant and, on the other hand, to the fact that the expected concentration in the groundwater for this element was modelled by employing the equation associated to equilibrium conditions (eq. 4.15a).

4.3.2 Road Scenario

Table 4.9 reports the input parameters calculated for the road scenario and used for the estimation of the $C_{POC}(t)$. The risks for the groundwater evaluated for the road scenario for the three types of BA are shown in Figure 4.4. As previously mentioned, for this scenario, the risks for the groundwater resources were first estimated accounting for the attenuation of contaminant concentration resulting from the mass redistribution in the soil layer below the source (SAM) and the dilution occurring when the contaminant is transferred from the leachate to the groundwater (LDF). Then the same simulation was re-run in a worst case scenario assuming that both SAM and LDF are negligible (i.e. SAM= 1 and LDF= 1).

As it can be noticed from Fig. 4.4, for the case accounting for soil attenuation and dilution in the groundwater, the risks calculated for the groundwater resource for the three types of BA are all below the reference value (i.e. $R_{gw} < 1$). On the contrary, for the worst case scenario (i.e. assuming LDF=1 and SAM=1) for both RDF-I BA and HW-I BA, some elements (i.e. Al, Cr and Pb for RDF-I BA and Al for HW-I BA) have shown to pose a possible risk already for a time framework of 50 years.

Table 4.9 Calculated input parameters for the modelling of the road scenario.

Parameters	**Symbol**	**Unit**	**RDF-I BA**	**RDF-G BA**	**HW-I BA**
Darcy velocity	v_{gw}	m/s	2.1E-06	2.1E-06	2.1E-06
Height of the groundwater mixing zone	δ_{gw}	m	0.71	0.71	0.71
Leachate dilution factor	*LDF*	-	8.6E+01	8.6E+01	8.6E+01
Soil attenuation model	*SAM*	-	0.065	0.065	0.065
Depth of the water table	L_f	m	5	5	5
Vertical dispersivity	α_z	m	0.16	0.16	0.16

However, in this case, conversely to what observed for the landfill scenario, it can be seen that moving from a time frame of 50 years to 100 years, the increase of risks is not significant and this is due to the occurrence of near steady state conditions. Furthermore, the obtained results highlighted higher risks compared to the landfill scenario. This is mainly due to the fact that for this scenario the contaminants' concentrations in the groundwater were modelled by employing the equation associated to equilibrium conditions (eq. 4.15a). In addition, the other assumption that led to higher calculated risks for the road scenario is the leachate infiltration rate (I_{eff}) considered ($2.54 \cdot 10^{-9}$ m/s) that is significantly higher than the one used to simulate landfill infiltration in the presence of a geomembrane ($2.94 \cdot 10^{-10}$ m/s). On the contrary, for the landfill scenario assuming that no geomembrane is present in the bottom liner, the infiltration rate assumed ($2 \cdot 10^{-9}$ m/s) is similar to the one used to simulate the infiltration through the road sub-base and consequently the risks calculated are similar. For instance, making reference to Pb for RDF-I BA, that was modelled in both scenarios with equation 4.17a, it can be noticed that the risks after 100 years, related to the worst case alternative for both the landfill (without the geomembrane) and the road scenarios, are very similar, i.e. $R_{gw}(t)$= 100 and $R_{gw}(t)$= 119, respectively.

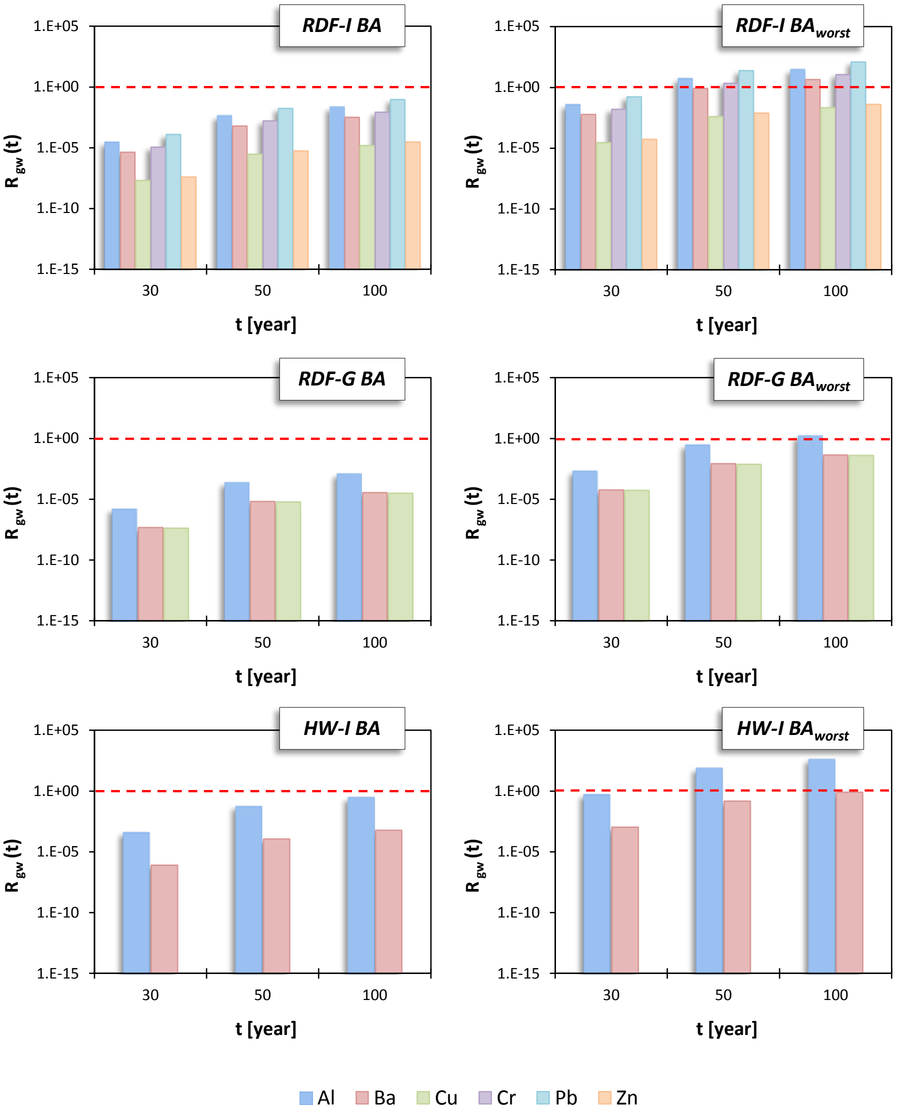

Figure 4.4 Results of the risk assessment for the road scenario. The graphs on the left side refer to the case in which LDF and SAM were included in the calculation, for RDF-I BA, RDF-G BA and HW-I BA from the top to the bottom, respectively. The graphs on the right represent the results obtained for SAM and LDF equal to 1. The red dashed line indicates the reference value ($R_{GW}(t)$= 1).

Another aspect that should be kept in mind is that the results shown in Fig. 4.4 were obtained assuming a constant rainfall rate, i.e. considering that water percolating through the road is uniformly distributed across the year. This of course is not representative of what happens in a real case where the frequency and duration of each rain event vary over the year. Hence, in order to take into account of these variations, the risks for groundwater were also calculated by changing the rainfall rates and the duration of the events. For illustration purposes only and to highlight how the assumption of a constant infiltration rate can influence the estimated risks for groundwater, Figure 4.5 reports the risks for Pb contamination of the groundwater associated to RDF-I BA that were calculated on a monthly basis assuming the average monthly rainfall intensity of the site of concern and cyclic rainfall events during five days every five days. From the graph it can be seen, as expected, that the calculated risks are not constant throughout the year reaching the maximum values during the rainiest months (i.e. October-December).

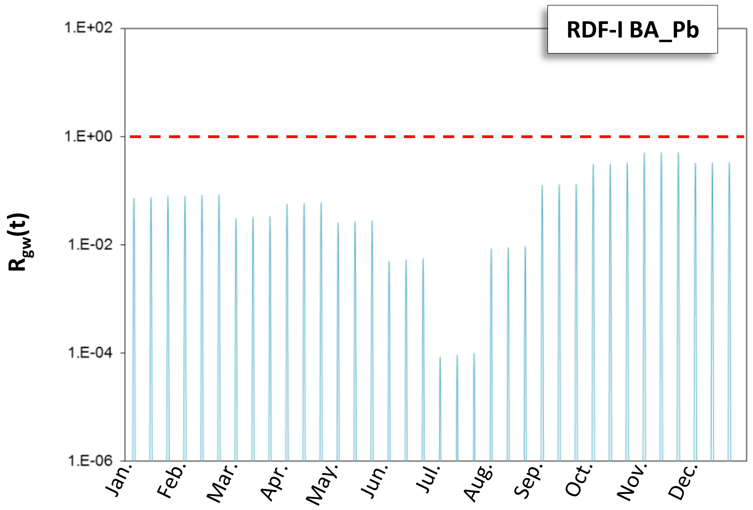

Figure 4.5 Risk trend of groundwater contamination during an average year associated to Pb leached from RDF-I BA (assuming variable rainfall events) in the road scenario. Risks refer to the alternative in which LDF and SAM were included in the calculation. The red dashed line indicates the reference value ($R_{GW}(t)$=1).

4.4 CONCLUSIONS

In this study potential risks for the groundwater due to the leaching of contaminants from the three types of considered BA in a specific disposal or reuse scenario were investigated. A different approach compared to standard risk assessment methodologies was proposed. Specifically the method used in this study is based on the results obtained from column leaching tests which allowed to estimate the main mechanisms controlling the leaching behaviour for the three types of BA. Indeed, it was observed that depending on the properties of the contaminants and the specific characteristics of the material, both equilibrium and non-equilibrium conditions can prevail during contaminant release and leaching concentrations vary with the time. Two different management scenarios were modelled for each type of BA i.e. landfilling and recycling as an unbound filler for road sub-base construction. Specific field conditions expected in the two scenarios (e.g. the infiltration rate and prevailing release mechanisms) were evaluated and, using the equations employed for the modelling of column test results and relevant estimated parameters, e.g. diffusion coefficients of contaminants, D_a (cm^2/s) and maximum available leaching concentrations, C_{sol} (mg/L), the amounts of contaminants expected to leach out from the BA and to reach the groundwater table, were calculated for a framework of concern of 100 years. The risk for the groundwater resource (R_{GW}) was finally assessed by comparing the calculated concentrations of the contaminants at the point of compliance with the reference values (CSC_{GW}) set by the Italian legislation for groundwater protection (Legislative Decree 152/06). Results showed that, for the considered scenarios (i.e. reuse in road sub-bases or landfill disposal) the leaching of metals and inorganic constituents from the three types of BA considered in this study, in nearly all cases seemed not to pose a risk for the groundwater resource. This is particularly true when contaminants attenuation due to sorption of constituents from the leachate onto clean soils underlying the affected soil zone (LDF) and the dilution of the concentration occurring when the contaminant is transferred from the leachate to the groundwater (SAM) are considered. However, making reference to the worst case for both landfill and road scenarios (e.g. no soil attenuation, no dilution in groundwater, no geomembrane in the bottom liner of the landfill), some contaminants, such as Al, Ba, Cr and Pb for the RDF-I BA and Al for both RDF-G BA and HW-I BA, may potentially pose a risk for the groundwater resource. Namely, generally higher risks associated to these contaminants were found for the road scenario. This was mainly attributed to the fact that for this scenario the concentrations of contaminants in the groundwater were modelled by employing the equation simulating a release under equilibrium conditions. However for this scenario, it should be kept in mind that the simulations were run assuming a constant rainfall rate, i.e. considering that water percolating through the road is uniformly distributed across the year. This of course is not representative of what happens in a real case and consequently the calculated risks for this scenario could be slightly overestimated. Overall, this first attempt indicated that the reuse of the different types of BA as an unbound filler material for road sub base construction may be a suitable alternative also from a risk-based point of view, especially for the RDF-G and HW-I BA. Nevertheless, the definitive evaluation of the environmental compatibility of this option should be performed case by case based on more detailed information regarding both the considered reuse scenario (e.g. infiltration rate through the road, thickness of the road sub-base material) and site-specific conditions (e.g. groundwater depth, rainfall intensity, type of soil in the vadose zone), since all of these factors showed to play an important role on the concentration of contaminants expected in the groundwater.

CONCLUSIONS AND FINAL REMARKS

In this study, two management options (i.e. landfilling and reuse as filling material in road sub-base construction) for bottom ash (BA) produced by different types of waste thermal treatment plants, were evaluated. Namely, BA generated at a dedicated hospital waste incineration plant (HW-I BA) and BA produced by both incineration and gasification of refuse derived fuel (RDF-I BA and RDF-G BA, respectively) were considered. To improve the basis for making decisions concerning BA management strategies, an in depth analysis of the leaching behaviour of these specific types of residues was firstly carried out (Section1) and then the most significant experimental leaching data were interpreted and used in evaluation tools such as LCA and risk assessment in order to evaluate the environmental consequences associated with the release of contaminants in the specific disposal/reuse scenario considered (Section 2).

First, the influence of the liquid-to-solid ratio (L/S) on the release of major components and potential contaminants from the three types of BA was examined (Chapter 1). Both batch (static) and column (dynamic) tests were performed and the results were compared as a function of both the type of analysed BA and the type of test carried out.

The experimental results showed that despite the relatively high content of contaminants measured in the solid matrix of the three types of BA, only a small amount of these elements was actually available for the leaching process. A generally lower release of contaminants was observed for the RDF-G BA which showed to comply with acceptance criteria for inert waste landfilling, while HW-I BA and RDF-I BA only met limit values set for disposal in non-hazardous waste landfills. Moreover, RDF-I BA displayed a generally higher release of amphoteric metals (i.e. Pb, Zn and Cu) and chlorides. As to the different leaching test methods applied, the obtained results showed that although for most of the elements considered a relatively good correlation between batch and column leaching tests results was observed, the release obtained from batch tests was generally higher (for some elements of up to two orders of magnitude) than the one obtained from column tests. This finding was mainly attributed to the different mode of execution of the two types of tests. In fact, while at the end of the batch tests the material can be assumed to be in a pseudo-equilibrium condition with the water phase solution, in the column tests the continuous renewal of the leachant solution can lead to non-equilibrium release conditions. This hypothesis was also supported by the application of an analytical model that indicated that most of the leaching trends observed in the different column experiments could be described quite well assuming the release to be limited by mass-transfer leading to concentrations in the eluates below equilibrium values. This was recognized as a crucial aspect to be considered for the interpretation and application of the lab-scale results for the assessment of the management options and long-term leaching behaviour of the material in field conditions. In fact, although in this specific case the type of leaching test applied showed not to affect the final result in terms of compliance with the limits set for landfill disposal or reuse, the critical contaminants and the leaching trends showed to vary depending on the type of test considered.

A step forward for the evaluation of the leaching properties of the three types of considered BA was addressed in Chapter 2. Specifically, acid neutralization capacity (ANC) and release of major compounds and trace contaminants as a function of pH was evaluated in order to derive a suitable description of the leaching behaviour of BA under environmental conditions that may occur in disposal/reuse scenarios. In addition, due to the higher heterogeneity and release of contaminants observed for the RDF-I BA compared to the other two types of BA, only for this material, the leaching behaviour as a function of both the L/S ratio and pH was assessed for two particle size classes (coarse: 0.425-12 mm and fine <0.425 mm), as well as after a weathering process carried out at laboratory scale for 12 months. Results indicated a remarkable difference in the ANC of RDF-I BA compared to the other two analysed types of BA. Indeed, RDF-G BA and HW-I BA displayed an almost negligible and low ANC, respectively. This was mainly associated to their mineralogy, which showed to be principally made up by amorphous phases. In light of this, the low ANC observed could be a parameter that may prove critical for the reuse of these two types of BA. In fact, the environmental conditions to which the materials may be subjected to in specific application scenarios, e.g. in contact with acidic rainwater (pH 5-6), could lead to a rapid drop of the native pH, resulting in an increase of the mobility of some contaminants such as Pb and Zn, which instead were not detected or found in very low concentrations at the BA native pH (pH= 10.4 and 7.3 for the HW-I BA and RDF-G BA, respectively). On the contrary, due to the abundance of hydrated phases, a significant ANC for pH values between 11 and 12 was found for the RDF-I BA, meaning that for modifications in environmental conditions corresponding to up to 2 meqH^+/g d.m., a quite stable leaching process can be expected. However, this type of BA showed fairly high release values already at its strongly alkaline native pH (12.4).

Regarding the effects of particle size on the leaching behaviour of RDF-I BA, while the release of contaminants as a function of pH, was shown not to be affected by the particle size distribution of the tested material, significant differences were instead found for the release as a function of the L/S ratio. Indeed, the obtained results showed a generally higher and faster release of contaminants (e.g. Cr, DOC and Cl^-) for the fine particle size fraction, which showed to exceed the limit values for hazardous waste landfill when the results of the first eluate of the column test were considered. This was mainly related to the higher surface area available for the leaching process for this particle size fraction compared to the coarse one. However, the removal of the fine particle size fraction from the bulk sample of the RDF-I BA was shown not to improve the leaching of contaminants, since the coarse particle size fraction exhibited quite a similar release compared to the bulk sample of the RDF-I BA, exceeding the landfill criteria for inert waste for the same contaminants. This was principally related to the fact that the coarse fraction represents 92% by weight of the bulk sample of RDF-I BA (i.e. mixed fraction).

As to the effect of natural weathering on RDF-I BA, the findings of this study evidenced that this treatment was able to modify the release of some metals as a function of the L/S ratio, likely due to the reaction with CO_2 by the mineral phases present in this type of residue, such as portlandite. In particular, although the native pH of the weathered sample showed not to differ significantly from the one observed for the fresh sample, weathering resulted in a relevant immobilization effect for Ba and Cu, which, contrarily to what observed for the fresh sample, showed to comply with the limit values for both inert waste landfilling and Italian limits for reuse. In addition a significant decrease (of up to one order of magnitude) was also observed for Pb release, which however, for both batch compliance leaching tests, still demonstrated to exceed the acceptance criteria for inert waste landfilling and reuse. On the other hand, the weathering process favoured the mobilization of oxyanionic metalloids such as Cr and Mo. However, while

Cr exceeded the limit values for inert waste landfilling for all the three types of leaching tests considered, for Mo only the release value detected in the first eluate of the column test was above those limits. Another interesting finding from the pH dependence and column leaching tests, was that although the pH dependent leaching patterns of the fresh and aged BA samples were rather similar, indicating that the phases controlling the solubility of the different components were probably the same, the release mechanism as a function of the L/S ratio for some elements (i.e. Pb and Zn) shifted from percolation to mass-transfer upon weathering, possibly indicating sorption of these contaminants onto phases such as carbonates.

In Chapter 3 potential environmental impacts associated to landfilling and reuse in road sub-base construction for the RDF-I and RDF-G BA were evaluated and compared by life-cycle assessment (LCA). Both non-toxicity related impact categories (i.e. global warming and mineral abiotic resource depletion) and toxic impact categories (i.e. human toxicity and ecotoxicity to freshwater) were assessed. The system boundaries included BA transport from the incineration/gasification plants to the landfills and road construction sites, leaching of potentially toxic metals from the BA, the avoided extraction, crushing, transport and leaching of virgin raw materials for the road scenarios, and material and energy consumption for the construction of the landfills. To provide a quantitative assessment of the leaching properties of the two types of BA, the experimental leaching data obtained in Chapter 1 (i.e. column percolation tests), were employed to estimate the cumulative release of potentially toxic metals from these waste materials in each scenario and used as input for the LCA model. Specific attention was placed on the sensitivity of leaching properties and the determination of emissions by leaching, including: leaching data selection, material properties and assumptions related to emission modelling. For all non toxicity-related impact categories and both types of BA, reuse of BA as a filler in road sub-base construction appeared to be beneficial with respect to landfilling. Whereas, toxicity-related impacts showed to differ significantly depending on both the type of BA and the management scenario considered, as a function of the leaching behaviour of the material. Specifically, for RDF-I BA leaching proved to be the major contributor to the total environmental impacts and reuse in road appeared to yield significant impacts in all the toxicity-related categories that were found to be higher than those obtained for the landfill scenario. For the RDF-G BA, instead, the contribution of leaching to the toxicity related impacts was negligible, making reuse in road particularly interesting. However, the low acid neutralization capacity observed for this type of BA (in Chapter 2) may represent a limiting factor. Indeed, leaching impacts were significantly affected by pH conditions, and decreases in pH could lead to increased environmental impacts related to RDF gasification bottom ash. The selection of the type of leaching data to use for determining the release of contaminants from the two types of BA (batch leaching test data instead of column leaching data) showed to significantly influence the quantified environmental impacts (batch data yielding higher emissions), however the overall ranking of the scenarios was not affected. The most critical modelling assumptions were: the distribution of contaminants between the environmental compartments (i.e. soil vs. surface water) and the net infiltration of rain water into the waste body, while the overall conclusions of the LCA were robust with respect to changes in the evaluated parameters.

A further step towards the evaluation of environmental impacts related to the two different management options assumed (i.e. landfilling and recycling in road sub-base construction) for the three types of analysed BA, was made by employing a risk-based approach (Chapter 4). Specifically, potential risks for the groundwater due to the emission of contaminants from the considered BA were investigated. A different approach compared to standard risk assessment methodologies was proposed. Specifically, the developed method was based on the results obtained by the column leaching tests which allowed to estimate the main mechanisms controlling the leaching behaviour of the three types of BA, i.e. the prevailing of equilibrium (percolation controlled release) or non-equilibrium (mass-transfer controlled release) conditions during contaminant release (Chapter 1). Specific field conditions expected in the two scenarios (e.g. the infiltration rate and prevailing release mechanisms) were evaluated and using the equations employed for the modelling of column test results and relevant estimated parameters, e.g. diffusion coefficients of contaminants, D_a (cm^2/s) and maximum available leaching concentrations, C_{sol} (mg/L), the amounts of contaminants expected to leach out from the BA and to reach the groundwater table, were calculated for a framework of concern of 100 years. The risk for the groundwater resource $R_{GW}(t)$ was finally assessed by comparing the calculated concentrations of the contaminants at the point of compliance with the reference values (CSC_{GW}) set by the Italian legislation for groundwater protection (Legislative Decree 152/06). Results showed that, for both of the considered scenarios the leaching of metals and inorganic constituents from the three types of BA, in nearly all cases seemed to not pose a risk for the groundwater resource. This is particularly true when contaminants attenuation due to sorption onto clean soils underlying the affected soil zone (LDF) and the dilution of the concentration occurring when the contaminant is transferred from the leachate to the groundwater (SAM) are considered. However, making reference to the worst case scenarios for both landfill and road (e.g. no soil attenuation, no dilution in groundwater, no geomembrane in the bottom liner of the landfill), some contaminants, such as Al, Ba, Cr and Pb for the RDF-I BA and Al for both RDF-G BA and HW-I BA, may potentially pose a risk for the groundwater resource. A generally higher risk associated to these contaminants was found for the road scenario. This was mainly attributed to the fact that for this scenario the concentrations of contaminants in the groundwater were modelled by employing the equation simulating release under equilibrium conditions. However for this scenario, it should be kept in mind that the simulations were run assuming a constant rainfall rate, i.e. considering that the water percolating through the road is uniformly distributed during the year. This of course is not representative of what happens in a real case and consequently the calculated risks for this scenario could be slightly overestimated.

The overall results of this study show that the environmental behaviour of BA generated from different waste to energy plants may vary significantly depending on the characteristics of the feed waste, but especially of the type of thermal treatment process applied. This finding may have important implications for the management of the analysed types of BA, since currently up to now, at least in Italy, no distinction is made for BA management based on the type of feed waste or thermal treatment that originated it, and the only option adopted besides non-hazardous waste landfilling is as additive in cement production. However, it appears that, depending on the specific origin of the BA, alternative management options such as reuse in road construction as unbound material may be viable. In particular, from an environmental perspective, the residues that showed the lowest impacts and hence may potentially be the most fit for reuse applications are the RDF-G BA, although as also found by LCA its negligible ANC could represent a limiting factor. Anyhow, from a risk-based point of view, the obtained results highlighted that reuse in road may be a suitable alternative to landfilling also for the other two types of BA (i.e. RDF-I BA and HW-I BA), since the leaching of metals and inorganic constituents from the BA, in nearly all cases seemed not to pose a risk for the groundwater resource.

Thus, in conclusion the methodological approach proposed in this work represents a first attempt to improve the basis for making decisions regarding solid residues management, contributing to fill a gap in current Italian practice. In fact, up to now evaluations concerning waste disposal or reuse have been solely based on a tabular approach and on the results of a simple batch leaching tests. Moreover, the proposed approach that here was developed for specific types of BA is intended to assess the potential environmental impacts of a wide range of waste materials and for different disposal or reuse scenarios. However, the results showed that, depending on the specific type of BA considered, its leaching behaviour may significantly affect the results of environmental implications involving its management strategies. Hence it is highly recommended that, LCA and risk-based assessment studies on these residues include careful evaluation of the specific environmental properties of each material. To this regard, the methodology proposed for carrying out the LCA and risk assessment studies may be refined by for example using the results of field leaching tests instead of laboratory ones, or employing more sophisticated models to estimate the amount of water in contact with the material (especially for the road scenario). Finally, it should be considered that the types of analysed bottom ash presented quite different physical characteristics besides environmental properties. Hence, also their technical performance should be specifically examined in order to identify the most suitable reuse applications and the maximum substitution ratios with respect to virgin raw materials applicable in each case.

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ANNEX A

SUPPLEMENTARY INFORMATION TO SECTION 1

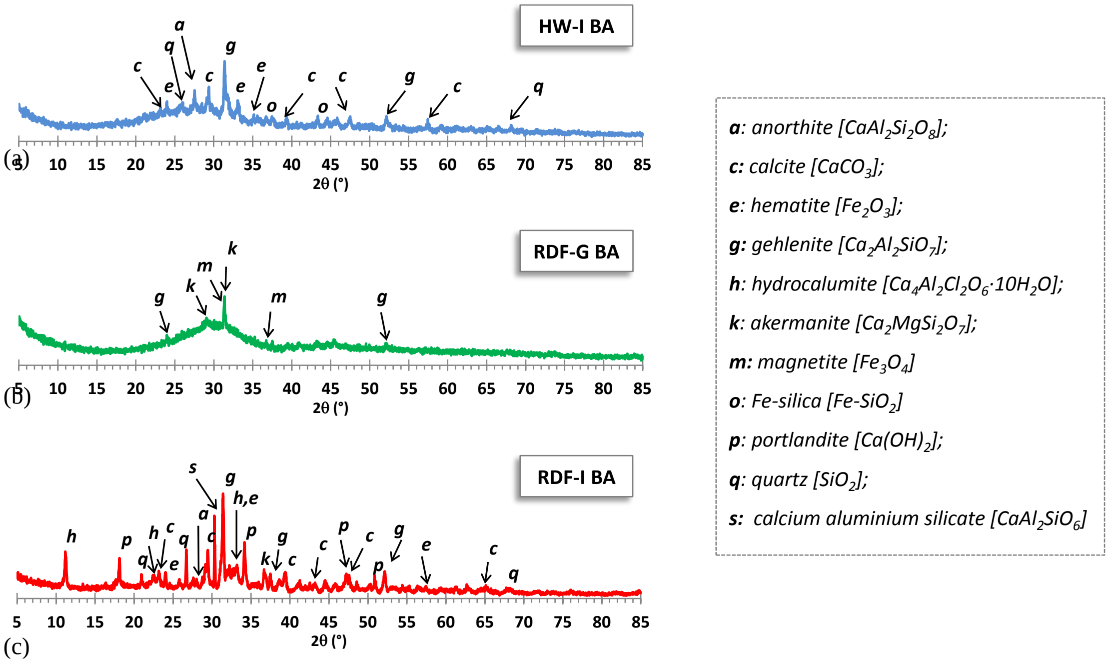


Fig. A.1 XRD patterns for HW-I BA (a), RDF-G BA (b) and RDF-I BA (c).

Table A.1 Leaching data (mg/l) for HW-I BA, obtained by column tests (CEN/TS 14405), batch tests (SR 003.1) on ground and unground BA and the two compliance leaching tests at L/S = 2 l/kg (UNI/EN 12457-1) and L/S = 10 l/kg (UNI/EN 12457-2). Limit of quantification (LOQ): reported below the table.

Type of Test	L/S [l/kg]	Amount of material [g dry matter]	Particle size [mm]	Time interval [h]	pH	Al [mg/l]	As [mg/l]	Ba [mg/l]	Ca [mg/l]	Cr [mg/l]	K [mg/l]	Mg [mg/l]	Mo [mg/l]	Na [mg/l]	Sb [mg/l]	Si [mg/l]	V [mg/l]	Zn [mg/l]	Cl^- [mg/l]	DOC [mg/l]
CEN/TS 14405_I°	0.09	3043	<12	5.25	11.18	99.30	0.00045	1.051	265.87	0.046	55.46	0.0758	0.1698	507.53	0.08018	1.758	<0.005	0.0323	943.77	29.25
CEN/TS 14405_I°	0.20	3043	<12	10.00	11.16	61.40	0.00059	1.855	357.05	<0.004	33.45	0.0458	0.1408	252.09	0.05756	1.356	<0.005	0.0141	787.84	17.94
CEN/TS 14405_I°	0.50	3043	<12	24.50	10.97	53.40	0.00073	1.042	247.95	<0.004	12.80	0.0258	0.0207	103.21	0.02250	1.385	<0.005	<0.01	172.34	16.24
CEN/TS 14405_I°	1.00	3043	<12	48.25	10.94	64.40	0.00059	0.555	142.15	<0.004	3.14	0.0193	0.0942	30.30	0.02071	1.672	<0.005	<0.01	99.40	6.85
CEN/TS 14405_I°	1.91	3043	<12	106.00	10.46	60.30	0.00059	0.465	89.89	<0.004	1.16	0.0164	0.0276	7.95	0.03059	1.492	<0.005	<0.01	82.83	3.47
CEN/TS 14405_I°	5.02	3043	<12	263.50	10.58	43.39	0.00117	0.293	53.90	<0.004	0.58	0.0183	<0.01	4.40	0.01385	2.196	<0.005	<0.01	74.55	14.28
CEN/TS 14405_I°	10.20	3043	<12	561.00	10.99	17.84	0.00188	0.199	42.42	<0.004	0.32	0.0285	<0.01	3.83	0.01081	5.306	<0.005	<0.01	21.54	10.19
CEN/TS 14405_II°	0.10	3056	<12	5.50	11.28	60.70	0.00049	0.866	335.76	0.023	54.54	0.0581	0.1673	508.66	0.10477	1.759	<0.005	0.0256	1060.25	32.85
CEN/TS 14405_II°	0.20	3056	<12	10.00	11.20	46.11	0.00065	1.319	374.20	<0.004	32.60	0.0413	0.1318	258.39	0.06033	1.586	<0.005	0.0107	828.32	21.90
CEN/TS 14405_II°	0.51	3056	<12	24.25	10.97	57.40	0.00062	0.732	225.84	<0.004	13.45	0.0305	0.0130	108.26	0.07758	1.558	<0.005	<0.01	124.25	10.71
CEN/TS 14405_II°	1.01	3056	<12	48.50	10.93	70.00	0.00051	0.532	131.02	<0.004	3.32	0.0160	0.0730	31.65	0.00438	1.885	<0.005	<0.01	49.70	5.50
CEN/TS 14405_II°	1.97	3056	<12	99.00	10.87	63.50	0.00054	0.506	95.02	<0.004	1.15	0.0172	0.0143	7.32	0.02175	1.730	<0.005	<0.01	36.45	8.62
CEN/TS 14405_II°	5.05	3056	<12	264.50	10.61	38.57	0.00134	0.303	57.12	<0.004	0.58	0.0150	<0.01	4.32	0.01641	2.775	<0.005	<0.01	14.91	13.87
CEN/TS 14405_II°	9.94	3056	<12	537.50	11.22	19.46	0.00211	0.220	52.37	<0.004	0.35	0.0334	<0.01	7.84	0.00778	6.354	<0.005	<0.01	11.60	10.82
CEN/TS 14405_Mean value	0.10	3050	<12	5.38	11.23	80.00	0.00047	0.958	300.81	0.035	55.00	0.0669	0.1686	508.10	0.09247	1.759	<0.005	0.0289	1002.01	31.05
CEN/TS 14405_Mean value	0.20	3050	<12	10.00	11.18	53.76	0.00062	1.587	365.62	<0.004	33.02	0.0436	0.1363	255.24	0.05894	1.471	<0.005	0.0124	808.08	19.92
CEN/TS 14405_Mean value	0.51	3050	<12	24.38	10.97	55.40	0.00068	0.887	236.90	<0.004	13.13	0.0281	0.0168	105.74	0.05004	1.472	<0.005	<0.01	148.29	13.47
CEN/TS 14405_Mean value	1.00	3050	<12	48.38	10.94	67.20	0.00055	0.543	136.58	<0.004	3.23	0.0177	0.0836	30.97	0.01254	1.778	<0.005	<0.01	74.55	6.17
CEN/TS 14405_Mean value	1.94	3050	<12	102.50	10.67	61.90	0.00057	0.485	92.46	<0.004	1.15	0.0168	0.0209	7.63	0.02617	1.611	<0.005	<0.01	59.64	6.04
CEN/TS 14405_Mean value	5.03	3050	<12	264.00	10.60	40.98	0.00125	0.298	55.51	<0.004	0.58	0.0166	<0.01	4.36	0.01513	2.486	<0.005	<0.01	44.73	14.08
CEN/TS 14405_Mean value	10.07	3050	<12	549.25	11.11	18.65	0.00200	0.209	47.40	<0.004	0.33	0.0310	<0.01	5.83	0.00930	5.830	<0.005	<0.01	16.57	10.51
SR 003.1 ground	0.5	159.98	<2	48	9.82	13.64	0.00082	0.420	359.68	0.024	17.40	1.9515	0.1699	172.29	0.06409	1.063	0.0075	0.0290	n.a.	n.a.
SR 003.1 ground	1	79.98	<2	48	10.29	7.01	0.00166	0.203	268.38	0.062	11.49	1.2483	0.1091	100.95	0.04670	2.107	0.0123	<0.01	262.38	38.77
SR 003.1 ground	2	39.99	<2	48	10.01	25.36	0.00074	0.151	141.73	0.013	5.87	1.1405	0.0471	46.81	0.04817	1.100	<0.005	<0.01	203.03	24.46
SR 003.1 ground	5	16.02	<2	48	10.02	19.41	0.00106	0.103	94.96	0.078	3.27	1.5477	<0.01	30.87	0.05141	1.216	0.0056	<0.01	118.70	23.36
SR 003.1 ground	10	8.01	<2	48	10.16	14.66	0.00164	0.075	54.31	0.112	1.92	1.6726	<0.01	15.57	0.04163	1.434	0.0089	<0.01	87.46	2.586
SR 003.1 unground	0.5	159.99	<12	48	9.94	15.97	0.00076	0.570	296.73	0.023	16.75	1.1630	0.1305	157.97	0.03396	1.110	0.0072	0.0291	n.a.	n.a.
SR 003.1 unground	1	79.98	<12	48	10.19	16.85	0.00113	0.209	175.82	0.017	9.45	1.0477	0.0746	99.41	0.10490	1.404	0.0062	<0.01	259.26	30.845
SR 003.1 unground	2	40.02	<12	48	10.51	22.05	0.00084	0.144	137.84	0.0045	5.25	0.4387	0.0365	47.80	0.03123	1.411	0.0057	<0.01	168.68	21.52
SR 003.1 unground	5	15.98	<12	48	10.11	14.82	0.00136	0.083	56.41	0.062	3.06	1.5284	<0.01	20.82	0.02629	1.267	0.0069	<0.01	99.96	17.016
SR 003.1 unground	10	8.01	<12	48	10.62	3.88	0.00262	0.077	47.35	0.119	1.24	1.2106	<0.01	10.51	0.02305	5.333	0.0128	<0.01	74.97	2.198
UNI EN 12457-1_I°	2	30	<4	24	10.62	2.02	0.00970	0.123	136.59	0.035	4.80	3.2295	0.0457	45.76	0.06484	6.270	0.0120	0.0220	107.68	33.74
UNI EN 12457-1_II°	2	30.02	<4	24	10.62	1.77	0.00880	0.120	126.48	0.050	4.27	3.2646	0.0495	44.39	0.06621	5.288	0.0104	0.0220	107.68	31.44
UNI EN 12457-1_Mean value	2	30.01	<4	24	10.62	1.89	0.00925	0.121	131.54	0.042	4.53	3.2471	0.0476	45.08	0.06553	5.779	0.0112	0.0220	107.68	32.59
UNI EN 12457-2_I°	10	7.99	<4	24	10.34	6.06	0.00207	0.073	45.46	0.070	1.15	1.3419	<0.01	8.61	0.03845	2.397	0.0086	<0.01	102.53	1.81
UNI EN 12457-2_II°	10	7.99	<4	24	10.51	3.96	0.00255	0.073	49.56	0.149	2.53	1.6359	<0.01	12.01	0.05466	4.851	0.0145	<0.01	74.55	1.73
UNI EN 12457-2_III°	10	8.01	<4	24	10.37	5.17	0.00283	0.063	43.65	0.128	1.65	1.7321	<0.01	10.21	0.03463	3.388	0.0115	<0.01	95.61	n.a.
UNI EN 12457-2_Mean value	10	8.00	<4	24	10.41	5.06	0.00248	0.070	46.22	0.116	1.78	1.5700	<0.01	10.28	0.04258	3.545	0.0115	<0.01	90.90	1.77

LOQ (mg/l): Be (0.0007); Cd (0.002); Co (0.005); Cu (0.005); Hg (0.0008); Mo (0.01); Ni (0.008); Pb (0.03); Se (0.002). **n.a.**: not available value. Note that L/S [l/kg] and the time interval [h] for the column tests are reported in terms of cumulative values

Table A.2 Leaching data (mg/l) for RDF-G BA, obtained by column tests (CEN/TS 14405), batch tests (SR 003.1) on ground and unground BA and the two compliance leaching tests at L/S = 2 l/kg (UNI/EN 12457-1) and L/S = 10 l/kg (UNI/EN 12457-2). Limit of quantification (LOQ): reported below the table.

Type of Test	L/S [l/kg]	Amount of material [g dry matter]	Particle size [mm]	Time interval [h]	pH	Al [mg/l]	As [mg/l]	Ba [mg/l]	Ca [mg/l]	Cu [mg/l]	Fe [mg/l]	Hg [mg/l]	K [mg/l]	Mg [mg/l]	Mn [mg/l]	Na [mg/l]	Pb [mg/l]	Sb [mg/l]	Se [mg/l]	Si [mg/l]	DOC [mg/l]
CEN/TS 14405_I°	0.12	4271	<12	10.5	7.35	0.03	0.00189	0.052	48.38	0.01551	<0.015	<0.0004	3.00	3.19388	0.009917	6.44	<0.02	0.00811	<0.002	5.849	10.89
CEN/TS 14405_I°	0.24	4271	<12	22.25	7.31	0.03	0.00126	0.033	43.62	0.01632	<0.015	<0.0004	2.34	1.99911	0.008791	5.27	<0.02	0.00703	<0.002	5.188	2.79
CEN/TS 14405_I°	0.52	4271	<12	50.5	7.84	0.05	0.00109	0.019	26.65	0.01900	<0.015	<0.0004	1.22	0.83292	<0.005	2.93	<0.02	0.00439	<0.002	3.563	1.87
CEN/TS 14405_I°	0.97	4271	<12	95	7.53	0.04	0.00088	0.008	12.39	0.02219	<0.015	<0.0004	0.50	0.32700	<0.005	1.29	<0.02	0.00271	<0.002	1.944	0.66
CEN/TS 14405_I°	1.88	4271	<12	172.5	7.54	0.22	0.00076	0.005	10.45	0.01888	<0.015	<0.0004	0.31	0.34339	<0.005	0.81	<0.02	0.00162	<0.002	1.543	1.66
CEN/TS 14405_I°	4.85	4271	<12	456	6.96	0.21	<0.0007	<0.004	6.97	0.01022	<0.015	<0.0004	0.18	0.24718	<0.005	0.34	<0.02	0.00129	<0.002	1.578	5.53
CEN/TS 14405_I°	9.92	4271	<12	869.5	7.05	0.32	<0.0007	<0.004	10.31	0.00577	<0.015	<0.0004	0.11	0.28815	<0.005	0.22	<0.02	0.00144	<0.002	1.239	6.26
CEN/TS 14405_II°	0.09	4281	<12	10.5	7.09	0.08	0.00164	0.133	48.21	0.03124	<0.015	<0.0004	2.99	3.18864	<0.005	6.53	<0.02	0.00819	<0.002	6.079	11.41
CEN/TS 14405_II°	0.22	4281	<12	22.0	7.49	0.07	0.00236	0.047	39.41	0.05181	<0.015	<0.0004	1.61	1.77291	<0.005	2.57	<0.02	0.00713	<0.002	5.651	3.04
CEN/TS 14405_II°	0.54	4281	<12	49.5	7.38	0.09	0.00261	0.022	21.33	0.06497	<0.015	<0.0004	0.75	0.67359	<0.005	1.17	<0.02	0.00354	<0.002	3.325	2.27
CEN/TS 14405_II°	1.05	4281	<12	95.75	7.40	0.05	0.00078	0.022	17.21	0.03057	<0.015	<0.0004	0.43	0.44766	<0.005	0.82	<0.02	0.00233	<0.002	2.487	1.49
CEN/TS 14405_II°	1.89	4281	<12	173.5	7.00	0.09	<0.0007	0.010	13.84	0.01930	<0.015	<0.0004	0.27	0.34969	<0.005	0.36	<0.02	0.00161	<0.002	1.399	0.90
CEN/TS 14405_II°	4.91	4281	<12	457.5	7.15	0.16	<0.0007	0.006	14.01	0.01062	<0.015	<0.0004	0.22	0.37956	<0.005	0.51	<0.02	0.00193	<0.002	0.952	1.63
CEN/TS 14405_II°	10.04	4281	<12	961.5	7.29	0.31	<0.0007	<0.004	8.06	0.00550	<0.015	<0.0004	0.13	0.24677	<0.005	0.31	<0.02	0.00198	<0.002	1.324	4.47
CEN/TS 14405_Mean value	0.11	4276	<12	10.5	7.22	0.06	0.00177	0.093	48.30	0.02337	<0.015	<0.0004	2.99	3.19126	0.00992	6.48	<0.02	0.00815	<0.002	5.964	11.15
CEN/TS 14405_Mean value	0.23	4276	<12	22.1	7.40	0.05	0.00181	0.040	41.51	0.03407	<0.015	<0.0004	1.98	1.88601	0.00879	3.92	<0.02	0.00708	<0.002	5.419	2.91
CEN/TS 14405_Mean value	0.53	4276	<12	50.0	7.61	0.07	0.00185	0.020	23.99	0.04199	<0.015	<0.0004	0.98	0.75325	<0.005	2.05	<0.02	0.00397	<0.002	3.444	2.07
CEN/TS 14405_Mean value	1.01	4276	<12	95.4	7.47	0.05	0.00083	0.015	14.80	0.02638	<0.015	<0.0004	0.47	0.38733	<0.005	1.06	<0.02	0.00252	<0.002	2.215	1.08
CEN/TS 14405_Mean value	1.89	4276	<12	173.0	7.27	0.15	0.00076	0.007	12.15	0.01909	<0.015	<0.0004	0.29	0.34654	<0.005	0.59	<0.02	0.00161	<0.002	1.471	1.28
CEN/TS 14405_Mean value	4.88	4276	<12	456.8	7.06	0.19	<0.0007	0.006	10.49	0.01042	<0.015	<0.0004	0.20	0.31337	<0.005	0.43	<0.02	0.00161	<0.002	1.265	3.58
CEN/TS 14405_Mean value	9.98	4276	<12	915.5	7.17	0.31	<0.0007	<0.004	9.19	0.00564	<0.015	<0.0004	0.12	0.26746	<0.005	0.27	<0.02	0.00171	<0.002	1.281	5.37
SR 003.1 ground	0.5	80.07	<2	48	8.66	0.61	n.a.	0.018	35.26	0.71157	0.317595	n.a.	2.42	2.01652	0.02614	5.73	0.04534	n.a.	n.a.	3.421	165.10
SR 003.1 ground	1	40.07	<2	48	9.32	1.68	n.a.	0.010	20.05	0.82461	0.324834	n.a.	1.57	1.15474	0.00981	3.08	0.04211	n.a.	n.a.	2.982	104.40
SR 003.1 ground	2	20.04	<2	48	9.26	1.77	n.a.	0.012	15.14	0.56724	0.269803	n.a.	1.82	0.86381	0.00584	3.75	0.03194	n.a.	n.a.	2.742	44.47
SR 003.1 ground	5	8	<2	48	8.34	1.84	n.a.	0.011	13.32	0.85587	0.233778	n.a.	1.10	0.84243	0.00925	1.96	0.03782	n.a.	n.a.	2.502	35.86
SR 003.1 ground	10	4.01	<2	48	8.95	0.98	n.a.	0.005	7.88	0.16320	0.0305751	n.a.	1.51	0.36165	<0.005	2.44	<0.02	n.a.	n.a.	1.652	29.12
SR 003.1 unground	0.5	80.01	<12	48	6.32	0.10	n.a.	0.029	29.37	0.27385	<0.015	n.a.	1.42	0.97059	0.05602	1.57	<0.02	n.a.	n.a.	2.319	83.71
SR 003.1 unground	1	40.01	<12	48	6.47	0.11	n.a.	0.015	18.31	0.13397	<0.015	n.a.	1.28	0.50730	0.02662	0.68	<0.02	n.a.	n.a.	1.307	58.05
SR 003.1 unground	2	20.07	<12	48	6.66	0.15	n.a.	0.012	16.71	0.08712	<0.015	n.a.	0.79	0.39317	0.01619	0.51	<0.02	n.a.	n.a.	0.815	118.10
SR 003.1 unground	5	8	<12	48	6.83	0.03	n.a.	0.011	11.68	0.10453	<0.015	n.a.	0.67	0.21369	0.03774	0.29	<0.02	n.a.	n.a.	0.531	45.65
SR 003.1 unground	10	4.02	<12	48	6.84	0.02	n.a.	0.007	9.06	0.07605	<0.015	n.a.	1.43	0.15672	0.02659	0.23	<0.02	n.a.	n.a.	0.404	34.25
UNI EN 12457-1_I°	2	29.99	<4	24	8.68	0.46	0.0005423	0.013	11.29	0.404826	0.094632	<0.0004	1.07	0.4763	0.0145	2.84	<0.02	0.00329	<0.002	2.134	86.10
UNI EN 12457-1_II°	2	29.98	<4	24	8.69	0.60	0.0005225	0.014	12.47	0.48338	0.157729	<0.0004	1.02	0.5162	0.0155	3.02	<0.02	0.00304	<0.002	2.332	68.15
UNI EN 12457-1_Mean value	2	29.99	<4	24	8.69	0.53	0.0005324	0.013	11.88	0.444	0.1261805	<0.0004	1.04	0.4962	0.0150	2.93	<0.02	0.00316	<0.002	2.233	77.13
UNI EN 12457-2_I°	10	4.06	<4	24	7.14	0.04	<0.0007	0.015	7.80	0.12201	<0.015	<0.0004	4.57	0.3833	0.0182	3.80	<0.02	0.00062	<0.002	0.818	22.26
UNI EN 12457-2_II°	10	4	<4	24	7.29	0.03	<0.0007	0.009	9.58	0.12959	<0.015	<0.0004	1.14	0.3116	0.0232	4.02	<0.02	0.00064	<0.002	0.868	5.56
UNI EN 12457-2_III°	10	4.04	<4	24	7.36	0.02	<0.0007	0.008	9.84	0.10621	<0.015	<0.0004	1.14	0.3048	0.0262	4.01	<0.02	0.00067	<0.002	0.877	n.a.
UNI EN 12457-2_Mean value	10	4.03	<4	24	7.26	0.03	<0.0007	0.011	9.08	0.11927	<0.015	<0.0004	2.29	0.3332	0.0225	3.95	<0.02	0.00064	<0.002	0.854	13.91

LOQ (mg/l): Be (0.001); Cd (0.005); Co (0.005); Cr (0.007); Mo (0.01); Ni (0.009); V (0.005); Zn (0.01); Cl^- (20). **n.a.**: not available value. Note that L/S [l/kg] and the time interval [h] for the column tests are reported in terms of cumulative values

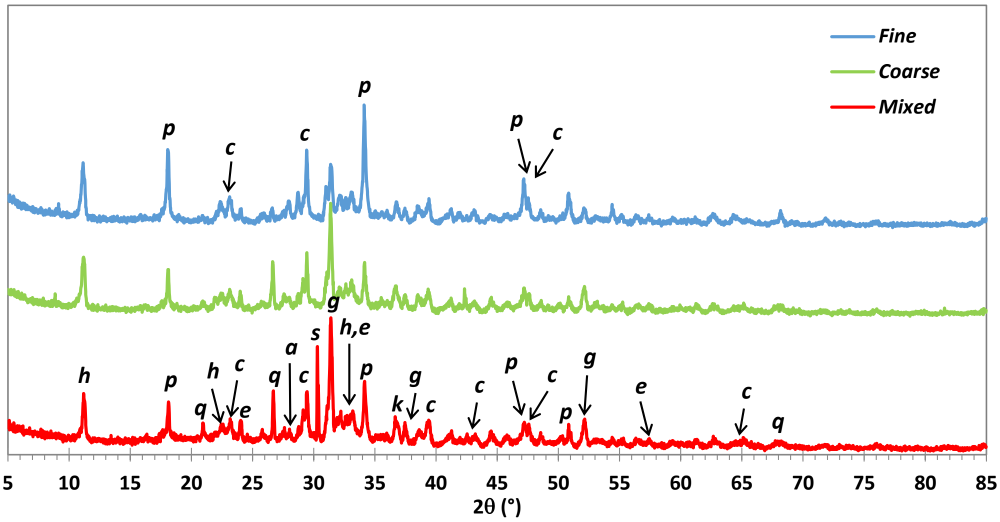
Table A.3 Leaching data (mg/l) for RDF-I BA, obtained by column tests (CEN/TS 14405), batch tests (SR 003.1) on ground and unground BA and the two compliance leaching tests at L/S = 2 l/kg (UNI/EN 12457-1) and L/S = 10 l/kg (UNI/EN 12457-2). Limit of quantification (LOQ): reported below the table.

Type of Test	L/S [l/kg]	Amount of material [g dry matter]	Particle size [mm]	Time interval [h]	pH	Al [mg/l]	As [mg/l]	Ba [mg/l]	Ca [mg/l]	Cr [mg/l]	Cu [mg/l]	Hg [mg/l]	K [mg/l]	Mg [mg/l]	Mo [mg/l]	Na [mg/l]	Pb [mg/l]	Sb [mg/l]	Se [mg/l]	Si [mg/l]	Zn [mg/l]	Cl^- [mg/l]	DOC [mg/l]
CEN/TS 14405_I°	0.10	2786	<12	4	12.8	6.94	0.0012	1.15	26.29	0.0500	0.0190	<0.001	540.70	<0.009	0.0158	1127.75	0.2231	0.29178	0.0072	2.2904	0.0177	2076.30	34.61
CEN/TS 14405_I°	0.20	2786	<12	9.5	12.86	2.99	0.0014	3.05	200.82	0.0388	0.0203	<0.001	589.00	<0.009	0.0145	1227.95	0.6821	0.19138	0.0069	1.5689	0.0500	2595.38	36.29
CEN/TS 14405_I°	0.51	2786	<12	26.5	12.82	1.67	0.0015	3.02	206.13	0.0342	0.0213	<0.001	582.36	<0.009	0.0136	1158.54	1.2592	0.18581	0.0077	0.8664	0.1075	2275.95	31.81
CEN/TS 14405_I°	1.02	2786	<12	54.5	12.54	0.68	0.0012	3.03	561.97	0.0119	0.0098	<0.001	125.16	<0.009	<0.01	229.15	0.9103	0.08517	0.0084	0.2413	0.0622	1078.08	8.56
CEN/TS 14405_I°	1.92	2786	<12	104.75	12.51	0.56	0.0011	8.72	689.06	0.0087	0.0109	<0.001	36.49	<0.009	<0.01	60.51	1.1013	0.09426	0.0083	0.1488	0.1107	998.22	1.11
CEN/TS 14405_I°	4.85	2786	<12	270.75	12.53	0.57	<0.001	6.11	792.21	0.0069	0.0104	<0.001	15.76	<0.009	<0.01	24.73	0.9635	0.07563	0.0100	0.2794	0.1134	598.93	1.61
CEN/TS 14405_I°	10.05	2786	<12	537	12.49	0.55	0.0012	3.44	777.54	0.0070	0.0088	<0.001	9.31	<0.009	<0.01	14.21	0.9019	0.07697	0.0048	0.1506	0.1286	479.15	1.91
CEN/TS 14405_II°	0.10	2745	<12	4	12.82	4.57	0.00362	0.39	37.16	0.0622	0.0212	<0.001	593.11	<0.009	0.0193	1322.26	0.0960	0.26956	0.0077	2.8096	0.0159	2116.23	41.63
CEN/TS 14405_II°	0.19	2745	<12	9	12.93	2.10	0.00235	2.79	185.74	0.0510	0.0204	<0.001	638.55	<0.009	0.0190	1447.23	0.5145	0.13070	0.0081	1.3338	0.0271	2874.88	40.28
CEN/TS 14405_II°	0.52	2745	<12	27	12.87	1.11	0.00153	2.42	135.84	0.0400	0.0176	<0.001	606.48	<0.009	0.0156	1303.66	1.1807	0.14783	0.0077	0.9044	0.0356	2595.38	34.43
CEN/TS 14405_II°	1.03	2745	<12	55.25	12.5	0.60	0.00000	7.83	639.96	0.0112	0.0059	<0.001	148.64	<0.009	<0.01	243.41	0.8340	0.07771	0.0072	0.5632	0.0401	958.29	5.33
CEN/TS 14405_II°	1.81	2745	<12	121.5	12.52	0.56	<0.001	8.54	739.09	0.0089	0.0058	<0.001	46.64	<0.009	<0.01	86.91	0.9056	0.07081	0.0088	0.3801	0.0959	838.51	1.63
CEN/TS 14405_II°	4.99	2745	<12	294.25	12.49	0.57	<0.001	5.42	767.41	0.0081	0.0071	<0.001	16.70	<0.009	<0.01	25.59	0.8165	0.09287	0.0064	0.2037	0.1056	519.08	1.88
CEN/TS 14405_II°	10.03	2745	<12	575	12.47	0.55	0.00101	3.29	807.97	0.0076	0.0065	<0.001	10.34	<0.009	<0.01	15.47	0.7038	0.09073	0.0073	0.1467	0.1075	598.93	2.92
CEN/TS 14405_Mean value	0.10	2766	<12	4.00	12.81	5.76	0.00241	0.77	31.72	0.0561	0.0201	<0.001	566.91	<0.009	0.0176	1225.01	0.1595	0.28067	0.0075	2.5500	0.0168	2096.27	38.12
CEN/TS 14405_Mean value	0.20	2766	<12	9.25	12.895	2.54	0.00187	2.92	193.28	0.0449	0.0204	<0.001	613.78	<0.009	0.0168	1337.59	0.5983	0.16104	0.0075	1.4514	0.0386	2735.13	38.28
CEN/TS 14405_Mean value	0.52	2766	<12	26.75	12.845	1.39	0.00150	2.72	170.99	0.0371	0.0194	<0.001	594.42	<0.009	0.0146	1231.10	1.2200	0.16682	0.0077	0.8854	0.0715	2435.67	33.12
CEN/TS 14405_Mean value	1.03	2766	<12	54.88	12.52	0.64	0.00060	5.43	600.97	0.0116	0.0078	<0.001	136.90	<0.009	<0.01	236.28	0.8722	0.08144	0.0078	0.4022	0.0511	1018.19	6.94
CEN/TS 14405_Mean value	1.87	2766	<12	113.13	12.515	0.56	0.00109	8.63	714.08	0.0088	0.0084	<0.001	41.57	<0.009	<0.01	73.71	1.0035	0.08253	0.0085	0.2645	0.1033	918.37	1.37
CEN/TS 14405_Mean value	4.92	2766	<12	282.50	12.51	0.57	<0.001	5.76	779.81	0.0075	0.0088	<0.001	16.23	<0.009	<0.01	25.16	0.8900	0.08425	0.0082	0.2415	0.1095	559.01	1.75
CEN/TS 14405_Mean value	10.04	2766	<12	556.13	12.48	0.55	0.00112	3.36	792.76	0.0073	0.0077	<0.001	9.83	<0.009	<0.01	14.84	0.8029	0.08385	0.0061	0.1487	0.1180	539.04	2.41
SR 003.1 ground	0.5	80.03	<2	48	12.44	0.7779	n.a.	3.49	518.28	0.2243	0.0810	n.a.	797.63	<0.009	0.0795	1432.32	0.1610	n.a.	n.a.	14.28	0.1254	1208.77	n.a.
SR 003.1 ground	1	40.01	<2	48	12.54	0.0363	n.a.	8.63	761.60	0.0965	0.2208	n.a.	399.63	<0.009	0.0391	949.38	1.1560	n.a.	n.a.	4.89	0.3828	1168.48	68.99
SR 003.1 ground	2	20.09	<2	48	12.43	0.0583	n.a.	10.44	778.92	0.0601	0.1589	n.a.	203.92	<0.009	0.0288	486.04	0.8222	n.a.	n.a.	3.69	0.5153	866.29	49.62
SR 003.1 ground	5	8.06	<2	48	12.54	0.1043	n.a.	9.27	783.71	0.0444	0.1289	n.a.	90.20	<0.009	0.0201	202.46	0.8321	n.a.	n.a.	3.70	0.4065	745.41	106.95
SR 003.1 ground	10	4.03	<2	48	12.45	0.1124	n.a.	8.98	775.87	0.0301	0.1262	n.a.	52.68	<0.009	0.0148	109.17	0.7231	n.a.	n.a.	2.77	0.3895	684.97	6.59
SR 003.1 unground	0.5	80.03	<12	48	12.54	0.1716	n.a.	6.04	564.43	0.0872	0.1004	n.a.	270.21	0.02846	0.0300	564.01	0.64674	n.a.	n.a.	0.392	0.3453	1716.94	113.30
SR 003.1 unground	1	40.01	<12	48	12.54	0.1150	n.a.	7.76	672.60	0.0618	0.1154	n.a.	131.55	0.02007	0.0135	267.03	0.70555	n.a.	n.a.	0.235	0.456803	1237.80	68.44
SR 003.1 unground	2	20.07	<12	48	12.54	0.1204	n.a.	10.12	843.49	0.0479	0.2087	n.a.	93.20	0.03633	<0.01	177.52	0.53678	n.a.	n.a.	0.165	0.218305	958.29	58.18
SR 003.1 unground	5	8.05	<12	48	12.54	0.1295	n.a.	7.68	719.29	0.0289	0.1272	n.a.	33.23	<0.009	<0.01	77.40	0.49061	n.a.	n.a.	0.115	0.222422	678.79	32.08
SR 003.1 unground	10	4	<12	48	12.53	0.1545	n.a.	5.60	690.35	0.0276	0.0632	n.a.	17.99	<0.009	<0.01	56.27	2.04572	n.a.	n.a.	0.101	0.188337	598.93	34.54
UNI EN 12457-1_I°	2	30	<4	24	12.49	0.1107	<0.001	8.790	940.65	0.0507	0.0757	<0.001	126.43	<0.009	0.0201	289.13	0.6752	0.00198	<0.002	0.3350	0.3275	1682.15	117.80
UNI EN 12457-1_II°	2	30.02	<4	24	12.49	0.1150	<0.001	8.296	946.83	0.0579	0.0804	<0.001	137.51	<0.009	0.0217	315.30	1.2961	0.00189	<0.002	0.3599	0.3413	1846.26	96.74
UNI EN 12457-1_Mean value	2	30.01	<4	24	12.49	0.1129	<0.001	8.543	943.74	0.0543	0.0781	<0.001	131.97	<0.009	0.0209	302.22	0.98569	0.00194	<0.002	0.3475	0.3344	1764.20	107.27
UNI EN 12457-2_I°	10	4	<4	24	12.42	0.1408	<0.001	7.827	860.90	0.0336	0.0435	<0.001	35.98	0.0049	0.0134	69.05	0.5840	0.00264	<0.002	<0.1	0.2486	714.78	11.38
UNI EN 12457-2_II°	10	4.07	<4	24	12.42	0.1333	<0.001	7.284	839.72	0.0353	0.0479	<0.001	31.20	0.0055	0.0128	59.25	0.5821	0.00275	<0.002	<0.1	0.2799	686.19	14.36
UNI EN 12457-2_III°	10	4.04	<4	24	12.39	0.1531	<0.001	7.452	836.03	0.0371	0.0606	<0.001	33.75	0.0328	0.0106	63.28	0.6455	0.00240	<0.002	<0.1	0.2571	686.19	n.a.
UNI EN 12457-2_Mean value	10	4.04	<4	24	12.41	0.1424	<0.001	7.521	845.55	0.0353	0.0507	<0.001	33.64	0.0144	0.0123	63.86	0.60385	0.00260	<0.002	<0.1	0.2619	695.72	12.87

LOQ (mg/l): Be (0.001); Cd (0.005); Co (0.005); Ni (0.009); V (0.005). **n.a.**: not available value. Note that L/S [l/kg] and the time interval [h] for the column tests are reported in terms of cumulative values

Table A.4 Limit values (expressed in mg/kg) reported in the European Landfill Directive (2003/33/EC, EU LFD) for waste acceptable at landfills for inert, non-hazardous and hazardous waste, calculated at L/S of 2 l/kg (UNI/EN 12457 part 1), at L/S of 10 l/kg (UNI/EN 12457 part 2) and for C_0, the first eluate of percolation test (CEN/TS 14405) at L/S = 0.1 l/kg. In the table also the limit values reported in the Italian legislation for reuse of waste materials (M.D. 186/2006) calculated at L/S of 10 l/kg (UNI/EN 12457 part 2) are shown. (n.r. not regulated element).

	Reuse	**Inert waste**			**Non-hazardous waste**			**Hazardous waste**		
Element	**L/S = 10 l/kg**	**C_0**	**L/S = 2 l/kg**	**L/S = 10 l/kg**	**C_0**	**L/S = 2 l/kg**	**L/S = 10 l/kg**	**C_0**	**L/S = 2 l/kg**	**L/S = 10 l/kg**
pH	5.5-12	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
As	0.5	0.006	0.1	0.5	0.03	0.4	2	0.3	6	25
Ba	10	0.4	7	20	2	30	100	6	100	300
Be	0.1	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
Cd	0.05	0.002	0.03	0.04	0.03	0.6	1	0.17	3	5
Co	2.5	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
Cr	0.5	0.01	0.2	0.5	0.25	4	10	1.5	25	70
Cu	0.5	0.06	0.9	2	3	25	50	6	50	100
Hg	0.01	0.0002	0.003	0.01	0.003	0.05	0.2	0.03	0.5	2
Mo	n.r.	0.02	0.3	0.5	0.35	5	10	1	20	30
Ni	0.1	0.012	0.2	0.4	0.3	5	10	1.2	20	40
Pb	0.5	0.015	0.2	0.5	0.3	5	10	1.5	25	50
Sb	n.r.	0.01	0.02	0.06	0.015	0.2	0.7	0.1	2	5
Se	0.1	0.004	0.06	0.1	0.02	0.3	0.5	0.3	4	7
V	2.5	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
Zn	30	0.12	2	4	1.5	25	50	6	90	200
DOC	300	16	240	500	25	380	800	32	480	1000
Cl^-	1000	46	550	800	850	10000	15000	1500	17000	25000



a: *anorthite [$CaAl_2Si_2O_8$];* ***c:*** *calcite [$CaCO_3$];* ***e***: *hematite [Fe_2O_3];* ***g:*** *gehlenite [$Ca_2Al_2SiO_7$];*
h: *hydrocalumite [$Ca_4Al_2Cl_2O_6 \cdot 10H_2O$];* ***k:*** *akermanite [$Ca_2MgSi_2O_7$];* ***p***: *portlandite [$Ca(OH)_2$];*
q: *quartz [SiO_2];* ***s:*** *calcium aluminium silicate [$CaAl_2SiO_6$]*

Fig. A.2 XRD patterns for the fine, coarse and mixed sample of RDF-I BA.

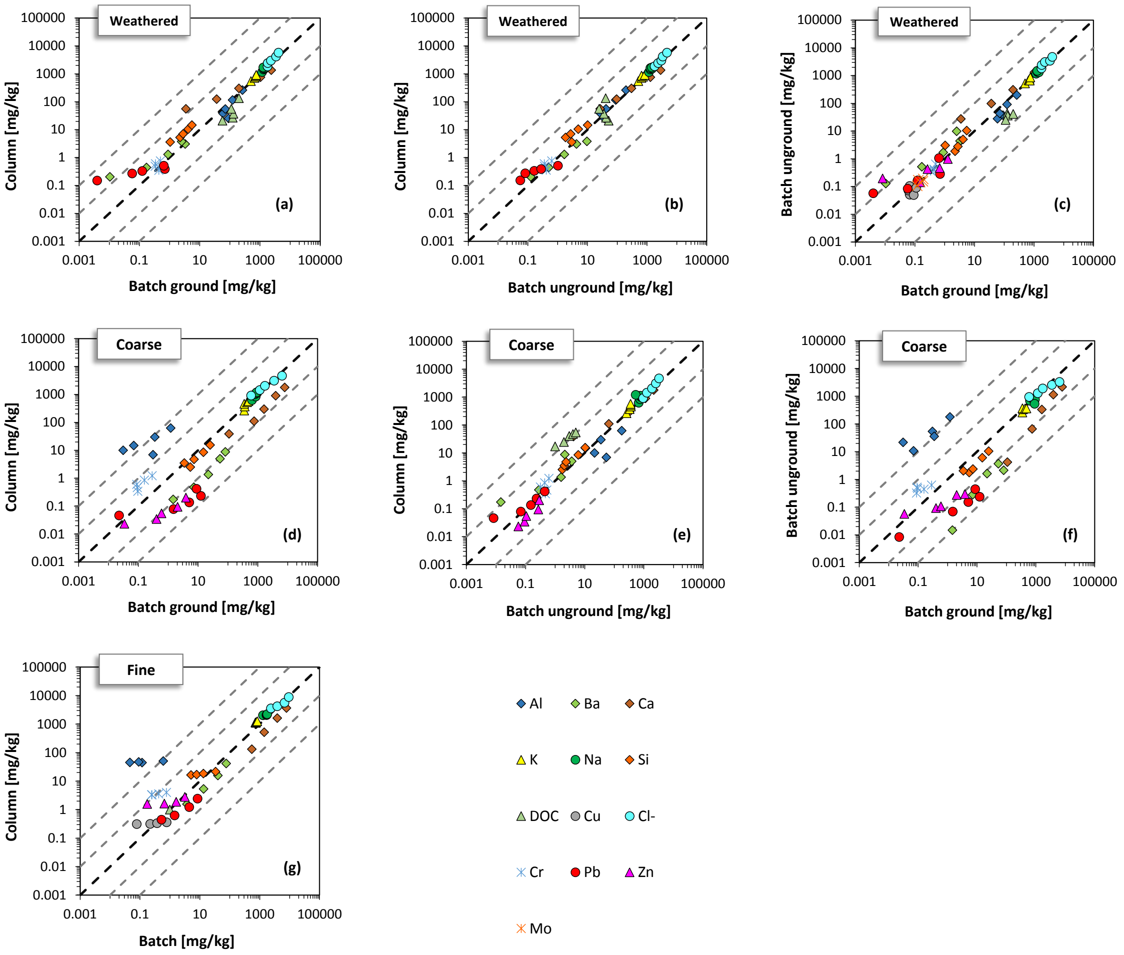


Fig. A.3 Correlations between column and batch tests conducted on unground and ground material for the weathered sample (a, b and c), the coarse fraction (d, e and f) and between column and batch tests for the fine fraction (g) of the RDF-I BA. The diagonal black line denotes a linear correlation ratio of 1:1.

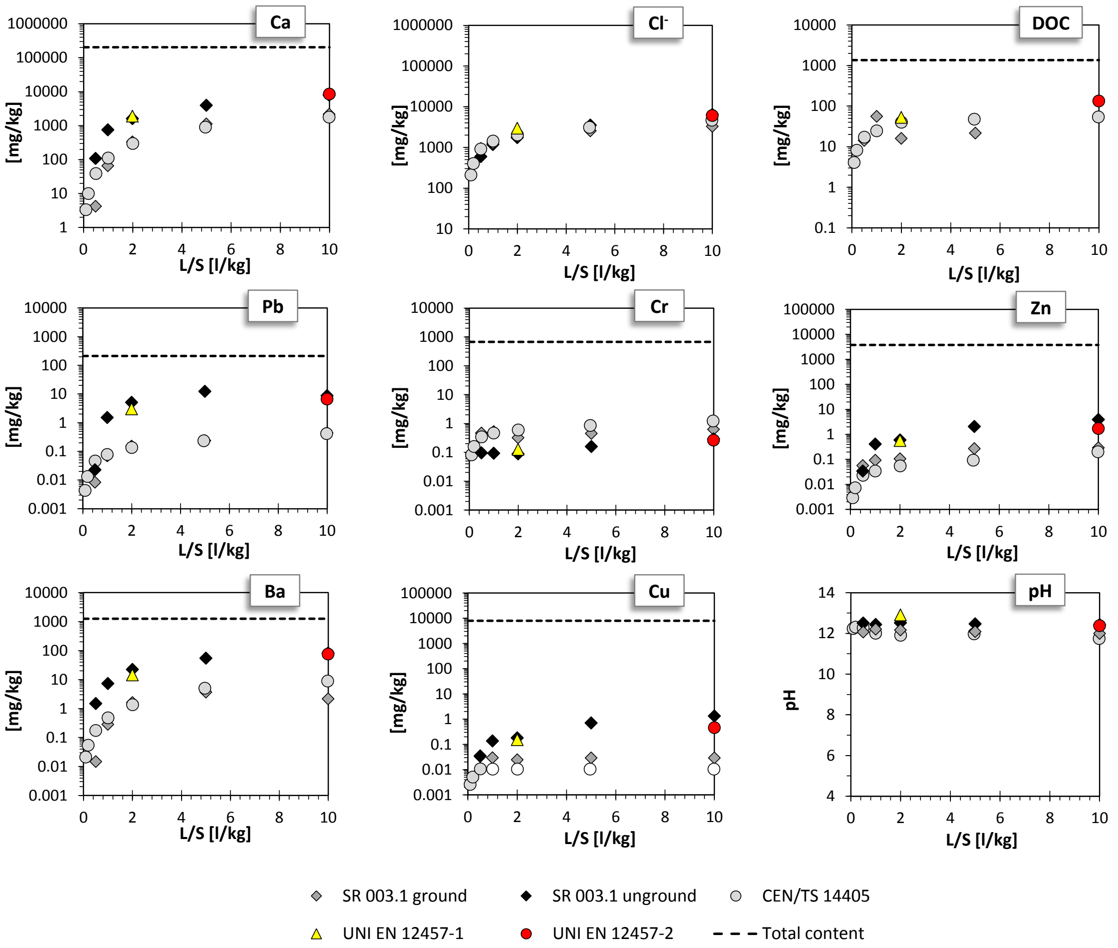


Fig. A.4 Release of Ca, Cl^-, DOC, Pb, Cr, Zn, Ba and Cu (mg/kg dry wt.), and pH as a function of the applied L/S ratio (l/kg) for the coarse fraction of RDF-I BA.

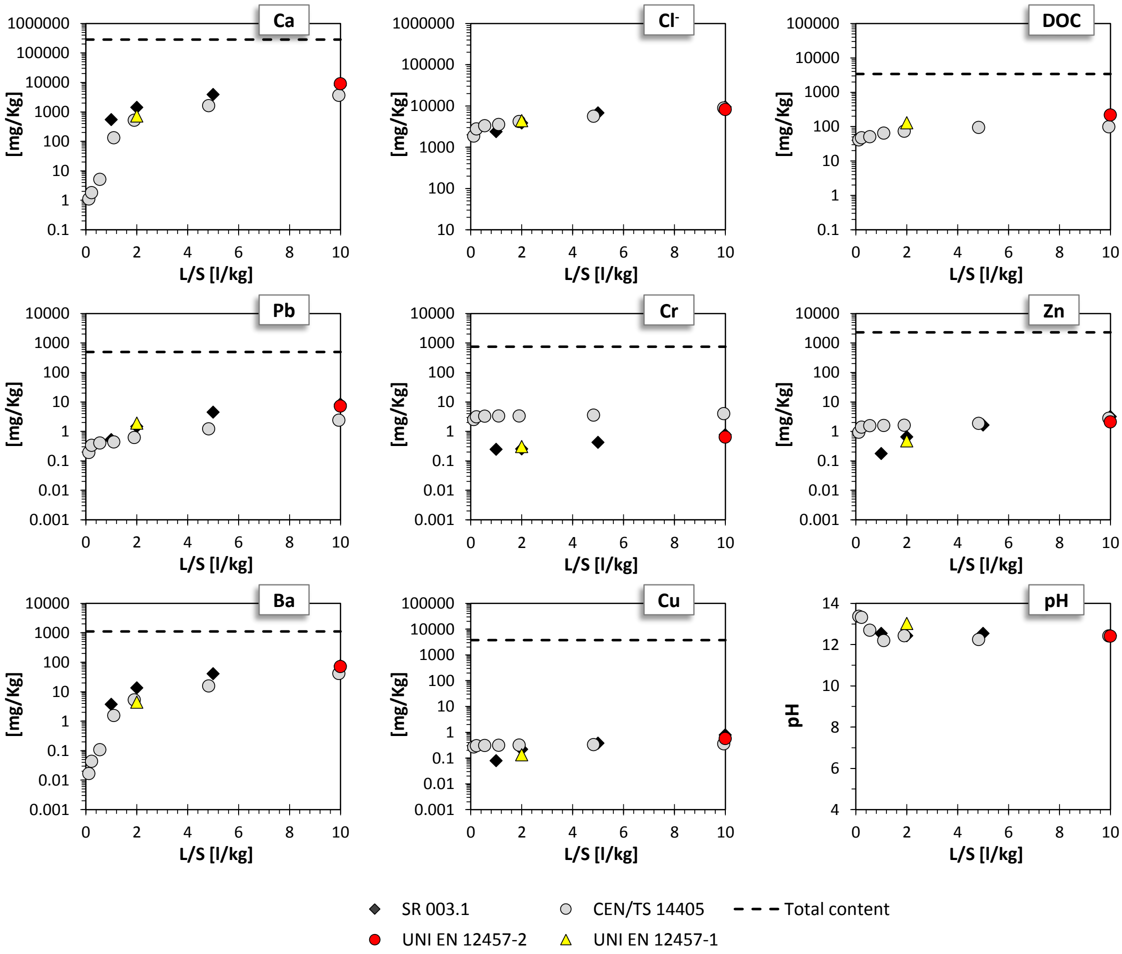


Fig. A.5 Release of Ca, Cl^-, DOC, Pb, Cr, Zn, Ba and Cu (mg/kg dry wt.), and pH as a function of the applied L/S ratio (l/kg) for the fine fraction of RDF-I BA.

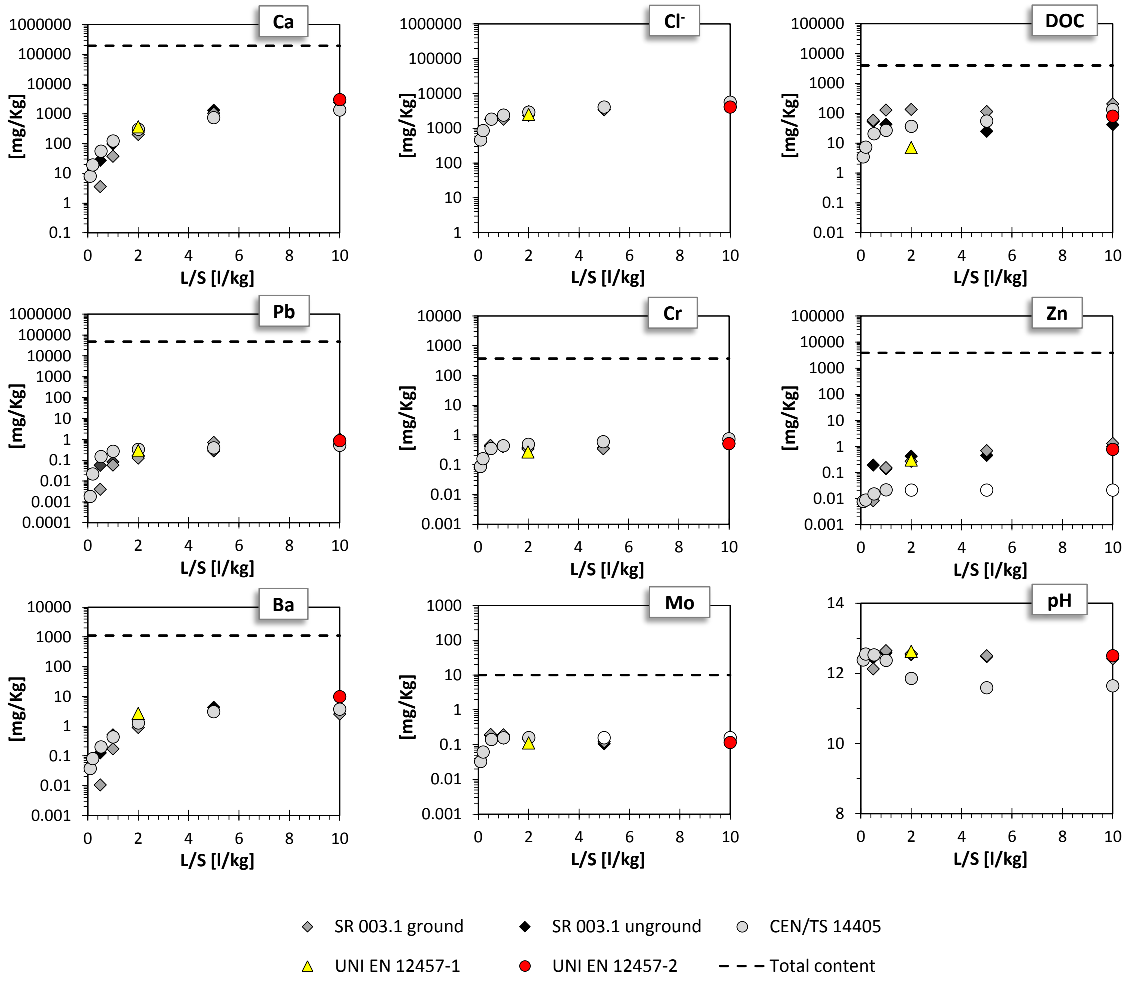


Fig. A.6 Release of Ca, Cl^-, DOC, Pb, Cr, Zn, Ba and Cu (mg/kg dry wt.), and pH as a function of the applied L/S ratio (l/kg) for the weathered sample of RDF-I BA. For illustration purposes only, the values lower than the limit of quantification (LOQ) were also reported (white dots).

ANNEX B

SUPPLEMENTARY INFORMATION TO SECTION 2

Table B.1 Overview of the LCIA methods employed.

Impact category	**Characterization method**	**Unit**	**Acronym**
Global warming	IPCC 2007, GWP 100a	kg CO_2 Eq	GWP
Ozone depletion	EDIP, ODP 100a	kg CFC-11-Eq	OD
Photochemical oxidant formation	ReCiPe Midpoint, POFP	kg NMVOC	POF
Terrestrial acidification	ILCD 2011	AE	TA
Eutrophication in terrestrial environments	ILCD 2011	AE	EP
Eutrophication in freshwater environments	ReCiPe Midpoint, FEP	kg P-Eq	EF
Eutrophication in marine environments	ReCiPe Midpoint, MEP	kg N-Eq	EM
Abiotic depletion of fossil resources	CML 2012	MJ	AD Fossil
Abiotic depletion of mineral resources	CML 2013	kg Sb-Eq	AD Mineral
Human toxicity, carcinogenic effects	USEtox	CTUh	HTc
Human toxicity, non-carcinogenic effects	USEtox	CTUh	HTnc
Freshwater ecotoxicity	USEtox	CTUe	ET

Table B.2 Total emissions for the landfill scenario related to leaching (results expressed in terms of kg of contaminant released per Mg of dry BA).

	RDF-I BA			**RDF-G BA**		
	Cumulative L/S = 2 l/kg			Cumulative L/S = 1.7 l/kg		
	Total Emissions	**From WWTP**	**From Uncollected Leachate**	**Total Emissions**	**From WWTP**	**From Uncollected Leachate**
As	9.45E-07	2.99E-07	6.46E-07	6.36E-07	3.47E-07	2.89E-07
Ba	6.55E-03	9.23E-04	5.63E-03	1.23E-05	3.13E-06	9.21E-06
Cr*	2.52E-05	1.28E-05	1.23E-05	<LOQ**	<LOQ	<LOQ
Cu	1.57E-05	6.46E-06	9.22E-06	3.67E-05	1.83E-05	1.84E-05
Mo	2.57E-06	9.65E-07	1.61E-06	<LOQ	<LOQ	<LOQ
Pb	9.88E-04	1.47E-04	8.41E-04	<LOQ	<LOQ	<LOQ
Sb	1.07E-04	1.89E-05	8.84E-05	2.36E-06	4.68E-07	1.89E-06
Se	8.90E-06	1.35E-06	7.55E-06	<LOQ	<LOQ	<LOQ
Zn	1.04E-04	2.45E-05	7.95E-05	<LOQ	<LOQ	<LOQ

*Cr assumed as Cr(VI)

**Limit of quantification (LOQ) in mg/l: Cr (0.0065), Mo (0.004), Pb (0.025), Se (0.0005), Zn (0.005)

Table B.3 Removal efficiencies of contaminants in the WWTP.

Compound	**Removal in WWTP [%]**
As	70
Ba	85
Cl^-	85
Cr(VI)	40
Cu	50
DOC	70
Mo	85
Pb	85
Se	85
Sb	85
Zn	70

Table B.4 Materials and energy used for the construction of an excavated-type landfill of 1E^{+06} Mg of humid bottom ash.

	Energy		Materials					
	Diesel consumptionn at site	Diesel consumption to site	Concrete	Minerals (clay, gravel and soil)	Metals (steel, Al, reinf. Steel and Cu)	Plastic (HDPE, PP, PVC)	Asphalt	Cables
Description	[l]	[l]	[t]	[t]	[t]	[t]	[m^2]	[m]
Total amount of materials	**193974**	**142761**	**811**	**390098**	**126**	**301**	**2904**	**3835**
Preparing earthwork								
Clear cutting of bushes, trees etc.	4880	0	0	0	0	0	0	0
Topsoil stripping and transport to deposit at site	4188	0	0	0	0	0	0	0
Soil for top cover, stripping and transport to deposit at site	111187	0	0	0	0	0	0	0
Membrane system								
Geological barrier (clay), delivered and built into the membrane system	16977	47812	0	106250	0	0	0	0
Plastic membrane, HDPE, t = 1.5 mm, delivered and built into the membrane system	0	59	0	0	0	79	0	0
Drainage gravel, 0-4 mm, t = 0.5 m, delivered and built into the leachate system	1388	23906	0	53125	0	0	0	0
Leachate system								
Drainage pipes, ф 110 HDPE Pn 10, delivered and built into the leachate system	20	14	0	0	0	18	0	0
Stone fascines, 4-8 mm, delivered and built into the leachate system	157	1279	0	2854	0	0	0	0
Concrete plate for protection at outlet	0	6	8	0	0.4	0	0	0
Geo-textile munder stone fascines, t = 1.5 mm, HDPE	0	3	0	0	0	4	0	0
Collection and inspection wells								
Concrete wells, h = 2.5 m, delivered and built	0	315	201	0	10	0	0	0
Pipes for leachate transport and wells								
Pipes ф 250 mm HDPE, Pn 10, transport pipes, delivered and built into the leachate system	1476	14	0	0	0	20	0	
Wells for cleaning transport pipes, ф 315 mm HDPE, delivered and built into the leachate system	0	0	0	0	0	0.51	0	0
Pumping station								
Concrete wells/structure, delivered and built into the leachate system	0	28	33	0	2	0	0	0
Pipe work, fitting and values	0	0	0	0	0	0.018	0	0
Pumps	0	0.20	0	0	0.11	0	0	0
Electrical installations (breaker panel, SCDA-system)	0	0	0	0	0.01	0	0	16
Various stairs and other metal parts	0	0	0	0	0.002	0	0	0
Leachate tank								
Concrete tank, ф 30 m, delivered and installed	0	649	413	0	20	0	0	0
Electrical installations (SCDA-system)	0	0	0	0	0.03	0	0	20
Surface water systems								
Excavating intercepting ditches, d = 1.0 m	166	0	0	0	0	0	0	0
Collection reservior								
Fence and gates								
Fence h = 2.2 m, delivered and installed	0	75	0	0	49	0	0	0
Gates, 2 x 3 m, delivered and installed	0	10	0	0	1	0	0	0
Monitoring wells								
Establishment of 6 monitoring wells, d = 15 m	0	500	10	0	40	180	0	0
Reception Area								
Weighbridges, delivered and installed	0	150	100	0	0.41	0	0	0
Office building [200 m^2]								
Garage building , Truck wash building [300 m^2]								
Access road - asphalt, b= 6m	0	0	0	0	0	0	2904	0
Interim roads - gravel, b = 6m	6500	3950	0	8800	0	0	0	0
Lighting	0	73	45	0	3	0	0	0
Power supply and data cables	0	1	0	0	0	0	0	3800
Top cover								
Planing of waste surface	3351	0	0	0	0	0	0	0
Compacted Clay t = 1m, delivered and installed	14617	41166	0	91480	0	0	0	0
Gravel layer t = 0.5 m, delivered and installed	5585	22750	0	50555	0	0	0	0
Soil cover (t = 0.8 m) built in from deposit at site	18786	0	0	65480	0	0	0	0
Top soil (t = 0.2 m) built in from deposit at site	4696	0	0	11555	0	0	0	0

Table B.5 Aggregated quantified amounts of materials used per Mg of humid bottom ash (FU) landfilled and material processes used in modeling of the environmental profile of the capital goods. Geographical area: (E): Europe; (S): Switzerland; (I): Italy. Eco: Ecoinvent; EASETE: EASETECH.

Material	**Amount**	**Unit**	**Process**	**Reference**
Aluminium	3.91E-11	kg/FU	Aluminium production, primary (E)	Eco. v.3.
Clay	1.98E-04	kg/FU	Clay pit operation (S)	Eco. v.3.
Concrete	3.41E-04	m^3/FU	Concrete production normal (S)	Eco. v.3.
Copper	1.20E-11	kg/FU	Copper production, primary (E)	Eco. v.3.
Gravel	1.15E-04	kg/FU	Gravel and Sand quarry operation (S)	Eco. v.3.
HDPE (High density polyethylene)	1.84E-07	kg/FU	Polyethylene production, high density (E)	Eco. v.3.
PP (Polypropylene)	2.74E-11	kg/FU	Polypropylene production (E)	Eco. v.3.
PVC (Polyvinylchloride)	1.47E-08	kg/FU	Polyvinylchloride (E)	Eco. v.2.
Reinforcement steel (Cast Iron)	3.54E-08	kg/FU	Cast iron (E)	Eco. v.2.
Roads	2.90E-02	m^2*year/FU	Road construction, company, internal (S)	Eco. v.3.
Steel	9.02E-08	kg/FU	Steel (E)	Eco. v.2.
Cables				
Copper	1.61E-04	kg/FU	Copper production, primary (E)	Eco. v.3.
PVC	1.80E-04	kg/FU	Polyvinylchloride (E)	Eco. v.2.
Limestone	2.24E-04	kg/FU	Limestone milled and packed (S)	Eco. v.2.
Electricity	4.40E-04	kWh/FU	Electricity production, natural gas (I)	Eco. v.3.
Diesel consumption				
Diesel consumption *at site*	0.1940	l diesel/FU	Road, Long haul truck, Euro3, 25t	EASETE.
Diesel consumption *to the site*	0.1195	kg diesel/FU	Operation, lorry > 32t, EUR 4	Eco. v.2.
Buildings				
Office building [200 m^2]	2.00E-04	m^2/FU	Building, hall steel construction (S)	Eco. v.3.
Garage building, truck wash building [1000 m^2]	1.00E-03	m^3/FU	Building, construction, multy-storey (E)	Eco. v.3.

Table B.6 Total emissions for the road scenario related to leaching (results expressed in terms of kg of contaminant released per Mg of dry BA).

	RDF-I BA	**RDF-G BA**
	L/S = 16.3 l/kg	L/S = 13 l/kg
As	1.93E-05	1.38E-06
Ba	4.94E-02	4.72E-05
Cr*	1.08E-04	<LOQ**
Cu	1.16E-04	1.09E-04
Mo	8.04E-06	<LOQ
Pb	1.27E-02	<LOQ
Sb	1.34E-03	2.38E-05
Se	9.47E-05	<LOQ
Zn	2.01E-03	<LOQ

*Cr assumed as Cr(VI)

**Limit of quantification (LOQ) in mg/l: Cr (0.0065), Mo (0.004), Pb (0.025), Se (0.0005), Zn (0.005)

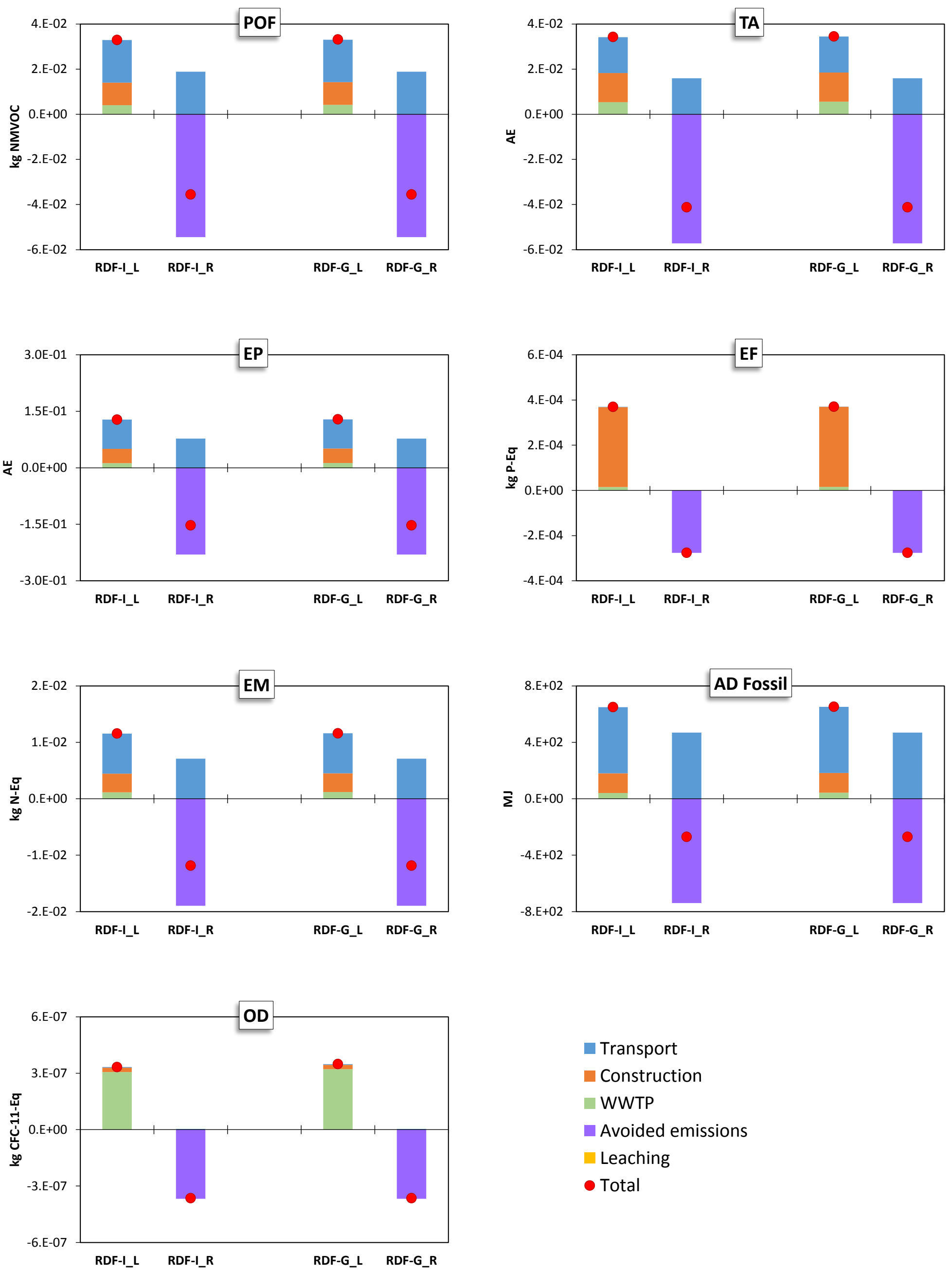


Fig. B.1 Characterized potential environmental impacts for the baseline scenarios obtained for photochemical oxidant formation (POF), terrestrial acidification (TA), eutrophication in terrestrial environments (EP), eutrophication in freshwater environments (EF), eutrophication in marine environments (EM), abiotic depletion of fossil resources (AD Fossil), ozone depletion (OD). RDF-I: Refuse Derived Fuel incineration bottom ash; RDF-G: Refuse Derived Fuel gasification bottom ash; L: landfill; R: road.

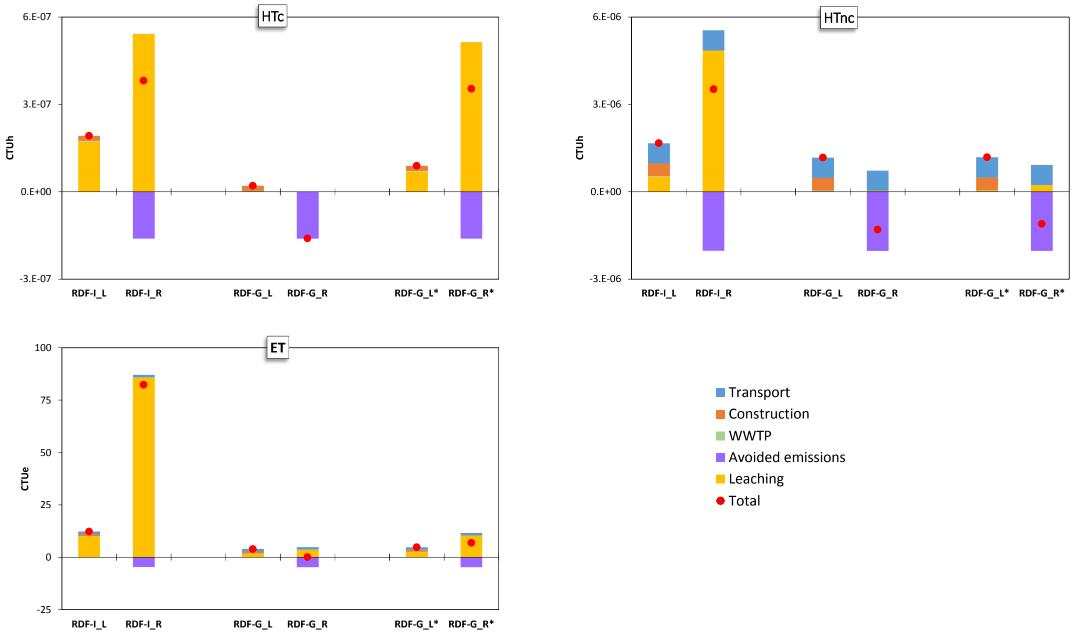


Fig. B.2 Comparison of the total characterized toxicity-related impacts of the baseline scenarios with the results obtained for the RDF gasification bottom ash considering quantification limit values (RDF-G_L* and RDF-G_R*) for the calculation of the release of contaminants.

Table B.7 Total emissions related to leaching obtained from the batch tests and used for the sensitivity analysis (results expressed in terms of kg of contaminant released per Mg of dry BA).

	RDF-I BA		**RDF-G BA**	
	Landfill	Road	Landfill	Road
	L/S =2 l/kg	L/S =10 l/kg	L/S =2 l/kg	L/S =10 l/kg
	Batch Test	Batch Test	Batch Test	Batch Test
As	<LOQ**	<LOQ	4.69E-07	<LOQ
Ba	5.47E-03	7.52E-02	8.49E-06	1.08E-04
Cr*	7.39E-05	3.53E-04	<LOQ**	<LOQ
Cu	9.37E-05	5.07E-04	5.33E-04	1.19E-03
Mo	1.34E-06	1.23E-04	<LOQ	<LOQ
Pb	6.31E-04	6.04E-03	<LOQ	<LOQ
Sb	1.24E-06	2.60E-05	2.02E-06	6.39E-06
Se	<LOQ	<LOQ	<LOQ	<LOQ
Zn	2.94E-04	2.62E-03	<LOQ	<LOQ

*Cr assumed as Cr(VI)
**Limit of quantification (LOQ) in mg/l: As (0.0008), Cr (0.003), Mo (0.01), Pb (0.02), Se (0.07), Zn (0.025)

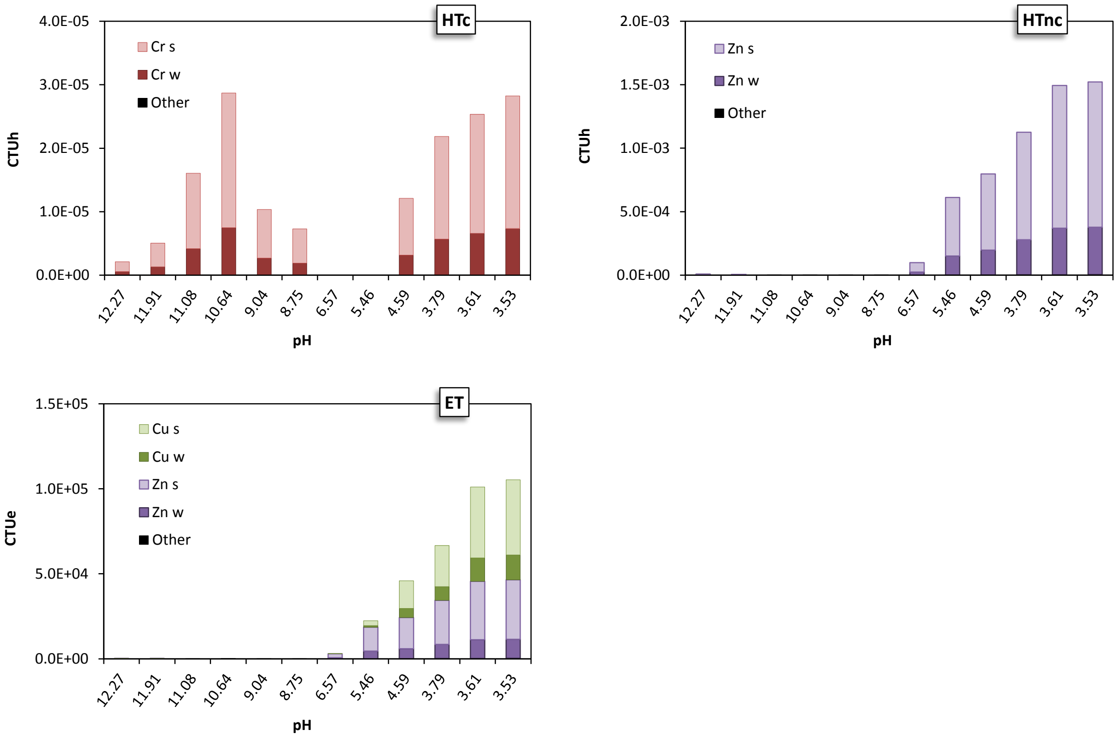


Figure B.3 Characterized potential toxicity-related impacts related to leaching from incineration bottom ash as a function of pH. s: soil industrial; w: surface water.

Table B.8 Total environmental impacts obtained from the sensitivity analysis performed for the incineration bottom ash. (-) Best case scenario; (+) Worst case scenario.

	Landfill Scenario RDF-I BA			**Road Scenario RDF-I BA**		
	HTc [CTUh]	**HTnc [CTUh]**	**ET [CTUe]**	**HTc [CTUh]**	**HTnc [CTUh]**	**ET [CTUe]**
Baseline	1.92E-07	1.67E-06	1.23E+01	3.81E-07	3.52E-06	8.24E+01
CD (-/+)	1.84E-07/2.37E-07	1.62E-06/1.93E-06	1.15E+01/1.7E+01	3.11E-07/7.77E-07	2.95E-06/6.74E-06	7.2E+01/1.41E+02
i (-/+)	1.3E-07/1.96E-07	1.33E-06/1.69E-06	6.31E+00/1.27E+01	2.68E-07/3.85E-07	1.77E-06/5.08E-06	5.01E+01/1.13E+02
ρ (-)	1.75E-07	1.59E-06	1.09E+01	3.77E-07	3.16E-06	7.54E+01
TD (-/+)	1.92E-07/1.92E-07	1.47E-06/1.97E-06	1.19E+01/1.28E+01	3.81E-07/3.81E-07	3.32E-06/3.82E-06	8.2E+01/8.29E+01
H (-/+)	1.66E-07/2.11E-07	1.54E-06/1.77E-06	9.97+00/1.4E+01	/	/	/

Table B.9 Total environmental impacts obtained from the sensitivity analysis performed for the gasification bottom ash. (-) Best case scenario; (+) Worst case scenario.

	Landfill Scenario RDF-G BA			**Road Scenario RDF-G BA**		
	HTc [CTUh]	**HTnc [CTUh]**	**ET [CTUe]**	**HTc [CTUh]**	**HTnc [CTUh]**	**ET [CTUe]**
Baseline	2.03E-08	1.17E-06	3.93E+00	-1.6E-07	-1.3E-06	7.4E-02
CD (-/+)	2.03E-08/2.03E-08	1.17E-06/1.18E-06	3.85E+00/4.34E+00	-1.6E-07/-1.6E-07	-1.3E-06/-1.29E-06	-3.29E-01/2.36E+00
i (-/+)	1.9E-08/2.04E-08	1.16E-06/1.17E-06	3.31E+00/3.96E+00	-1.6E-07/-1.6E-07	-1.3E-06/-1.3E-06	-6.55E-01/2.05E-01
ρ (-)	1.97E-08	1.17E-06	3.59E+00	-1.6E-07	-1.3E-06	7.3E-02
TD (-/+)	2.02E-08/2.03E-08	9.73E-07/1.47E-06	3.58E+00/4.45E+00	-1.6E-07/-1.6E-07	-1.5E-06/-1E-06	-2.7E-01/5.92E-01
H (-/+)	1.97E-08/2.07E-08	1.17E-06/1.18E-06	3.37E+00/4.05E+00	/	/	/

PUBLICATIONS WITHIN THE PHD RESEARCH

Scientific journals

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

Di Gianfilippo, M., Costa, G., Verginelli, I., Gavasci, R., Lombardi, F., 2015. Analysis and interpretation of the leaching behaviour of waste thermal treatment bottom ash by batch and column tests. *Submitted for publication to Waste Management.*

Conference Proceedings

Di Gianfilippo, M., Costa, G., Lombardi, F., Gavasci, R., 2013. Leaching behaviour of waste thermal treatment bottom ash as a function of material properties and environmental conditions. In Proceedings: Sardinia 2013. 14th International Waste Management and Landfill Symposium, 30 September-4 October 2013, S. Margherita di Pula (CA), Sardinia, Italy.

Di Gianfilippo, M., Costa, G., Lombardi, F., Astrup, T., 2014. The use of leaching data in LCA: landfilling of Hospital Waste incineration bottom ash. In Proceedings of the 8th Conference of the Italian network of LCA (VIII Convegno della Rete Italiana di LCA), 19-20 June 2014, Florence, Italy.

Di Gianfilippo, M., Costa, G., Pantini, S., Lombardi, F., Allegrini, E., Astrup, F.T., 2014. Life cycle assessment of landfilling of two different types of RDF thermal treatment bottom ash. In Proceedings: Venice 2014. 5th International Symposium on Energy from Biomass and Waste, 17-20 November 2014, San Servolo, Venice, Italy.

OTHER PUBLICATIONS

Scientific journals

Baciocchi, R., Costa, G., Di Gianfilippo, M., Polettini, A., Pomi, R., Stramazzo, A., 2015. Thin-film versus slurry-phase carbonation of steel slag: CO_2 uptake and effects on mineralogy. *Journal of Hazardous Materials*, 283, 302-313.

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Baciocchi, R., Costa, G., Di Gianfilippo, M., Polettini, A., Pomi, R., Stramazzo A., 2012. Evaluation of the CO_2 storage capacity of different types of steel slag subjected to accelerated carbonation. In Proceedings: Crete 2012. 3rd International Conference on Industrial and Hazardous waste management, 12-14 September 2012, Chania, Crete, Greece.

Baciocchi, R., Costa, G., Di Gianfilippo, M., Polettini, A., Pomi, R., Stramazzo A., Zingaretti, D., 2013. Influence of CO_2 partial pressure on direct accelerated carbonation of steel slag. In Proceedings: ACEME 2013. 4th International Conference on Accelerated Carbonation for Environmental and Materials Engineering, 10-12 April 2013, Leuven, Belgium.

Costa, G., Di Gianfilippo, M., Polettini, A., Pomi, R., Stramazzo A., 2013. Slurry-phase carbonation of different types of steel slag: CO_2 uptake and effects on mineralogy. In Proceedings: ACEME 2013. 4th International Conference on Accelerated Carbonation for Environmental and Materials Engineering, 10-12 April 2013, Leuven, Belgium.