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The recovery of industrial and urban waste for the valorisation of organic and mineral content in the fertiliser sector, adopting a circular economy model

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"*Il recupero dei rifiuti industriali e urbani per la valorizzazione del contenuto organico e minerale nel settore di fertilizzanti seguendo il modello di economia circolare*"

La ricerca si propone di indagare le potenzialità del riuso di rifiuti industriali di diversa natura con particolare riferimento a quelli derivanti da processi di ossidazione termica ai fini di una valorizzazione nell'ambito della produzione di fertilizzanti in un'ottica di economia circolare e sostenibilità ambientale.

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Abstract-English

Conventional fertilisers are primarily synthesised through industrial chemical processes that rely on non-renewable raw materials, such as natural gas and extracted minerals. Their extensive use has raised concerns regarding dependency on imported mineral raw materials from third countries and the associated environmental impacts arising from extraction, production, and transportation. In response to these challenges, the European Union (EU), in line with "*Circular Economy Principles*", has prioritised the transition towards sustainable fertilisers derived from secondary raw materials. Recent regulatory frameworks facilitate the incorporation of recycled components into fertiliser production, fostering the adoption of more sustainable alternatives. "*Circular Fertilisers*" offer numerous agronomic and environmental benefits, including improved soil structure, enhanced nutrient retention, and a reduced carbon footprint compared to conventional fertilisers. A particularly promising area of research is the valorisation of cogeneration ashes generated from biomass incineration for electricity production. These ashes represent a potentially valuable source of essential plant nutrients. Moreover, their high content of basic cations, in the form of oxides, hydroxides, and carbonates, enhances their effectiveness as soil amendments. With global biomass cogeneration ash production estimated at approximately 480 million tonnes per year, the development of sustainable strategies for their recovery and utilisation is of critical importance.

This thesis investigated the mineralogical and chemical properties of cogeneration ashes to evaluate their potential for nutrient recovery and agricultural application. The study was framed within the principles of the Circular Economy, aiming to reduce landfill disposal, minimise dependence on non-renewable mineral resources, and promote sustainable resource management practices. The research was conducted in collaboration with TIMAC AGRO Italia S.p.A., an Italian company of the French Roullier Group, specialising in plant nutrition and the production of mineral and organo-mineral fertiliser formulations.

Through a feasibility-oriented investigation, ashes derived from biomass combustion in several cogeneration plants were systematically characterised, considering the type of biomass used as fuel and the combustion technology employed. The study evaluated the ashes in terms of agronomic potential, physico-chemical safety, and source-plant characteristics, which collectively influence their functional performance for potential reuse in agriculture. Furthermore, the analysis aimed to identify the most promising ash types for subsequent industrial-scale trials, designed to assess their efficacy and behaviour as fertilisers.

In particular, eight biomass ash samples—four fly ashes and four bottom ashes—were collected from cogeneration plants across Italy and characterised through a multi-methodological approach. Chemical, mineralogical, and microstructural analyses, combined with physico-chemical treatments, were employed to determine the bioavailability of key nutrients, detect potentially hazardous substances, and evaluate their feasibility as secondary raw materials for sustainable fertiliser production. This comprehensive characterisation provides key insights into optimal treatment methods to ensure product safety, improve agronomic efficiency, enhance recycling strategies, and support practical implementation in the fertiliser industry.

The findings reveal significant physical and chemical variability in both fly and bottom ashes, influenced by key factors such as biomass type (*e.g.*, virgin wood *vs.* treated wood pellets), combustion temperature, and particle size distribution. Chemical analyses confirm that all samples contain substantial concentrations of plant-essential nutrients, particularly K_2O, CaO, and MgO. Furthermore, leaching tests and mineralogical analyses identify water-soluble elements that may contribute to plant nutrient availability. Crucially, the applied physico-chemical treatments effectively reduce heavy metal concentrations to levels compliant with the European Fertilising Products Regulation (EU) 2019/1009, which sets the qualitative standards for the commercialisation of fertiliser products.

Finally, the detailed characterisation enabled the selection of the most suitable ash sample for further industrial-scale experimentation. This involved an initial safety treatment to further minimise heavy metal content, followed by the integration of the ash with conventional and compatible mineral raw materials. The resulting formulation yielded a fertiliser product enriched with nutrients recovered from the ash, demonstrating its potential application in the fertiliser industry within a circular economy framework.

Overall, the results of this study, obtained through a comprehensive quantitative mineralogical characterisation, make a substantial contribution to the evaluation of the agronomic potential of ashes and to the development of sustainable waste-derived fertilisers. Such fertilisers, compliant with environmental regulations, have the potential to optimise resource efficiency and promote the long-term sustainability of the agricultural sector.

Abstract-Italiano

I fertilizzanti convenzionali sono prevalentemente ottenuti attraverso processi chimici industriali che impiegano materie prime non rinnovabili, quali gas naturale e minerali estratti. Il loro ampio utilizzo ha sollevato preoccupazioni in merito alla dipendenza dalle importazioni delle materie prime minerali da paesi terzi e agli impatti ambientali derivanti dalle fasi di estrazione, produzione e trasporto. Per far fronte a queste criticità, l'Unione Europea (UE), in linea con i *Principi dell'Economia Circolare*, ha posto tra le sue priorità la transizione verso i fertilizzanti sostenibili ottenuti da materie prime secondarie. I recenti quadri normativi favoriscono l'integrazione di materiali riciclati nella produzione di fertilizzanti, incentivando l'adozione di alternative più sostenibili. I "*Fertilizzanti Circolari*" offrono molteplici vantaggi agronomici e ambientali, tra cui il miglioramento della struttura del suolo, una maggiore ritenzione dei nutrienti e una significativa riduzione dell'impronta di carbonio rispetto ai fertilizzanti tradizionali. Un ambito di ricerca particolarmente promettente riguarda la valorizzazione delle ceneri di cogenerazione derivanti dall'incenerimento della biomassa per la produzione di elettricità. Queste ceneri costituiscono una fonte potenzialmente preziosa di nutrienti essenziali per le piante. Inoltre, il loro elevato contenuto di cationi basici, presenti sotto forma di ossidi, idrossidi e carbonati, ne migliora l'efficacia come ammendanti del suolo. Con una produzione globale stimata in circa 480 milioni di tonnellate all'anno, lo sviluppo di strategie sostenibili per il recupero e l'utilizzo di tali materiali risulta di cruciale importanza.

Questa tesi ha analizzato le proprietà mineralogiche e chimiche delle ceneri di cogenerazione al fine di valutarne il potenziale per il recupero dei nutrienti e la loro applicazione in ambito agricolo. Lo studio si inserisce nel contesto dei principi dell'Economia Circolare, con l'obiettivo di ridurre lo smaltimento in discarica, minimizzare la dipendenza dalle risorse minerali non rinnovabili e promuovere pratiche di gestione sostenibile delle risorse.

La ricerca è stata condotta in collaborazione con TIMAC AGRO Italia S.p.A., filiale italiana del Gruppo francese Roullier, specializzata in nutrizione vegetale e nella produzione di formulazioni di fertilizzanti minerali e organo minerali.

Attraverso un'indagine orientata alla fattibilità, le ceneri derivanti dalla combustione di biomassa in diversi impianti di cogenerazione sono state caratterizzate sistematicamente, tenendo conto sia del tipo di biomassa impiegata come combustibile sia della tecnologia di combustione adottata. Lo studio ha valutato le ceneri in termini di potenziale agronomico, sicurezza fisico-chimica e caratteristiche dell'impianto di origine, fattori che determinano congiuntamente le loro prestazioni funzionali per un

possibile riutilizzo in agricoltura. L'analisi ha inoltre mirato a identificare i tipi di cenere più promettenti per successivi test su scala industriale, volti a verificarne l'efficacia e il comportamento come fertilizzanti. Nello specifico, otto campioni di ceneri di biomassa—quattro ceneri volanti e quattro ceneri pesanti—provenienti da impianti di cogenerazione italiani sono stati sottoposti a una caratterizzazione multi-metodologica. Sono state condotte analisi chimiche, mineralogiche e microstrutturali, integrate con trattamenti fisico-chimici, per determinare la biodisponibilità dei nutrienti, individuare eventuali sostanze nocive e valutare la loro idoneità come materie prime secondarie per la produzione di fertilizzanti sostenibili. Questa caratterizzazione approfondita ha permesso di identificare i trattamenti ottimali, al fine di garantire la sicurezza, migliorare l'efficienza agronomica, ottimizzare le strategie di riciclo e supportare l'implementazione pratica delle ceneri di biomassa nel settore dei fertilizzanti.

I risultati hanno evidenziato una notevole variabilità fisica e chimica tra le ceneri volanti e le ceneri pesanti, influenzata da fattori chiave quali la tipologia di biomassa impiegata (es. legno vergine *vs.* legno trattato), la temperatura di combustione e la granulometria. Le analisi chimiche hanno confermato la presenza di concentrazioni elevate di nutrienti essenziali per le piante, in particolare K_2O, CaO e MgO. Inoltre, i test di lisciviazione e le analisi mineralogiche hanno permesso di identificare le fasi minerali solubili in acqua, evidenziando il contenuto di elementi potenzialmente biodisponibili per le piante. Di particolare rilevanza è l'aspetto che i trattamenti fisico-chimici adottati hanno consentito di ridurre efficacemente le concentrazioni di metalli pesanti al di sotto delle soglie previste dal Regolamento Europeo sui Prodotti Fertilizzanti (UE) 2019/1009, che stabilisce gli standard qualitativi per la commercializzazione delle formulazioni fertilizzanti.

Infine, la caratterizzazione dettagliata ha permesso di selezionare il campione di cenere più idoneo per una sperimentazione su scala industriale. Questo processo ha incluso un trattamento di sicurezza iniziale volto a ridurre ulteriormente il contenuto di metalli pesanti, seguito dall'integrazione della cenere con materie prime minerali convenzionali e compatibili. Il risultato è stato la formulazione di un fertilizzante innovativo arricchito con nutrienti recuperati dalla cenere, dimostrando la fattibilità della sua applicazione nel settore fertilizzanti all'interno di un contesto di economica circolare.

Complessivamente, i risultati di questo studio, ottenuti tramite una caratterizzazione mineralogica quantitativa dettagliata, forniscono un contributo significativo alla valutazione del potenziale agronomico delle ceneri e allo sviluppo di fertilizzanti sostenibili derivati da scarti, conformi alle normative ambientali, in grado di ottimizzare l'uso delle risorse e sostenere la sostenibilità a lungo termine del settore agricolo.

Section 1. Introduction

In the contemporary global landscape, characterised by increasing pressure on natural resources and heightened environmental awareness, the development of sustainable practices is an imperative across all productive sectors. Agriculture relies heavily on mineral fertilisers to maintain productivity and ensure global food security. However, the extraction of commercially valuable minerals, such as phosphorite – classified by the European Union as a Critical Raw Material (CRM) – entails substantial social, environmental, and economic costs. In response to this issue, there is a growing interest in promoting whenever possible the use of secondary raw materials and developing processes to transform waste into valuable products, thereby addressing both resource depletion and environmental concerns.

The application of "*Circular Fertilisers*" (*i.e*. products from secondary raw materials) in agriculture provides multiple benefits, as their use improves soil structure, nutrient retention, and significantly reduces the carbon footprint compared to the production of conventional fertilisers (Lam et al., 2020; El Chami et al., 2023; Culas et al., 2025). Over the last decade, various circular fertiliser value chains have emerged as promising alternatives to replace conventional fertilisers. These value chains differ in terms of the secondary raw materials used as inputs (*e.g*., wastewater, organic waste, manure), the production processes based on nutrient recovery technologies (*e.g*., composting, anaerobic digestion, precipitation, stripping), and the circular fertilisers produced as outputs (*e.g*., compost, struvite, ammonium sulphate, phosphates, etc.) (Paredes et al., 2025).

As part of the European Union's political priorities, the transition from conventional fertilisers towards fertilisers derived from renewable resources, obtained from locally available secondary raw materials, is being promoted in accordance with "*Circular Economy Principles"*. To facilitate the transition towards more sustainable agriculture, Regulation (EU) 2019/1009 on fertilising products, which has been in force since 2022, represents a fundamental pillar. This regulation governs the use of recycled or organic-origin materials in fertiliser production, fostering their placement on the EU market.

All these approaches contribute to aligning the availability of valuable nutrients contained in various secondary raw materials with the need to use circular fertilisers to replace conventional ones, thereby reinforcing the concept of the circular economy and enhancing the sustainability of industrial processes. Some of these value chains are already well-established, and the circular fertiliser market is operational (*e.g*., compost production from organic waste) (Czekała et al., 2020; Toledo et al., 2020). Others, however, remain in the research phase due to low technological maturity, persistently high operational costs or regulatory constraints that limit their introduction in the European market,

as in the case of vivianite (Wilfert et al., 2018; Wu et al., 2019) or struvite (Paredes et al., 2025) precipitation technologies for the recovery of phosphorus from urban wastewater and sludge.

In the context of developing value chains for circular fertilisers, the ashes originating from the biomass combustion inside energy cogeneration plants offer a substantial, albeit insufficiently exploited, opportunity as potential secondary raw material. Often destined to landfill disposal, these ashes are, in fact, rich in nutrients such as K, Ca, Mg and P essential for plant growth and represent a valuable opportunity to reduce the pressure exerted on traditional mineral resources.

Currently, biomass combustion for heat and energy production is steadily increasing, due to the limited availability of fossil fuels and the evidence concerning global warming caused by CO_2 emissions from the combustion of such fuels. Therefore, the management of biomass ashes constitutes an increasingly relevant issue and their utilisation in applications other than landfill disposal represents, consequently, a high priority. The accumulation of waste materials entails significant economic and environmental problems, requiring increased landfill utilisation with associated management costs and negative territorial impacts. Simultaneously, the extraction and intensive consumption of natural mineral resources for fertiliser production are unsustainable in the long term, highlighting the need for innovative solutions aimed at reducing dependence on these materials.

In line with the waste hierarchy of Legislative Decree 152/2006, the reuse or recycling of biomass ashes would be desirable. Nevertheless, the wide variety of fuels used in biomass power plants, including agricultural residues and wood waste, as well as their use in different energy production systems, influence the chemical and mineralogical composition of the ashes and, consequently, the quality and bioavailability of their components.

Under the European Fertilising Products Regulation (EU) 2019/1009, specifically CMC 13 (materials of thermal oxidation or their derivatives), the use of ashes as fertilisers is permitted, subject to compliance with stringent environmental safety and agronomic efficiency criteria. Frequently, the limited recycling of industrial ashes is primarily due to stringent legislative restrictions, concerns regarding their composition, and the costs associated with chemical analyses and quality documentation.

To optimise nutrient recovery from biomass ash, it is imperative to move beyond simplistic elemental chemical analysis and adopt a more comprehensive characterisation approach. An in-depth investigation into mineral speciation, employing advanced mineralogical methodologies, is paramount for the precise identification and quantification of elemental species and their distribution into different mineralogical soluble phases. Specifically, this methodological approach allows the detection of the chemical compounds present in the ashes which is essential for understanding their nutrient availability to plants and their compatibility with the mineral raw materials utilised in the

fertiliser industry, with the aim of partially substituting their usage. Furthermore, such analysis is indispensable for the elucidation of biomass ashes behaviour within biological and environmental systems. The direct application of ashes, albeit seemingly advantageous, exhibits salient limitations, attributed to compositional heterogeneity and the potential presence of inert mineral species and potential contaminants. Consequently, an alternative valorisation strategy is necessitated: the weighted integration of ash into balanced fertiliser formulations, predicated upon precise mineralogical characterisation. This approach facilitates the optimisation of controlled nutrient release and enhances agronomic efficacy.

In this context, this study aimed to conduct a comprehensive characterisation of biomass ashes, encompassing the analysis of chemical composition, mineralogical investigation, morphological and microstructural characteristics. Subsequently, specific treatments were applied to separate the nutrients present in the ashes, exploiting both water solubility and particle size distribution. The analysis was conducted on different samples of fly ashes and bottom ashes from four biomass cogeneration plants located in Italy, with the purpose of evaluating their potential use in mineral fertiliser industry and reduce landfill disposal in line with the objectives of the "*Circular Economy*". The study was conducted in close collaboration with the private company TIMAC AGRO Italia S.p.A., a worldwide leader in the production of fertilisers. The study also included an industrial trial which allowed an evaluation of the practical admixture of ash showing an optimal chemical profile with conventional mineral raw materials, for the development of a fertiliser product, demonstrating the feasibility potential of this practice.

This approach is based on scientific and technological principles aimed at maximising resource efficiency and minimising environmental impacts. Consequently, the knowledge obtained in this study is of fundamental importance for the development of sustainable, eco-responsible and cost-effective management strategies that facilitate the recovery of nutrients from waste materials and mitigate the environmental impact of agricultural and industrial activities.

Furthermore, it contributes to the creation of economic value through the reuse of materials that would otherwise be considered waste. The implementation of this strategy is of crucial importance, as it simultaneously addresses two of the main global challenges: the decrease in dependence on non-renewable mineral resources used in the fertiliser industry and the reduction of waste accumulation.

The research topic is inherently multidisciplinary, integrating methodologies and expertise from geosciences, chemistry, environmental sciences, and agronomy.

The following section will provide a review of the existing literature on the role of mineral fertilisers in plant nutrition, highlighting the main sustainability issues and challenges of modern agriculture that motivated this research.

Section 2. State of art

2.1 Issues and challenges of fertiliser industry

The optimal soil management and the balanced supply of nutrients are essential prerequisites to ensure the growth and development of agricultural crops and forests, as well as the productivity of harvests and the functionality of ecosystems. Currently, the application of fertilisers in agriculture is an essential practice to secure production and food security. These latter, serve the function of providing plants with essential nutrients while simultaneously enhancing soil fertility and crop productivity (Kathpalia & Bhatla, 2018).

Conventional fertilisers are produced through industrial chemical synthesis processes using raw materials such as natural gas and extracted minerals (Lu & Tian, 2017). The application of conventional fertilisers is widespread within the European Union (EU), covering 75 % of agricultural land, and their global use is expected to increase at an estimated annual growth rate of +2 % in the coming years (European Commission 2019). The EU heavily relies on imports for most fertiliser raw materials, sourced from non-renewable mineral reserves in third countries. Therefore, the use of conventional fertilisers is associated with negative environmental impacts related to nutrient extraction methods, production processes, and the significant CO_2 emissions linked to the transportation of fertiliser products from third countries to regions of use (Basosi et al., 2014).

Moreover, the global population has doubled since the 1960s, rising from three to seven billion by 2015, a trend projected to continue, potentially reaching ten billion by 2050 (Alexandratos & Bruinsma, 2012). This rapid expansion necessitates a substantial increase in agricultural production to meet future food and energy demands while simultaneously preserving the planet's ecological and energy resources, adhering to a sustainable agriculture paradigm (Tominc et al., 2023). Simultaneously, recent climate models predict an increasing frequency and duration of drought and heat stress in numerous regions, adversely affecting major crops and consequently threatening food security (Deryng et al., 2014). Therefore, the primary challenges for agriculture are to enhance crop yield within more resource-efficient systems and to stabilise plant development and yield formation under both biotic and abiotic stress conditions (El Chami & Galli, 2020).

Addressing the increasing demand for food has required enhancing agricultural productivity, not only by optimising yield per hectare but also by improving crop quality. Consequently, in recent decades, the use of fertilisers has substantially increased (Hemantaranjan, 2013).

Estimates suggest that due to global population growth and the associated increase in food demand, the availability of these natural resources will progressively decline in the coming decades, eventually proving insufficient (Weinzettel et al., 2013).

In detail, mineral fertilisers supply plants with essential nutrients which are classified into macronutrients, mesonutrients and micronutrients based on their required quantities. Each group are essential for maintaining vital biochemical processes. Macronutrients, required in larger quantities, include phosphorus (P), nitrogen (N), potassium (K). Mesonutrients, whose required amounts may vary depending on the plant species, include calcium (Ca), magnesium (Mg), and sulphur (S). Micronutrients, while needed in smaller amounts, are critical for enzymatic activity and plant structural stability. These include iron (Fe), copper (Cu), zinc (Zn), boron (B), manganese (Mn), molybdenum (Mo), and nickel (Ni) (Davis, 2015; Kathpalia & Bhatla, 2018).

According to Arnon & Stout, (1939): an element is considered essential if (1) its absence leads to abnormal growth, failure to complete the life cycle, or premature plant death; (2) it cannot be replaced by any other element; and (3) it has a direct impact on plant growth or metabolism. While all essential elements are crucial for plant life, their required amounts vary considerably, depending on the plant species and the specific element.

The three main sources of nutrients for plants are air, water, and soil. Elements, such as carbon, oxygen, and hydrogen, are known as structural elements. More precisely, carbon and a portion of oxygen are derived from atmospheric carbon dioxide (carbon nutrition), while hydrogen and the remaining oxygen originate from water absorbed from the soil (hydric nutrition) (Kathpalia & Bhatla, 2018). Plant mineral nutrition is the process by which inorganic nutrients are absorbed primarily through the roots from soil, with a marginal contribution from the stomatal pathway (Pandey, 2015). Macro, meso and microelements are assimilated in ionic form from the circulating soil solution via three principal mechanisms: active uptake, which requires metabolic energy; ion exchange, involving interactions between root surfaces and the soil solution; and diffusion, which follows concentration gradients (Lambers & Oliveira, 2019). Merely a limited proportion of the total pool of soil nutrients is readily bioavailable and can be taken up and metabolically exploited by plants (Marschner & Rengel, 2023). Nutrient availability is regulated by the dynamic equilibrium between soil fractions: the soluble fraction (immediately available ions and molecules), the exchangeable fraction (nutrients adsorbed onto colloidal surfaces and readily mobilised), the slowly available fraction (elements bound to organic or less complex mineral compounds), and the reserve fraction (nutrients incorporated into crystalline structures which are not directly bioavailable to plants). However, nutrients within crystalline structures can be gradually released through processes such as erosion or rock weathering, thus becoming progressively bioavailable to plants (Guggenberger, 2005; Sárdi, 2017; Marschner & Rengel, 2023).

A crucial parameter for nutrient bioavailability is soil pH, which governs salt solubility and cation exchange: in acidic soils, cations such as H^+ and Al^{3+} predominate, limiting the availability of

essential elements like phosphorus, calcium, and magnesium; conversely, in neutral and alkaline soils, high concentrations of calcium, magnesium, potassium, and sodium are observed, while iron and other micronutrients may be less accessible (Mengel et al., 2001; Colombo et al., 2014).

The ability of plants to adapt to specific pH conditions has resulted in ecological differences among species: acidophiles require acidic soils for effective iron assimilation, whereas other plant species favour neutral-alkaline soils (Tyler, 1996). Optimal management of mineral nutrition therefore necessitates a careful balancing of pH and elemental ratios, in order to optimise root uptake and ensure balanced vegetative growth.

Each element, notwithstanding the diversity in required quantities, fulfils a spectrum of fundamental functions, indispensable for the proper execution of biological activities.

Phosphorus is an essential element for life, as it is a fundamental component of several vital compounds, including adenosine triphosphate (ATP), adenosine diphosphate (ADP), and nucleic acids (DNA and RNA). Plants primarily absorb phosphorus as dihydrogen phosphate ($H_2PO_4^-$). Once absorbed, it contributes to cell division and reproduction, seed and fruit formation. The amount of phosphorus absorbed by plants is relatively low; however, its essentiality is indisputable. Phosphorus deficiency manifests as dwarfism, abnormal leaf coloration, and stunted growth (Malhotra et al., 2018).

Phosphorus exists in four allotropic forms—white (which occurs in two structural modifications, α and β), red, and black —but it is never found in its pure state in nature due to its high reactivity (Valsami-Jones, 2015). Instead, it occurs in various minerals, both from igneous and sedimentary rocks. Among these, deposits of pure phosphate minerals can be classified into three categories (De Boer et al., 2019), according to their increasing economic importance:

-*Iron and aluminium phosphates*, primarily represented by wavellite [$Al_3(PO_4)_2(OH,F)_3 \cdot 5(H_2O)$], variscite [$AlPO_4 \cdot 2(H_2O)$], and strengite [$FePO_4 \cdot 2(H_2O)$], which are widely distributed in Senegal, Brazil, and Utah. These minerals can be used for fertiliser production through nitric acid treatment or thermal processing (Notholt, 1994).

-*Calcium, iron, and aluminium phosphates*, which exhibit significant compositional variability and constitute an intermediate, less well-defined class. The primary minerals in this group include crandallite [$(CaAl_3(PO_4)_2(OH)_5 \cdot H_2O)$] and millisite [$(Na,K)CaAl_6(PO_4)_4(OH)_9 \cdot 3H_2O)$], often found in association with other phosphate minerals. The most significant deposits are located in Florida and Christmas Island, and their use in fertiliser production is similar to that of the previous class (Gilkes & Palmer, 1979; Krekeler et al., 2008).

-*Calcium phosphates*, largely known as 'phosphate rock', belonging to the apatite mineral group. The term 'apatite' encompasses a broad range of Ca-phosphate minerals sharing a similar crystalline

structure but varying in chemical composition, including fluoroapatite [$Ca_5(PO_4)_3F$], chloroapatite [$Ca_5(PO_4)_3Cl$], hydroxyapatite [$Ca_5(PO_4)_3(OH)$], and carbonate-fluorapatite [$(Ca_5(PO_4,CO_3)_3F)$] (White, 2005). These compositional variations arise from the geological origins of the deposits, which can be sedimentary, volcanic, or metamorphic. Volcanic and metamorphic phosphate deposits, often found in association with iron mines, are generally of higher grade but are limited to specific regions such as the Kola Peninsula and Brazil (Cathcart, 2015).

Conversely, sedimentary apatites constitute the primary source of phosphate and display significant compositional differences depending on their formation period, spanning from the Precambrian to the Miocene (Dar et al., 2017). Sedimentary phosphate deposits originate from marine and organic sources, as evidenced by the frequent presence of fossils in phosphate rock. The formation of these deposits is not merely the result of direct accumulation of animal remains but is primarily attributed to metasomatic transformations, where dissolved phosphate reacts with calcareous sediments, forming new phosphate minerals (Filippelli, 2011).

During the Cretaceous and Holocene periods, ammonium phosphate released from decaying animal remains dissolved in seawater and reacted with carbonate detritus, transforming them into calcium phosphates (Calzavara et al., 2005). The most significant phosphate deposits are located in the western United States, North Africa, Russia, Australia, and the Pacific Islands (Flicoteaux & Lucas, 1984; Harris, 2018).

However, the scarcity of geological phosphate reserves, concentrated in limited global regions, presents a major concern for long-term agricultural sustainability, making the phosphorus market vulnerable to political and economic instability (Lu & Tian, 2017). Future estimates suggest that the global phosphorus demand for arable land could reach 22 to 27 million tonnes annually by 2050, with an additional 4 to 12 million tonnes annually for pastures (Mogollón et al., 2018). Efficient phosphorus resource management is thus crucial to avert deficits that could compromise agricultural productivity. Industrially, phosphate rock is treated with sulphuric acid (H_2SO_4) to produce soluble fertilisers such as single superphosphate (SSP), monoammonium phosphate (MAP), and diammonium phosphate (DAP) (Delgado et al., 2016). The European Union has designated phosphorus as a critical raw material (CRM), highlighting the importance of sustainable management for its long-term availability (Smol, 2019).

Nitrogen is another essential element for plant growth, a constituent of amino acids, nucleotides, chlorophyll, and coenzymes. Plants primarily absorb nitrogen as nitrate ions (NO_3^-) and ammonium ions (NH_4^+) (Fathi, 2022). It is virtually absent in the lithosphere, constitutes 1 % of the hydrosphere, nearly 5 % of the biosphere, and 78 % of the atmosphere. In nature, nitrogen is predominantly present as a gas (N_2), both in the atmosphere and in water. Additionally, there are various inorganic nitrogen

compounds, though they represent only 0.01 % of atmospheric nitrogen, 2.5 % of nitrogen in water, and 6.3 % of nitrogen found in terrestrial systems. The most common inorganic nitrogen compounds include nitrous oxide (N_2O), nitrates (NO_3^-), and ammonia (NH_3), which are also present in water, soil, and certain rocks, albeit in relatively small quantities (Smil, 1985; Erisman et al., 2007).

Despite these various nitrogen forms, atmospheric nitrogen remains the most significant source of the element, both for industrial applications and as a nutrient supply. Small amounts of atmospheric nitrogen can be converted into oxides through natural or artificial electrical discharges (such as lightning), allowing nitrogen to enter the soil and biological cycles (Wong et al., 2017).

The most crucial natural process by which nitrogen transitions from its inert gaseous form to the living world is biological nitrogen fixation, carried out by numerous microorganisms. On a global scale, this process is of immense importance; estimates suggest that biologically fixed nitrogen on Earth amounts to at least 98 million tonnes per year, which is more than twice the total nitrogen fixation capacity of the entire global chemical industry (Stein & Klotz, 2016).

Furthermore, biological nitrogen fixation has historically been the sole nitrogen source in all natural ecosystems and remained so in agriculture until just a few decades ago. Even animal manure and natural organic fertilisers—before the introduction of synthetic fertilisers—contained exclusively nitrogen derived, either directly or indirectly, from biological fixation (Calzavara et al., 2005). However, with the advent of industrial processes, the reliance on biological nitrogen fixation has been significantly altered, leading to the dominance of synthetic nitrogen fertilisers.

Nitrogen fertiliser production is primarily based on the Haber-Bosch process, which converts atmospheric nitrogen into ammonia using natural gas as a hydrogen source. This highly energy-intensive process makes nitrogen production susceptible to natural gas price fluctuations. Although technological advancements have improved energy efficiency (Erfani et al., 2024), nitrogen fertiliser production still significantly contributes to greenhouse gas emissions (Menegat et al., 2022). Furthermore, intensive nitrogen fertiliser use can lead to nitrogen compound dispersion in the environment, negatively impacting aquatic (eutrophication) and atmospheric ecosystems (Jones et al., 2014).

Potassium, an essential osmotic and ionic regulator for enzymatic function, is absorbed by plants as K^+ cations. It is involved in various biochemical processes, such as protein synthesis (Sardans & Peñuelas, 2021). The element is found in numerous minerals; however, many of the most common ones are water-insoluble and therefore inaccessible to plants. Other minerals, primarily derived from marine deposits, such as sylvite (KCl), carnallite [$KMgCl_3 \bullet 6(H_2O)$], kainite [$MgSO_4 \bullet KCl \bullet 3(H_2O)$], and langbeinite [$K_2Mg_2(SO_4)_3$] can be more readily processed to extract potassium in plant-available

forms (Garrett, 1996; Calzavara et al., 2005). Sylvite, the most widely used potassium mineral worldwide, is typically found in association with halite (NaCl) (Castro-Suarez et al., 2022).

Global potassium reserves are substantial, with the largest deposits located in Canada, Russia, and Central Europe (Al Rawashdeh, 2020; Zimmer et al., 2020). In the Italian context, the most significant potash salt deposits are located in Sicily, particularly in the central-southern regions, where they historically represented a strategic resource for the extractive industry. A distinctive feature of these deposits is the considerable abundance of kainite [$MgSO_4 \bullet KCl \bullet_3(H_2O)$], which enabled the direct production of potassium sulphate, a fertiliser of high agronomic importance. Nevertheless, despite this unique characteristic, potash mining activities in Sicily have been discontinued for several years-(Schreiber et al., 1976; Calzavara et al., 2005).

Approximately 93 % of the extracted potassium is used for fertiliser production, which is subsequently exported from production centres to agricultural regions worldwide (Zörb et al., 2014). Potassium-based fertilisers derived from minerals are used to produce primarily potassium chloride (KCl) and, for chlorine-sensitive crops, potassium sulphate or potassium nitrate (Villalobos, 2016). Although potassium is relatively abundant, its extraction is costly and concentrated in a few geographic areas, resulting in a market dominated by a small number of producers (Manning, 2010).

Calcium plays a pivotal role in regulating osmotic pressure and ionic concentration within cellular fluids, thereby ensuring electrochemical equilibrium. Furthermore, calcium is an indispensable constituent of cell walls, and its deficiency precipitates specific pathologies, such as rachis desiccation, which arise from cellular collapse (Gilroy et al., 1993). Additionally, calcium serves to buffer excessive acidity. It is absorbed as the Ca^{2+} ion, and in non-acidic soils, which are prevalent in Italy, it is seldom deficient. However, the sequestration of this element within cell walls and in oxalate crystals can engender complications even in soils not deficient in calcium. In acidic soils, calcium may be deficient, and thus, pH amendments, typically executed with calcium and/or magnesium salts, also serve a fertilising function (Calzavara et al., 2005).

Magnesium is an essential constituent of chlorophyll and certain enzymes. It also functions in lipid metabolism and the regulation of osmotic pressure. Given the element's importance in chlorophyll, its deficiency manifests conspicuously, with the formation of chlorotic areas, particularly in older leaves. Magnesium is invariably absorbed as the Mg^{2+} ion. Soil availability is contingent upon the bedrock from which the soils are derived and is therefore highly variable. Deficiencies may occur in acidic soils or in those where excess calcium or potassium hinders root uptake (Gerendás & Führs, 2013; Huber & Jones, 2013).

Sulphur is an element widely distributed in nature, occurring in various forms such as sulphates—syngenite [$K_2Ca(SO_4)_2 \cdot H_2O$], gypsum [$Ca(SO_4) \cdot 2H_2O$] and barite ($BaSO_4$), as sulphides—pyrite

(FeS_2), galena (PbS), and as the native element (S). Its cycle is complex, involving both inorganic and biological processes, with the contribution of numerous microorganisms capable of oxidising and reducing its compounds to derive energy (Kroneck 2005).

Soil serves as the primary environment for sulphur transformation, where it exists in inorganic forms (sulphates, sulphites, thiosulphates, and elemental sulphur) and, predominantly, organic forms, which constitute the major reservoir (Rai et al., 2020). Plants absorb sulphur primarily as the sulphate ion (SO_4^{2-}) from the soil and, to a lesser extent, as sulphur dioxide (SO_2) from the atmosphere (Oksana et al., 2024). Biologically, sulphur is essential for all living organisms, participating in protein synthesis through its presence in the amino acids cysteine an methionine, which are fundamental for protein stability (Francioso et al., 2020). Furthermore, it is a component of vital vitamins (biotin, thiamine) and coenzymes. In plants, it is indispensable for metabolism and cellular regulation but is not accumulated, necessitating a constant intake (Ingenbleek & Kimura, 2013).

Copper primarily fulfils catalytic functions in plant metabolism, often synergistically with iron (Ravet & Pilon, 2013). Being a polyvalent element, it actively participates in oxidation-reduction processes and is an essential component of various enzymes. Furthermore, it is required for chlorophyll synthesis. In soil, it is present as an exchangeable cation or as a basic salt derived from bedrocks or phytosanitary treatments. Plants absorb it in its divalent form, both as a simple ion and as an organic complex. However, soil strongly retains copper, and in alkaline or organic-rich environments, its availability is reduced due to the formation of insoluble compounds (Calzavara et al., 2005).

Other micronutrients, including Zn, B, Mn, and Mo, all play crucial roles in plant physiology, contributing to growth, enzymatic regulation, protein synthesis, and cellular structure stabilisation. Their sources include natural minerals and industrial by-products, but their procurement and processing often involve high costs and environmental impacts (Villalobos, 2016).

The intensive use of mineral fertilisers while crucial for supporting crops under stress, is now considered unsustainable (Mogollón et al., 2018; Soumare et al., 2023). This unsustainability stems from the non-renewable nature of the mineral resources used, and the significant environmental, social, and economic implications associated with the procurement, transportation, and industrial processing required to convert these raw materials into plant-available nutrients (Blass et al., 2017).

To ensure an adequate supply of nutrients to crops and mitigate the challenges associated with the procurement of mineral raw materials, it is essential to develop sustainable alternatives that reduce dependence on mineral resources and high-impact industrial technologies.

Addressing these challenges necessitates enhancing nutrient recovery practices for healthy plant growth. This can be achieved by utilising waste materials and implementing processes that transform them into marketable products. This approach rooted in “Circular Economy Principles”, integrates

sustainability into production, promoting resource management that balances economic goals and long-term environmental priorities.

The European Union is intensifying its commitment to the transition from a linear to a circular economy, aiming to establish a system in which valuable resources—such as nutrients and organic matter present in materials traditionally classified as “waste”—are effectively recovered, recycled, and reintegrated into the economic cycle. The European Commission’s 2011 “End of Waste “strategy sets out the criteria under which waste materials can be reclassified as reusable resources, thereby fostering sustainable resource management and minimising waste generation (EC, 2011).

For use in fertiliser production, these materials must acquire characteristics that enhance soil quality and plant growth, while ensuring safety for human, animal, and environmental health.

A robust scientific foundation supports the potential of directing waste into fertiliser production where feasible. Numerous studies have established nutrient recovery for agricultural applications, particularly from organic waste such as the organic fraction of urban waste and sludge from wastewater treatment plants, processed under aerobic or anaerobic conditions (Lukehurst et al., 2010; Guedes et al., 2014; O’Connor et al., 2021).

However, recovering mineral nutrients from inorganic waste streams remains underdeveloped, despite the promising potential of biomass ashes as a mineral nutrient source (Vassilev et al., 2013b; Cruz et al., 2017). Nevertheless, the most common management practice for industrial ashes is landfill disposal, which carries significant economic and environmental drawbacks and precludes ash recycling, resulting in the inevitable loss of valuable mineral resources.

2.2 Overview of biomass ashes from cogeneration plant

The increasing adoption of renewable energy sources at the expense of fossil fuels is a growing trend in many European countries. The use of biomass for heat and power production has undergone significant development over the years due to multiple factors, such as the easy access to biomass feedstock, the promotion of European and global objectives for the sustainable development of energy sources, and the contribution to achieving energy independence for some states, including Italy, which relies primarily on other European Union states for its energy needs. Biomass as a fuel represents 14 % of the world's primary energy source and up to 35 % in some developing countries (Demirbas, 2007; Bowen et al., 2017).

Biomass, by definition, comprises all organic materials that have not undergone fossilisation processes. According to the Directive of the European Union (EU, 2018), biomass is defined as: "The biodegradable fraction of products, waste, and residues of biological origin from agriculture, including vegetal and animal substances, forestry and related industries, fisheries, and aquaculture,

as well as the biodegradable fraction of waste, including industrial and municipal waste of biological origin". Vassilev et al., (2013a) defined biomass as "a complex heterogeneous mixture of organic matter and, to a lesser extent, inorganic matter, containing various intimately associated solid and fluid phases with different contents and origins".

Biomass with low water content is ideal for thermochemical conversion processes, with lignocellulosic biomass—primarily sourced from wood and vegetal residues—being the most suitable type for energy production. Forests and harvested agricultural fields are the main suppliers, providing biomass in the form of wood and agricultural residues. Approximately 70 % of the biomass used for energy production comes from forests, highlighting their central role in this sector (Gambini et al., 2019). Wood biomass for energy production is prioritised in the form of wood chips, pellets, and sawdust, as these formats are specifically optimised for combustion processes and exhibit high compatibility with advanced energy production technologies (Saidur et al., 2011; S. V. Vassilev et al., 2013a; Maresca et al., 2017; Gielen et al., 2019).

These materials can be used in specific cogeneration plants to produce energy. The term "cogeneration" refers to the simultaneous production of heat and electricity from a single energy input. Types of employed power plants consist of steam power plants, gas turbines, combined cycle power plants, and internal combustion engines. The extracted heat largely varies in entity and temperature depending on technology, size, and operation parameters. Such a system has valuable properties to enhance the efficiency of fuel use: the combined production of electricity and heat turns out to be more efficient than the separate production of these two forms of energy (Gambini et al., 2019). The main technologies for biomass energy conversion remain thermochemical processes, such as combustion.

On an industrial scale, the most advanced technology is the fluidised-bed boiler, which uses a hot sandy bed to support biomass combustion at lower temperatures, with isothermal conditions and high fuel flexibility, ensuring excellent efficiency (Freire et al., 2015). Grate furnaces, on the other hand, operate at more variable temperatures and are suitable for biomass fuels with particles of varying sizes (Yongtie et al., 2022). Typically, the biomass is burned to produce high-pressure steam, which then drives a turbine to generate electricity. Cogeneration plants, through the combined production of electricity and heat, can achieve an overall efficiency of up to 80 %, optimising fuel utilisation and minimising energy losses compared to electricity-only generation systems (Zhai et al., 2021).

Biomass is clearly a wide category, comprising materials with various properties and shapes. However, in all cases, it has the noteworthy advantage of the non-fossil nature of its carbon.

The combustion of biomass does generate CO_2, but its emission does not alter the natural carbon cycle, contrary to fossil fuels (Moliner et al., 2021). For instance, in the case of wood biomass from

agro-forestry residues, the CO_2 released during combustion is identical to that absorbed by plants during their growth. This emission would naturally re-enter the environment through the decomposition of organic matter at the end of its life cycle (Demirbas, 2005; Demirbas et al., 2007).
Despite the virtuous principles and environmental benefits, it is not true that exploiting biomass for energetic purposes is an entirely carbon-neutral activity. A biomass conversion plant requires being built and supported by adequate infrastructure, and the biomass must be collected, pre-treated, and transported. Ideally, these steps could be reduced and powered with renewable energy, but unfortunately, this is not entirely feasible yet (Gambini et al., 2019).
The net calorific value (NCV) of dry biomass varies with feedstock. It is between 16 and 19 MJ/kg for hardwood, softwood, cereal crop straw, rape straw, and sunflower straw. Rice straw and sugarcane stalks have lower NCVs than other agricultural residues (12 and 8 MJ/kg, respectively). The NCV of recovered wood varies between 4 and 17 MJ/kg depending on the woody waste composition (Zhai et al., 2021).
In many countries, biomass for energy purposes is specifically cultivated, with certain crops, such as bamboo, proving particularly suitable for this purpose (Moliner et al., 2021). However, this practice can lead to soil nutrient depletion, as agro-forestry residues are not allowed to naturally decompose or mineralise (Achat et al., 2015; Hansen et al., 2018). Additionally, it increases the demand for fertilisers required to sustain so-called "energy forests" in certain regions of the world (Albuquerque et al., 2022).
Furthermore, the growing use of wood biomass as a bioenergy generates large quantities of ashes, estimated at around 476 million tons per year worldwide, creating the need to explore sustainable methodologies for the valorisation of these waste materials and reducing landfill disposal (Vassilev et al., 2013b; Zhai et al., 2021).
One of the fundamental distinctions regarding ashes is related to their bulk density and the consequent tendency either to be transported away from the combustion chamber by the flow of combustion gases or to accumulate at the bottom of the chamber.
Biomass ashes can be classified into three main types: bottom ash, which primarily consists of coarser particles that fall through the grate during combustion; fly ash, composed of fine particles carried by combustion gases and deposited in various sections of the boiler and the flue gas cleaning system; and air pollution control residue—a mixture of fly ash and reagents (such as lime and activated carbon) introduced to capture pollutants in the flue gas cleaning system. Before determining the appropriate application or disposal method, biomass ashes must be classified according to the European Waste Catalogue (EWC) (2000/532/CE). The relevant waste codes for biomass ashes classification include 10 01 01 (bottom ash, slag, and boiler dust, excluding the boiler dust specified

under 10 01 04), 10 01 03 (fly ash from peat and untreat (ed wood), 10 01 05 (solid-phase calcium-based reaction residues from flue gas desulphurisation), 10 01 07 (sludge-phase calcium-based reaction residues from flue gas desulphurisation), 10 01 18* (residues from gas cleaning containing hazardous substances), 10 01 19 (gas cleaning residues other than those classified under 10 01 05, 10 01 07, and 10 01 18), 19 01 07* (solid residues from gas treatment), 19 01 13* (fly ash containing hazardous substances), and 19 01 14 (fly ash not classified under 19 01 13) (Bogush et al., 2018).

The most common management practice for biomass ash is landfill disposal, which poses relevant economic and environmental drawbacks (Agrela et al., 2019). Legislative measures have been introduced to restrict this practice by increasing costs and penalties, with landfill taxes aimed at encouraging companies to divert their waste from landfills and seek alternative waste management options (Silva et al., 2019). The quantity of ash generated during biomass combustion varies widely, largely due to the type of feedstock, the combustion technology used, and the specific operating conditions of the process. These factors influence key quality characteristics of the ash, which in turn affect its suitability for further applications (Freire et al., 2015).

The utilisation of wood ash as a resource within the bioeconomy presents several challenges (Munawar et al., 2021). These include the complexity of current regulations, logistical issues stemming from decentralised collection, variability in product quality, and safety concerns related to storage and handling. Furthermore, many potential utilisation pathways remain in the developmental or pilot phases and lack widespread implementation (Bachmaier et al., 2021). Consequently, ash produced by biomass plants is frequently perceived not as a valuable by-product of wood-based energy production, but rather as waste, thus necessitating costly disposal.

In the future, ash management and disposal will be subject to increased scrutiny due to increasingly stringent environmental regulations, diminishing landfill availability, and rising disposal costs (Freire et al., 2015).

The following sections will explore the available literature addressing various aspects related to ashes produced from the combustion of wood and vegetal-based biomass. Specifically, the chemical and physical characteristics of these ashes, their potential forestry and agronomic applications, and the risks associated with contaminant presence.

2.3 Chemical and physical properties

The initial chemical profile of fuel directly determines the chemical composition of ash residues after combustion. According to Nunes et al., (2016), the elemental components that constitute biomass ashes are found in two primary forms. Firstly, they exist as mineral salts chemically bonded to the carbon structure of the biomass, representing the “inherent component”. Secondly, they can originate

from mineral soil particles incorporated during plant growth or introduced during harvesting and transport operations, thus forming the "foreign component". Following combustion at 550–600 °C, the ash yield from various biomass types, exhibits substantial variability, ranging from 0.1 % to 46 %, with a mean value of 6.8 %, expressed as weight percentage on a dry basis (Vassilev et al., 2013a). In general, the ash yield from biomass combustion is markedly lower than that generated from coal and shows considerable variation depending on the specific biomass source. Notably, the ash yield tends to decrease along the following sequence: animal-derived biomass, aquatic biomass (inclusive of algae and marine flora), contaminated biomass (*e.g.,* wood waste), herbaceous and agricultural biomass, and, lastly, lignocellulosic (woody) biomass (Bogush et al., 2018).

Specifically, it ranges from 2 % in some dry wood species to nearly 20 % in certain cereal crops (*e.g.*, rice husks) or forest residues. This variation is further pronounced when biomass materials are contaminated with inert substances, such as soil or small stones, which may mix with the fuel during collection, harvesting, handling, storage, and processing (Nunes et al., 2016; Bogush et al., 2018; Jenkins et al., 2019). Understanding the factors influencing biomass ash composition is crucial for assessing its potential applications and environmental impact, as these properties influence subsequent ash management strategies.

Several factors influence the chemical and physical properties of biomass ash, including the plant species, the specific plant components combusted, operational storage conditions, and, particularly in industrial power plants, combustion temperature (typically 800–1600°C) (Umamaheswaran & Batra, 2008; Dahl et al., 2009; Sarenbo, 2009; Saidur et al., 2011; Vassilev et al., 2013a; Freire et al., 2015; Zhai et al., 2021). Vassilev et al. (2013a) differentiate major elements which occur in concentration higher than 1 wt% (they include Ca, K, P, S, Mg, Al, and Si), minor elements occurring in concentration of 0.1–1 wt% (*e.g.*, Mn), and trace elements (<0.1 wt%, including Cu, Zn, Cr, and Ni). Potential environmental contaminants such as Hg, Cd, Sb, Se, V, Br, Cr, Pb, Zn, As, along with Cl and nutrient elements as S, K and Na, exhibit a high volatilisation potential and tend to get enriched in fly ash rather than bottom ash. These elements occur in various chemical forms Vassilev et al. (2013a) provided a comprehensive analysis of the mineralogical and phase composition of biomass ashes, contrasting them with coal ashes. Their investigations revealed a greater diversity of mineral and phase constituents in biomass ashes (291) compared to coal ashes (188). Biomass ashes are characterised by both inorganic phases (silicates, oxides and hydroxides, sulphates, phosphates, carbonates, chlorides, nitrates, glass, and amorphous (non-glass) phases) and organic phases (cellulose, hemicellulose, lignin, char, other organic phases). Commonly identified phases include glass, char, quartz, calcite, sylvite, lime, arcanite, anhydrite, portlandite, apatite, halite, clay minerals, gypsum, and amorphous (non-glass) material (Bogush et al 2018). The specific mineral and phase

assemblage varies considerably, primarily due to the aforementioned factors, notably the type of biomass fuel, combustion conditions, and ash handling. Vassilev et al. (2013a) also proposed a classification system for biomass ash phases and minerals based on the origin: primary (refractory silicates, oxyhydroxides, phosphates), secondary (all the other minerals, glass, char), and tertiary (carbonates, hydroxides). They also provided a detailed account of phase and mineral transformations during biomass combustion, highlighting the complexity of biomass ash composition.

Ash particle formation during biomass combustion involves a complex interplay of physical and chemical processes. During combustion, the inorganic ash fraction undergoes concurrent physical and chemical transformations, including segregation, evaporation, precipitation, nucleation, and coalescence, leading to ash particle formation. Consequently, ash particles vary significantly in size, morphology, and composition, influenced by fuel properties, combustion temperature, and residence time (Nunes et al., 2016). At elevated temperatures, mineral constituents undergo significant physicochemical changes (Abraham et al., 2013). Silica may melt (partially or completely) and react with other ash components to form alkali metal silicates (primarily K and Na). Aluminosilicates may undergo partial or complete fusion. Carbonates, oxalates, chlorides, and other salts decompose, while alkali and heavy metals volatilise. Thermal shock and rapid gas release contribute to particle fragmentation, whereas mineral particles may coalesce and agglomerate (Nunes et al., 2016). Ash characteristics also depend on the combustion system employed. Fluidised bed combustion generally results in lower ash fusion than fixed-bed configurations due to reduced molten particle coalescence. Comprehensive discussions of biomass combustion technologies are available elsewhere (Dahl et al., 2009; Abraham et al., 2013; Munawar et al., 2021).

Biomass ash chemical composition is closely related to the fuel type, as different feedstocks have distinct elemental compositions. Table 1 illustrates significant variations in major element oxide composition across various biomass fuels. Agricultural residues are a significant biomass source, primarily derived from maize (36 %), rice (18 %), wheat (14 %), sugarcane (9 %), and soybean (8 %). Maize, rice, and wheat account for 68% of total agricultural residues and are crucial for bioenergy generation, particularly in agriculturally intensive regions. Wood fuels, another major biomass category, are primarily sourced from tropical hardwood, temperate hardwood, and softwood species (Zhai et al., 2021). Plants with long reproductive cycles (*e.g.*, trees) typically have different ash compositions than plants harvested multiple times annually (*e.g.*, energy crops, cereals) due to nutrient cycling between trees and soil. Energy crops and cereals tend to contain higher concentrations of low-melting-point oxides (particularly of K_2O and P_2O_5), whereas tree ash is predominantly composed of SiO_2 and CaO (Nunes et al., 2016; Munawar et al., 2021; Zhai et al., 2021).

Table 1. Mean oxide compositions in biomass ashes from various feedstocks (wt%) (biomass residuals from the agri-food industry, forest biomass and wood waste) utilised for combined energy production, as reported in the literature (Nunes et al., 2016; Zhai et al., 2021; Munawar et al., 2021).

Material/Source	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	TiO_2	Reference
Olive husk	32.7	8.4	6.3	14.5	4.2	4.3	26.2	2.5	0.6	0.3	Nunes et al. 2016
Wheat straw	48	3.5	0.5	3.7	1.8	20	14.5	3.5	1.9	NA	Nunes et al.2016
Olive kernel	67.7	20.3	0.05	0.5	0.05	0.15	11.2	NA	NA	0.05	Nunes et al. 2016
Cereal crops	51	1.9	1.6	6.1	2.8	19	2.2	3.2	3.3	0.11	Zhai et al.2021
Sugarcane	54	11	8.0	5.3	3.1	8.41	1.1	2.4	3.3	2.1	Zhai et al.2021
Soybean	21	3.4	2.1	17	5.6	21	1.7	4.8	3.0	0.09	Zhai et al. 2021
Rice husk	89.3	0.22	0.4	1.3	0.57	5.04	0.35	0.87	NA	NA	Munawar et al. 2021
Bagasse	2.5	11.1	1.3	15.8	11.9	14.5	0.6	NA	NA	NA	Munawar et al. 2021
Grasses	53	0.7	0.70	6.4	4.0	22	0.6	4.0	2.1	0.3	Zhai et al. 2021
Tropical hardwood	14	2.7	2.2	27	4.7	24	1.3	5.5	3.2	0.33	Zhai et al. 2021
Temperate hardwood	11	3.01	1.5	38	6.9	17	0.53	8.2	2.9	0.1	Zhai et al. 2021
Temperate hardwood bark	9.8	1.4	1.2	64	7.6	5.9	1.6	2.0	1.6	0.1	Zhai et al. 2021
Conifer bark	6.8	3.6	2.3	59	5.2	6.0	2.0	3.2	2.0	0.13	Zhai et al. 2021
Woody crops	4.3	1.4	0.8	42	6.4	20	1.2	9.3	2.6	0.10	Zhai et al. 2021
Recovered wood	39	9.5	5.7	16	14	2.6	2.0	0.7	5.8	2.7	Zhai et al. 2021
Wood residue	2.5	11.1	1.3	15.8	11.9	14.5	0.6	NA	NA	NA	Munawar et al. 2021
Wood pellets	4.3	1.3	1.5	55.9	8.5	16.8	0.6	3.9	1.3	0.1	Nunes et al. 2016

Recovered wood from industrial activities and municipal waste collection (construction/demolition, furniture manufacturing, packaging, urban solid waste) is another bioenergy feedstock due to its high availability and potential for landfill waste reduction. Recovered wood ash typically exhibits higher MgO and Al_2O_3 concentrations but lower K_2O and P_2O_5 concentrations compared to other wood ash types, likely due to contamination with foreign materials (*e.g.*, construction debris, soil) (Zhai et al., 2021). Recovered wood may also contain high concentrations of heavy metals and organic contaminants from chemical treatments (*e.g.*, painting, impregnation, industrial adhesives). The potential presence of plastics can increase the risk of dioxin and furan (PCDD/F) formation during combustion, limiting the sustainable ash management and agricultural applications (Demeyer et al., 2001).

2.4 Agronomic applications

The application of wood biomass ashes from cogeneration plants in agricultural and forestry sectors has attracted increasing scientific interest due to its potential implications. Biomass ash may contain a variety of macronutrients, including P, N, K, mesonutrients such as Ca, Mg and S, as well as micronutrients such as Fe, Cu, Zn, B, Mn, Mo and Ni, which are resistant to incineration. However, biomass ashes are deficient in N as this element volatilises during the combustion process, primarily in the form of NOx gases. Overall, due to their chemical composition and, in particular, the presence of basic cations in the form of oxides, hydroxides, and carbonates, ashes exhibit high alkalinity (Obernberger et al., 2006; Reijnders, 2006; Karltun et al., 2008; Nzihou & Stanmore, 2013; Freire et al., 2015; Bogush et al., 2018; Lehmusto et al., 2024). As already pointed out, the increasing use of wood biomass as a source of bioenergy has led to the intensification of harvesting methods for agroforestry residues. In particular, the extensive removal of residues - including straw, branches and foliage - interrupts the natural cycle of decomposition and mineralisation, which is essential for replenishing essential soil nutrients. This leads to a reduction in soil fertility, with potential negative effects such as increased reliance on chemical fertilisers and increased vulnerability to erosion (Achat et al., 2015; Hansen et al., 2018; Albuquerque et al., 2022).

Therefore, closing mineral cycles through recycling biomass ashes as a fertiliser or soil amendment appears to be one of the most sustainable solutions. Annex II of Regulation (EU) 2019/1009 (European Commission, 2019) promotes the reuse of fertilising products based on ashes within the EU market under the Constituent Material Category (CMC) 13. This category includes thermal oxidation materials and their derivatives, establishing the relevant material standards. Nevertheless, the valorisation of this type of ash remains a highly complex issue.

Given the established influence of multiple factors on the chemical composition and properties of ash, a focused examination of biomass type's impact on nutrient bioavailability is warranted. Specifically, the type of biomass combusted significantly modulates the quality and nutrient profile of the resultant ash. This directly manifests as variations in the concentration and bioavailability of essential nutrients, critical for applications within forestry and agricultural domains.

Several studies have investigated variations in forest soil fertility and crop productivity following the application of wood biomass ash (Demeyer et al., 2001.; Omil et al., 2007; Augusto et al., 2008; Huotari et al., 2015; Hansen et al., 2018; Mortensen et al., 2020; Johansen et al., 2021).

The use of wood ash as a fertiliser and/or soil amendment has been primarily studied in Northern European countries, where ashes are commonly applied in boreal forests (Demeyer et al., 2001.; Augusto et al., 2008; Hansen et al., 2018; Johansen et al., 2021), particularly in sites where nitrogen (N) does not limit tree growth, such as peatland forests (Huotari et al., 2015). In these areas, which are characterised by intensive forest exploitation, the reuse of ashes has become necessary to counteract the depletion of basic elements in forest soils, mitigate acidification and has demonstrated significant potential as a liming material as well as an excellent alternative source of Ca, Mg, K, P and other nutrients (Huotari et al., 2015).

The liming effect primarily depends on the calcium content and may vary according to the combusted material. For instance, ashes derived from rape straw contained a higher calcium content and exhibited a more pronounced liming effect than ash obtained from cereal straw (Huotari et al., 2015).

The nutrient content of ashes depends not only on the feedstock used but also on the combustion process. A study by Etiégni & Campbell, (1991) reported that the phosphorus (P) concentration in wood ash ranged from 1.7 % at 538°C to 2.6 % at 1093°C, highlighting the influence of combustion temperature. Moreover, the effectiveness of wood ash as a lime alternative is influenced by the boiler combustion efficiency (Vance, 1996; Schiemenz & Eichler-Löbermann, 2010).

It should also be emphasised that regardless of the content of nutrients present in ashes, their availability for plants may vary significantly according to the physical form in which they occur. Ohno & Susan Erich (1990) observed that only a minimal fraction of the P supplied through wood ash was extractable and available to plants. Similarly, Pels et al. (2005) highlighted low phosphorus solubility in biomass ashes, whereas Onwuka et al. (2007) recorded increased available phosphorus in the soil and enhanced maize growth following fertilisation with cocoa husk ash. Likewise, Reuler & Janssen (1995) observed a significant improvement in both yield and phosphorus uptake in rice fertilised with wood ash.

In a more recent study (Schiemenz & Eichler-Löbermann, 2010), the potential of biomass ashes as a phosphorus source for agriculture was analysed, with the aim of optimising nutrient cycling and

reducing the use of synthetic fertilisers. The study involved two pot experiments conducted on a P-deficient sandy-clay soil, testing three types of biomass ash: rape meal ash, straw ash, and cereal ash. These treatments were compared with the application of triple superphosphate (TSP), a highly soluble P source, potassium chloride (KCl) for potassium supplementation, and a control treatment lacking P and K across various plant species, including maize, lupin, summer barley, phacelia, Italian ryegrass, and buckwheat. The results demonstrated that the effectiveness of biomass ashes in supplying P was comparable to that of triple superphosphate (TSP), and that the fertilisation effect also varied depending on the crop species.

Positive effects on yield were observed in winter wheat (Triticum aestivum L.), spinach (Spinacia oleracea L.), oats (Avena sativa L.), and beans (Phaseolus vulgaris L.) (Clapham & Zibilske, 1992; Krejsl & Scanlon, 1996). Furthermore, the phosphorus content and occurrence modes in eight types of biomass ashes were examined by Vassilev & Vassileva (2022). Their study revealed that biomass ashes are enriched in P, with concentrations ranging from 0.3 wt% to 4.4 wt% (mean 1.7 wt%). The highest P concentrations (>2 %) were found in ashes derived from agricultural residues, particularly plum pits, sunflower shells, and corn cobs. The study also identified that the primary forms of P in biomass ashes are associated with apatite and whitlockite. As a result, biomass ashes, sourced from renewable and carbon-neutral materials, represent a promising alternative for the sustainable recovery of P and its industrial application, offering a viable substitute for finite and non-renewable phosphate rock deposits.

Patterson et al. (2004) reported a 50 % increase in barley (Hordeum vulgare L.) yield and up to a 124 % increase in rape (Brassica rapa L.) seed yield following the application of wood ash. Furthermore, field experiments in Thailand showed an increase in rice yield by applying rice husk ash for tropical climates (Phongpan & Mosier, 2003). The research conducted by Etiegni et al., (1991) explored the effects of biomass-derived ash on wheat growth, evaluating different application rates (0, 2, 4, 8, 16, and 32 wt%). The results revealed a variable wheat yield response to ash treatments. Specifically, adding 2 wt% ash (40 mt/ha) promoted an increase in yield, suggesting a beneficial effect at low concentrations. However, higher doses triggered a progressive decline in yield, highlighting potential inhibitory effects associated with excessive ash application. This study underscores the importance of precise dosage management in the application of biomass ashes in agriculture, in order to maximise benefits while preventing negative impacts on crop production.

The study by Park et al. (2023) investigated how the application of bottom ashes significantly influences the growth and yield of “Chinese cabbage”. The results indicated a dose-dependent relationship, with growth increasing proportionally to the amount of bottom ash applied, up to a threshold of 100 kg/10a. Beyond this limit, a decline was observed, suggesting a counterproductive

effect of excessive doses. The yield index confirmed this trend, reaching its maximum value (138) at 100 kg/10a of bottom ash. Consequently, this amount was identified as optimal for maximising Chinese cabbage production.

These findings highlight the crucial role of accurate dosage management in biomass ashes applications to optimise agricultural outcomes while preventing adverse effects on crops.

The application of biomass ashes must be carefully monitored and managed, as an imbalanced application can influence the physical and chemical properties of soils, such as texture, pH, and the content of potentially harmful heavy metals that pose environmental risks (Pöykiö et al., 2009; Freire et al., 2015; Maresca et al., 2017). Therefore, it is essential to assess the potential risks associated with the use of this type of ash, as it could directly affect nutrient dynamics and ecosystem health (Maresca et al., 2019). Mtisi & Gwenzi (2019) observed a reduction in microbial activity in soils with high ash concentrations, leading to nutrient immobilisation and limited plant growth. This behaviour is similar to the effects of biochar, which has shown a comparable trend: while moderate application can enhance crop productivity, excessive amounts of biochar can be counterproductive, interfering with plant growth (Kang et al., 2021; Schmidt et al., 2021; Xie et al., 2021).

Several studies have highlighted that excessive biomass ashes application can lead to the accumulation of heavy metals in soil, increasing the risk of metal migration and toxicity to crops (Liu et al., 2018; Munawar et al., 2021). The overuse of ashes in agricultural fields can induce phytotoxicity due to the presence of potentially toxic elements in high concentrations, such as Cu and Zn, as well as highly soluble salts (Shaheen et al., 2014). These components can alter soil chemical properties, interfere with nutrient uptake by plants, cause stress, and potentially reduce crop yields.

Therefore, it is crucial to carefully monitor the amount of ash applied to soil to prevent negative effects on plant growth.

The use of recycled wood biomass ashes as a fertiliser can offer numerous environmental benefits, including reducing waste volumes destined for disposal, promoting nutrient recycling, enhancing tree growth (Ernfors et al., 2010) and counteracting soil acidification in forest ecosystems (Brunner et al., 2004). However, the analysis conducted by Aronsson & Ekelund, (2004) highlighted a degree of uncertainty regarding the biological effects of wood ash application on forest soils and aquatic ecosystems. Subsequent scientific research has made significant progress, generating a broad spectrum of new evidence concerning the impact of ash fertilisation. Among these findings, studies have examined heavy metal concentrations in wild berries and fungi (Moilanen et al., 2006), microbial processes in soil (Rosenberg et al., 2010; Saarsalmi et al., 2010) and surface water quality (Piirainen et al., 2013).

Although biomass ashes contain nutrients that may be beneficial for plant nutrition, their complex chemical composition necessitates a thorough evaluation prior to their application in agriculture. The bioavailability of nutrients, the potential presence of inorganic contaminants (*e.g.*, heavy metals) and organic pollutants (*e.g.*, dioxins, furans), as well as other challenges related to chemical-physical properties (high pH, salinity, and dust emissions), make it essential to conduct a detailed characterisation of both the ashes and the receiving soil. This ensures that the ashes are of consistent quality, safe, and suitable for the intended use (Vassilev et al., 2013b).

Such assessment must be carried out in accordance with Regulation (EU) 2019/1009 on fertilising products, which stipulates that an EU fertilising product must be composed exclusively of component materials that meet the requirements set out in one or more of the "Constituent Material Categories" (CMCs) listed in Annex II. Additionally, it is crucial that both the constituent materials and the secondary raw materials used are free from substances exceeding the maximum limits defined in Annex I, as such exceedances could compromise the compliance of the fertilising product with the EU regulatory framework.

The following section will explore the factors influencing ash quality, particularly hazardous elements posing risks to human health and the environment, which could represent a significant barrier to biomass ashes reuse.

2.5 Safety and risk assessment

Ashes resulting from the combustion of woody biomass in cogeneration plants, while representing a potentially useful byproduct, can pose environmental and human health risks due to the possible presence of heavy metals, polycyclic aromatic hydrocarbons (PAHs), and dioxins/furans (PCDD/Fs). The concentration of these contaminants is influenced by a complex interplay of factors. Firstly, the type and quality of the biomass play a crucial role: the wood species, its origin, and any pre-combustion treatments affect the chemical composition of the ash. Secondly, the combustion process is a determining factor: the technology used and the operating conditions of the plant (temperature, residence time, air/fuel ratio) (Nzihou & Stanmore, 2013; Vassilev et al., 2014; Freire et al., 2015; Cruz et al., 2017). According to Vassilev et al. (2014) the concentrations of environmentally significant heavy metals—Zn, Pb, Cu, Cd, Cr, Ni, As and Hg—can be bioaccumulated in the biomass at trace concentrations during normal growth through various biological and environmental mechanisms. Some of these elements are present in the biomass due to their role as nutrients for plants; in particular, very high values for Cu and Zn have been observed in some biomass ashes from power plants that fired coconut and wood wastes (Masto et al., 2015).

Plant species show a different capacity to accumulate heavy metals, a phenomenon influenced by factors such as plant physiology, soil characteristics, and sources of contamination (Nzihou & Stanmore, 2013). Among the most studied metals, Cd, Pb, Cu and Zn are particularly relevant due to their association with anthropogenic activities and the use of fertilisers.

Cadmium, derived from industrial processes such as metal smelting and the combustion of fossil fuels, is sometimes also present in the superphosphate used in fertilisers (Niño-Savala et al., 2019). Phytotoxic and harmful to human health, it can cause kidney dysfunction, bone damage, and other negative effects. It impairs plant growth and accumulates in the food chain (Benavides et al., 2005). Species such as poplars and willows demonstrate a marked capacity for Cd accumulation, making them suitable for phytoremediation (Nzihou & Stanmore, 2013).

Lead mainly originates from traffic emissions and industrial activities, proving highly toxic to the human nervous system and kidneys (Raj & Das, 2023). “Dactylis” (cocksfoot) was found to accumulate the highest amounts of Pb (over 5 mg/kg dry weight), while “Triticale” (cross between wheat 'Triticum' and 'Secale'”) and some tree species show much lower absorption, often below the detection limit (1 mg/kg). However, the low mobility of Pb in the soil limits its long-term absorption (Nzihou & Stanmore, 2013).

Zinc and copper are released during metal smelting, but also derive from other sources: Zn is present in tyre abrasion, engine oils, and exhaust gases from coal-fired plants, while Cu can come from pipes, power lines, and copper sulphate-based fungicides (Zhang et al., 2012; Rehman et al., 2019). Both are essential micronutrients, but are toxic in high concentrations (Yruela, 2005). Zn concentrations in plants vary significantly, from 15 mg/kg (Secale) to 135 mg/kg (Dactylis), while Cu ranges from 2.6 mg/kg (Poplar) to 22.6 mg/kg (Dactylis) (Nzihou & Stanmore, 2013).

Among toxic metals, mercury is poorly retained in the ash because it is particularly volatile and is almost entirely emitted as vapour, both as Hg^0 element and in its oxidised form, $HgCl_2$. Oxidised mercury represents between 80 % and 97 % of Hg emissions that enter the atmosphere (Nzihou & Stanmore, 2013).

Wood treated with resins and preservatives can indeed contain high amounts of heavy metals, as confirmed by various scientific sources (Hasan et al., 2010; Jones et al., 2019). These treatments, which aim to protect wood from weathering, fungi, and insects, may involve the use of chemical compounds containing heavy metals, such as As, Cr, and Cu.

Arsenic, in particular, is a highly toxic element that can cause damage to various organs and systems, including the skin, liver, kidneys, and nervous system (Mohammed Abdul et al., 2015), and its presence is generally associated with wood treatment processes The different chemical forms in which arsenic can be present in wood treated with chromated copper arsenate (CCA), a widely used

preservative in the past, highlighting the complexity of its speciation and potential release into the environment.

It is estimated that in 2005 the global wood preservation industry treated approximately 30 million cubic metres of wood, consuming approximately 500,000 tonnes of chemical preservatives. About two-thirds of this volume was treated with chromated copper arsenate (CCA) (Helsen & Van Den Bulck, 2005).

Chromium, depending on its chemical form (*i.e.* Cr VI), can be carcinogenic and cause allergic reactions (Hossini et al., 2022).

It is important to emphasise that these heavy metals can be present in high concentrations in the ash resulting from the combustion of recovered wood, often used as an energy source in cogeneration plants (Demirbas, 2007).

The combustion of treated wood, in fact, can concentrate heavy metals in the ash, representing an additional risk to the environment and health. Therefore, it is essential to carefully monitor the composition of the ash resulting from the combustion of recovered wood and adopt appropriate management measures to prevent the dispersion of such contaminants.

Despite being often considered a renewable energy source, the combustion of virgin untreated wood is not without risks, as highlighted in Obernberger et al. (2006). In their study, the authors report elevated levels of cadmium, zinc, and lead, particularly in bark, wood chips, and sawdust. These findings are attributed to increased environmental pollution in recent decades—resulting in higher concentrations of heavy metals in biomass fuels.

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) are persistent organic pollutants (POPs) with high toxicity, regulated under various legislative frameworks. According to Annex C of the Stockholm Convention on POPs, PCDDs and PCDFs are classified as "unintentional" POPs (UPOPs), as they are unintentionally generated during various anthropogenic activities, including combustion processes involving wood and other biomass-derived fuels (Wu et al., 2020). Bioaccumulation through the food chain represents the most critical pathway for human exposure to PCDDs and PCDFs. The contamination of food-producing animals and edible plants primarily occurs through soil absorption (Lopes & Proença, 2020).

In Europe, the recent harmonisation of EU fertiliser regulations aims to valorise certain waste materials as component material categories (CMC) for use as alternative fertilisers (EU Regulation 2019/1009). Among these, materials derived from thermal oxidation, particularly ash-based materials (CMC 13), are included. In addition to the control of heavy metals, proposed concentration limits for Σ_{16} PAHs and PCDDs/PCDFs are set at 6 mg/kg and 20 ng TEQ/kg, respectively. Toxic equivalency

factors (TEQs) are calculated based on the World Health Organisation's 2005 revision (Van Den Berg et al., 2006). The toxicity of a complex mixture of PCDDs and PCDFs is typically expressed as a toxic equivalency (TEQ), which is an aggregate measure obtained by multiplying the concentration of individual congeners by their respective toxic equivalency factor (TEF). The TEF values indicate the relative toxicity of each congener in comparison to the most toxic compound, 2,3,7,8-TCDD (Ahlborg et al., 1992).

Despite the low solubility of PCDDs/PCDFs and PAHs, which suggests limited environmental availability, it has been demonstrated that the leachability of dioxins depends on the composition and sorption properties of soils (Gul et al., 2018).

The formation of PCDDs/PCDFs in combustion processes was first reported in 1977 in waste incineration systems (Olie et al., 1977). Since then, these compounds have been extensively studied, despite the complexity and high costs associated with their characterisation.

During combustion processes, PCDDs and PCDFs can form through two main pathways: primary formation via the precursor mechanism and secondary formation through de novo synthesis (Tuppurainen et al., 1998). These two mechanisms operate simultaneously and independently in different zones of combustion systems and are influenced by various factors, including fuel composition (notably the presence of Cl, Cu, and S), the presence of organic contaminants, furnace conditions, and the applied flue gas treatment technologies (Yasuhara et al., 2003; Stanmore, 2004; Tame et al., 2007; Zhang et al., 2012).

In the higher-temperature regions of the furnace (>650°C) with low oxygen levels, PCDDs/PCDFs originate from precursors such as biomass lignin, wood preservatives containing pentachlorophenol (PCP), polychlorinated biphenyls (PCBs), and other compounds, including chlorobenzenes, chlorophenols, and PAHs, which may also form due to incomplete combustion (Tame et al., 2007). In post-combustion zones, such as baghouse filters, de novo synthesis involves the catalysed chlorination of carbonaceous structures in fly ash between 250–500°C, peaking at approximately 300°C, where Cu is the most significant catalyst (Addink & Altwicker, 1998; Bruce et al., 1991).

A high chlorine content in fuels is often associated with poorer combustion conditions, leading to increased production of chlorinated intermediates that further react to form PCDFs in post-combustion zones (WikstrÖm et al., 1999). Consequently, the potential presence of dioxins and furans rises with increasing Cl levels.

During combustion, Cl is released from inorganic or organic matrices, predominantly generating HCl, though metal chlorides may also form. HCl can be converted into Cl_2 through the Deacon catalysed reaction, which is maximised at approximately 300°C in the presence of O_2 and Cu. Cl_2 is considered

a more potent chlorinating agent than HCl due to its enhanced capability to generate highly reactive Cl radicals (Gullett et al., 2000; Duo & Leclerc, 2007).

Simultaneously, metal chlorides that may be present in fly ash, such as $CuCl_2$, can act as Cl donors, directly chlorinating carbon structures in the presence of O_2 (WikstrÖm et al., 1999).

Wood biomass with low Cl content typically produces lower levels of PCDDs/PCDFs, whereas co-combustion with Cl- and metal-containing materials (*e.g.*, salt-laden wood biomass, straw and cereal residues, wood treated with PCP-based or other metal-based preservatives) enhances PCDD/F formation (Wunderli et al., 2000; Lopes et al., 2009; Bai et al., 2017; Lopes & Proença, 2020).

Tame et al. (2007) observed that the combustion of waste wood treated with Cu-based preservatives increased baseline PCDD/F levels by two to three orders of magnitude compared to untreated wood ash. Oehme & Müller (1995) similarly reported that TEQ concentrations in filter ashes from waste wood incineration can be three orders of magnitude higher than those from untreated wood. Studies conducted in waste wood chip incinerators in Taiwan revealed that PCDDs/PCDFs in fly ash collected from baghouse filters were extremely high (Bai et al., 2017).

Duo & Leclerc (2007) reported that the combustion of salt-laden wood containing NaCl in coastal boilers resulted in PCDD/F emissions that were two to three orders of magnitude higher than those from wood with lower Cl content. Similarly, Someshwar, (1996) observed that PCDD/F concentrations in fly ash were higher in European boilers burning forest biomass compared to similar United States boilers, likely due to the elevated Cl levels in European forest biomass collected near oceanic coastlines. In addition to Cu, other metals present in fuels—such as Fe, Ni, Cr, Zn, Pb, and Al—serve as catalysts in the formation and chlorination of PCDD/Fs (Altarawneh et al., 2009; M. Zhang et al., 2016). Regarding metal chlorides, Zhang et al., (2016) identified two primary functions: catalysis and Cl donation, with $CuCl_2$ being the most active, followed by $CrCl_3$, $NiCl_2$, and $ZnCl_2$. (Addink & Altwicker, 1998) found that $CuCl_2$ acted more effectively as Cl donors than as catalysts at 353°C in the presence of O_2. Conversely, alkaline earth metals such as Ca and Mg exhibited an inhibitory effect on PCDD/F formation (Qian et al., 2005; Altarawneh et al., 2009). Calcium can capture HCl, forming liquid $CaCl_2$ in the bottom zones and/or absorbing HCl in post-combustion zones, thereby preventing Cl_2 formation (Xie et al., 1999). Similarly, NaOH and KOH have demonstrated analogous effects (Naikwadi et al., 1993). However, ash is primarily composed of alumina and aluminosilicates, which can act as catalytically active surfaces for PCDD/F formation in post-flame zones (Potter et al., 2016).

Polycyclic aromatic hydrocarbons (PAHs) are formed through complex mechanisms involving the cyclisation and aromatisation of carbonaceous matter during the pyrolysis phase of combustion, typically occurring at temperatures above 400°C, with an optimal range between 700–900°C (Lima

et al., 2005). The thermal destruction of PAHs necessitates higher temperatures and more oxidising conditions (Van Caneghem & Vandecasteele, 2014). Consequently, PAH yields depend on fuel composition and contamination, combustion conditions (temperature, oxygen availability and residence time), and post-combustion gas treatment (Van Caneghem & Vandecasteele, 2014).

Fuel contaminants such as creosote (a wood preservative) can serve as significant PAH sources in combustion systems (Johansson & Van Bavel, 2003). Straka & Havelcová (2012) detected substantial PAH concentrations in biomass ash containing unburnt material (14.5 %) and, therefore, recommended measuring PAHs in ash intended for soil application when unburnt content exceeds 9 %. However, elevated PAH levels, including carcinogenic compounds, were found in porous fly ash particles from rice husk combustion, irrespective of their unburnt content (Janvijitsakul & Kuprianov, 2007).

Sarenbo (2009) identified high levels of polycyclic aromatic hydrocarbons (PAHs) in biomass fly ash produced during the winter season, with unburned carbon content ranging between 25 % and 45 %. Conversely, Rey-Salgueiro et al. (2016) reported relatively low PAH concentrations in biomass ash, although these compounds were present in bottom ash containing 26 % organic matter. The correlation between PAH content in ash and its unburned carbon fraction is frequently documented. For instance, Košnář et al. (2016) observed an exponential relationship between PAHs and unburned material, as indicated by loss on ignition (LOI) values of 55 % in wood fly ash.

To effectively minimise polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) emissions from biomass boilers, it is crucial to optimise combustion conditions and implement appropriate flue gas treatment. Additionally, fuel composition plays a fundamental role in emission control. Besides regulating the content of metals and chlorine (as well as other halogens), it is essential to ensure that the fuel does not contain pre-existing PCDD/F. Furthermore, the use of wood preservatives, pesticides, and fertilisers—potential precursors of PCDD/F—should be avoided. Consequently, the inclusion of treated wood waste and other waste materials in biomass boilers should be prevented to mitigate the unintentional formation of highly toxic persistent organic pollutants (POPs), such as PCDD/F, and carcinogenic PAHs (Lopes & Proença, 2020).

Section 3. Materials and methods

3.1 Samples description and plant technologies

This study was conceived as a feasibility-oriented investigation aimed at characterising the principal solid residues arising from biomass combustion in a thermoelectric power plant, with the specific objective of identifying the most appropriate material for potential industrial-scale applications.
For this purpose, samples of fly ash (FA) and bottom ash (BA) were collected directly from four Italian plants engaged in the combined production of electric and thermal energy from biomass combustion, in order to provide a systematic evaluation of the chemical, physical, and mineralogical properties of these residues, while also accounting for the operational characteristics and peculiarities of cogeneration plants distributed across the Italian territory.
The investigated samples consist of four fly ashes and the respective four bottom ashes collected from the grate boiler of the same plant, resulting from the combustion of various vegetal materials and wood waste through different combustion technologies as summarised in Table 2. This table contains also information about the abatement systems implemented at each plant and specific codes under which the ashes are categorised into hazardous and non-hazardous within the European Waste Code (EWC) according to 2000/532/CE.
The two samples, BaF and FaF, originate from a thermoelectric power plant that processes approximately 500 tonnes per day of untreated solid vegetal biomass, consisting of 92 wt% cereal straw and 8 wt% wood chips obtained from agro-forestry prunings, for the combined production of electrical and thermal energy. The plant includes a biomass combustion system, a boiler, a steam turbine, an electricity generator, and a heat distribution system. For electric production, the plant generates high-temperature, high-pressure steam in the boiler, which drives a steam turbine connected to an electrical generator. This process results in an output of approximately 25.2 MW of electrical energy, with an internal consumption of 2.2 MW. The steam exiting the turbine at low pressure is condensed and recycled in the boiler, repeating the cycle. The operational principle is based on the Clausius-Rankine cycle, a thermodynamic cycle used to convert heat into mechanical work by expanding and compressing a working fluid—in this case, water. Water is particularly efficient for biomass cogeneration plants due to its availability, non-toxicity, non-flammability, chemical stability, and low viscosity (Abbas et al., 2020). The plant employs a mobile grate firing furnace in its combustion chamber, enabling efficient biomass combustion through an airflow regulation system. The ashes are removed and cooled in a water bath before storage. The bottom ashes are classified under EWC 10 01 01 ("bottom ashes, sludges, and boiler powders"), with the BaF sample considered non-hazardous waste. Combustion gases are cooled in a cyclone and subjected to a purification

system through the combined action of hydrated lime and activated carbon, while dust is captured by a bag filter for emission control. Hydrated lime reduces sulphur oxides in combustion fumes through the formation of calcium sulphate (Wang et al., 2005). Activated carbon has a highly porous surface that effectively traps a wide range of contaminants, such as heavy metals, PCCD/F, and IPA (Mariana et al., 2021).

The bag filter, a gas filtration device, utilises fabric bags to capture solid particles in combustion gases, ensuring only clean gases are released into the atmosphere (Matteson, 2017). Dust collected by the bag filter is classified under EWC 10 01 05 ("solid waste produced from calcium-based reactions in flue gas desulphurisation processes"), with the FaF sample considered non-hazardous waste.

The samples BaC and FaC come from a cogeneration plant producing electrical and thermal energy from the combustion of wood waste, including old furniture, various packaging and pruning residues obtained from urban recycling. This plant operates on the Organic Rankine Cycle (ORC). Organic Rankine Cycle ORC, instead of using water, employs an organic fluid with favourable thermodynamic properties as the heat transfer medium. The evaporation temperature of organic fluids is lower than that of water, resulting in higher efficiency in ORC cogeneration installations. The ORC system consists of two circuits: one for thermal oil and the other for the organic fluid. Heat released from biomass combustion is transferred through an oil cycle to an organic fluid, which evaporates at high temperature and pressure. The ORC system includes a pump, an evaporator, a turbine, and a condenser. Overheated organic vapor is expanded in a turbine, then condensed in a condenser before returning to the circulation pump to start a new cycle (Quoilin et al., 2013). The plant has an electric capacity of 1 MW and provides 5.5 MW of thermal power to the district heating network of the city. The combustion chamber includes a fuel feeding system, a grate assembly, a secondary air system for regulating airflow, and an ash discharge system for removing ash by gravity through hoppers. Bottom ashes removed from the grate-fired boilers are classified under EWC 19 01 12 ("bottom ashes and slag"), with the BaC sample considered non-hazardous waste. The plant employs pollutant abatement systems that operate before the gases are released into the atmosphere. In the combustion gas purification process, sodium bicarbonate neutralises acids (such as hydrochloric acid and sulphur dioxide) in the gases, and activated carbon adsorbs pollutants such as heavy metals and volatile organic compounds. The bag filter removes solid particles. Dust trapped by the bag filter is classified under EWC 19 01 13* ("fly ashes containing hazardous substances"), with the FaC sample considered hazardous waste.

The samples BaL and FaL originate from the combustion of virgin wood biomass and end-of-waste wood, including agroforestry residues and urban pruning. The plant from which they are produced

operates on the Organic Rankine Cycle (ORC). The plant boasts a thermal capacity of 5980 kW and a gross electrical power of 999 kW. The infrastructure includes a combustion chamber outfitted with a mobile grate firing furnace, similar to the systems in the other plants. Ashes extracted from the grate-fired boilers are categorised under EWC 10 01 01 ("bottom ashes, slag, and boiler powders"), with the BaL sample considered non-hazardous waste. Combustion gases traverse a treatment section featuring a bag filter, where dust removal procedures are executed before expulsion through the chimney. Dust collected by the bag filter falls under EWC 10 01 03 ("peat and untreated wood fly ashes"), encompassing the FaL sample, which is also regarded as non-hazardous waste.

The samples BaR and FaR originate from a cogeneration plant that utilizes woody waste and forestry residues, virgin wood processing, and the maintenance of ornamental greenery (considered end-of-waste wood) for thermal valorisation. This plant operates with a thermal capacity of 5.99 kW and a gross electrical power output of 1,000 kW, running an average of 8,000 hours per year. The plant uses a heat transfer fluid (thermal oil) that transfers heat to the organic oil circuit (using silicone oil), facilitating evaporation and subsequent turbine expansion according to the Organic Rankine Cycle principles. The combustion chamber has a fuel feeding system, a grate assembly, an airflow regulation system, and a gravity-based ash removal system. Bottom ashes extracted from the grate-fired boilers are classified under EWC 10 01 01 ("bottom ashes, slag, and boiler powders"), with the BaR sample considered non-hazardous waste. Combustion fumes undergo treatment in an electrostatic precipitator before being expelled through the chimney. This device, devoid of a filter, uses an electric charge to eliminate impurities from the air in solid, droplet, gas, or liquid form. As the gas exits the combustion chamber, it passes over wires or plates in the electrostatic precipitator, imparting a static charge to the smoke or gas. This charged gas is then collected on a second plate with an opposite charge, trapping the pollutant particles (Lichtfouse et al 2015).

Dust collected through electrostatic precipitation is classified under EWC 10 01 18* ("waste generated from flue gas purification containing hazardous substances"), with the FaR sample considered hazardous waste.

Table 2. Description of study materials.

Type of ash	Samples	EWC	Combustion technology	Type of fuel	Combustion temperature (°C)	Ash handling
Fly ashes	FaF	100105	Steam turbine	Straw and wood chips	>900	Hydrated Lime/Activated carbon/Bag filter
	FaC	190113*	[1]ORC	Wood waste	>900	Bicarbonate/ Activated carbon/Bag filter
	FaL	100103	ORC	Virgin wood and end-of-waste wood	>900	Bag filter
	FaR	100118*	ORC	[2]End-of-waste wood	>900	Electrostatic precipitator
Bottom ashes	BaF	100101	Steam turbine	Straw and wood chips	>900	Grate firings
	BaC	190112	ORC	Wood waste	>900	Grate firings
	BaR	100101	ORC	Virgin wood and end-of-waste wood	>900	Grate firings
	BaR	100101	ORC	End-of-waste wood	>900	Grate firings

* Hazardous waste

[1] Organic Rankine Cycle

[2] End-of-waste wood: the concept of end of waste was born at the EU level with the Waste Framework Directive (2008/98/EC). Art. 6 states that "waste ceases to be waste" when it undergoes a recovery operation, including recycling, and meets specific criteria

3.2 Sample preparation and laboratory analyses

Bottom ash was collected at the boiler outlet, while fly ash was sampled either from bag filters or, where available, from the electrostatic precipitator, in accordance with the manual stockpile sampling procedure as described in Møller (2004). Sampling was conducted at each plant between June and September 2022, under standard operating conditions characterised by typical oxygen concentrations and temperature values. For each of the four plants investigated, a bulk sample of approximately 2 kg (wet weight) was collected for both bottom ash and fly ash and all the samples were stored in polyethylene containers, kept in the dark at room temperature, in order to preserve their original physicochemical properties. Before laboratory analyses, each bulk sample was homogenised by agitation and manually subdivided using the quartering method to obtain representative subsamples for the analyses. These subsamples were then oven-dried at 105 °C for one hour to reduce their moisture content. Dried bottom ash samples were subsequently sieved using a 2 mm mesh and mechanically ground prior to analysis. All samples were characterised through a multi-analytical approach using the methodologies described hereafter.

Chemical composition of biomass ashes was determined by X-ray fluorescence (XRF) using a Panalytical AXIOS Advanced (PAN Alytical, Almelo, The Netherlands) automatic spectrometer, equipped with an X-ray tube X SST-mAX (Rh anode). The detection limit for major element oxides was 0.01 wt%. Oxide concentrations were determined on powder pellets obtained by pulverising 5 g of the sample with an Elvacite polymer resin dissolved in acetone and pressing under a hydraulic press for 15 s at 15 ton/m^2. Loss on ignition (L.o.I.), determined by mass losses at 950°C, was used to measure the volatile components.

Mineralogical characterisations of biomass ash samples were performed using X-ray powder diffraction (XRPD) which was conducted with a PANalytical Empyrean diffractometer (Malvern, PANalytical, Almelo, The Netherlands) equipped with a real time multiple strip (RTMS) PIXcel^{3D} detector and Cu-Kα radiation. The operating conditions were 40 kV and 40 mA, range was 3–80° 2θ, virtual scan was 0.026° 2θ, and counting time was 360 s per step. The incident beam pathway included a 0.125° divergence slit, a 0.25° antiscattering slit, and a soller slit (0.02 rad), whereas a Ni filter, a soller slit (0.02 rad), and an antiscatter blade (7.5 mm) were mounted in the diffracted pathway. X-ray patterns were collected from powders milled using a Retsch MM 400 vibratory mill (20 Hz, 120 s) and backloaded in aluminium sample holders.

The collected X-ray patterns were analysed using the software X'Pert High Score version 3.0 e (Malvern PANalytical, Almelo, The Netherland) which includes the ICSD database. Quantitative phase analyses (QPA) were carried out using the Rietveld method (Rietveld, 2014) by means of the Rietveld refinement software BGMN (J. Bergmann, Dresden, Germany) (Bergmann et al. 1998),

implemented in the graphical user interface Profex (Doebelin & Kleeberg, 2015). The amorphous phase quantification was carried out by combining Rietveld and reference intensity ratio (RIR) methods (Gualtieri, 2000), adding 10 wt% of corundum as internal standard (Buehler, α-Al_2O_3 > 99%). To obtain a more realistic estimation of standard deviations in quantitative phase analysis, X-ray powder diffraction measurements were repeated three times on the same powder sample, which was backloaded into the sample holder prior to each measurement. The standard deviation was then calculated from the quantitative phase results obtained through independent Rietveld refinements of the resulting three diffraction datasets.

Thermogravimetric, differential thermogravimetric and differential thermal analyses (TG- DTG-DTA-) were conducted using a Seiko thermal analyser SSC 5200 combined with a TG/DTA 320U module (Seiko, New Castle, DE, USA). Analyses were performed in air atmosphere on approximately 20 mg of powder within the temperature range of 26–1100°C (with a heating rate of 10°C/min) to determine the physical and chemical properties, quantify moisture content, residual organic carbon, volatile substances, and identify phase transitions, crystallisation, and sublimation of biomass ashes.

A Bruker spectrometer was used for identifying different functional groups and molecular bonds characterising the ashes. Fourier Transform Infrared (FTIR) analyses were carried out, at room temperature, on KBr - crushed sample pellets. The acquisition range was between 400 and 4000 cm^{-1} with 4 cm^{-1} of resolution; 16 scans were averaged for each sample and background.

A Nikon SMZ800 (Nikon Corp., Tokyo, Japan) stereomicroscope, magnification range 10x - 60x, was used for microscopic observations of the samples.

A scanning electron microscope (SEM) LEO model EVO-50XVP (Zeiss, Cambridge, UK), coupled with an X-max (80 mm^2) Silicon drift Oxford instruments detector EDX system (SEM-EDX) (Oxford Instruments, High Wycombe, UK), was used for morphological and microchemical analyses. Analyses were performed, in vacuum mode, using the powder of samples fixed on metal supports and coated by carbon. Images were collected using a secondary electron (SE) and backscattered electrons (BSE) at working distances between 7.5–8.5 mm with an acceleration voltage of 10–15 kV and a beam current of 10 μA. EDX analyses were done with an accelerating voltage of 10–15 kV on spots and variable areas, acquiring a minimum of 60 s per spot analysis.

Inductively Coupled Plasma Atomic Emission Spectrometry with argon plasma (ICP) using an ICP-MS 7900 Agilent Technologies instrument was performed according to the UNI EN 13657:2004 standard for the determination of heavy metal content. 1 g of sample was mineralised with 9 mL of HCl and 3 mL of HNO_3 in a microwave system and subsequently filtered through filter paper. The resulting solution was diluted to 50 mL with UPW (ultrapure water). During the mineralisation

process, a procedural blank and a reference material in matrix (0.5 % Fe solution) were included to check for any contaminations for the blank and to evaluate the analytical process in matrix.

Organic Gas Chromatography with Mass Spectrometry detection (GC/MS) using a 7890B (GC) 5977B (MS) MPS-XL was performed to evaluate the presence of persistent organic compounds, specifically Polycyclic Aromatic Hydrocarbons (PAHs) in accordance with the UNI EN 15527:2008 standard, and Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans (PCDD/PCDF) in accordance with the Legislative Decree No. 121 of 03/09/2020 + UNEP/POPS/CAP3/INF27 07+NATO CCMS ITEF1988.

The PAH content was determined for the eight samples across twenty compounds (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, benzo(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(ghi)perylene, chrysene, dibenzo(ae)pyrene, dibenzo(al)pyrene, dibenzo(ai)pyrene, dibenzo(ah)pyrene, dibenzo(ah)anthracene, indeno(1-2-3-cd)pyrene, pyrene, naphthalene) to compare against the EU 2019/1009 fertiliser limit, which specifies 6 mg/kg of dry matter for the sum of the following compounds (IPA_{16}): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, and benzo[ghi]perylene.

The PCDD/F content was determined by measuring the concentration of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in dry matter samples. These concentrations were then expressed in World Health Organization Toxic Equivalent (WHO-TEQ) units (Van den Berg et al., 2006). The WHO-TEQ system quantifies the toxicity of different PCDD/F congeners by comparing them to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the most toxic congener. This allows comparison with the EU Regulation 2019/1009 limit of 20 ng/kg dry matter WHO-TEQ for fertilisers.

For the extraction of persistent organic compounds (PAHs and PCDD/F), samples of fly and bottom ashes were treated with 50 ml of a solvent mixture (acetone and hexane) and subjected to sonication for one hour. During the process, a blank sample and two surrogate standards were included to ensure the accuracy of the procedure. Subsequently, the obtained solution was filtered through a folded paper filter and concentrated to a reduced volume using a multi-position evaporator. The latter allows blocking evaporation, bringing the final volume to 1 ml by operating under a nitrogen flow. Finally, the solution was adjusted to a final volume of 1 ml before proceeding with instrumental analysis.

3.3 Water leaching test

Water leaching tests were performed to assess the leachability behaviour of fly ash and bottom ash samples following the guidelines of the EN 12457-2:2002 (EN, 2002). This procedure involves a one-stage batch leaching test at a liquid to solid ratio (L/S) of 10 L/kg with deionised water, during 24 h, with particle size below 4 mm in diameter. Bottom ash samples were pre-ground to ensure dimensional homogeneity.

A 1 g aliquot of each sample was suspended in 10 mL of deionised water and subjected to continuous stirring on a magnetic plate for 5 hours. The resulting eluates were collected via a two-step filtration process: the first step employed 2.5 µm Whatman filter paper, followed by filtration through a PTFE membrane with a pore size of 0.45 µm. The pH of the solution was measured both before and after filtration using a pH meter (HI 98127, Hanna Instruments, Woonsocket, USA) and stored at 4 ± 1°C for subsequent analysis. The solid residues retained on the 2.5 µm filters were oven-dried at 80°C for one hour and subsequently weighed to determine the solubilisation percentage, calculated as the difference between the initial sample weight and the post-filtration residue weight.

Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed to quantify target metals in both eluates and solid residues obtained from the tests. X-ray powder diffraction (XRPD) and quantitative mineral phase analyses were conducted on the solid residues, employing the same methodology previously applied to bulk samples, to achieve a comprehensive characterisation of the mineral phases.

In addition to the standard leaching procedure specified by EN 12457-2:2002, an additional water leaching tests was conducted exclusively on fly ash samples (FaC, FaF, FaL, and FaR) to determine the maximum water-solubilisation potential of these specific ash types. This supplementary test followed the same methodology as before and employed an increased liquid-to-solid (L/S) ratio of 100 L/kg to enhance the release of target components and assess their maximum solubilisation potential under dilute conditions. Specifically, 5 g of each sample was suspended in 500 mL of deionised water and stirred on a magnetic plate for 5 hours before being filtered. The solid residues collected on the 2.5 µm filters were dried in an oven at 80°C for one hour and then weighed to calculate the solubilisation percentage. This was determined by subtracting the weight of the post-filtration residue from the initial sample weight.

3.4 Grain size separation and analysis

Grain size separations were performed through direct sieving under dry conditions, with mechanical shaking for one hour, using ASTM stainless steel sieves with ½ phi mesh sizes, covering the following particle size ranges: >2mm, 2-1 mm, 1-0.5mm, 0.5–0.25 mm, 0.25–0.125 mm, 0.125–0.063 mm, and <0.063 mm. They included the sole bottom ash samples as all fly ashes showed granulometry below 0.063 mm.

No separation of the finer fraction (below 0.063 mm) was performed due to the occurrence of water-soluble phases in the studied material which did not permit the use of wet separation methods.

After sieving, the mass of each size fraction was recorded, and the weight distribution percentage for each fraction was calculated. Element concentrations within the different particle size fractions were then determined using an ICP-MS 7900 Agilent Technologies instrument according to previously described procedures. Mineral phases in each granulometric fraction were identified by XRPD measurements and quantitative mineralogical analyses, according to the same procedures previously described for the analysis of bulk samples.

Section 4. Results: characterisation of the investigated ashes

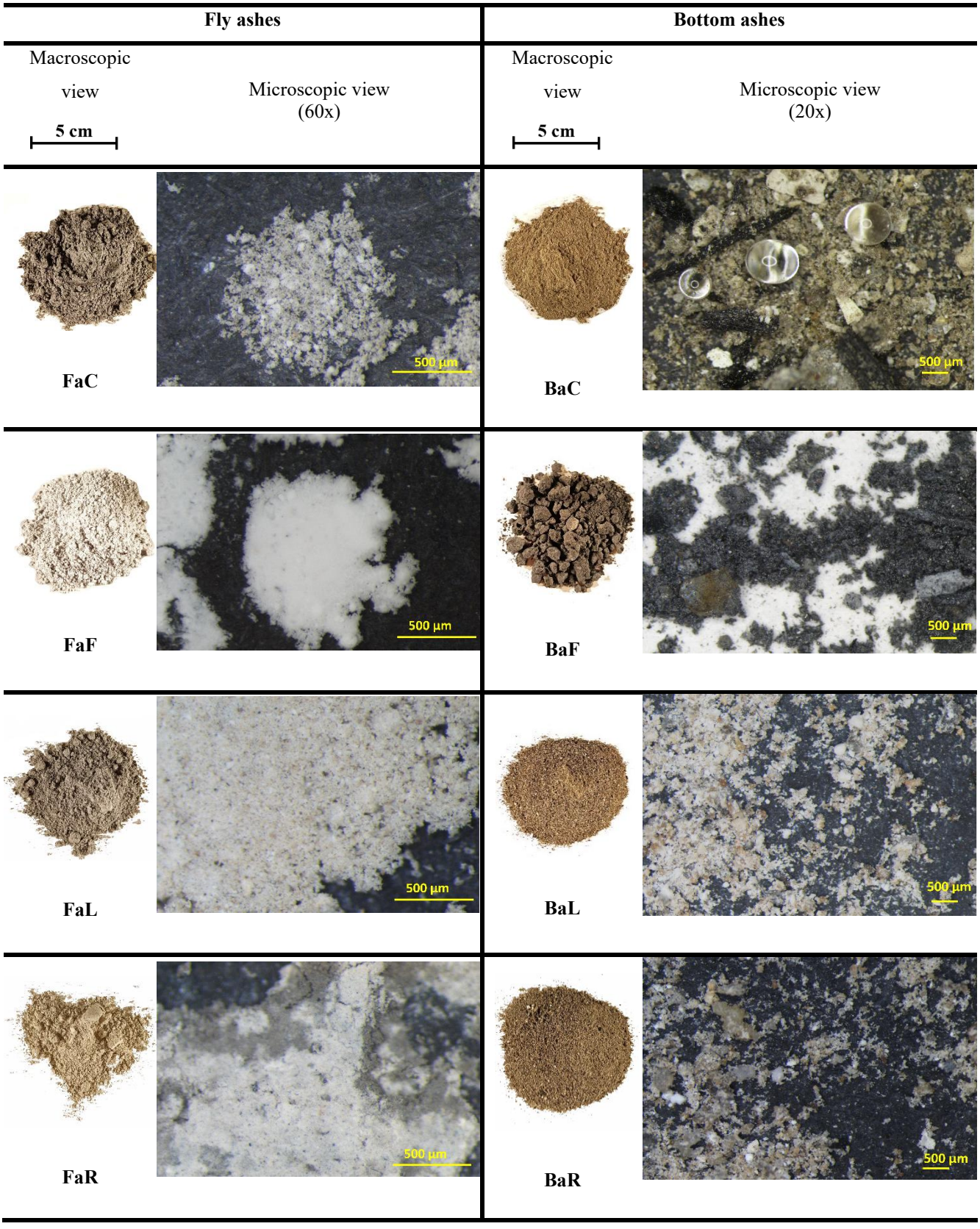


Figure 1- Macroscopic images and microscopic view under stereomicroscope of fly ashes and bottom ashes.

A macroscopic and microscopic view of the ashes investigated in this work is reported in Figure 1, showing the microstructure and morphology of each fly ash sample and the corresponding bottom ashes from the same plant. The colour of these samples ranged from light grey and brown to black. They include fine-grained and dusty powders (FaC, FaF, FaL and FaR) and mixtures of sandy materials and fine-grained dusty powders (BaC, BaL and BaR). Darker-coloured biomass ashes generally contain char, such as the BaF sample, which appears as a black-dark grey slag. Some biomass ashes had friable agglomerated chunks with spots of black, grey, brown, and/or white particles. Overall, all fly ash samples appear as micro-aggregates of fine particles with homogeneous shapes. Bottom ashes consist of coarse granular particles with heterogeneous, irregular shapes, as well as spherical vitreous particles.

4.1 Chemical composition of ashes

Table 3. Major oxide (wt%) and heavy metal (mg kg^{-1}) concentrations in the investigated ash samples.

		Fly ashes				Bottom ashes			
Unit	Oxide	FaC	FaF	FaL	FaR	BaC	BaF	BaL	BaR
Major oxides[1] (wt%)	Na_2O	31.78	5.51	4.14	10.7	5.62	1.19	0.8	1.13
	MgO	0.81	0.04	6.72	2.86	5.09	1.84	6.86	5.68
	Al_2O_3	0.54	0.11	2.05	1.3	5.17	5.47	5.94	8.18
	SiO_2	1.59	2.26	6.91	4.85	31.72	58.31	30.01	43.79
	P_2O_5	0.62	1.53	2.82	1.88	2.06	0.86	1.34	1.82
	K_2O	0.68	16.05	19.7	19.8	5.29	13.93	6.57	6.83
	CaO	1.46	21.28	28.26	7.12	23.87	9.31	35.77	23.64
	TiO_2	0.25	0	0.12	0.05	3.98	0.3	0.4	0.6
	MnO	0.02	0.01	0.17	0.07	0.26	0.14	0.18	0.2
	Fe_2O_3	0.18	0.08	1.39	0.92	4.68	2.63	3.8	5.06
	L.o.I [3]	62.07	53.13	27.71	50.45	12.26	5.3	8.34	3.08
Heavy metals[2] (mg/kg)	Pb	7745	983	1354	606	603	621	3245	478
	Ni	34	6	31	43	86	21	31	55
	Cd	140	18	32	75	45	4	1	0,7
	As	111	27	90	222	113	12	6	8
	Cu	495	132	295	991	717	92	122	15774
	Zn	41688	5204	7504	20017	9416	872	193	239
	Cr (VI)	<0.5	<0.5	<0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	Hg	13.34	2.28	0.325	1.4	0.311	<0.1	<0.1	<0.1
	Cr (Tot)	90	23	127	201	209	35	72	94
	Co	18	3	7	9	28	7	8	14

[1] Determined from XRF; [2] Determined by ICP-MS; [3]L.o.I. at 950°C.

The chemical composition of biomass ashes is presented in Table 3. All the investigated ash samples show a significantly different chemical composition, although fly ashes and the respective bottom ashes show a generally distinct composition regardless of the type of combustion furnace and fuel used.

Fly ashes show significant amounts of alkali elements: potassium oxide (K_2O) content ranges from 16.05 wt% to 19.8 wt% in FaR, FaL and FaF, while very high content of sodium (Na_2O) is observed in FaC (up 31.78 w%). The two samples FaF and FaL are also characterised by a relevant amount of CaO (28.26 wt% and 21.28 wt%, respectively), compared with samples FaC and FaR showing less than 2 wt% and 8 wt% of Ca-oxide, respectively. Both FaF and FaR samples are also characterised by significantly higher content of MgO, SiO_2, Al_2O_3 and P_2O_5 with respect to the other ashes.

Silicon is the predominant element in all bottom ashes, with concentrations of Si_2O ranging from 30.01 wt% in BaL to 58.31 w% in BaF. Significant content of CaO is also present in all the samples with values exceeding 20 wt% in three of the samples (BaC, BaL and BaR), while other oxides (*i.e.* K_2O, Al_2O_3, MgO, Fe_2O_3, Na_2O, P_2O_5, MnO and TiO_2) are found in concentrations less than 10 wt%. Overall, fly ash shows significant amounts of potassium and sodium, while bottom ashes are richer in silicon, calcium, aluminium and iron. Both fly ash and bottom ash samples show also significant and almost similar amounts of magnesium and phosphorus. The Loss on Ignition (L.o.I) value determined at 950°C (Table 3) resulted from ~62 wt% (FaC) to ~28 wt% (FaL) in fly ashes suggesting high content of volatile compounds. Conversely, lower values of L.o.I. were observed for the bottom ashes (from ~3 wt% in BaR to ~12 wt% in BaC).

Chemical analyses of trace elements by ICP-MS indicated relatively high concentrations of heavy metals, although the type and content of metals differ significantly from sample to sample. Zinc represents the predominant heavy metal in all fly ashes and in BaC bottom ash, with concentrations peaking at 41688 mg/kg and 9416 mg/kg in FaC and BaC, respectively. Lead is a very abundant heavy metal as well, reaching a concentration up to 7745 mg/kg in fly ash and up to 3245 mg/kg in bottom ash. The Cu content ranges from a maximum of 991 mg/kg to a minimum of 132 mg/kg in fly ashes, whereas in bottom ashes its content span from 15774 mg/kg in BaR to 92 mg/kg in BaF.

Overall, nickel (Ni), cadmium (Cd), arsenic (As), mercury (Hg), and total chromium (Cr tot) exhibit significantly lower values compared to zinc, lead, and copper in both fly ashes and bottom ashes, as detailed in Table 3. Nickel varies from 43 mg/kg in fly ashes to 86 mg/kg in bottom ashes. Slightly higher concentrations are observed for cadmium (up to 140 mg/kg), arsenic (up to 222 mg/kg), and total chromium (up to 209 mg/kg). Mercury's highest concentration is reached 13.34 mg/kg in fly ashes, with less than 0.1 mg/kg in all bottom ash samples. Hexavalent chromium (Cr VI) measures below 0.5 mg/kg (LOQ) in all the samples investigated.

A comparison of the collected data with the limits of heavy metals for various fertiliser types according to European fertiliser regulation (2019/1009) (Table 4) show some exceedances depending on the sample and fertiliser type. The highest concentrations of heavy metals were observed for the fly ash sample FaC and the bottom ash sample BaC, while the lowest concentrations were found in FaF and BaF.

Table 4. EU Regulation 2019/1009 establishing criteria for the placing on the market of fertiliser.

Metals (mg/kg)	Pb	Ni	Cd	As	Cu	Zn	Cr (VI)	Hg
Organo-mineral fertilisers	120	50	3	40	600	1500	2	1
Inorganic fertilisers based on macroelements	120	100	3	40	600	1500	2	1
Inorganic fertilisers based on microelements	600	2000	200	1000				100
Calcium and/or magnesium correctives	120	90	2	40	300	800	2	1
Inorganic amendment	120	100	1.5	40	300	800	2	1

Table 5 shows the concentrations of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs). Notably, the fly ash sample collected by the electrostatic precipitator (FaR) exhibits the highest PCDD/F concentration, reaching 40 ng/kg dry matter WHO-TEQ (Van den Berg et al., 2005). This value significantly exceeds the European Union Regulation 2019/1009 limit of 20 ng/kg dry matter WHO-TEQ for PCDD/Fs in fertilisers.

Table 5. Bulk chemical (GC-MS) composition ng /kg WHO-TEQ of PCDD/PCDF.

	Fly ashes				Bottom ashes			
	FaC	FaF	FaL	FaR	BaC	BaF	BaL	BaR
PCDD/PCDF (ng /kg)	< 10	< 10	< 10	40	< 10	< 10	< 10	< 10

The polycyclic aromatic hydrocarbons (PAHs) were calculated for the eight samples to compare with the EU 2019/1009 fertiliser limit, which specifies a maximum of 6 mg/kg of dry matter for the sum of the following compounds (PAH16): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, and benzo[ghi]perylene. All these compounds showed concentrations below 0.2 mg/kg (LOQ), indicating that their sum in all the investigated sample falls within the limit of 6 mg/kg determined by Regulation EU 2019/1009.

4.2 Mineralogical composition of ashes

The X-ray powder diffraction pattern (XRPD) patterns showing the mineralogical composition of different ash samples is report in Figure 2 and 3, while quantitative phase analysis according to Rietveld refinement of XRPD data are displayed in Tables 6 and 7 (Diagram outputs from BGMN refinement are in Appendix 1). XRPD data of fly ashes (Figure 2) suggested that the type and content of crystalline phases changes significantly from sample to sample. The most intense peaks in all the measured diffraction patterns are related to chloride phases. The potassium chloride sylvite (KCl) is the main crystalline phase in both FaF and FaR samples showing a content of ~25 wt% and 35 wt%, respectively in these two samples, while ~13 wt% of this phase was determined in FaL. Instead, in FaC halite (NaCl) is the main mineral component, while it is present only in concentration below 2 wt% in the other fly ash samples.

In addition to chlorides, the investigated fly ashes showed the presence of several calcium minerals such as calcite ($CaCO_3$), common to all samples (from 2.1 to 10.5 wt %), portlandite [$Ca(OH)_2$] contained in amounts ranging from 1 to 18.7 wt%, anhydrite ($CaSO_4$), from 1.1 to 6.6 wt%, and hydroxyapatite $Ca_5(PO_4)_3(OH)$ from 1.4 to 7.5 wt%, present in four samples. Furthermore, soluble K-bearing sulfates such as aphthitalite [$(K,Na)_3Na(SO_4)_2$] and syngenite [$K_2Ca(SO_4)_2•(H_2O)$] are also present, the former in all the samples (from 1.4 % to 5.8 wt%), the latter only in FaL and FaR (19.0 wt% and 10,1 wt%, respectively). The Na-sulfate thenardite (Na_2SO_4) was instead detected in FaC (3.9 wt%). The highest content of Na-rich phases in FaC compared to the other samples characterised by K- and Ca-rich mineral phases is in well agreement with chemical analysis showing an enrichment of Na in the former sample and of K and Ca in the others.

Minor mineral phases corresponding to oxides such as periclase (MgO) and zincite (ZnO) were also detected. The former in three out of four samples with amounts ranging from 0.9 wt% to 4.3 wt%, the latter only in FaC sample (1.6 wt%). This evidence further agrees with the chemical data showing an higher concentration of zinc in FaC compared to the other samples. Lastly, only two silicon-based mineral phases are detected: Ca-silicates in FaC (3.4 wt%) and quartz (0.8 wt%) in FaR.

Overall, a very significant amount of amorphous phase was found in all the investigated fly ashes, with values estimated from 30.2 wt% to 46.8 wt%.

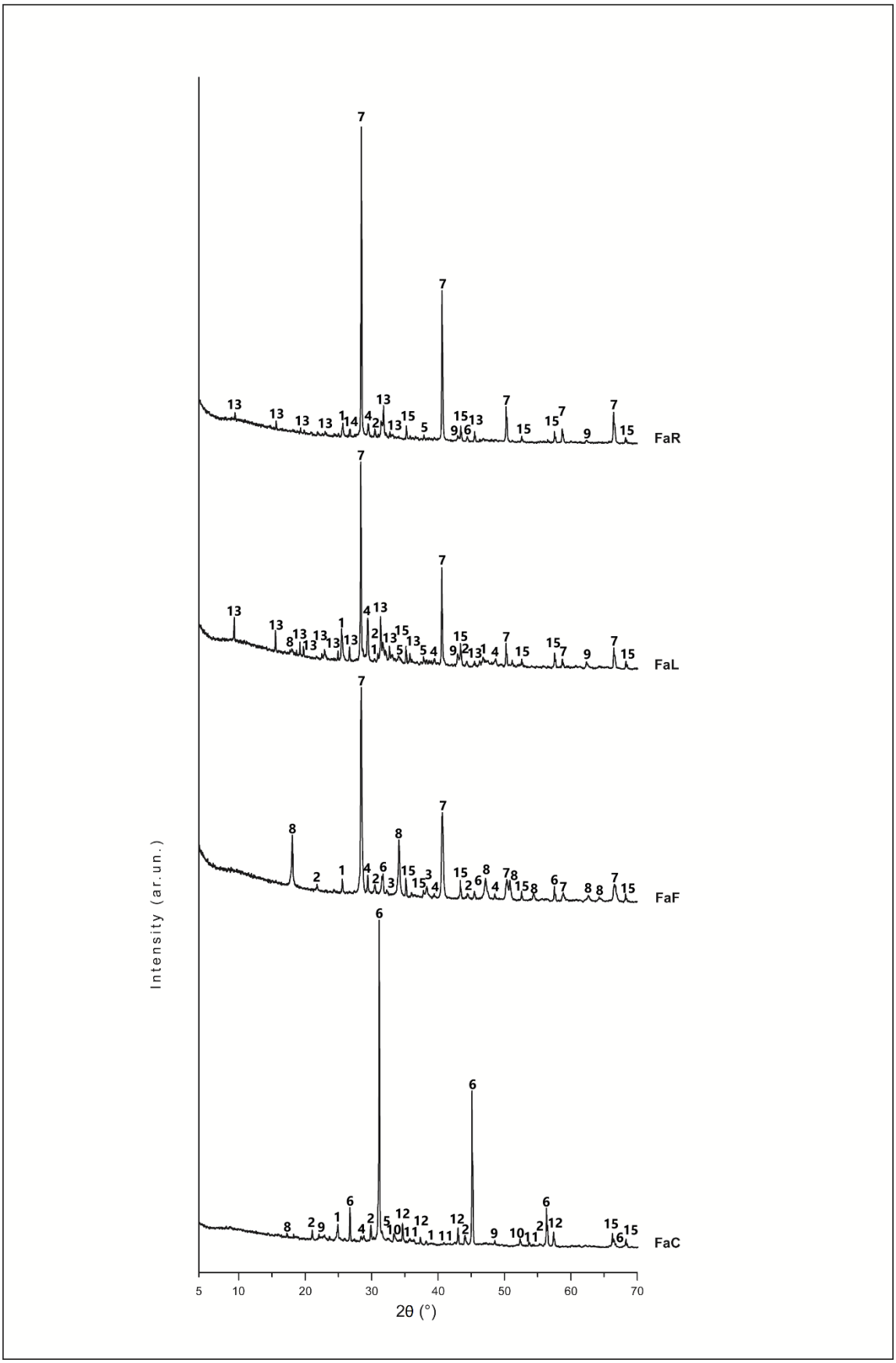


Figure 2. XRPD patterns of fly ashes: anhydrite (1); aphthitalite (2); CaClOH (3); calcite (4); hydroxyapatite (5); halite (6); sylvite (7); portlandite (8); periclase (9); thenardite (10); zincite (11); Ca-silicate (12); syngenite (13); quartz (14); corindone (15).

Table 6. Mineralogical composition (wt%) of fly ashes obtained by Rietveld refinement.

Mineral name, formula	FaC	FaF	FaL	FaR
anhydrite, $Ca(SO_4)$	1.4 ±0.1*	1.3 ±0.6**	6.6 ±1.5*	1.7 ±0.3*
aphthitalite, $(K,Na)_3Na(SO_4)_2$	5.8 ±0.4	5.7 ±0.6	1.4 ±0.8	5.5 ±1.0
calcite, $CaCO_3$	2.1 ±0.2	5.0 ±0.5	10.5 ±0.9	5.3 ±1.8
CaClOH		4.5 ±0.9		
halite, NaCl	30.4 ± 1.0	2.3 ±0.2		2.4 ±0.3
hydroxyapatite, $Ca_5(PO_4)_3(OH)$	2.7 ±0.2	1.4 ±0.4	7.5 ±0.3	5.6 ±0.4
silvite, KCl		25.5 ±1.1	13.3 ±1.0	35.3 ±0.9
periclase, MgO	0.9 ±0.3		4.3 ±0.3	3.1 ±0.5
thernadite, Na_2SO_4	3.9 ±1.7			
portlandite, $Ca(OH)_2$	1.0 ±0.1	18.7 ±0.6	3.0 ±0.8	
zincite, ZnO	1.6 ±0.2			
Ca-silicate	3.4 ±0.5			
syngenite, $K_2Ca(SO_4)_2•(H_2O)$			19.0 ±1.7	10.1 ±2.1
quartz, SiO_2				0.8 ±0.4
amorph	46.8 ±3.8	35.6 ±1.7	34.4 ±1.9	30.2 ±4.5
Rwp	9.08; 7.6; 7.72	7.19; 7.04; 7.28	6.48; 6.63; 6.40	7.68; 7.58; 7.01
χ^2	1.60; 2.98; 2.96	2.69; 2.27; 2.78	2.13, 2.02; 1.80	2.89; 2.59; 2.06
GOF	1.26; 1.73; 1.72	1.64; 1.51; 1.67	1.46; 1.42; 1.34	1.70; 1.61; 1.44

* Insoluble phase; ** soluble phase
Notes: standard deviations were determined experimentally through multiple, independent measurements and Rietveld refinements of each sample.
Rwp, $\chi 2$ and GOF values for each independent refinement replicas are reported.

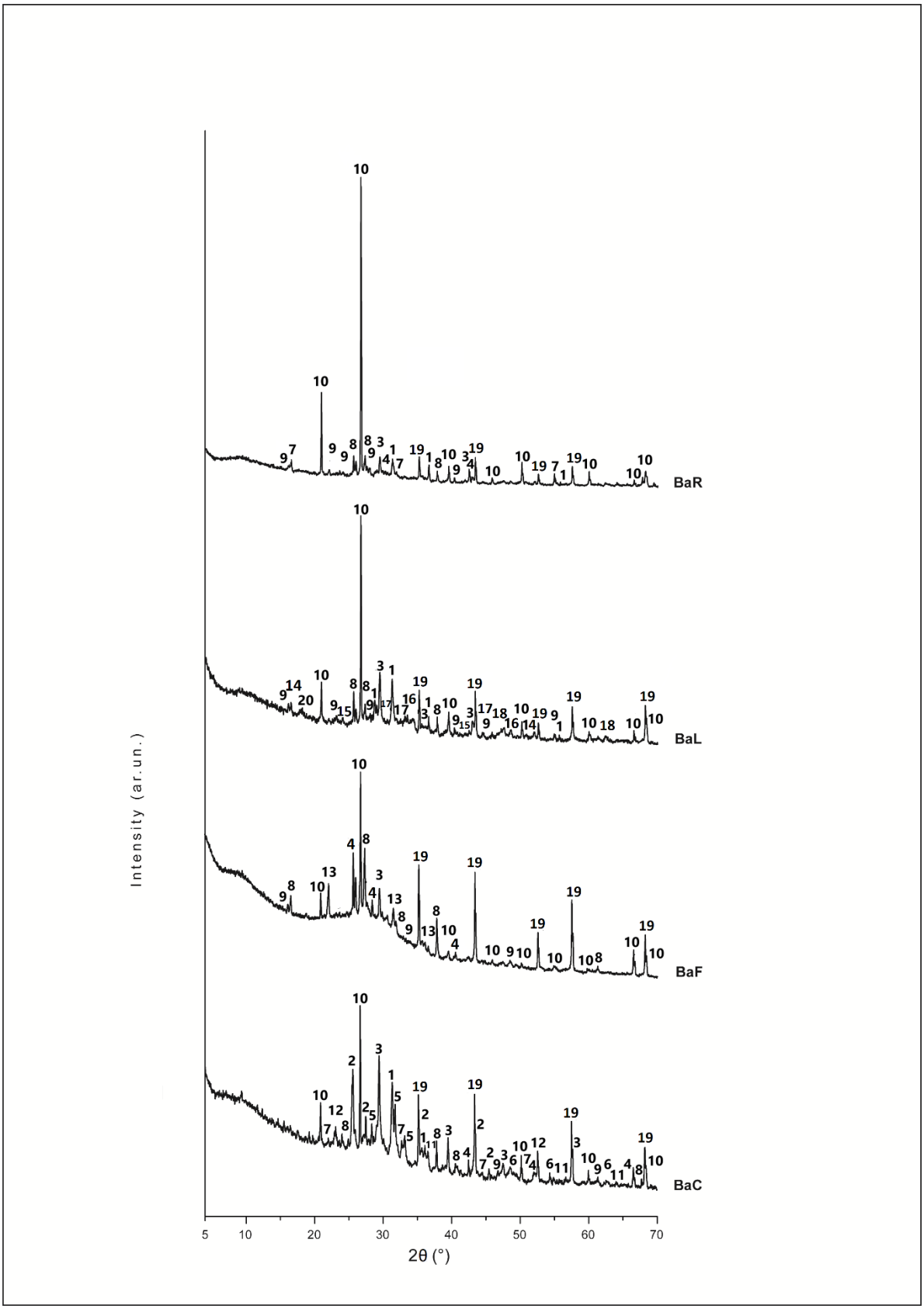


Figure 3. XRPD patterns of bottom ashes: akermanite (1); anhydrite (2); calcite (3); pyroxene (4); gypsum (5); hematite (6); hydroxyapatite (7); leucite (8); plagioclase (9); quartz (10); rutile (11); syngenite (12); cristobalite (13); hatrurite (14); monocalcium aluminate (15); merwinite (16); periclase (17); portlandite (18); corindone (19).

Table 7. Mineralogical composition (wt%) of bottom ashes obtained by Rietveld refinement.

Mineral name, formula	BaC	BaF	BaL	BaR
akermanite, $Ca_2MgSi_2O_7$	4.1 ± 0.4		6.4 ± 2.0	6,6±1.2
anhydrite, $Ca(SO_4)$	4.3 ± 0.7 *			
pyroxene, $(Ca,Mg,Fe)_2Si_2O_6$	3.2 ± 0.3	2.2 ± 0.3		4.2±0.3
hatrurite, Ca_3SiO_5			1.2±0.2	
monocalcium aluminate, $CaAl_2O_4$			3.5±0.7	
calcite, $CaCO_3$	7.6 ±0.6	1.8 ± 0.7	5.4±1.6	3.2±1.2
cristobalite, SiO_2	1.1 ±0.2	1.8 ±0.2		
gypsum, $CaSO_4 \cdot 2H_2O$	1.6 ±0.2			
hematite, Fe_2O_3	1.5 ±0.2			
hydroxyapatite, $Ca_5(PO_4)_3(OH)$	4.0 ±0.2		2.2±0.5	2.2 ±0.2
leucite, $KAlSi_2O_6$	3.2 ± 0.3	6.5 ± 2.0	5.5± 0.5	9.8± 1.8
merwinite, $Ca_3Mg(SiO_4)_2$			4.8± 0.7	
periclase, MgO			1.7± 0.5	1.5± 0.1
plagioclase, $(Na,Ca)(Si,Al)_4O_8$	3.2 ± 0.9	6.7 ± 1.6	7.7± 2.0	5.9± 0.3
portlandite, $Ca(OH)_2$			2.9± 0.1	
quartz, SiO_2	6.3 ± 1.3	2.1 ± 1.1	8.8± 0.3	23.4± 2.4
rutile, TiO_2	1.8 ± 0.1			
syngenite, $K_2Ca(SO_4)_2 \bullet (H_2O)$	5.0 ± 0.6			
amorph	54.1 ± 0.6	78.9 ± 5.1	49.8 ± 3.5	43.2 ±5.1
Rwp	5.52; 4.13; 4.89	2.31; 3.18; 3.06	6.11; 6.57; 6.75	6.86; 6.85; 6.57
χ^2	2.0; 2.99; 3.92	2.34; 3.76; 3.32	2.34; 2.44; 2.56	3.05; 2.78; 2.57
GOF	1.42; 1.73; 1.98	1.53 ;1.94; 1.82	1.53; 1.56; 1.60	1.75; 1.67; 1.60

* Insoluble phase;
Notes: standard deviations were determined experimentally through multiple, independent measurements and Rietveld refinements of each sample.
Rwp, χ2 and GOF values for each independent refinement replicas are reported.

The X-ray powder diffraction data of bottom ashes (Figure 3, Table 7) showed a high content of silicate phase in accordance with high silicon content identified by chemical analyses (Table 3). Quartz is present in all the samples with amounts ranging from 2.1 wt% to 23.4 wt%. Depending on the sample, various silicate phase such as leucite ($KAlSi_2O_6$), and cristobalite (SiO_2), are present, the former in all investigated samples (from 9.8 wt% to 3.2 wt%), the latter in only two samples with concentrations below 2 wt%. Additionally, the XRPD analyses highlighted the presence of several calcium-based silicates, in well agreement with the generally high content of calcium observed in all the investigated bottom ash samples (CaO = 9.3-37.77 wt%). Plagioclase is common in all samples in percentage ranging from 3.2 wt% to 7.7 wt%, akermanite ($Ca_2MgSi_2O_7$) was detected in three

samples with concentrations ranging from 4.1 wt% to 6.6 wt%, whereas depending on the samples, other silicate phase such as pyroxene [$(Ca,Mg,Fe)_2Si_2O_6$], hatrurite (Ca_3SiO_5), and merwinite [$Ca_3Mg(SiO_4)_2$] were also found. The occurrence of several oxide phases as hematite (Fe_2O_3), periclase (MgO), and rutile (TiO_2) was also detected in concentrations generally below 2 wt%, while portlandite [$Ca(OH)_2$] only in BaL (2.9 wt%). Other detected Ca-bearing minerals are calcite $CaCO_3$, which is a common constituent of all the samples (from 1.8 wt% to 7.6 wt%), apatite [$Ca_5(PO_4)_3(OH)$], present in three out of four samples (from 2.2 wt% to 4.0 wt%), while only in BaC the Ca-bearing sulfates syngenite [$(K_2Ca(SO_4)_2•(H_2O)$] and gypsum ($CaSO_4·H_2O$) were also found 5.0 wt% and 1.6 wt%, respectively.

Finally, a content of amorphous material ranging from 43.2 wt% to 78.9 wt% was estimated in the examined bottom ash samples.

4.3 Thermal characterisation through TG-DTA analysis

The behaviour of the ashes under study as a function of temperature, recorded in air atmosphere, is shown in Figure 4 and Figure 5, for fly ashes and bottom ashes, respectively. In the whole, some general aspects can be noted:

- despite some similarities in chemical and mineral compositions, the thermal behaviours of each individual ash were found different, with some exception.
- fly ashes exhibited significantly higher total weight losses compared to bottom ashes.
- all samples show a quite continuous weight loss by heating with a significant increase of the slope from 600°C.
-the decomposition of calcite ($CaCO_3$) was the principal thermal event clearly observed in all samples, as indicated by endothermic peaks occurring at different temperatures between 600 and 750 °C.
-Thermal event related to silicates (*e.g.*, quartz, cristobalite, leucite), which are quite abundant especially in bottom ashes, were not fully appreciated as most of these phases are quite stable in the considered thermal range (Vassilev et al., 2013b, 2022).

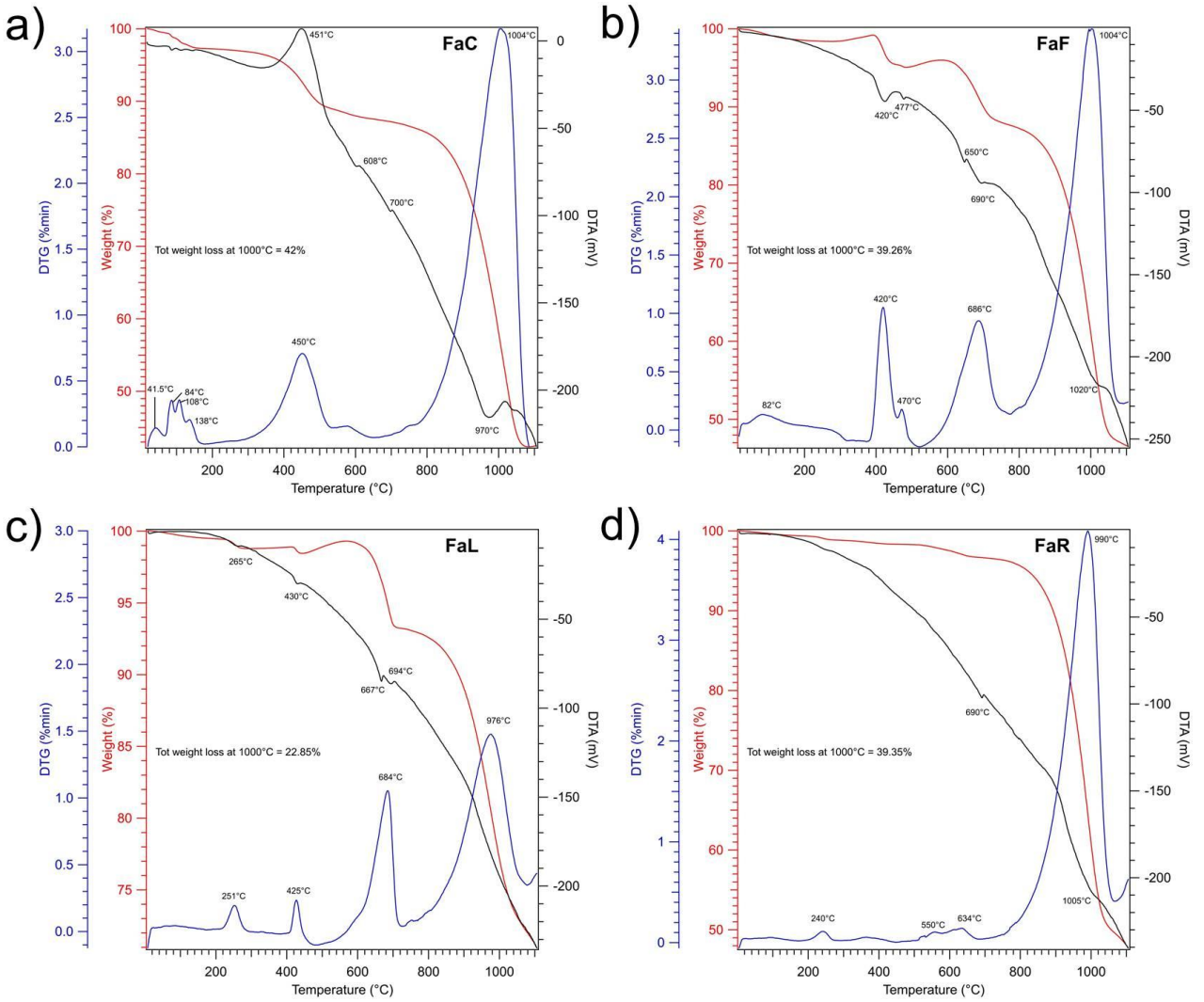


Figure 4. TG (red line, left axis), DTA (black line, right axis) and DTG (blue line, external axis) curves of fly ashes: (a) FaC, (b) FaF, (c) FaL and (d) FaR.

The TG analysis of FaC sample (Figure 4a) showed a total weight loss of about 57 % at 1100°C, corresponding to four different losses. The first, in the region between 25-200°C with a mass loss of about 2.7 % is associated to slights endothermic effects mainly due to evaporation of adsorbed water. A second weight loss of 8.4 % was observed in the range 200-530°C (DTG peak at 450 °C). This mass variation corresponded to an exothermic peak centred at 450°C and may be attributed to the combustion of residual char (exothermic process occurring between 200 and 600°C (Umamaheswaran & Batra, 2008; Vassilev et al., 2022b). A weight loss of ~ 1.5 % between 530-700°C can be considered as the contribute of dehydroxylation of hydroxides, portlandite and hydroxyapatite according to mineralogical analyses, and calcite decomposition, as also suggested by the endothermic DTA peaks at about 600 and 700°C, respectively. The last and significant mass loss of about 45 %, occurred within the analysis range, can be considered as the sum of desulphurisation

of minerals as anhydrite, aphthitalite and thernadite, and chloride melting (Vassilev et al., 2022). Results are in agreement with XRPD data, since halite (NaCl) resulted the most abundant mineralogical phase (~30 wt%).

FaF sample (Figure 4b) showed a total weight loss of 53 % at 1110 °C, corresponding to five flections of TG curve. Within 500°C three weight losses were observed (1.45 %, 3 % and 0.4 %), the former related to decomposition of hydrated phases or physically adsorbed water from the sample, the remaining ones due to the decomposition of hydroxides, which commonly occurs in the range of 450-550°C, especially of portlandite, present as abundant phase (see mineralogical analysis). As further confirmation, DTA curve showed in this range two endothermic peaks centred at 420°C and 470°C, respectively. The mass loss of 7 %, occurring in the range 500-750°C, corresponds to calcite degradation. The presence of two endothermic processes centred at 650°C and 690°C may corresponds to calcite with different crystallisation degree formed during the combustion process. Between 750°C and 1100°C, the TG curve showed a significant weight loss up to 41.4 %, corresponding to a sharp DTG peak at ~ 1000°C and a DTA endothermic flection at 1020°C, related, similarly to FaC ash, both to the partial degradation of sulphates and chlorides fusion (*i.e.* silvite and halite minerals) (Thy et al., 2006). The thermal behaviour of FaL (Figure 4c) resulted quite similar to FaF ash, although its total mass loss (28.76 %) resulted the lowest among all fly ashes object of study. The weight losses were collected in the follow ranges: within 300°C (~ 1.18 %), 300-440°C (~ 0.35 %), 440-715°C (~ 5.2 %), 715-1100°C (~22.1 %). At thermal losses corresponded four endothermic events occurred at 265°C, 430°C, 667°C and 694°C which can be attributed respectively to dehydration of hydrated sulphate syngenite, dehydroxylation of portlandite, calcite decarbonation, fusion of sylvite and desulphurisation of sulphates. It is worth to note that the last and larger weight loss reached the maximum at 976°C (see DTG curve).

The TG curve of the FaR sample (Figure 4d) showed a total weight loss of 51.97 % up to 1100°C. The trend of the curve is more continuous than other fly ashes and three weight losses were observed. The first in the region between 25-300°C with a mass loss of about 1,15 % was related to dehydration of syngenite; the second in the range 300-700°C with a mass loss of about 2%, included the dehydroxylation and decarbonation processes already discusses for other ashes. DTA curve, in this range, marked only a slightly endothermic peak at 690°C. In the range 700-1100°C occurred the third and significant loss (48,7 %) due to sulphates and chlorides, as further confirmed by the derivative thermogravimetry (peak at about 990°C) and endothermic inflection of DTA curve at about 1000°C.

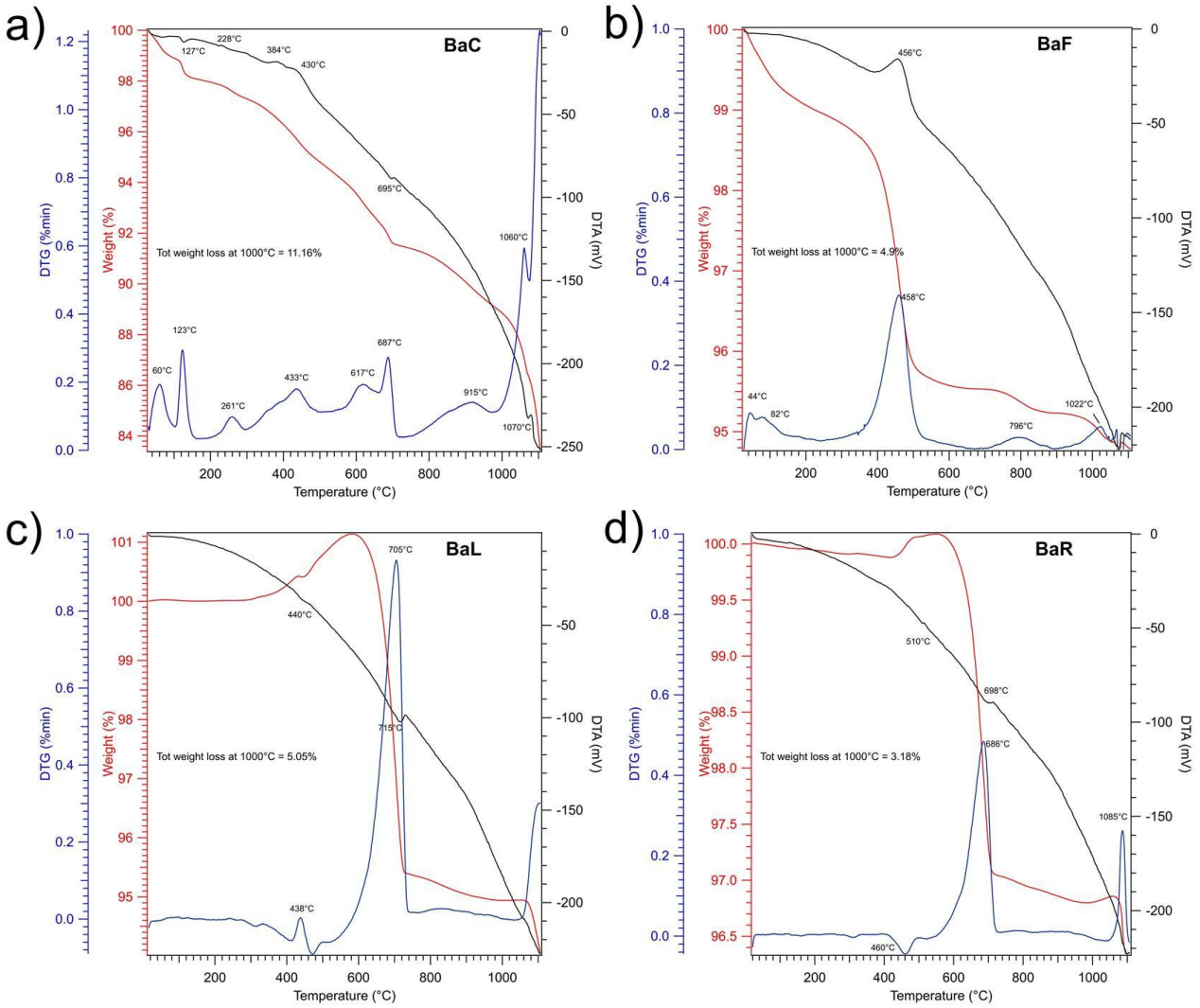


Figure 5. TG (red line, left axis), DTA (black line, right axis) and DTG (blue line, external axis) curves of bottom ashes: (a) BaC (b) BaF (c) BaL and (d) BaR.

The thermal behaviours of the bottom ashes (Figure 5) appeared quite different from each other and showed total weight losses ranging from 3 to 15% up to 1100°C.

The total weight loss of BaC sample (Figure 5a) was the sum of six contributions, as consequence of its heterogeneous mineralogical composition (see Figure 3 and Table 6). In the range 25 -145°C a loss of ~ 1.9 %, may be attributed to decomposition of hydrated phases (*e.g.*, syngenite and gypsum) and physically adsorbed water in the ash. In this range, an endothermic event was collected at 127°C. In the range 145-280°C was observed a loss lesser than 1 % in weight attributed to further dehydration of gypsum as confirms the flection by DTA at 280°C. Between 280-470°C the weight loss of about 2.3 % are the sum of different exothermic events (384°C and 430°C) related to the combustion of residual chars. The endothermic peak at 695°C was due to carbonates decomposition and corresponded to a weight loss of 3.6 %, occurred between 470-710°C. The other weight losses (2.3 % and 5.1 %) occurred in the range 710-960°C and 960-1100°C, as evidence by two DTG peaks with

maxima at 915°C and 1060°C, respectively, which can be attributed to degradation of sulphates which commonly occurs above 800–900°C and silicates present in this sample. These minerals are stable up to 1000°C, hence indications of their transformations were observed at the second weight loss phase, occurring beyond 1000°C at an endothermic peak due to fusion at high temperatures (Abraham et al., 2013; Vassilev et al., 2022b).

Similarly to BaC, BaF ash (Figure 5b) showed a multistep weight loss (in the complex 5.2 % at 1100°C). In the ranges 25-200°C, 600-870°C and 870-1100°C sample lost amounts lesser than 1 %, whereas between 200-600°C occurred the main loss of ~ 3,5 % in weight, with a maximum event at about 450°C. The occurrence of an evident exothermic peak, the sole revealed in a quite continuous DTA curve, allowed to attribute this variation to the residual of coal combustion. Is worth to be noted that the occurrence of some char in BaF was also confirmed by SEM investigations, as showed below in Figure 9a.

BaL and BaR samples (Figure 5c-d) thermal behaviours appeared quite similar. Both TG curves evidenced until 540 and 590°C an apparent weight increase up to 1.15 %, probably due to oxidative phenomena (Mobili et al., 2020). The main weight losses occurred between 550-750°C, equal to 4.6% and 2.95 % for BaL and BaR, respectively. The endothermic variations, detected in DTA curves, allowed to attribute these weight losses to calcite decomposition. The different silicates present in the samples remained stable up to 900°C, whereas indications of others slight phase transformations were observed between 980-1100°C, with weight losses minor than 1 %.

4.4 Fourier Transform Infrared Spectroscopy (FTIR) analysis

The FTIR analyses of the ashes (Figure 6 and Table 7) confirmed the presence of various compounds, resulting in different molecular vibrations, as already revealed by chemical and mineralogical analyses. The main vibrations observed by FTIR analyses are in Table 7. Due to the complexity of the ash composition, the overlapping of some vibrations, mainly observed in the broader bands and making complex the spectra interpretations, is outlined.

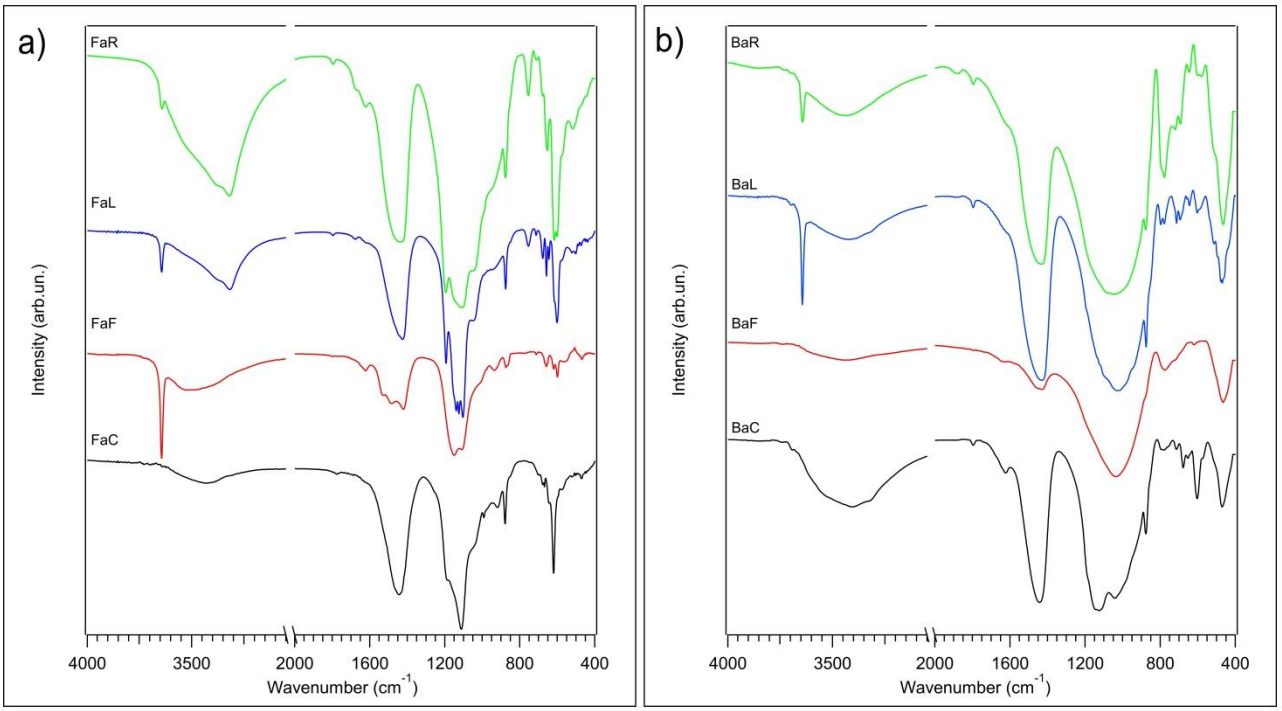


Figure 6. FTIR spectra of a) fly ashes, b) bottom ashes.

The narrow absorption peaks centred in the range 3646 - 3642 cm^{-1}, detected in FaF, FaL, FaR, BaL and BaR, are associated with the O-H bond stretching in hydroxyl linkage related to minerals such as portlandite or hydroxyapatite.

All ashes showed a broad band centred between 3450-3400 cm^{-1} and a weak peak or a shoulder at about 1650-1620 cm^{-1}, related to stretching and bending vibration respectively of O-H bonds of water molecules. These peaks are more prominent when structural water molecules occur in ashes (*i.e.* in FaL, FaR and BaC which contain gypsum and/or syngenite).

Table 8. Characteristic bands of fly and bottom ashes identified from FTIR spectra.

	Fly ashes				Bottom ashes			
	FaC	FaF	FaL	FaR	BaC	BaF	BaL	BaR
Peaks (cm^{-1})	3440 (br)	3646 (s-sh)	3643(s-sh)	3641(w-sh)	3690 (w)	3470 (w)	3643 (s-sh)	3642 (sh)
	1443 (s)	3470 (br)	3320 (s-br)	3320 (s-br)	3450 (br)	1640 (w)	3400 (m)	3430 (br)
	1190 (d)	1623 (w)	1795 (w)	1798 (w)	1795(w)	1439 (m)	1795 (w-sh)	1795 (w-sh)
	1114 (s-sh)	1528 (w-M)	1677 (w)	1678 (w)	1623 (w)	1035(s)	1635 (w)	1638 (w)
	1035 (w)	1484 (w-M)	1426 (s)	1620 (w)	1443 (s)	877 (w)	1430 (s)	1430 (s)
	995 (w)	1420 (s-M)	1193 (m-sh)	1440 (s)	1130 (s)	744(m)	1026 (s)	1046 (s)
	919 (w)	1150 (s-d)	1138 (s-M)	1195(sh-M)	1040 (s)	617 (s)	874 (sh)	878 (sh)
	878 (sh)	1109 (s-d)	1125 (s-M)	1105 (s-M)	877 (sh)	464 (sh)	798 (d)	778 (s)
	677 (w)	935 (w)	1103 (s-M)	1043 (s-M)	790 (w)		778 (d)	720 (w-sh)
	618 (s-sh)	874 (sh)	1042 (w)	877 (m-sh)	717 (w)		714 (sh-d)	694 (w-sh)
	570 (w)	865 (sh)	875 (m-sh)	754 (m-sh)	680 (sh)		693(sh-d)	646 (w-sh)
	472 (w)	713 (w)	755 (m-sh)	711 (w)	604 (sh)		646 (sh)	604 (w)
		657 (m)	714 (w)	654 (sh)	470 (sh)		604 (sh)	580 (d)
		620 (d)	680 (w-sh)	616 (s-sh-d)			516 (w)	514 (d)
		600 (sh-d)	657 (m-sh)	603 (s-sh-d)			472 (sh)	466 (s-sh)
		547 (w)	600 (s-sh)	574 (w)				
		467 (w)	526 (w-d)	517 (w)				
			502 (w-d)					

Legend of peak features: (s) = strong; (w) = weak; (br) = broad; (sh) = sharp; (m) = medium; (d) = doublet; (M) = multiplet.

The pronounced peaks at about 1440-1420 cm^{-1} are related to CO_3^{2-} stretching vibration of calcium carbonates which are present in all samples according to XRPD. Instead, further peaks related to C-O vibrations, can be generally observed at 1795 cm^{-1}, 875 cm^{-1} and ~ 710 cm^{-1} according to the relative concentrations of carbonate phases in the materials.

Calcium and sodium sulphates in FaC, FaF, FaL, FaR gave rise to strong SO_4^{2-} vibrational bands near 1190, 1150-1110 cm^{-1} as doublet or triplet peaks, and well-defined peaks between 680–600 cm^{-1}, respectively. Additional weaker peaks are observed at about 1030-1000 cm^{-1} and near 470-500 cm^{-1}. In BaC sample, the existence of calcium and potassium sulphates in the form of anhydrite, gypsum and syngenite can be noticed by a prominent band at 1130 cm^{-1} and two sharp peaks at 680 cm^{-1} and 604 cm^{-1}.

In all bottom ashes the IR spectra showed the main and widest band at around 1030-1040 cm^{-1} related to Si-O-T (T = Si, Al) vibrations, including different contributions associated to bonds of silicate species.

Phosphate group (PO_4^{3-}) group forms IR absorption bands in the regions at about 600 cm^{-1}, 570-560 cm^{-1} and ~ 470 cm^{-1} (evident in samples FaC, FaL, FaR, BaC, BaL and BaR). Is worth to note that other typical peaks of the group, as those at 960 cm^{-1}, 1030 and 1095 cm^{-1} can be considered overlapped and hidden in the broad bands between 1000-1200 cm^{-1}.

Other peaks revealed in ashes below 800 cm^{-1} can be attributed to different T-O vibrations (T = Ca, Mg, Fe, Mn) (Abraham et al., 2013).

4.5 Microstructural and microchemical characterisation by SEM-EDS

Under microscopic examination by scanning electron microscopy fly ash (Figure 7) exhibits quite homogeneous and well-defined aggregates of fine particles, consisting of intimately intermixed phases. Microchemical analysis revealed the occurrence of K, Ca, Mg, S, Cl, and P as main chemical components attributable to the occurrence of minerals phases such as hydroxyapatite [$Ca_5(PO_4)_3(OH)$], sylvite (KCl) (point analysis 2), syngenite [$K_2Ca(SO_4)_2 \bullet (H_2O)$] (point analysis 3), and periclase (MgO) (point analyses 1 and 3) in high concentrations in well agreement with bulk analyses.

Bottom ashes are characterised by high granulometric heterogeneity with either irregular, spherical, or lamellar shaped particles. Microchemical analysis revealed a composition rich in Si, Al, Ca, Mg, and Fe, consistent with the results of chemical and mineralogical analyses. A more detailed examination by scanning electron microscopy allowed the identification of several characteristic morphologies such as the spherules with high concentrations of Si, Ca, Al, Mg, and K, in Figure 8 (a) or lamellar aggregates in Figure 8(c) and (d). These particles can be attributed to silicates such as merwinite [$Ca_3Mg(SiO_4)_2$] when primarily enriched in Si, Mg, and Ca Figure 8 (c). The significant presence of iron-rich particles probably attributable to hematite (Fe_2O_3) Figure 8 (d) has also been detected, as well as the occurrence of unburned woody structures with potassium-rich mineral phases deposits on them in Figure 9 (a).

The clear identification of the polymeric structure of lignin, confirming the presence of vegetal origin residues with high abundance of calcium has also been observed in Figure 9 (b).

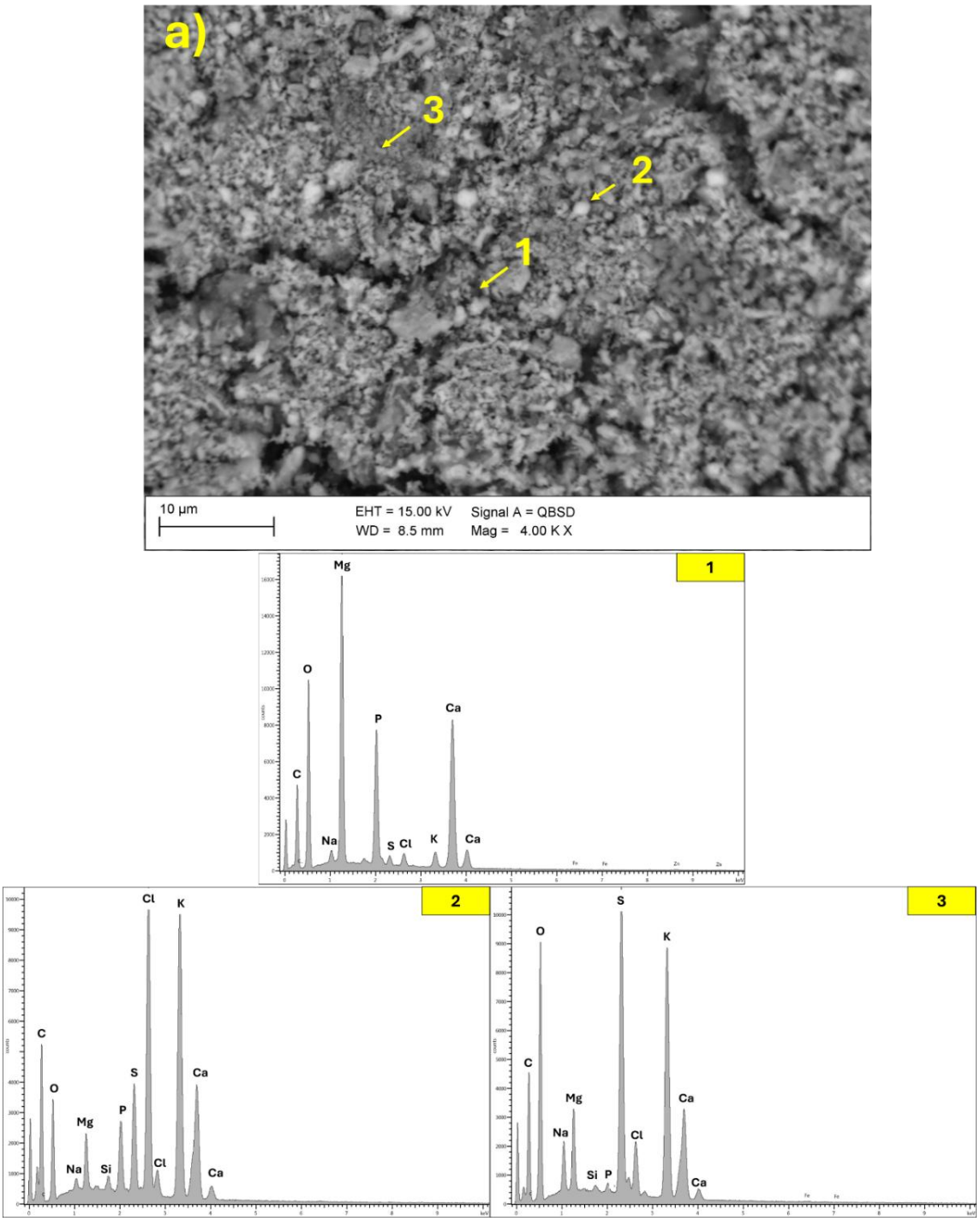


Figure 7. Scanning electron microscope image and EDS spectra of the FaL sample.

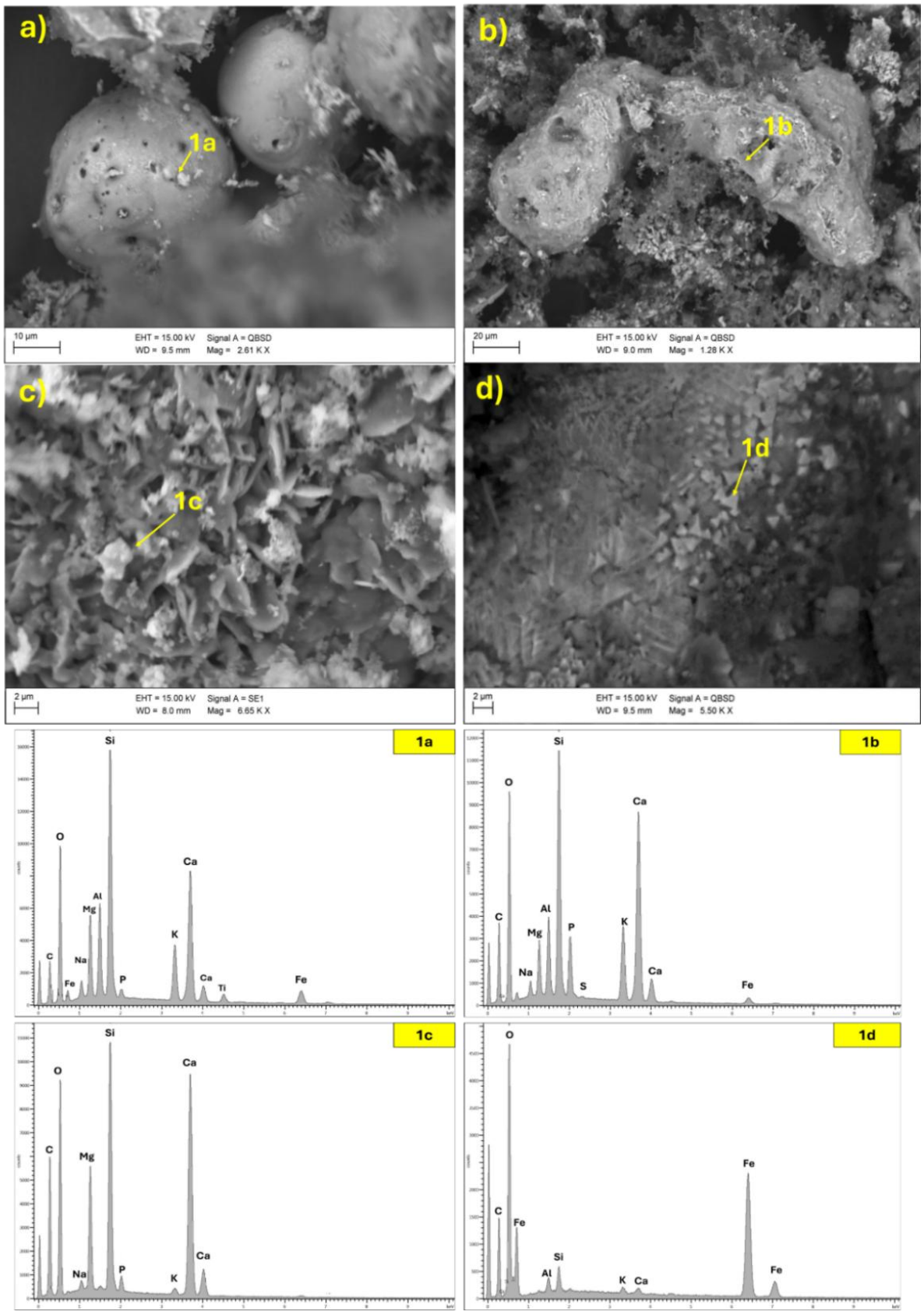


Figure 8. Scanning Electron Microscope (SEM) images of the morphological characteristics of ash particles, with corresponding EDS spectra for the BaL sample.

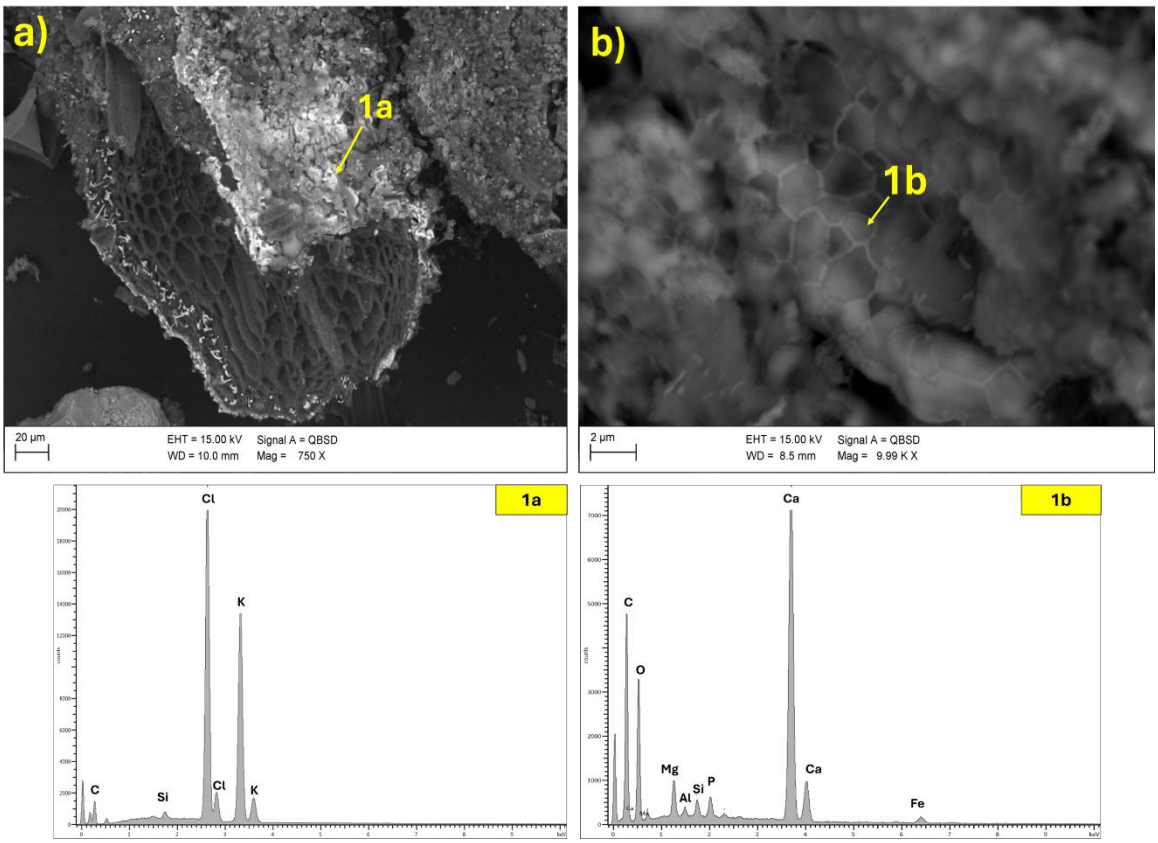


Figure 9. Scanning Electron Microscope (SEM) images of unburned wood residues and EDS spectra in BaF sample.

4.6 Water leaching test

4.6.1 Characterisation of eluates

The chemical composition of eluates obtained from water leaching tests with liquid-to-solid (L/S) = 10 L/kg for all samples + L/S = 100 L/kg conducted only for fly ash (FaC, FaF, FaL and FaR) samples is reported in Table 9.

Table 9. Chemical composition of eluates.

		Fly ashes				Bottom ashes			
mg/L	Element	FaC	FaF	FaL	FaR	BaC	BaF	BaL	BaR
Nutrients	K	2194	12056	11689	18549	455.27	694.09	185.73	229.34
	Ca	32.04	1400	321.08	865.14	223.97	30.67	45.5	94.79
	P	<1	<1	<1	<1	<1	<1	<1	<1
	Mg	7.8	<1	<1	1.78	25.09	1.45	1.08	2.07
	Na	17202	1282	520,2	1363	147.27	119.46	16.63	27.62
	Fe	7.08	<1	<1	<1	<1	<1	<1	<1
	B	9.43	6.4	9.35	2.58	2.05	1.42	<1	1.68
	Zn	15.86	<1	<1	<1	<1	<1	<1	<1
	Mn	<1	<1	<1	<1	<1	<1	<1	<1
	Mo	<1	<1	1.49	1.80	<1	<1	<1	<1
	Cu	<1	<1	<1	<1	<1	<1	<1	<1
Heavy metals	Co	<1	<1	<1	<1	<1	<1	<1	<1
	Pb	1.07	<1	<1	<1	<1	<1	<1	<1
	Ni	<1	<1	<1	<1	<1	<1	<1	<1
	Cd	<1	<1	<1	<1	<1	<1	<1	<1
	As	<1	<1	<1	<1	<1	<1	<1	<1
	Cr (Tot)	<1	<1	2.67	1.33	<1	<1	<1	<1
	Hg	<1	<1	<1	<1	<1	<1	<1	<1
	PSSW (%)[1]	72.22	54	40.90	64.72	7.43	1.79	2.82	4.32
	pH[2]	12	14	12	14	9	10	11	11
	PSSW (%)[3]	70.19	68.15	52.92	66.27	-	-	-	-
	pH[4]	10	12	12	12	-	-	-	-

[1] percentage of solubilised sample in water (PSSW) at the liquid to solid ratio (L/S) of 10 L/kg
[2] pH of the eluate resulting from the water leaching test at a liquid-to-solid ratio (L/S) of 10 L/kg
[3] percentage of solubilised sample in water (PSSW) at the liquid to solid ratio (L/S) of 100 L/kg
[4] pH of the eluate resulting from the water leaching test at a liquid-to-solid ratio (L/S) of 100 L/kg

Eluates from fly ashes showed higher concentration of nutrients (mainly K and Ca) compared to bottom ashes, in agreement with their higher content of variably soluble phases such as sylvite, portlandite, halite, and so on. Potassium and calcium reach concentrations up to 18549 mg/L and 1400 mg/L, respectively, in eluates from FaR sample, whereas eluates from bottom ashes showed notably lower content of solubilised nutrients (up to K = 694.09 mg/L in BaF, Ca = 223.97 mg/L in BaC). Mg, B, Fe, Zn, and Mo exhibited low solubilisation, mostly below the limit of quantification or in trace concentrations ranging from 1 to 25 mg/L, with slightly higher values in FaC and BaC. P, Mn, and Cu remained consistently below the detection limit in all samples.

Heavy metals, including Co, Pb, Ni, Cd, As, Cr (tot), and Hg, were consistently below detection limits (<1 mg/L) in all samples, with the exception of FaC, where up to 1.07 mg/L of Pb was detected, while Cr (tot) of 2.67 mg/L and 1.33 mg/L was measured in FaL and FaR, respectively.

Table 9 also shows the percentage of solubilised sample in water (PSSW) and the pH of the eluates at the L/S ratio of 10 L/kg for all the investigated ashes. All fly ashes exhibit significantly higher solubility compared to bottom ashes, with PSSW ranging from 40.90 % (FaL) to a maximum of 72.22 % (FaC), in contrast to values from 1.79 % (BaF) to 7.43 % (BaC) of bottom ashes.

The pH of the eluates with values ranging from 12 (FaC and FaL) to 14 (FaF and FaR) reflect the strongly alkaline nature of fly ashes, whereas bottom ashes eluates exhibit more moderate alkalinity, with pH values ranging from 9 (BaC) to 11 (BaL).

When the L/S ratio increased to 100 L/kg, the PSSW values of the fly ashes generally showed an increase, *i.e.* from 54.0 % to 69.15 % in the case of FaF or from 40.90 % to 52.92 % in the case of FaL, which is clearly related to the type and relative content of soluble phases in each fly ash sample. A moderate decrease in pH was observed at the higher L/S ratio, reflecting the dilution effect and a reduction in eluate alkalinity. However, all eluates from the fly ash samples retained their alkaline character.

These results highlight the variability in solubility behaviour among different fly ash samples. FaF and FaL demonstrated greater sensitivity to the increased L/S ratio, while FaC and FaR maintained relatively consistent solubilisation profiles. Overall, increasing the L/S ratio enhances the solubility of most fly ashes, accompanied by a slight moderation in pH under more dilute conditions.

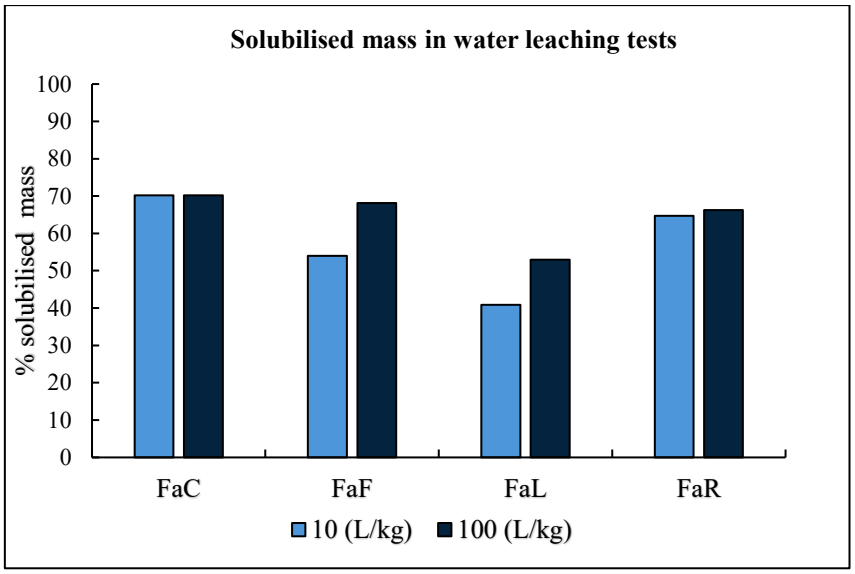


Figure 10. Comparison between the percentage of the solubilised sample in water at liquid-to-solid (L/S) ratios of 10 L/kg and 100 L/kg**.**

4.6.2 Characterisation of solid residues

The chemical composition of solid residues obtained from water leaching tests on fly ash (FaC, FaF, FaL and FaR) and bottom ash (BaC, BaF, BaL and BaR) samples is reported in Table 10.

The percentage of solid residue remaining (SR) after leaching at a liquid-to-solid (L/S) ratio of 10 L/kg for bottom ashes and at L/S = 100 L/kg for fly ashes is reported in Table 10 as well.

In the case of fly ashes, the choice of considering leaching at L/S of 100 L/kg is justified by the necessity to analyse solid residues after the maximum solubility of ashes, given the presence of several water-soluble components, as revealed by mineralogical analyses.

Table 10. Chemical composition of solid residues.

		Fly ashes				Bottom ashes			
	Element (mg/kg)	FaC	FaF	FaL	FaR	BaC	BaF	BaL	BaR
Nutrients	K	36376	39062	29077	25597	26133	41396	31551	27569
	Ca	132959	136358	164108	234508	71943	135857	146372	71307
	P	12850	17950	17570	24790	6449	2831	5401	5756
	Mg	23051	24613	24525	32714	13123	26084	27434	14976
	Na	3882	4322	3288	2654	3512	4881	4127	3687
	Fe	14607	2393	12632	28453	18442	9565	14395	19583
	B	625.14	232.35	753.99	873.73	185.78	33.55	99.46	115.61
	Mn	1635	191	1712	2604	1125	348	817	779
	Mo	14.11	7.19	13.9	59.49	10.91	6.9	4.05	9.07
Regulated heavy metals [1]	Zn[1]	89453	671	11182	42984	6403	25	180	206
	Cu[1]	1017	148	430	2032	564	26	105	130
	Pb	13567	113	1633	9132	4307	4	35	53
	Ni	74	5	49	87	130	15	27	36
	Cd	299	4	49	163	35	< 1	< 1	< 1
	As	204	31	154	512	101	3	5	7
	Cr VI	< 0.2	< 0.2	9	10	10	< 0.2	< 0.2	1.1
	Hg	30.65	0.79	0.649	2.21	0.202	0.121	0.107	0.206
Additional metals	Si	20500	17000	31000	15000	23500	14000	22500	15500
	Al	11755	1429	14843	22838	16976	11163	21492	25372
	Co	39	1	11	17	26	5	6	8
	Bi	33.89	1.68	7.46	57.43	4.63	< 0.004	< 0.004	< 0.004
	Sb	552.33	2.01	85.38	438.09	52.9	< 1	2.49	3.31
	Ba	2929	32.91	561.98	554.25	189.54	182.23	313.47	281.46
	V	37	9	43	76	29	22	37	42
	Ti	1271	75.08	616.96	942.43	6489	388.18	1176	1285
	Cr (Tot)	179	17	128	347	274	75	74	120
	SR (%)	29.81 [2]	31.85 [2]	47.08 [2]	33.73 [2]	92.57 [3]	98.21 [3]	97.18 [3]	95.68 [3]

[1] The elements included in this category are regulated under EU Regulation 2019/1009. Copper (Cu) and Zinc (Zn) are regulated for all fertiliser categories, with the exception of "inorganic fertilisers based on micronutrients". Nevertheless, these elements are essential micronutrients
[2] solid residues (SR) obtained from leaching at L/S ratio of 100 L/kg
[3]solid residues (SR) obtained from leaching at L/S ratio of 10 L/kg

K, Ca, P, Mg, Na and Fe show the highest concentrations in solid residues of both fly and bottom ashes although corresponding to significantly different percentages of un-solubilised component of

the original material. Other elements such as B, Mn, Mo, Zn, and Cu, show significant variations among different samples and according to the ash category. B and Cu are preferentially concentrated in residues of fly ashes, whereas Zn and Mn show very high concentration in the solid residue of samples FaC, FaL, FaR and BaC, reaching up 89453 mg/kg of Zn (FaC) and up 2604 mg/kg of Mn (FaR).

Heavy metals, including Pb, Ni, Cd, As, Cr VI, and Hg, exhibit notable variability between the two ash types. Lead shows generally low concentrations in residual fractions of bottom ashes, except for sample BaC, having almost similar Pb content to fly ash residues. Cd, As and Cr (tot) show almost similar trend, with generally highest concentrations in sample FaC.

The chemical analysis of solid residues provides a clear understanding of the distribution of elements within the insoluble fraction of the sample. The data clearly demonstrate that heavy metals regulated under ER 2019/1009 are predominantly concentrated in the insoluble fraction of the samples, represented by the solid residues obtained from water leaching tests (Figure 11). However, specific patterns emerge for individual elements. Cr (VI) is below the limit of quantification (LOQ) in FaC, FaF, BaF, and BaL, while Cd remains below the LOQ in BaF, BaL, and BaR. Similarly, Hg is consistently below 1 mg/kg in FaF, FaL, BaC, BaF, BaL, and BaR.

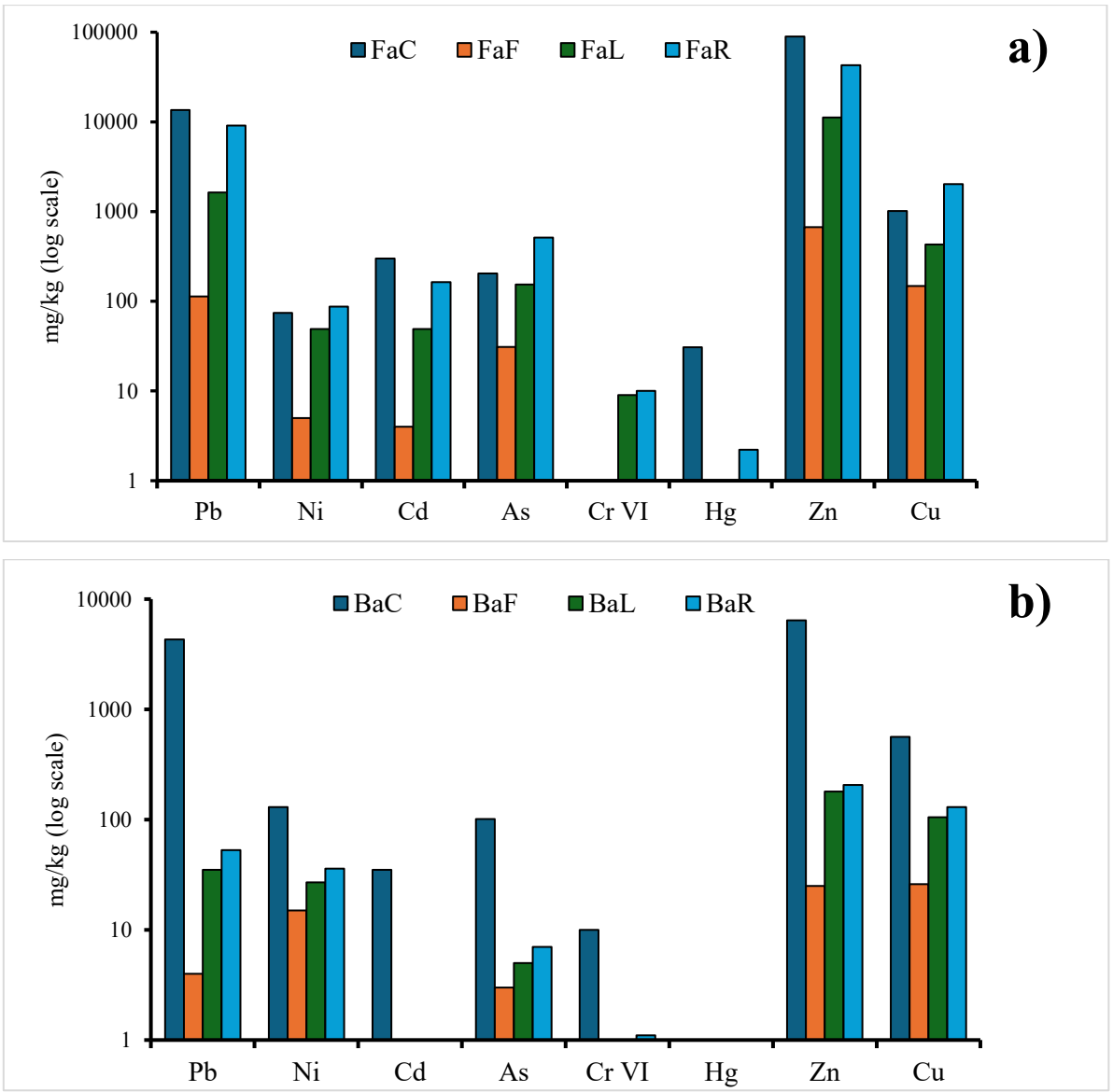


Figure 11. Content of metals regulated under European Regulation 2019/1009 of fertiliser present in solid residues of (a) fly ashes and (b) bottom ashes.

Additional elements investigated, including Si, Al, Co, Bi, Sb, Ba, V, Ti, and Cr (tot), also exhibit quite variable content in each residual material, with general enrichment of Bi, Sb, Ba and Ti corresponding to fly ash. Among the bottom ash, the residual fraction from sample BaC show a composition more similar to fly ash samples than others bottom ash samples.

Table 11. Mineralogical composition of solid residue of fly ashes obtained by Rietveld refinement.

Mineralogical composition (wt%, 3σ*)				
Mineral	FaC	FaF	FaL	FaR
anhydrite, Ca (SO_4)	1.7±0.4		3.2±0.7	2.1±0.6
aphthitalite, $(K,Na)_3$ $Na(SO_4)_2$		2.1±0.5		
calcite, $CaCO_3$	8.6±1.1	31.4±2.1	22.7±1.9	10.3±1.1
hydroxylapatite, $Ca_5(PO_4)_3(OH)$	4.3 ±0.6	7.5±0.7	11.7±1.0	9.8±0.9
periclase, MgO	1.12±0.7		8.3±0.8	6.6±0.8
portlandite, Ca $(OH)_2$		11.5±0.9		
zincite, ZnO	4.0±0.4			2.2±0.3
syngenite, K_2Ca $(SO_4)_2•(H_2O)$				5.6±1
quartz, SiO_2	1.4±0.3		1.30±0.3	2.6±0.4
rutile, TiO_2	0.9±0.2			
defernite, $Ca_6(CO_3)_{1.5}(SiO_4)_{0.5}(OH)_{7.5}Cl0._5$		8.7±1.1		
whitlockite, $Ca_3(PO_4)_2$	5.4±1.1			
sodalite, $Na_8Al_6Si_6O_{24}Cl_2$	1.0 ±0.3			
akermanite, $Ca_2MgSi_2O_7$			8.4±1.2	
pyrolusite, MnO_2			1.1±0.4	
brownmillerite, $Ca_2(Al,Fe)_2O_5$			6.1±0.7	4.9±0.7
grossular, $Ca_3Al_2(SiO_4)_3$			0.7±0.3	
hematite, Fe_2O_3	5.9 ±1.8			
yeelimite, $Ca_4Al_6O_{12}SO_4$	1.9 ±0.4			
K-feldspar, KAl_3O_8				2.0±0.8
amorph	63.8±3.9	38.8±3.9	36.6±5.1	53.9±4.2
Rwp	6.07	6	5.37	5.43
χ^2	2.65	2.11	2.03	1.95
GOF	1.63	1.45	1.42	1.39

*Standard deviation calculated as 3σ

The mineralogical analysis of fly ash solid residues obtained from water leaching tests revealed significant compositional variations with respect to the original bulk ashes, highlighting the extent of dissolution processes and the crucial role of solubilisation in reshaping the mineralogy of the solid residues as illustrated in Table 11. Mineral phases having relatively high water-solubility such as silvite KCl, aphthitalite [$(K,Na)_3Na(SO_4)_2$], syngenite [$K_2Ca(SO_4)_2·(H_2O)$], and portlandite [$Ca(OH)_2$], originally present in the bulk composition (Table 6) reduced drastically or were absent in the solid residues. Specifically, silvite, initially present at high concentrations (25.5 wt% in FaF, 13.3 wt% in FaL, and 35.3 wt% in FaR), was completely dissolved in all samples. Syngenite underwent a

sharp reduction, decreasing from initial concentrations of 19.0 wt% (FaL) and 10.1 wt% (FaR) to about 5.6 wt% exclusively in FaR. Similarly, aphthitalite, present in the bulk at concentrations ranging from 5.8 wt% to 1.4 wt%, was only detected in FaF. Portlandite, initially characterised by a concentration of 18.7 wt.% in FaF, was significantly reduced in the solid residue of the same sample 11.5 wt.%, while disappearing completely in the other samples. Insoluble mineral phases, such as calcite ($CaCO_3$), hydroxyapatite [$Ca_5(PO_4)_3(OH)$], zincite (ZnO), and periclase (MgO), showed, as expected, a relative enrichment in the solid residues.

Moreover, several mineral phases that were present in trace amounts in the bulk samples,making their unequivocal detection difficult, were clearly identified in the solid residues due to their enhanced enrichment. They include oxides such as rutile (TiO_2), hematite (Fe_2O_3), pyrolusite (MnO_2) or brownmillerite [$Ca_2(Al,Fe)_2O_5$], silicates such as defernite, [$Ca_6(CO_3)_{1.5}(SiO_4)_{0.5}(OH)_{7.5}Cl_{0.5}$], sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) in FaC (1 wt%) or akermanite ($Ca_2MgSi_2O_7$), the whitlockite [$Ca_3(PO_4)_2$] or calcium yeelimite ($Ca_4Al_6O_{12}SO_4$), and other phases detected as traces.

Finally, the amorphous phase exhibited an overall increase in the solid residues, rising from initial values of 30.2 wt% (FaR bulk) and 46.8 wt% (FaC bulk) to about ~ 53 wt% and ~ 64 wt %, respectively, in the corresponding solid residues.

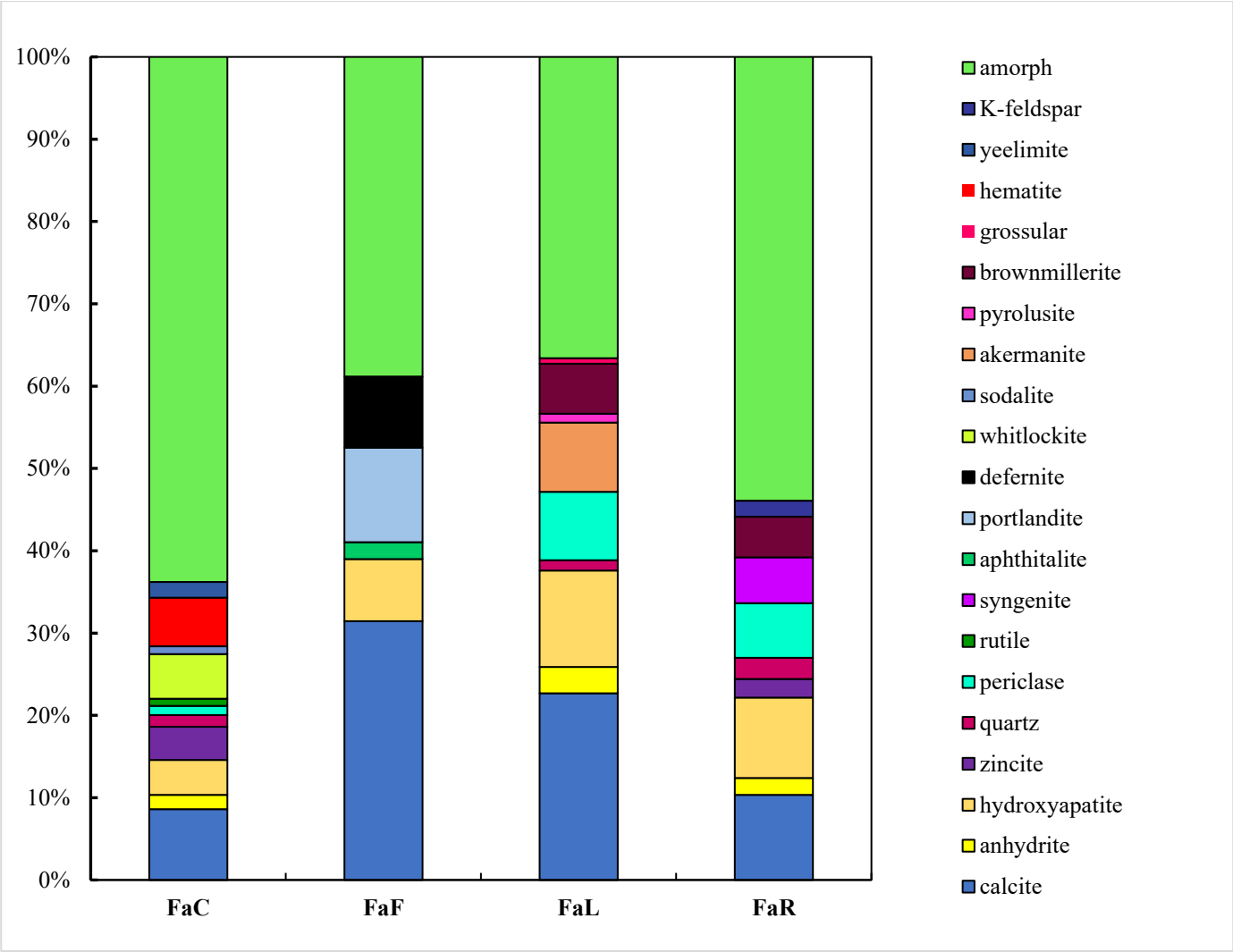


Figure 12. Mineral content of fly ash solid residues (wt%).

Table 12. Mineralogical composition of solid residue of bottom ashes obtained by Rietveld refinement.

Mineralogical composition (wt%, 3σ*)				
Mineral	BaC	BaF	BaL	BaR
akermanite, $Ca_2MgSi_2O_7$	5.9±0.9		11.2±1.1	5.7±0.6
anhydrite, $Ca(SO_4)$	3.0±0.6			
pyroxene, $(Ca,Mg,Fe)_2Si_2O_6$	4.1±0.8	1.3±0.4		4.1±0.7
hatrurite, Ca_3SiO_5			1.2±0.4	
monocalcium aluminate, $CaAl_2O_4$			6.2±1.1	
calcite, $CaCO_3$	6.8±0.8	0.5±0.2	6.6±0.8	4.0±0.5
cristobalite, SiO_2		1.4±0.3		
gypsum, $CaSO_4 \cdot 2H_2O$	4.4±0.8			
hematite, Fe_2O_3	0.5±0.4			
hydroxylapatite, $Ca_5(PO_4)_3(OH)$	2.6±0.5		2.6±0.6	2.0±0.4
leucite, $KAlSi_2O_6$	3.3±1	3.6±0.8	5.3±1.2	9.6±1.2
merwinite, $Ca_3Mg(SiO_4)_2$			2.6 ±0.6	
periclase, MgO			1.6 ±0.5	0.9±0.3
plagioclase, $(Na,Ca)(Si,Al)_4O_8$	2.3±0.5	0.8±0.3	4.7±0.7	7.0±1.0
quartz, SiO_2	7.9±0.5	1.7±0.2	13.7±1	25.3±1.8
rutile, TiO_2	2.0±0.5			
brownmillerite, $Ca_2(Al,Fe)_2O_5$			4.4±0.7	
massicot, PbO			0.4±0.1	
grossular, $Ca_3Al_2(SiO_4)_3$	0.1±0.1			
amorph	57.1±3.3	90.7±1.1	39.3±4.8	41.3±4.2
Rwp	4.90	4.34	6.36	5.31
$\chi 2$	1.62	1.26	2.52	1.86
GOF	1.27	1.12	1.58	1.36

*Standard deviation calculated as 3σ is reported

Due the low content of water-soluble phases in bottom ashes the mineralogical composition of their solid residues after leaching test (Table 12) was not significantly different from the initial bulk samples (Table 9), in agreement with the low PSSW of these ashes, which ranged from a minimum of 1.79 wt% in BaF to 7.43 wt% in BaC (Table 9). Water-soluble mineral phases such as syngenite and portlandite were the only phase originally present in the bottom ashes which were not detected in their solid residues (Table 7).

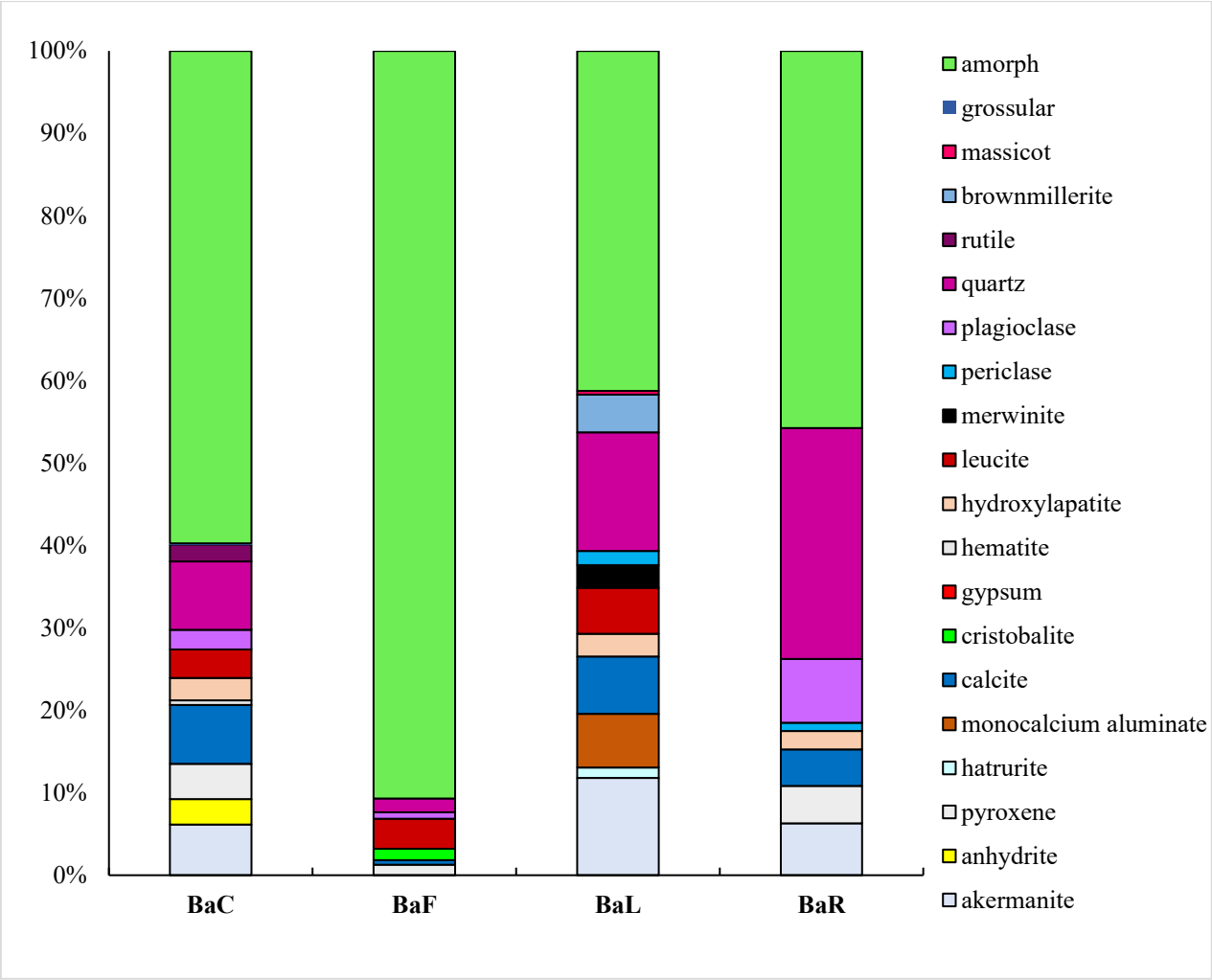


Figure 13. Mineral phase composition of bottom ash solid residues (wt%).

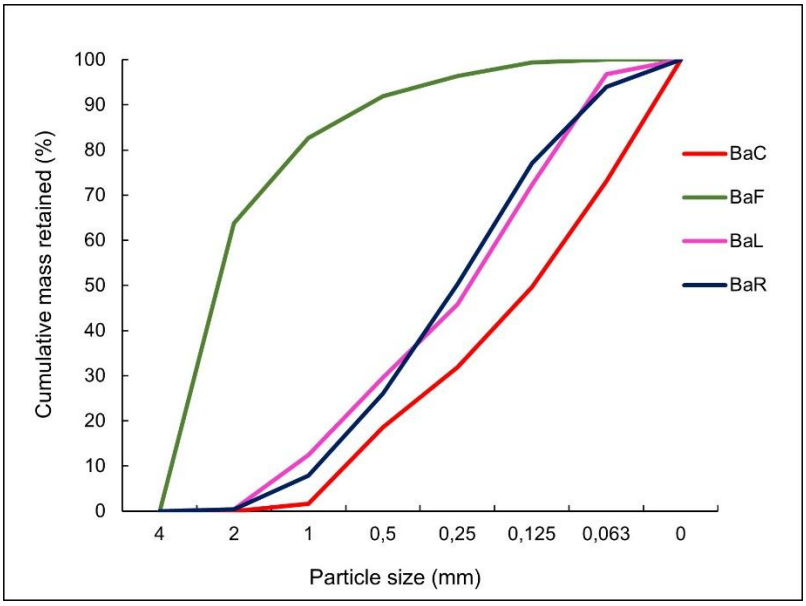
4.7 Chemical and mineralogical characterisation of particle size fractions

4.7.1 Particle size determination of bottom ashes

Particle size separation of bottom ashes was performed under dry conditions to assess the distribution of major and minor elements, with a particular focus on the content of nutrients, heavy metals, and mineralogical phases across different granulometric fractions. The BaF sample was excluded from this procedure due to its physical consistency as it is composed of highly friable, predominantly scorified material, which is not well suited for the chemical and mineralogical characterisation of the different grain sizes. All results of chemical and mineralogical analyses performed for each grain size fraction separated from the bottom ashes are provided in Appendix 2 (Table A2.1 and Table A2.2).

Table 13. Size distribution of bottom ash particles (wt%) and corresponding graphic representation.

Particle size (mm)	BaC	BaF	BaL	BaR
>2	0	63.7	0.4	0.3
2-1	1.6	18.9	12	7.5
1-0.5	17	9.3	17.1	18.2
0.5-0.25	13.2	4.4	16.2	24.2
0.25-0.125	17.8	3	26.5	26.9
0.125-0.063	23.5	0.6	24.6	16.9
< 0.063	26.8	0	3.2	6



Notes: Cumulative mass retained (%) of the BaC, BaF, BaL and BaR samples across the investigated particle size classes (mm). BaF consists mainly of particles >2 mm, while BaC, BaL and BaR show a more uniform distribution across intermediate and fine classes.

4.7.2 Chemical and mineralogical composition of granulometric fraction

The chemical and mineralogical analyses of the granulometric fractions do not indicate a systematic segregation of elements and mineral phases. They reveal distinct trends in concentration variations across different grain size classes, which vary depending on the sample. Nevertheless, some general variations have been identified: in the BaC sample, the decrease in calcite and akermanite content (Figure14a) with increasing grain size corresponds to the progressive reduction in Ca concentration (Figure 14b), confirming the preferential enrichment of this element in finer fractions. Similarly, periclase is more concentrated in finer granulometric fractions, aligning with the observed diminution in magnesium concentration as grain size increases.

In the BaL sample (Figure 15a), leucite content increases with granulometry, mirroring the gradual rise in potassium concentration for particle size higher than 0.063 mm (Figure 15b). No reliable explanation can be given for the high K content in grain size <0.063 mm, which cannot be strictly related to any crystalline phase.

In the BaC and BaR (Figure 14-16) samples, the reduction of hydroxyapatite in the coarsest fractions is consistent with the decrease in phosphorus concentration in these granulometric classes.

Finally, while Si does not exhibit clear granulometric segregation, quartz and feldspars show higher concentrations in coarser particle sizes, particularly in the BaL and BaR samples.

Some minor elements generally exhibit a progressive decrease in concentration with increasing grain size, indicating their preferential enrichment in finer fractions. This is mainly observed for Cd, Cr, Cu, B, and As, in BaC (Figure 14c), whereas it is less prominent in BaL and BaR samples where only B shows a progressive decreasing by increasing grain size and to a lesser extent Ba in BaR (Figures 15-16). Notably, in BaC sample, an opposite situation is observed, with Ba exclusively enriched only in the coarser fractions. Other elements such as Hg, Cd, Sb, V and Cr were generally detected in very low concentrations or below the limit of quantification (LOQ) in most analysed samples. The trends of Hg, Cd, V, Sb and Cr, in addition to other pollutants regulated by the European Fertiliser Regulation 2019/1009 are further illustrated in Figure 18 where separate graphs for each element are plotted to better highlight the variation of several elements through different granulometries.

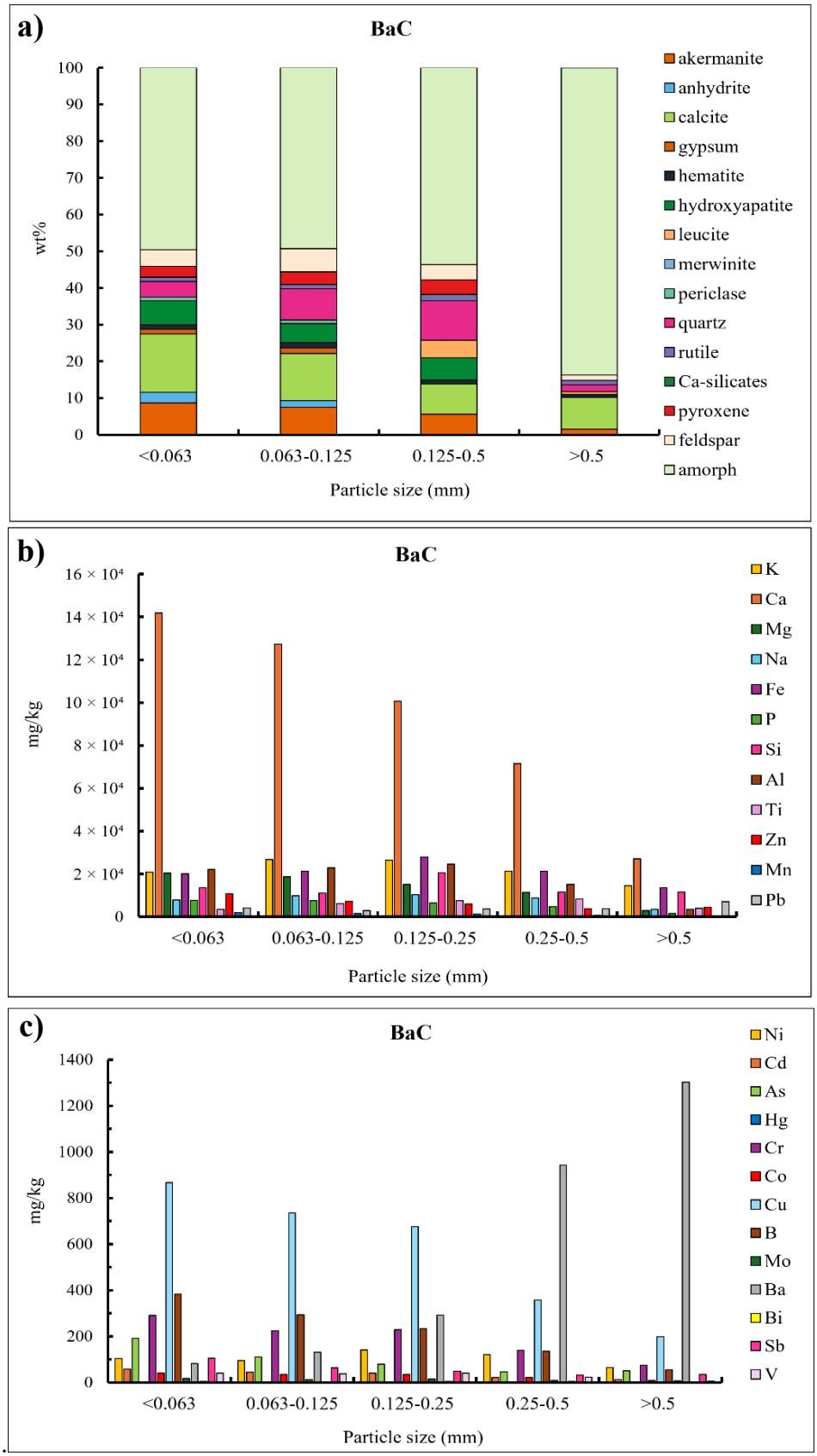


Figure 14. Phase speciation (a), major elements (b), and minor elements (c) in the different particle size classes of BaC samples.

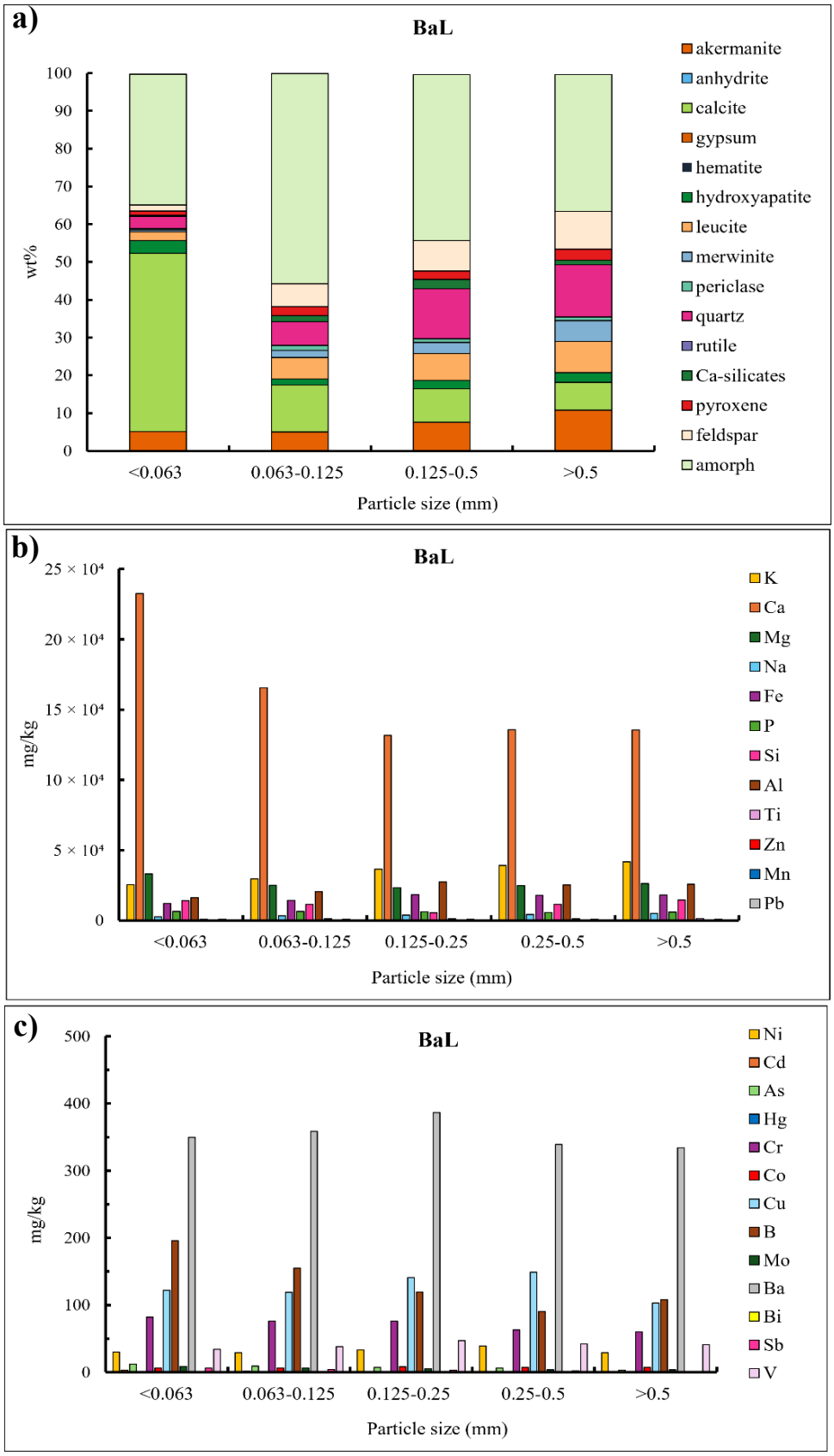


Figure 15. Phase speciation (a), major elements (b), and minor elements (c) in the different particle size classes of BaL samples.

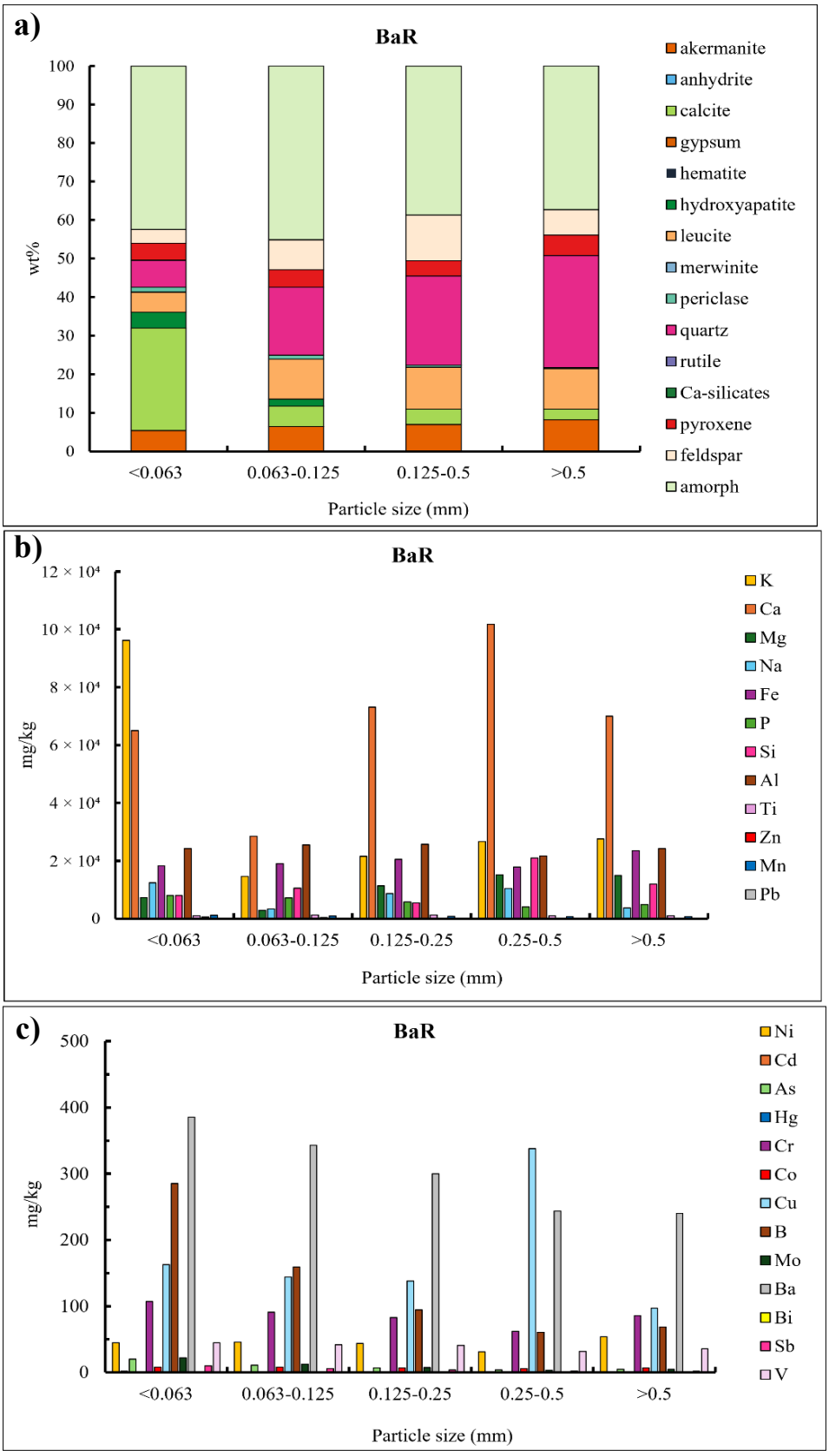


Figure 16. Phase speciation (a), major elements (b), and minor elements (c) in the different particle size classes of BaR samples.

When considering the distribution of nutrients across the different grain size fractions (Figure 17) it can be observed that nutrients represent the predominant component of each fraction, with weigth relative percentages ranging from a minimum of approximately ~70 % (BaR 0.063-0.125 mm) to a maximum of approximately ~90 % (BaL <0.063 mm), depending on the sample. Moreover, although no clear distribution of different nutrients in each grain size fraction of samples can be universally observed, some trends can be outlined when considering individual samples. In BaC sample the content of Fe and K generally increases in coarser fractions while that of Ca, Mn, Mg and P is higher in finer fractions. Specifically, major decreasing Mg and P occur for grain sizes higher than 0.5 mm. A similar trend for Fe and K was also observed in the BaL sample, but in this sample, all other elements, such as Mg, Na, P and Ca show almost equal distributions in each grain size fraction. Instead in BaR a quite opposite trend for Ca, Mg and K is observed with respect to the other samples, that can be related to the relatively high and variable concentrations of Si and Al in each grain size fractions.

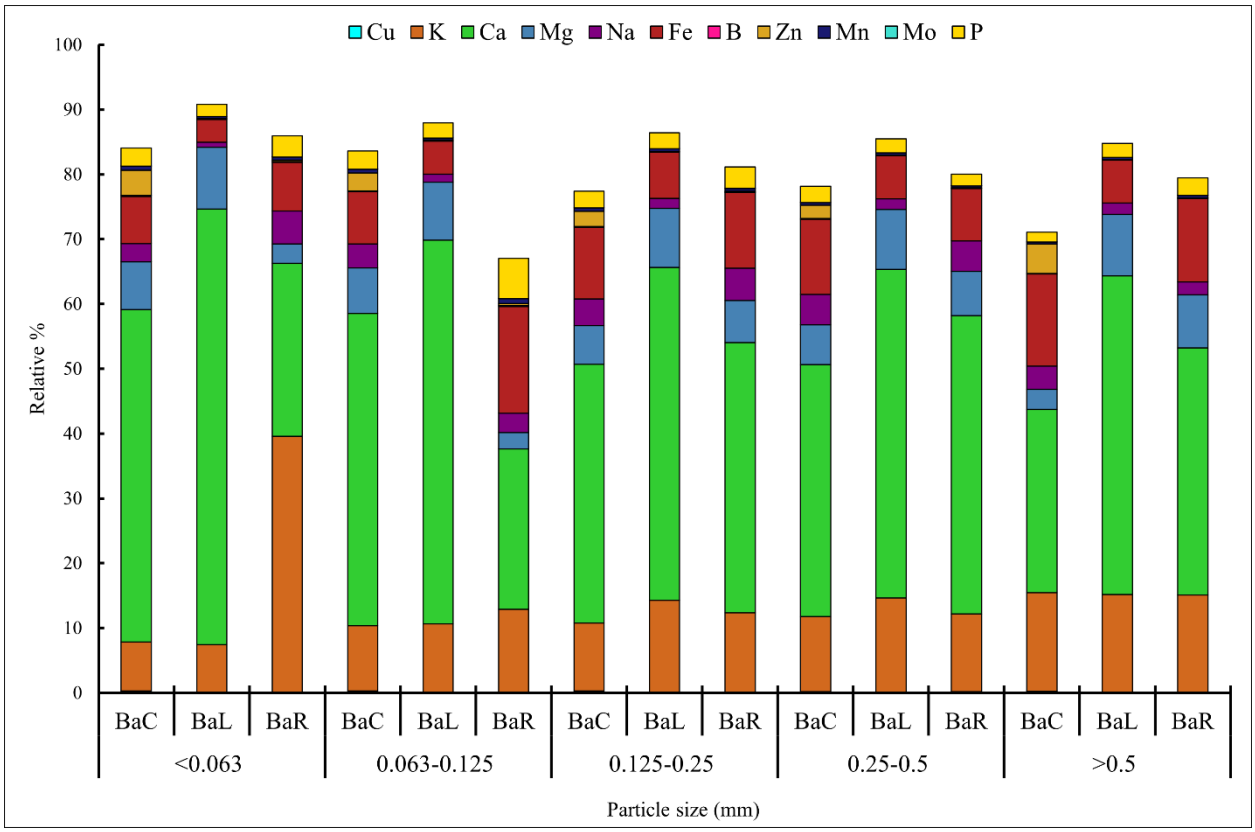


Figure 17. Relative percentage of nutrients distribution in different grain size classes.

Figure 18 shows a comparative analysis of heavy metal concentrations regulated by the European Fertiliser Regulation (excluding Co, Cr, Sb and V, which lack specific limits) across different granulometric fractions in the investigated samples, expressed in mg/kg. The data reveal frequent

exceedances of the thresholds established by European Regulation 2019/1009 (Table 4), particularly in BaC, for which the distribution of pollutant consistently surpasses regulatory limits across all fractions. Specifically, Pb concentrations in BaC exceed the maximum limit of 600 mg/kg for "inorganic fertilisers based on microelements" in all fractions, whereas in BaL and BaR the content of this element remains generally below the threshold limit of the of ER 2019/1009, showing only a slight enrichment in the <0.063 mm fraction (Figure 18(a)).

Figure 18(b) displays that, Ni in the BaC sample, surpasses the minimum threshold of 50 mg/kg for "organo-mineral fertilisers" in all granulometric fractions. However, it remains within the upper limit of 100 mg/kg for "inorganic fertilisers based on macroelements" and "inorganic amendment" fractions 0.063–0.125 mm (95 mg/kg) and >0.5 mm (65 mg/kg), which applies to two fertiliser categories mentioned above. In contrast, BaL and BaR exhibit Ni concentrations below the minimum threshold in all fractions (with the only exception of >0.5 mm fraction in BaR) and do not show any specific trends through them. The content of Cd exceeds the minimum threshold of 3 mg/kg for "organo-mineral fertilisers" and inorganic fertilisers based on macroelements in all granulometric fractions of the BaC sample, although a progressive decreasing of this element is observed by increasing grain size. In all the other two samples, the Cd concentration remains within permissible limits and becomes negligible at grain sizes greater than 0.125 mm (Figure 18(c)). As already observed for the other elements, the As content in BaC consistently exceeds the minimum threshold of 40 mg/kg throughout all fractions, whereas it remains below the limits in all granulometric classes of BaL and BaR and, generally, its content is negligible for grain sizes higher than 0.125 mm.

Zn and Cu, which can be considered as nutrients for contents below the threshold limit of 1500 mg/kg and 600 mg/kg, respectively, exceed these limits only in BaC, although showing a progressive decreasing content by increasing the grain size, as already outlined for As and Cd. Therefore, the content of Cu results significantly below the minimum threshold for grain size higher than 0.5 mm. Instead, in the case of BaL and BaR, the content of these two nutrients/pollutants is below the minimum threshold across all granulometric fractions.

Hg and Cr VI were detected only in trace amounts, often below the limit of quantification, across all granulometric fractions of the investigated samples. The only exception is Cr VI in BaC, where concentrations exceed the regulatory limit of 2 mg/kg in the <0.063 mm to 0.125–0.25 mm fractions. Overall, the only granulometric fractions that comply fully with both minimum and maximum regulatory limits across all fertiliser categories are the 0.063–0.125 mm and 0.125–0.25 mm fractions of the BaL and BaR samples.

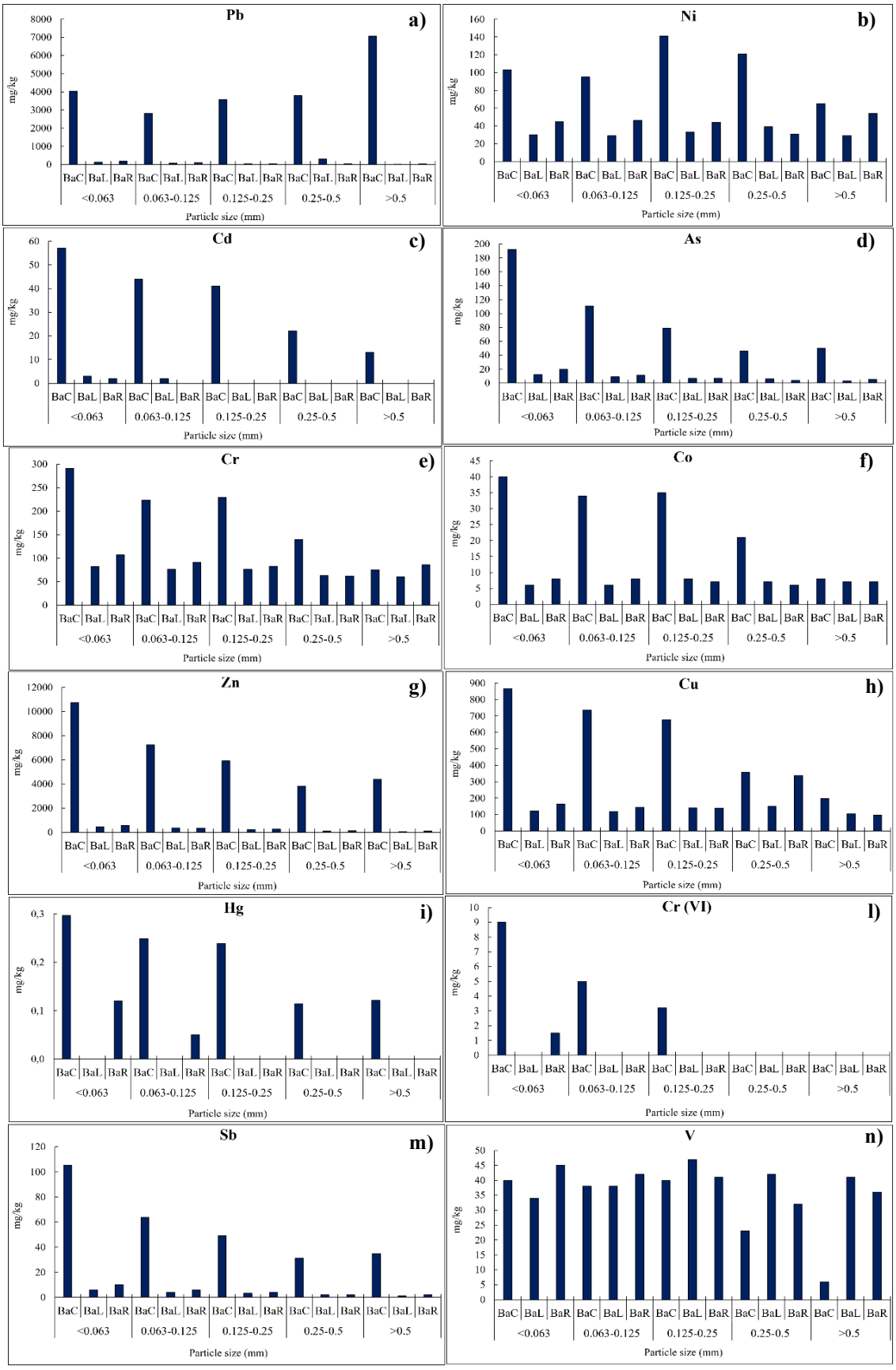


Figure 18. Heavy metals in different grain size.

Section 5. Discussion

5.1 Physicochemical properties of biomass ashes from italian cogeneration plants

The multi-methodological analysis revealed significant concentrations of essential macronutrients for plant growth, including Ca, K, Mg, and P, as well as micronutrients such as Fe, Cu, and Zn, across all examined samples. Notably, the highest concentrations of Ca and Mg were identified in bottom ash (*e.g.*, CaO=35.77 wt% and MgO=6.86 wt% in BaL sample), while the maximum potassium content was recorded in fly ash (up to K_2O=19.8 wt% in FaR). Similarly, fly ash had quite a high content of P (up to P_2O_5=2.82 wt% in FaL). Considering micronutrients, the most substantial concentrations of Fe and Cu were detected in bottom ash (*i.e.* Fe_2O_3=5.06 wt% and Cu=15774 mg/kg in BaR). Conversely, the highest Zn content was measured in fly ash (up to 41688 mg/kg in FaC). Therefore, Ca, Mg, and Fe are significantly enriched in bottom ash samples, whereas K and Zn are predominantly concentrated in fly ash. This distribution pattern is consistent with previous studies investigating the speciation of metals within different types of ash (Obernberger et al., 2006; Jenkins et al., 2019; Vassilev et al., 2010, 2013a). Phosphorus exhibited a uniform distribution across all analysed samples, with no significant variation. Copper concentrations, except for BaR, were comparable among the other samples examined.

Overall, fly ashes exhibit a high level of homogeneity, consisting of particles smaller than 0.063 mm and composed of intermixed mineral microphases, as demonstrated by SEM-EDS analyses in Figure 7. Chemical analyses (Table 3) reveal significant concentrations of alkali elements, including K, Na and Ca. The potassium oxide (K_2O) content ranged between 16.05 wt% and 19.8 wt% in the FaR, FaL, and FaF samples, while an exceptionally high sodium oxide (Na_2O) concentration of 31.78 wt% was recorded in FaC, significantly exceeding that of other samples, which did not exceed 10 wt% of Na_2O. Calcium content, in contrast, varied from a minimum of CaO=1.46 wt% in FaC to CaO=28.26 wt% in FaL.

Mineralogical analyses indicated that these elements are predominantly present as chlorides (sylvite, halite), sulphates (aphthitalite, syngenite, thenardite), and hydroxides (portlandite), as demonstrated by Rietveld refinement data (Table 6).

Thermogravimetric analyses (TG-DTA) identified substantial mass losses attributable to the dehydration of hydrated sulphates at approximately 250°C, dehydroxylation of hydroxides around 450°C, degradation of sulphates, and melting of chlorides within a temperature range of 700 to 1100°C, depending on the sample (Figure 4).

FTIR analyses allowed to support these findings by identifying characteristic peaks associated with O-H bonds in the range of 3646–3642 cm^{-1}, corresponding to minerals such as portlandite, while calcium and sodium sulphates were identified near 1190 cm^{-1}, 1150–1110 cm^{-1}, and between 680–600 cm^{-1}, respectively (Figure 6a).

The presence of alkaline mineral phases in fly ash reflects the complex physicochemical processes occurring during combustion. In particular, literature reports, indicate that alkali metals volatilise during high-temperature combustion and recondense into the finer particulate matter comprising fly ash, thereby promoting the accumulation of K, Na, Cl, and S in these ash fractions (Vassilev et al., 2013b; Staničić et al., 2023). The process is strongly influenced by the nature of the fuel and the operating conditions of the plant, including combustion temperature and the efficiency of flue gas treatment systems, which modulate the formation and adhesion of alkali salts to fine particles. Several studies reported that the concentration of K, Na, Ca, and the anions Cl^- and SO_4^{2-} is typically associated with fine particle classes and decreases in coarse particle classes.

Volatile components in the combustion process may recondense in-flight as particles or react with the fly ash as the flue gases cool down. These processes occur on the surface of the fly ash particles. Due to the higher specific surface area of smaller particles, volatile components become enriched in the fine fractions of the fly ash. For the metals Fe, Al, Si, and Ti, the size dependence exhibits the opposite trend, with lower concentrations in the fine particle classes and higher concentrations in the coarse particle classes (Linak & Wendt, 1993; Zacco et al., 2014; Lanzerstorfer, 2015; Bogush et al., 2018). According to Cruz et al., (2019), ash particles smaller than 0.200 μm are generally enriched with alkaline metals in their composition.

The chemical and mineralogical composition of the fly ash analysed is notably impacted by the use of specific reagents in flue gas purification systems for atmospheric emission control (Bogush et al., 2018). Specifically, the particularly high Na_2O content (31.78 wt%) and the significant presence of halite (30.4 wt%) in FaC can be attributed to the use of sodium bicarbonate combined with activated carbon for the removal of dioxins/furans and heavy metals via a physico-chemical adsorption process. This process precipitates acidic components from the combustion gases generated by the ORC plant. Similarly, the significant CaO content observed in FaF (28.26 wt%) and the presence of portlandite (18.7 wt%) are associated with the use of hydrated lime to remove sulphur oxides during flue gas purification operations (Chang & Wey, 2006).

As a rule, the presence of alkali sulphates in fly ash can be attributed to processes occurring during combustion, where sulphur (S) is predominantly oxidised to gaseous sulphur dioxide (SO_2) and subsequently converted into alkali sulphates through condensation reactions and interactions with alkali metals present in the combustible matrix (Obernberger et al., 2006). The high Loss on Ignition

(L.o.I.) values, ranging from 28 wt% (FaL) to approximately 62 wt% (FaC) in the investigated samples, confirmed the significant content of volatile components and easily decomposable salts (Patwardhan et al., 2010).

In addition to the presence of alkali salts, fly ashes exhibit specific Ca, Mg, and Zn-mineral bearing phases. Calcium is also present in all samples as calcite and anhydrite, with concentrations ranging from 2.1 to 10.5 wt% (FaC–FaL) and from 1.4 to 6.6 wt% (FaC–FaL), respectively.XRPD data (Table 6) and SEM-EDS analysis indicate that magnesium is primarily associated with periclase MgO, which was identified in three samples with concentrations ranging from 0.9 wt% to 4.3 wt% (Figure 7). Finally, zinc is present as zincite, detected exclusively in sample FaC, the richest in this element.

The high concentrations of alkaline metals in biomass feedstocks, along with volatilisation mechanisms and the subsequent flue gas treatment systems, facilitate the formation of chlorides, sulfates, and hydroxides, which are prevalent in fly ashes generated from the combustion of wood biomass in a cogeneration plant.

The high solubility of these mineral phases, which are potentially bioavailable to plants, is further evidenced by water leaching tests (Table 9), which reveal that fly ashes produce highly alkaline eluates, with pH values ranging from 12 to 14 at a liquid-to-solid (L/S) ratio of 10. Additionally, leaching experiments indicate significant solubilisation, with 40 % to 72 % of the sample mass dissolving in water, highlighting the influence of mineralogical composition on leachate chemistry. These results are consistent with the findings of Vassilev et al. (2013b), who reported that the water-soluble fraction of biomass ashes can reach up to 61 %, whereas the values for this characteristic in coal ashes range from 0.2 % to 7.2 %.

A clearer understanding of these dissolution processes can be achieved by analysing the mineralogical composition of the solid residues remaining after leaching, as shown in Figure 12.

Fly ash solid residues revealed substantial mineralogical changes compared with the original ashes, reflecting extensive dissolution of highly water-soluble phases such as sylvite, aphthitalite, syngenite, and portlandite. Conversely, insoluble minerals, including calcite, hydroxyapatite, zincite, and periclase, became relatively enriched in the residues, highlighting the role of leaching in reshaping ash mineralogy. Notably, several mineral phases that were present in trace amounts in the bulk samples became clearly detectable in the solid residues due to their relative enrichment. These included oxides such as rutile (TiO_2) 0.9 wt% in FaC, hematite (Fe_2O_3) 5.9 wt% in FaC, pyrolusite (MnO_2) 1.1 wt% in FaL, and brownmillerite [$Ca_2(Al,Fe)_2O_5$] 6.1 wt% in FaL, silicates such as defernite [$Ca_6(CO_3)_{1.5}(SiO_4)_{0.5}(OH)_{7.5}Cl_{0.5}$] 8.7 wt% in FaF, sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) 1 wt% in FaC and akermanite ($Ca_2MgSi_2O_7$) 8.4 wt% in FaL or other trace compounds such as whitlockite

[$Ca_3(PO_4)_2$] 5.4 wt% in FaC, yeelimite ($Ca_4Al_6O_{12}SO_4$) 1.9 wt% in FaC and K-feldspar (KAl_3O_8) 2 wt% in FaR.

Building on these observations, the mineralogical evolution of the solid residues after leaching was examined in greater detail. A comparison of the phase assemblage, accounting for the mass loss due to dissolution, is further displayed in Figure 19. In the figure, the percentage of solubilised mineral phases (grey bars on the left) and unleached residual phases (blue bars on the right) from the bulk (before leaching tests) are plotted in comparison with the phase assemblage in solid residue after leaching tests (red bars on the right). Although the displayed comparisons are necessarily based on certain assumptions, they enable a clearer and more quantitative evaluation of the relative amounts of different phases before and after leaching, yielding important insights into processes such as the dissolution of the amorphous fraction, the extent of carbonation, and other secondary transformations which occurred in the samples.

Based on this recalculation, it is possible to assess, for example that the amount of amorphous phase in the fly ash samples (specifically FaC, FaR, and FaL) remains essentially unchanged after leaching. This suggests that the amorphous material is only slightly, or not at all, affected by the dissolution process. The possible hydration of Ca-silicates (Lothenbach & Nonat, 2015) may also explain the absence of these phases in the residue of FaC (Figure 19a). Furthermore, the increase in calcite content observed in all samples clearly indicates carbonation effects, which are particularly evident in FaF due to the carbonation of portlandite (Galan et al., 2015).

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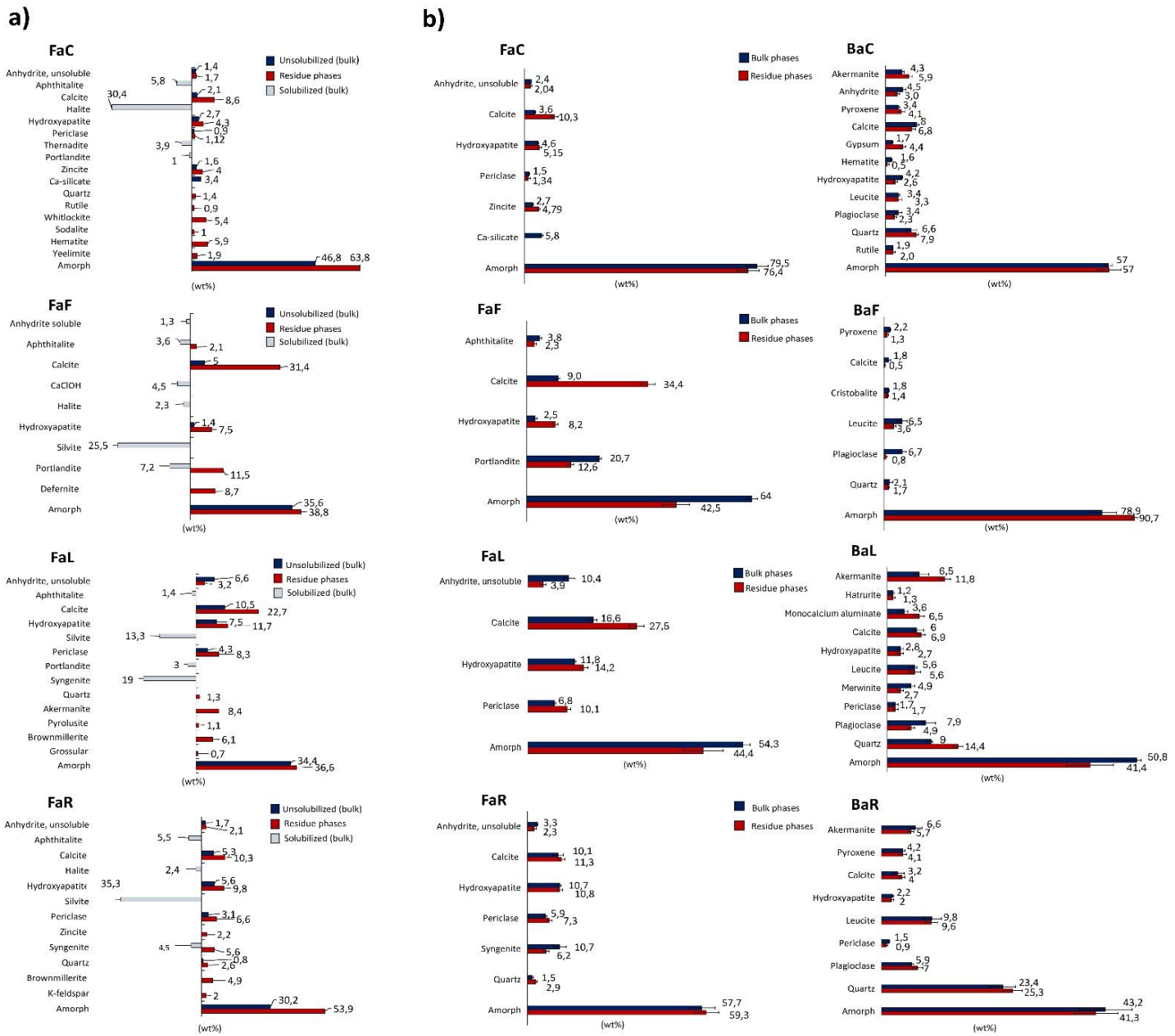


Figure 19. Phase composition of the solid residue of FA and BA after leaching tests. a) Diagrams showing the percentage of solubilised mineral phases (grey bars on the left) and unleached residual phases (blue bars on the right) from the bulk (before leaching tests) in comparison with the phase assemblage in solid residue after leaching tests (red bars on the right); b) diagrams showing the phase assemblage before and after leaching in FA and BA, normalised for mass losses due to dissolution of soluble phases.

In contrast to the fly ash samples discussed above, the following section focuses on the characterisation of the bottom ashes, which exhibit distinct compositional and mineralogical features In particular, the elevated concentrations of silicon (expressed as SiO_2) and calcium (CaO) in bottom ash samples are particularly noteworthy. The SiO_2 content varies between 30.01 wt% (BaL) and 58.31 wt% (BaF), while CaO exceeds 20 wt% in three samples (BaC, BaL, BaR). Depending on the sample, these elements predominantly occur as silicates (pyroxene, leucite, plagioclase, akermanite, merwinite), oxides (quartz, cristobalite), and carbonates (calcite), as identified through mineralogical analyses (Table 7). Supporting these findings, thermogravimetric analyses (TG-DTA) indicate lower mass losses in comparison to fly ash (Figure 5), suggesting the thermal stability of silico-calcic and oxide components occurring in bottom ash (Umamaheswaran & Batra, 2008; Abraham et al., 2013; Vassilev et al., 2022b). Consequently, bottom ash retains the thermally stable minerals of the original fuel, forming a predominantly silico-calcic matrix that is chemically and mineralogically distinct from fly ash. This differentiation is further corroborated by the higher concentrations of lithophile elements (Si, Ca, Al, Mg) in bottom ash compared to fly ash (Chang & Wey, 2006; Bunt et al., 2012; Bogush et al., 2018).

In all analysed samples, the concentrations of Al_2O_3, Fe_2O_3, MgO, P_2O_5, MnO, and TiO_2 are generally below 10 wt% (Table 3). However, Fe_2O_3 (ranging from 2.63 wt% in BaF to 5.06 wt% in BaR) and Al_2O_3 (from 5.17 wt% in BaC to 8.18 wt% in BaR) exhibit higher concentrations in bottom ash, likely due to their thermal stability, which facilitates their retention in the combustion bed (Wei et al., 2011). These elements are associated with various aluminosilicates, including leucite ($KAlSi_2O_6$), and plagioclase [$(Na,Ca)(Si, Al)_4O_8$] (Table 7).

Thermogravimetric studies (TG-DTA) indicate the occurrence in the samples of phases with stability up to a temperature of approximately 900°C, which is consistent with the high content of silicate phases detected by the mineralogical analyses. This is in accordance with the findings reported by Vassilev et al. (2022), which did not indicate any evidence of transformation within this temperature range due to the occurrence of silicates such as quartz, plagioclase, leucite, and kalsilite remaining stable up to 900°C.

Minor phase transformations occurring between 980–1100°C (Figure 5) were associated with partial melting processes at 1000°C of silicates and the interaction between alkaline oxides and aluminosilicates (Kirnbauer et al., 2013). Furthermore, in all bottom ash samples, IR spectra exhibit a dominant and broad band around 1030–1040 cm^{-1}, associated with Si-O-T vibrations (T = Si, Al), reflecting contributions from various silicate phases (Figure 6b).

Scanning electron microscopy (SEM-EDS) further supports these findings, confirming a composition rich in Si, Al, Ca, Mg, and Fe, in alignment with chemical and mineralogical analyses. SEM imaging

reveals distinctive microstructural features, including spherules with high concentrations of Si, Ca, Al, Mg, and K, associated with plagioclase [$(Na,Ca)(Si,Al)_4\ O_8$] and leucite ($KAlSi_2O_6$) (Figure 8a). Additionally, lamellar aggregates, predominantly enriched in Si, Mg, and Ca, are identified as merwinite [$Ca_3Mg(SiO_4)_2$] (Figure 8c). The presence of iron-rich particles, likely attributable to hematite (Fe_2O_3), is also observed (Figure 8d), further supporting the chemical and mineralogical characterisation.

According to several previous studies (Steenari et al., 1999; Vassilev et al., 2013b; Nunes et al., 2016) the predominance of quartz and other aluminosilicate minerals in bottom ash is only partially attributable to the original biomass composition. For instance, the decomposition of silicon-based minerals derived from plant tissue during incineration, such as phytoliths ($SiO_2 \times nH_2O$)—which are often structural components of plant tissue deposited between and within plant cells (Yapuchura et al., 2019) —is largely the result of contamination by sand and soil particles introduced during biomass harvesting.

In contrast to fly ashes, bottom ashes exhibit pronounced morphological and granulometric heterogeneity, as demonstrated by SEM-EDS analyses (Figure 8) and particle size distribution data (Table 13). BaF is primarily composed of highly friable predominantly scorified material, with most particles belonging to coarse size classes (>2 mm), whereas BaC exhibits a higher proportion of fine particles in the <0.063 mm class fraction. The BaL and BaR samples display a more homogeneous granulometric distribution, with the 0.25–0.125 mm fraction predominating. The substantial granulometric heterogeneity of bottom ashes underscores the influence of fuel composition and combustion parameters on their physical characteristics, distinguishing them from fly ashes, which are typically finer and more homogeneous in texture, as illustrated in paragraph 2.3.

From an agronomic perspective, phosphorus was predominantly identified as hydroxyapatite [$Ca_5(PO_4)_3(OH)$], with concentrations ranging from 1.4 wt% to 7.5 wt% in fly ash samples and between 2.2 wt% and 4 wt% in three bottom ash samples. The presence of hydroxyapatite can be attributed to the thermal stability of calcium phosphates and their tendency to persist in the solid phase during combustion processes (Tõnsuaadu et al., 2012). Furthermore, the accumulation of apatite in ash is closely linked to the nature of the biomass used, as illustrated in paragraph 2.3 and summarised in Table 1, owing to the different capacity of plant species employed as fuel to absorb phosphorus throughout their life cycle and store it in their tissues (Vassilev et al., 2022b, 2023).

Regarding bottom ash, only two samples exhibited the presence of water-soluble mineral phases that are potentially bioavailable to plants. Sample BaC contains gypsum (1.6 wt%), and syngenite (5 wt%), whereas sample BaL shows portlandite at a concentration of 2.9 wt%. This limited presence of soluble mineral phases is further corroborated by the water leaching tests, as illustrated (in Table

9), which clearly demonstrate the low solubility of bottom ashes, which showing a dissolution in water ranging from a minimum of 1.79 % to a maximum of 7.43 % (at L/S = 10), which is significantly lower than that observed for fly ashes. Due to the low content of water-soluble phases in the bottom ashes, the mineralogical composition of the solid residues after leaching remained largely unchanged relative to the bulk samples, with syngenite and portlandite being the only phases initially present that were not detected after leaching (Table 12-Figure 19).

Additionally, the pH of the eluate solution varies between 9 and 11, indicating a moderately alkaline character compared to fly ashes, which generally exhibit higher solubility and stronger alkalinity.

This finding confirms that bottom ashes are predominantly composed of insoluble compounds, with only a minor fraction influencing the chemical composition of the leachates and the alkalinity of the solution, albeit to a lesser extent than fly ashes.

In agreement with findings reported in the literature (Nurmesniemi et al., 2012; Vassilev et al., 2014; Freire et al., 2015; Bogush et al., 2018), the results from the eight analysed samples demonstrate a clear compositional separation between fly ash and bottom ash. Fly ash is enriched with elements such as potassium, sodium, sulphur, and chlorine, predominantly present as water-soluble mineral phases, which are bioavailable to plants. In contrast, bottom ash is richer in silicon, calcium, and aluminium, which are mainly found in water-insoluble mineral phases. The high dependence on the chemical composition of both fly and bottom ash and the nature of the combustible material, as well as the combustion technique and post-combustion management practices, is strongly reflected in the high compositional heterogeneity of ashes (Jenkins et al., 2019). According to Vassilev et al. (2010), the chemical composition of biomass is primarily composed, in decreasing order, of C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti, with variations in their concentrations depending on the type of biomass. The chemical differences between natural and anthropogenic biomass are related to their sources (vegetal, animal, or a combination of vegetal, animal, and manufactured materials). In general, natural biomass is characterised by higher levels of Mn, K, P, Cl, and Ca, and lower levels of Al, C, Fe, N, S, Si, and Ti compared to coal.

In this study, the analysed samples clearly illustrate these differences: some are derived from the combustion of untreated virgin wood, composed of straw and wood chips (FaF, BaF), others originate from wood waste of various origins (FaC, BaC), while others come from a mix of virgin wood and recycled "end-of-waste" wood (FaL, BaL). In some cases, exclusively recycled wood was used (FaR, BaR). Notably, ashes derived from herbaceous materials tend to exhibit higher potassium levels (*i.e.* samples FaF and BaF). Conversely, ashes produced from woody biomass display higher calcium (Saidur et al., 2011; Zhai et al., 2021) as in FaL (CaO=28,26 wt%) and BaL (CaO=35,77 wt%).

This differentiation is further supported by SEM microchemical analysis, which reveals residual unburned woody structures with potassium-rich mineral deposits (Figure 9a) and vegetal-origin residues characterised by lignin's polymeric structure and high calcium content (Figure 9b). The presence of such organic remnants aligns with the distinct mineral composition of woody and herbaceous biomass ashes. Additionally, thermogravimetric analysis (TG-DTA) indicates the presence of unburned carbon (Figure 5a and b), reinforcing the persistence of organic residues and confirming the influence of biomass type on the mineralogical and chemical properties of the resulting ash.

Moreover, the specific combustion conditions, particularly temperature, further affect the chemical and mineralogical properties of the residue (WikstrÖm et al., 1999; Vassilev et al., 2005; Umamaheswaran & Batra, 2008; Monti et al., 2008; Zhai et al., 2021). During the combustion process, the organic components of biomass undergo oxidation, while metals and other inorganic constituents concentrate in the solid phase, shaping the final chemical composition of the ash.

These findings are in concordance with the existing literature (Dahl et al., 2009; Vassilev et al., 2010; Nunes et al., 2016), which underscores the relationship between the formation and distribution of mineral phases and the chemical composition of the biomass fuel, as well as the thermal dynamics of the combustion process. Consequently, the variability of the aforementioned factors—biomass type, plant part used, combustion conditions, and post-combustion management practices—plays a decisive role in the distribution and concentration of the primary inorganic elements present in ash. This differentiation also extends to compositional variability (Chang & Wey, 2006; Bogush et al., 2018; Maresca et al., 2019) within the same ash type (fly or bottom ash), which explain the differences in chemical properties (major oxide and heavy metal content), mineralogical characteristics, thermal behaviour and water solubility observed in the investigated samples.

5.2 Standard quality of investigated biomass ashes as fertiliser raw materials

The utilisation of vegetal and various wood waste biomass ashes as fertilisers or soil amendments represents a multifaceted opportunity for nutrient recycling and environmental sustainability. However, a critical assessment of their chemical composition is essential, particularly concerning potentially harmful contaminants, to ensure safe application. Despite their significant content of essential plant nutrients (K, Ca, Mg, P and Fe), biomass ashes may also contain heavy metals such as Cd, Pb, As, and Ni, which may restrict their use (Pöykiö et al., 2009; Nzihou & Stanmore, 2013; S. V. Vassilev et al., 2014; Freire et al., 2015).

Chemical analyses of trace elements conducted using ICP-MS (Table 3) revealed substantial variability in both the type and concentration of heavy metals across samples of fly ash (FaC, FaF,

FaL and FaR) and bottom ash (BaC, BaF, BaL and BaR), relative to the regulatory limits established for different fertiliser categories. As reported in Table 4, European Regulation 2019/1009 specifies threshold values for each metal based on the fertiliser type. Comparing these standards is particularly valuable for decision-making processes concerning waste declassification and recovery in the fertiliser sector.

All analysed samples exceeded the Pb limit of 120 mg/kg set for organo-mineral fertilisers, macroelement-based fertilisers, correctives, and amendments. Additionally, fly ash samples FaC, FaF, FaL, FaR, and bottom ash sample BaL surpassed the upper limit of 600 mg/kg established for inorganic fertilisers based on micronutrients. Regarding Ni, only BaC sample exceeded the limits of 50 mg/kg for organo-mineral fertilisers, and all samples complied with 100 mg/kg for macroelement-based fertilisers.

Cadmium concentrations exceeded the limits of 3 mg/kg for organo-mineral and macroelement-based fertilisers and 1.5 mg/kg for inorganic correctives in all fly ash samples (FaC, FaF, FaL and FaR) as well as in bottom ash samples BaC and BaF. However, no sample exceeded the 200 mg/kg limit set for inorganic micronutrient-based fertilisers, and samples BaL and BaR complied with the limits across all categories.

Concerning As, samples FaC, FaL, FaR, and BaC exceeded the 40 mg/kg threshold applicable to all categories except "inorganic micronutrient-based fertilisers", while FaF, BaF, BaL and BaR remained within the regulatory limits.

In the case of Cu samples FaC, FaF, FaL, BaF and BaL were within the 600 mg/kg threshold established for organo-mineral and macroelement-based fertilisers, whereas FaR, BaC and particularly BaR significantly exceeded this limit, reaching 15774 mg/kg. Regarding Zn, all fly ash samples surpassed the maximum permissible concentration of 1500 mg/kg, while all bottom ash samples complied with the regulatory thresholds. No sample exceeded the limits for hexavalent chromium (Cr VI), whereas for mercury (Hg), fly ash samples FaC, FaF and FaR exceeded the 1 mg/kg limit set for four fertiliser categories. Conversely, FaL and all bottom ash samples remained within the regulatory limits.

Among the analysed samples, FaC, FaR and BaC were identified as the most critical, exhibiting the highest number of regulatory exceedances for heavy metals. This behaviour is closely linked to the nature of the fuel used, which primarily consists of wood waste from various sources, including materials classified as “wood waste” and “end-of-waste wood”, both of which are known to potentially contain elevated contaminant concentrations (Tame et al., 2007; Hasan et al., 2010; Nzihou & Stanmore, 2013).

The BaR sample, derived from the combustion of wood classified as “end-of-waste wood,” exhibited a less problematic profile compared to the most critical samples. It only exceeded the regulatory threshold for copper, a recognised micronutrient, and remained within the permissible limit for lead, even in the inorganic micronutrient-based fertiliser category. This outcome highlights the variability in waste wood quality and the differentiated impact of combustion on contaminant levels (Nzihou & Stanmore, 2013; Vassilev et al., 2014).

Samples BaF and FaF, originating from the combustion of straw and virgin wood chips, exhibited the most favourable chemical profiles. These samples complied with regulatory limits for a greater number of heavy metals and showed significantly lower contaminant concentrations, confirming the positive impact of using untreated woody biomass as a fuel source (Bachmaier et al., 2021). Finally, intermediate samples FaL and BaL displayed a moderate number of exceedances. These resulted from the combustion of a mixture of virgin wood and recycled wood classified as “end-of-waste”, reflecting an intermediate behaviour corresponding to the mixed nature of the fuel. These findings underscore the importance of fuel composition in determining the chemical characteristics of the resulting ashes.

Overall, the concentrations of environmentally significant heavy metals—Zn, Pb, Cu, Cd, Cr and Hg—are markedly higher in fly ashes compared to bottom ashes. In the comparison conducted by Dalh et al. (2009) on the characteristics of bottom ash and fly ash produced by a medium-sized (32 MW) municipal heating plant using forest biomass and peat in a fluidised bed boiler, it was found that over 90 % of the heavy metals in the fly ash are concentrated in the finest fraction, less than 0.074 mm. This phenomenon is attributed to the transformation of more volatile heavy metals during combustion, which subsequently condense or react to form new fine aerosols or accumulate on the surface of fly ash particles (Dahl et al., 2009; Nurmesniemi et al., 2012; Nzihou & Stanmore, 2013; Bogush et al., 2018; Agrela et al., 2019).

Despite certain challenges associated with specific fertiliser categories, inorganic micronutrient-based fertilisers appear to present the most favourable potential for the reuse of the studied ashes. Within this category, only Pb exceeds the regulatory limit of 600 mg/kg in the samples. Moreover, a majority of the samples slightly exceed this limit, such as BaC (603 mg/kg), BaF (621 mg/kg) and FaR (606 mg/kg), FaF (983 mg/kg). Instead, the concentrations of other regulated metals remain within the established thresholds. It suggests that possible reusing of such kind of ashes within this category might be adopted after a reduction of the lead content by specific pre-treatments. Heavy metals such as Pb, Cd, Zn, Cu and Cr can be extracted using various methods, including the use of organic (ossalic acid $C_2H_2O_4$) and inorganic acids (HCl; H_2SO_4; HNO_3), chelating agents (EDTA), as well as electrochemical techniques such as electrodialytic separation (EDS) (Tominc et al., 2023).

In particular, in acid leaching techniques, the efficiency of heavy metal depletion is influenced by the binding environment of the metals and the leaching conditions, including redox conditions, the pH of the ash slurry, the liquid-to-solid ratio (LS), temperature, and leaching duration (Weibel et al., 2017). However, it is important to note that within this category, specific limits for copper and zinc are not defined, highlighting the necessity for further studies to ensure the safe and effective agronomic use of these ashes.

Additionally, it is worth considering that zinc and copper, when appropriately managed, are recognised as essential micronutrients for plants (Zając et al., 2018) suggesting a potential value in the agronomic application of these ashes.

The management of contaminants is thus crucial, as the presence of heavy metals can compromise soil quality and food safety (Vassilev et al., 2013b) emphasise that while biomass ashes hold significant potential for various applications, including fertilisers and soil amendments, their effectiveness is closely linked to the management of heavy metals and organic pollutants. The effective utilisation of these ashes requires an integrated approach that considers both agronomic benefits and the environmental risks associated with their contaminants.

As previously reported, the composition of biomass ashes varies significantly depending on several factors, including the type of biomass used, combustion techniques, and post-combustion management practices (Demirbas, 2005; Sarenbo, 2009; Vamvuka & Kakaras, 2011). The samples under investigation reflect these variations; some originate from the combustion of virgin wood (FaF and BaF), which exhibit the fewest exceedances of heavy metal limits, whereas others are derived from the combustion of urban waste, wood industry residues, or a combination of these fuels (FaC and BaC) and are the most enriched in heavy metals.

Treated wood, often sourced from industrial processing residues, construction or demolition waste, and discarded furniture, represents a potential resource for thermal and electrical energy production through cogeneration processes. However, the use of ashes derived from this material presents specific challenges due to its chemical composition and contaminant content. Treated wood is frequently subjected to processes such as impregnation, painting, or gluing, which can lead to the accumulation of heavy metals (arsenic, chromium, copper, lead) or persistent organic compounds (synthetic resins, adhesives, and paints) in the resulting ashes (Jones et al., 2019; Lehmusto et al., 2024).

During combustion, these contaminants can accumulate at high concentrations in the resulting ashes, as observed in samples FaC and BaC, which exhibit the highest zinc concentrations (41688 mg/kg for FaC and 9416 mg/kg for BaC), consistent with findings from other studies (Nzihou & Stanmore, 2013; Bachmaier et al., 2021). According to Vassilev et al. (2013b), the application of ash derived

from contaminated biomass (*e.g.*, municipal solid waste, sewage sludge, demolition wood) to soil may pose several risks, including alterations in nutrient availability, the presence of toxic trace elements (As, Cd, Pb and Hg), groundwater contamination, and negative impacts on soil pH and microbiology. Additionally, issues such as salinity and dust emissions, may arise, often necessitating pre-treatment. Therefore, the utilisation of biomass ash should be carefully assessed on a case-by-case basis.

While the bulk composition of the samples indicates significant contamination with heavy metals particularly in ashes derived from treated wood, the behaviour of these elements in aqueous environments differs considerably. Water leaching tests have demonstrated that the resulting eluates are highly alkaline at an L/S ratio of 10, with pH values ranging from 12 to 14 for fly ashes and 10 to 11 for bottom ashes, as illustrated in Table 9. Despite this pronounced alkalinity, the eluates contain only trace concentrations or levels below the quantification limit for regulated heavy metals. This suggests that these metals predominantly remain in the insoluble fraction of the sample, as confirmed by the chemical analysis of the solid residues presented in Table 10 for all studied samples. Furthermore, particularly in fly ashes, nutrients such as K and Ca exhibit high water solubility, underscoring their potential availability in aqueous environments. These findings align with previous studies in the literature, which consistently report that heavy metals demonstrate limited solubility in the water-soluble fraction, primarily remaining in the insoluble phase and becoming more susceptible to leaching under acidic pH conditions. Conversely, elements such as K, Ca and Na readily dissolve, leading to higher concentrations in aqueous solutions (Supancic et al., 2014; Maresca et al., 2017; Bogush et al., 2018).

Rigorous management practices are essential to maximise the benefits of biomass ashes and minimise associated risks. Bachmaier et al., (2021) recommend the exclusive use of untreated wood for combustion to mitigate the presence of heavy metals and to obtain ashes with high agronomic potential. Additionally, practices such as regular quality monitoring and the separation of the more contaminated ash fractions can contribute to ensuring that materials are safe for agricultural application (Zacco et al., 2014; Voshell et al., 2018).

Figure 17 depicts the distribution of nutrients across the different grain size fractions. It can be observed that nutrients constitute the primary component of each fraction, with relative percentages varying from a minimum of approximately ~70 % (BaR 0.063-0.125 mm) to a maximum of around ~90 % (BaL <0.063 mm). However, as highlighted by the mineralogical analyses (Figures 14-15-16), the nutrients are primarily silicates, carbonates, and oxides, which are insoluble in water and, consequently, not bioavailable to plants.

According to Barbosa et al., (2013), the concentration of regulated metals (Zn, Cr VI, As, Sb, Se, Hg, Cd, Ni, Mo, Pb, Cu, Ba, and total Cr) tends to decrease with increasing particle size, leading to lower ecotoxicity levels in coarser fractions. In line with this, the present study also identified instances where finer granulometric fractions showed enrichment of specific heavy metals, with distinct variation patterns in concentration across different grain size classes, varying depending on the sample. This trend is particularly pronounced for Cd, Cr, Cu, B, and As in BaC (Figure 14c), whereas it is less pronounced in the BaL and BaR samples, where only B exhibits a consistent decrease in concentration with increasing grain size, and Ba shows a weaker trend in BaR (Figures 15–16). Only two granulometric fractions (0.063–0.125 mm and 0.125–0.25 mm in the BaL and BaR samples) exhibited no contamination, with heavy metal concentrations remaining within the limits set by the European Regulation on fertilisers 2019/1009 (Fig. 18).

Studies conducted by Cruz et al. (2019) indicate that, although the nutritional content of biomass ashes—such as calcium, potassium, and magnesium—may be beneficial for soil amendment, concerns regarding heavy metal content persist. Bachmaier et al., (2021) specifically highlight cases in which heavy metals such as cadmium, chromium, and lead exceeded the limits established by the German Fertiliser Ordinance, necessitating stringent quality control measures to safeguard soil and human health.

In addition to heavy metal analyses, in-depth investigations into organic micropollutants were conducted, with particular attention to polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). Analyses performed using GC/MS revealed that none of the samples exceeded the limit of 6 mg/kg for the 16 PAHs established by Regulation 2019/1009. However, the highest PCDD/F value, 40 ng/kg WHO, was detected in fly ash from the electrostatic precipitator (FaR), surpassing the regulatory limit of 20 ng/kg WHO imposed by the same regulation for dioxins and furans, as illustrated in Table 5.

This result is consistent with the high loss-on-ignition (L.o.I) value (50.45 %) observed in the sample, which could indicate a significant presence of unburned organic material (Paya et al., 1998). The formation of PCDD/Fs could be attributed to insufficient combustion efficiency in the plant, as frequently reported in the literature (Naikwadi et al., 1993; Stanmore, 2004; Demirbas, 2005; Sarenbo, 2009; Košnář et al., 2016). Consequently, the use of these ashes, characterised by high levels of unburned carbon, as soil amendments could pose significant environmental risks due to the direct release of persistent organic pollutants of anthropogenic origin (Freire et al., 2015; Lopes & Proença, 2020).

Although the combustion temperature was the same for all the samples (900°C, Table 2) the sample FaR consists exclusively of fly ash collected via electrostatic precipitators, in contrast to the other fly

ash samples (FaC, FaF and FaL), which were collected using bag filtration systems combined with activated carbon. The presence of these filters could explain the lower PCDD/F values observed in the latter samples, due to a dilution effect and enhanced contaminant retention capacity (Li et al., 2023). These findings highlight the importance of accurate separation and management of contaminated fractions to prevent environmental dispersion risks.

These data align with the study by Freire et al. (2015), which highlights that although bottom ash and fly ash from Portuguese thermal plants generally comply with limits for inorganic contaminants, PCDD/Fs remain a concern due to the elevated concentrations found in some fly ash samples. The detection of values exceeding regulatory thresholds underscores the need to adopt rigorous monitoring and management practices during fly ash recycling.

Given the persistence and potential bioaccumulation of these compounds in the environment, it is essential to implement stringent quality control measures to ensure the safety of reuse operations. This includes regular contaminant monitoring, optimisation of combustion processes, and the use of advanced filtration systems to minimise the formation and release of organic pollutants.

Furthermore, the recycling potential of fly ash should be evaluated on a case-by-case basis, considering both the chemical composition of the material and its compliance with existing regulatory frameworks. Enhanced management practices, such as the segregation of highly contaminated fractions and the promotion of research into alternative treatment technologies, could further mitigate environmental risks and promote the sustainable utilisation of these materials in agriculture and other applications.

5.3 Critical assessment and valorisation of biomass ashes from cogeneration plant in fertiliser industry

The valorisation of biomass ashes represents a strategic opportunity for integrating industrial by-products into the circular economy, particularly within the fertiliser industry, which predominantly depends on finite, non-renewable mineral resources for crop nutrition. However, the practical utility of biomass ashes is inherently linked to the capacity to address critical challenges, including compositional variability, the presence of contaminants, and strict compliance with environmental and agronomic regulations.

Comprehensive analyses have demonstrated significant concentrations of essential plant nutrients across all examined samples. The most prominent macronutrients identified include K, Ca, Mg, and P, mesonutrients such as Ca and Mg, while notable micronutrients comprise Cu, Zn, and Fe. Despite the promising agronomic potential suggested by this chemical composition, the presence of contaminants considerably constrains their applicability. Fly ash samples FaC, FaL and FaR, as well

as bottom ash samples BaC and BaL, exhibit contamination levels exceeding the thresholds established by EU Regulation 2019/1009 for fertilisers.

Extensive literature (Reijnders, 2006; Obernberger et al., 2006; Febrero et al., 2014; Bogush et al., 2018; Maschowski et al., 2019; Lehmusto et al., 2024) has consistently highlighted that the nature of the biomass fuel used—particularly wood waste and end-of-waste wood—is the primary determinant of the elevated contaminant levels detected in these samples. Consequently, the sustainable agronomic application of such materials necessitates the implementation of advanced remediation processes to reduce contaminant concentrations and ensure the safe utilisation of the product. These measures are essential for compliance with regulatory and environmental standards, minimising risks to soil integrity, crop productivity, and surrounding ecosystems, and promoting the responsible use of residual ashes.

The detailed characterisation conducted in this study identifies fly ash FaF and bottom ashes BaF and BaR as the samples with the greatest agronomic potential. Although their potassium and calcium contents are not the highest among the analysed samples (FaF: K_2O 16.05 wt%, CaO 21.28 wt%; BaF: K_2O 13.93 wt%, CaO 9.31 wt%; BaR: K_2O 683 wt%, CaO 23,64 wt%), their lower concentrations of heavy metals represent a potential advantage. Specifically, these samples exhibit only minor exceedances for lead (983 mg/kg in FaF and 621 mg/kg in BaF), slightly surpassing the regulatory limit of 600 mg/kg established by EU Regulation 2019/1009 for inorganic micronutrient-based fertilisers.

This combination of favourable chemical composition and reduced contaminant levels, as highlighted in Table 3, positions these samples as more viable candidates for agronomic use, provided rigorous evaluation and monitoring are conducted to ensure their safe and sustainable application as fertilisers or soil amendments.

These findings underscore the necessity of tailored management strategies to enhance the agronomic value of biomass ashes while minimising associated environmental risks. Future research should prioritise the development of innovative treatment technologies aimed at reducing contaminant levels, alongside the refinement of regulatory frameworks and quality control protocols. Such efforts will be pivotal in facilitating the integration of biomass ashes into sustainable agricultural systems, thereby contributing to the advancement of circular resource management and reducing dependence on non-renewable inputs.

These results align with existing literature, which identifies ashes derived from virgin biomass as the most suitable for agronomic applications due to their nutrient-rich composition and reduced contaminant levels (Nurmesniemi et al., 2012; Freire et al., 2015; Bachmaier et al., 2021). Furthermore, the presence of water-soluble compounds identified in FaF, primarily in the form of

potassium chloride (sylvite 25.5 wt%) and potassium sulphate (aphthitalite 5.8 wt%), enhances plant bioavailability, further reinforcing its agronomic value and rendering FaF particularly suitable for the formulation of potassium-based fertilisers.

The presence of such soluble minerals, as also highlighted in previous studies (Wang et al., 2015; Bogush et al., 2018), underscores the potential of fly ashes derived from virgin biomass to ensure the rapid and efficient release of potassium chloride and potassium sulphate for agronomic purposes. The occurrence of salts such as potassium chloride and potassium sulphate is particularly significant for the fertiliser industry, as these compounds could partially substitute synthetic potassium chloride and potassium sulphate commonly used in granular and liquid mineral formulations (Wang et al., 2015). Similarly, the substantial calcium content suggests its potential use as a soil amendment. Calcium is a crucial element for improving the physical and chemical structure of the soil, promoting soil particle aggregation and enhancing cation exchange capacity—key factors for optimising soil fertility (Augusto et al., 2008).

The ability to correct soil acidity through the neutralisation of hydrogen ions is another key property of calcium, making these samples particularly suitable for application in contexts characterised by acidic soils. Numerous studies have demonstrated the efficacy of wood biomass ashes as amendments in sustainable soil management strategies (Karltun et al., 2008; Schiemenz & Eichler-Löbermann, 2010; Maresca et al., 2019; Zhai et al., 2021).

In particular, fly ashes exhibit a Neutralising Value (NV) of 26.1 %, significantly higher than the 8.7 % measured for bottom ashes (Nurmesniemi et al., 2012).

This characteristic provides fly ashes with a markedly greater capacity to neutralise soil acidity, making them particularly suitable for enhancing soil chemical properties and overall soil quality. These properties are especially relevant in forestry contexts, where soil acidity is a frequent and significant issue (Hannam et al., 2018). The application of wood ash in silviculture aims to counteract soil acidification and nutrient depletion, thereby ensuring the long-term maintenance of productivity (Augusto et al., 2008; Rosenberg et al., 2010; Knapp & Insam, 2011).

Furthermore, the ability of these ashes to neutralise acidity facilitates the precipitation of heavy metals as less soluble compounds, particularly in soils affected by mining activities and acid mine drainage phenomena (Mendes et al., 2021).

In the case of bottom ashes, which are characterised by a composition particularly rich in silicon, this feature does not constitute a significant limitation for their use in agronomic applications. As highlighted by (Steenari et al., 1999), the high silica concentration, while reducing the efficacy of bottom ashes as direct fertilisers compared to fly ashes, does not necessarily compromise their

potential for agronomic use. This aspect, as previously discussed, suggests further opportunities for their utilisation in specific contexts.

The application of wood biomass ash in agriculture has garnered increasing scientific interest due to its potential implications for soil fertility and crop productivity, as documented in numerous studies (Augusto et al., 2008; Hansen et al., 2018; Mortensen et al., 2020; Johansen et al., 2021).

Augusto et al. (2008) identified two primary conditions where wood ash application can be particularly beneficial. Firstly, in soils depleted of Ca and Mg, the high content of these nutrients in ash allows for the restoration of soil fertility, which is often compromised by chronic acidification. Secondly, in soils where K is a limiting factor for plant growth, the high concentration and solubility of potassium in wood ash can significantly enhance forest productivity. However, the effects of wood ash in mineral soils tend to be temporary, leading to a short-term increase in mineralisation fluxes. In contrast, in organic soils, such as peat-rich soils, wood ash application can induce profound and long-lasting modifications in biogeochemical cycles, significantly influencing nutrient availability and the dynamics of forest ecosystems. These findings emphasise the importance of a thorough assessment of soil characteristics to optimise wood ash interventions in forestry.

Among the associated risks, it is essential to ensure that the application rates of wood biomass ash are carefully determined in relation to specific soil characteristics to mitigate the risk of heavy metal accumulation. Studies conducted in Denmark (Hansen et al., 2018) demonstrated that the application of wood biomass ash increases soil pH and nutrient concentrations in the O horizon. However, doses exceeding 6 Mg ha^{-1} can promote the accumulation of heavy metals in the soil. Specifically, Cd concentrations exceeding the regulatory limit of 0.5 ppm in the O horizon were observed, in accordance with the threshold values defined by Danish legislation.

Although the absence of N in ash may limit its efficacy as a fertiliser, it has been demonstrated that an increase in soil pH stimulates nitrogen mineralisation, making inorganic nitrogen more available for plant uptake and thereby enhancing the fertiliser potential of ash (Mortensen et al., 2020). It has also been shown that the application of wood ash as a fertiliser significantly influences soil decomposer organisms and nitrogen mineralisation. Mortensen et al. (2020) highlighted, through the analysis of soil physicochemical factors and biological communities, that ash stimulates the basal decomposer food web and ecological dynamics, increasing the pool of inorganic N available for plants. Furthermore, two years after ash application, a decline in enchytraeid abundance (small worms) and a significant increase in earthworm populations (larger organisms known for their critical role in decomposition and soil aeration) were observed, suggesting a positive effect of ash on soil dynamics and nutrient availability.

Johansen et al. (2021) confirmed that wood ash application increases soil pH and enhances the levels of essential nutrients, including K, P, Ca, and Zn, in the surface layers. Additionally, an increase in organic nitrogen mineralisation was observed, accompanied by a significant increase in plant biomass, up to 270 %. However, extremely high doses, such as 33,7 t ha^{-1}, were associated with an increase in Cd concentration in the leaves of "Deschampsia flexuosa". Doses exceeding 10 t ha^{-1} are considered impractical in forest management, as they surpass regulatory limits designed to prevent soil contamination.

The regulatory landscape, as emphasised by Silva et al. (2019) reveals significant gaps in addressing the complexities of using biomass ash as fertilisers within the EU framework. Current legislation does not adequately harmonise standards to account for the unique characteristics of biomass ashes, including the specific contaminant profiles associated with different combustion practices. This inadequacy hinders the safe recycling of these materials and limits their potential to improve soil quality. Mayer et al. (2022) supported these concerns, noting that ashes derived from untreated wood are considered suitable for fertilisation, whereas ashes from waste wood are subject to stricter regulations due to higher contamination levels. This underscores the importance of regulatory compliance and the need to differentiate ash types based on their origin and composition.

The presence of heavy metals and organic pollutants, such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), in biomass ashes highlights the need for targeted research on their chemical behaviour under varying soil conditions. Observations by Freire et al. (2015) suggest that blending different types of ashes could dilute pollutant concentrations, offering a practical approach to mitigating environmental risks; however, this strategy must be evaluated against the potential introduction of contaminants from diverse sources.

Overall, biomass ashes present promising opportunities for sustainable soil management and nutrient recycling. However, it is critical to carefully consider their contamination profiles—particularly heavy metals, PCDD/Fs, and polycyclic aromatic hydrocarbons (PAHs). Regulatory frameworks must evolve to ensure that ash recycling practices optimise not only the benefits to soil but also the mitigation of environmental and health risks. Future research should prioritise the development of standardised protocols for ash assessment, effective methods for reducing harmful contaminants, and the establishment of best practices for safe application across diverse soil types.

The future of biomass ash utilisation will depend on a deeper understanding of its chemical and biological properties, alongside the implementation of coherent and clear regulations. Research must focus on developing techniques to separate nutrients from contaminants, enabling broader and safer reuse. Additionally, fostering dialogue among scientists, policymakers, and farmers is crucial to building consensus on the valorisation of biomass ashes as sustainable resources.

Biomass ashes possess significant potential to enhance soil health and contribute to agricultural sustainability. However, realising this potential requires addressing the challenges associated with contamination and regulation. Careful management, rigorous monitoring, and updated regulations can enable the adoption of biomass ashes as valuable materials within the framework of a circular economy, promoting more sustainable and responsible agricultural practices.

Section 6. Industrial trials

6.1 Sample selection for industrial trials

The multi-methodological characterisation of the analysed ashes allowed for the identification of the material exhibiting the optimal features for some industrial experimental tests, which were carried out at from 30 to 31 July 2024 at the Timac Agro Italia plant in Barletta (BT).

The purpose of these tests was to develop a standard fertiliser formulation incorporating one selected ash type among those investigated in this thesis. The integration of ash into a standard fertiliser formulation performed in this study represents an initial step toward the sustainable valorisation of this kind of waste within the Italian fertiliser industry, with the aim of partially replacing conventional mineral raw materials.

Based on the previous discussed results, **FaF** was chosen as the most suitable material for the experimental phase. This ash, classified under the European Waste Code (EWC) 10 01 05, originates from calcium-based reactions in flue gas desulphurisation processes (see Section 3.1). Since it is derived from the combustion of untreated vegetal biomass (*e.g.*, straw and wood chips), FaF shows considerable potential for integration into fertiliser formulations, thanks to its high content of nutrients present in water-soluble mineral phases (such as sylvite, aphthitalite, and portlandite), which are potentially bioavailable to plants. However, the decisive factor for its selection was the high operational reliability of the combustion plant, which processes only virgin biomass under strictly controlled and standardised procedures. Its operating parameters and ingoing fuels are in fact rigorously monitored and maintained within narrow variability ranges, ensuring both the reproducibility and stability of operating conditions. This ensures the consistent production of ashes with highly controlled and homogeneous composition, which is essential for ensuring reproducible experimental results and reliable integration into fertiliser formulations. Although specific operational details of the plants cannot be disclosed due to confidentiality restrictions, it can be stated that the other investigated ashes were excluded from the preliminary industrial trial conducted in this study, as the heterogeneity of biomass feedstocks and the combustion technologies employed in those plants, did not provide the same level of operational control and compositional consistency as observed for FaF.

However, one of the main limitations to incorporating FaF ash into standard fertiliser formulations was its heavy-metal content, which exceeded the limits established by fertiliser regulations (although still present at lower concentrations than in the other samples analysed). For this reason, in 2024, the plant managers implemented an upstream intervention in the combustion process aimed at reducing

heavy metal contamination in the ashes mostly through the selection of more efficient fuels. To optimise the combustion process and minimise the heavy metal content of the resulting ash, the composition of the biomass feedstock was adjusted.

In the plant configuration used during 2022–2023, the input fuel consisted of approximately 92% straw and 8% virgin wood chips, despite the relatively low calorific value of straw. In the revised blend introduced in 2024, virgin wood chips sourced from agricultural and forestry pruning residues accounted for 28% of the fuel, with the remaining 72% being straw. Increasing the proportion of virgin wood has been reported to stabilise combustion and help maintain operating temperatures below 900 °C. In addition, because of its higher calorific value, virgin wood improves overall energy efficiency and is considered more suitable for producing ash with substantially lower contaminant concentrations than straw (Alakangas, 2016).

Further chemical and mineralogical investigation of the FaF ash, following the plant intervention carried out in 2024 (hereafter referred to as FaF-2024), was conducted before the test for their integration into fertilizer formulations. The new analyses were performed the same methodological approach applied to the previously described samples and the obtained results are presented and discussed in the following section.

6.2 Chemical and mineralogical characterisation of ash used for industrial trials

The chemical and mineralogical composition of the fly ash sample FaF-2024 is reported in Tables 14 and 15 in comparison with the corresponding ash from the same plant before the modification of operational parameters and specific fuels carried out in 2024 (FaF).

The most pronounced compositional change concerns silicon, with the FaF 2025 sample exhibiting a marked enrichment in SiO_2, increasing to 19.81 wt% compared with 4.82 wt% in the FaF sample. This enhancement is likely attributable to the higher proportion of woody biomass in the fuel, in which silicon is primarily present as phytoliths ($SiO_2 \cdot nH_2O$), structurally incorporated into plant tissues and released during incineration (Yapuchura et al., 2019). MgO and P_2O_5 also show substantial increases, reaching 11.46 wt% and 6.26 wt%, respectively, compared with initial values of 0.09 wt% and 3.26 wt%, consistent with literature reports of higher concentrations of these oxides in wood-derived ashes compared with straw ashes (see Table 1).Among the other major oxides, Al_2O_3 exhibits a moderate increase (1.99 wt% *vs* 0.23 wt%), whereas CaO decreases slightly (41.26 wt% *vs* 45.40 wt% in FaF). In contrast, Na_2O and K_2O decrease markedly, from 11.76 to 2.25 wt% and from 34.24 to 16.08 wt%, respectively, reflecting reduced volatilisation of alkali elements, in agreement with

previous studies reporting lower alkali contents in wood ashes than in straw-derived ashes (Porbatzki et al., 2011).

Minor oxides, including TiO_2, MnO, and Fe_2O_3, display only marginal and quantitatively negligible variations.

Collectively, these compositional shifts indicate that optimisation of operational parameters combined with adjustments in fuel composition promotes the accumulation of siliceous and refractory components, while limiting the volatilisation of alkali elements (Na, K), a key factor in fouling of combustion systems. Such modifications expected to enhance both plant efficiency and operational reliability (Gogolev et al., 2022).

Concerning heavy metals, the FaF 2024 sample exhibits a pronounced reduction in concentrations of all regulated heavy metals analysed, compared with the FaF sample, particularly for Zn, Pb, and Cd, showing that modifications in fuel composition and operational conditions may significantly influence the accumulation of potentially toxic elements in the resulting ash. As shown in Table 14, these adjustments effectively minimised pollutant concentrations, ensuring full compliance with the regulatory limits for Constituent Material Categories (CMCs) established by EU Regulation 2019/1009, which consequently allowed the production of ash with a well-defined chemical profile suitable for experimental applications.

Table 14. Main oxides (wt%) and heavy metal content (mg/kg), of FaF 2024 and FaF before the modification of operational parameters and fuels at the plant. The pH (measured as described in Section 3.2) and regulatory limits for different categories of fertilisers and soil amendments according to Regulation (EU) 2019/1009 are reported.

Main oxides (wt%)										
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
[1]FaF-2024	2.25	11.46	1.99	19.81	6.26	16.08	41.26	0.08	0.05	0.78
FaF	11.76	0.09	0.23	4.82	3.26	34.24	45.40	0	0.02	0.17
Heavy metals (mg/kg)										
	Pb	Ni	Cd	As	Cu	Zn	Cr (VI)	Hg		p H
FaF-2024	44	4	1.4	11	48	230	< 0.2	0.312		13
FaF	983	6	18	27	132	5204	<0.5	2.28		14
Regulatory limit (EU) 2019/1009 (mg/kg)	120	50	3	40	600	1500	2	1	OMF	
	120	100	3	40	600	1500	2	1	IF-Macro	
	600	2000	200	1000				100	IF-Micro	
	120	90	2	40	300	800	2	1	Ca/Mg corr.	
	120	100	1.5	40	300	800	2	1	IA	

[1]FaF-2024: ashes after the modification of operational parameters carried out at the plant on 2024.

Notes: OMF: Organo-Mineral Fertilisers; IF-Macro: Inorganic Fertilisers based on Macronutrients; IF-Micro: Inorganic Fertilisers based on Micronutrients; Ca/Mg Corr: Calcium and/or Magnesium Correctives; IA: Inorganic Amendment.

The mineralogical composition of the ash samples, reported in Table 15, shows that some minerals are retained, while others undergo significant changes between FaF 2024 and FaF, following modifications to the combustion parameters and fuel blend. In both samples, portlandite (FaF 2024: 21.4 wt%; FaF: 18.7 wt%) and calcite (FaF 2024: 4.7 wt%; FaF: 5 wt%) are present in comparable amounts, indicating that the primary calcium-bearing phases remain largely unchanged. Similarly, sylvite (FaF 2024: 6.8 wt%; FaF: 25.5 wt%) is still detectable, albeit at substantially reduced content. Following the operational adjustments, a decrease in halite (FaF 2024: 0.8 wt%; FaF: 2.3 wt%) and a moderate increase in anhydrite (FaF 2024: 2.5 wt%; FaF: 1.3 wt%) are also observed.

Conversely, several minerals present in FaF such as aphthitalite (5.7 wt%), hydroxyapatite (1.4 wt%), and CaClOH (4.5 wt%), are absent in the modified FaF 2024, while new phases including wollastonite (5.3 wt%), dawsonite (1.8 wt%), and defernite (13.4 wt%) appear in its mineral assemblage. The occurrence of silicate phases wollastonite and defernite, are consistent with the higher SiO_2 content in FaF 2024 compared to FaF (19.81 wt% vs 4.82 wt%). Likewise, the decrease in alkali chlorides aligns with the reduced concentrations of Na_2O (2.25 wt% vs 11.76 wt%) and K_2O (16.08 wt% vs 34.24 wt%). The comparable contents of portlandite and calcite reflect the similar CaO contents in the two samples (FaF 2024: 41.26 wt%; FaF: 45.40 wt%).

As previously noted, these differences clearly highlight the influence of the feedstock: the increased proportion of woody biomass in FaF 2024 promotes the formation of silicate phases, while reducing the prevalence of alkali-rich minerals typical of straw-derived ashes. Finally, the amorphous fraction remains largely unchanged between the two samples (FaF 2024: 43.3 wt%; FaF: 35.6 wt%).

Table 15. Comparison of mineralogical composition of ash samples after the modification of combustion parameters and fuel blend (FaF-2024) and (FaF).

Mineralogical composition (wt%)		
Mineral	FaF-2024*	FaF
silvite, KCl	6.8 ±0.5	25.5 ±1.1
portlandite, Ca $(OH)_2$	21.4 ±1.4	18.7 ±0.6
calcite, $CaCO_3$	4.7 ±0.7	5.0 ±0.5
halite, NaCl	0.8 ±0.2	2.3 ±0.2
defernite, $Ca_6(CO_3)_{1.5}(SiO_4)_{0.5}(OH)_{7.5}Cl0.5$	13.4 ±1.1	
anhydrite, Ca (SO_4)	2.5 ±0.4	1.3 ±0.6
wollastonite, $CaSiO_3$	5.3 ±0.9	
dawsonite, $NaAl(CO_3)(OH)_2$	1.8 ±0.6	
aphthitalite, $(K,Na)_3Na(SO_4)_2$		5.7 ±0.6
CaClOH		4.5 ±0.9
hydroxyapatite, $Ca_5(PO_4)_3(OH)$		1.4 ±0.4
amorph	43.3 ±3.6	35.6 ±1.7
Rwp	6	7.17
χ^2	2.11	2.58
GOF	1.45	1.61

* Estimated standard deviations (e.s.d.) calculated using a 3-sigma correction.

6.3 Formulation process and results obtained

For the industrial experimental test, an NPK 30-20-50 fertiliser was selected — a standard formulation containing 30 wt% nitrogen, 20 wt% phosphorus, and 50 wt% potassium. This formulation was chosen not only because it represents a widely adopted industrial benchmark in terms of composition and agronomic performance, but also because it provides a well-established reference framework for assessing the behaviour of integrated alternative raw materials such as the investigated ashes, under realistic production conditions. Furthermore, the constituent compounds of this NPK mixture are characterised by a high degree of chemical and physical compatibility with most conventional fertiliser materials including mineral and chemical components. This intrinsic compatibility helps maintain the structural stability and overall integrity of the granulated product, aiming to achieve performance and consistency comparable to that of the conventional formulation, even when ashes are incorporated.

Prior to transfer to the industrial fertiliser plant, the ash underwent a high-pressure roll compaction process, designed to optimise transport logistics and reduce the risk of dust dispersion. This pre-

treatment step ensured a more uniform particle size distribution and improved the handling characteristics of the ash during blending with the NPK mixture.

Two experimental batches were carried out to evaluate the incorporation of ashes into the NPK fertiliser. A total of 250 t of product was prepared in two batches: (1) 100 t for an initial trial containing 5 wt% ash, conducted as a preliminary test to evaluate process performance and blending reproducibility under slightly adjusted parameters; and (2) approximately 150 t with a higher ash addition of 10 wt%. The ash content in the second batch was chosen to be high enough to assess the compatibility of the ash with the fertiliser matrix while still ensuring that the declared nutrient content of the product remained unaffected. In both batches, the conventional potassium chloride (KCl) content was reduced proportionally to the ash addition, resulting in 15 wt% KCl in the 5 wt% ash batch and 10 wt% KCl in the 10 wt% ash batch. The primary objective of these trials was to evaluate the compatibility and influence of the ash on the physico-chemical properties of the final fertiliser, analysing key aspects such as granulation behaviour, moisture content, and pH. This sequential approach allowed for a systematic assessment of the effects of varying ash content on the processing behaviour of the mixture while maintaining consistency with the standard industrial formulation.

The raw materials used in the formulation of the ash-based NPK fertiliser included ammonium sulphate [$(NH_4)_2SO_4$], potassium chloride (KCl), single superphosphate (SSP), [$Ca(H_2PO_4)_2 \cdot H_2O$], talc, and oil as summarised in Table 16. The appearance of the raw materials prior to their incorporation into the granulation process can be appreciated in Figures 20-21.

Ammonium sulphate contains 20 wt% ammoniacal nitrogen and 24 wt% sulphur. It is synthesised in the dedicated chemical industry by directly neutralising sulphuric acid with ammonia. The reaction is highly exothermic, leading to the direct crystallisation of the salt and the evaporation of excess water. Superphosphate is a fertiliser containing 17 wt% phosphorus, 28 wt% sulphur, and 24 wt% calcium. It is produced by treating "phosphorites", the sedimentary rocks with 15–20 wt% phosphorus, composed of minerals such as fluoroapatite or hydroxyapatite [$Ca_5(PO_4,CO_3)_3(F,OH)$], with sulphuric acid (H_2SO_4) in a mixer, followed by a maturation period of approximately four days. As a result of the chemical reaction, calcium dihydrogen phosphate [$Ca(H_2PO_4)_2$], also known as monocalcium phosphate or superphosphate, is released. This compound is water-soluble and typically appears as a powder with a characteristic odour, which arises from the reaction between sulphuric acid and phosphorite. Potassium chloride contains 60 wt% of K. In nature, it is found in evaporitic rocks composed of various potassium salts, such as sylvite (KCl), carnallite $KMgCl_3 \bullet 6(H_2O)$, kainite $MgSO_4 \bullet KCl \bullet_3(H_2O)$, and others. Potassium salts extracted from mines are not pure but consist of various components that must be separated to produce fertilisers with agronomic value. Finally, talc and oil are used in granulated fertilisers to facilitate the granulation process.

Table 16. Fertiliser production formulas.

Component	Conventional formula of fertiliser (wt%)	Formula with ash (wt%)	
Ammonium sulfate $(NH_4)_2SO_4$	30	30	30
Potassium chloride (KCl)	20	15	10
SSP (Superphosphate) $Ca(H_2PO_4)_2 \cdot H_2O$	50	50	50
Talc	0.3	0.3	0.3
Oil	0.3	0.3	0.3
Ash		5	10



Figure 20. Components of the formulation: a) superphosphate (SSP), b) ammonium sulphate, c) potassium chloride, d) ashes.

During the production process, the raw materials were transported along the conveyor belt to the granulator, as illustrated in Figure 21. The granulation procedure follows the "wet and dry" principle, which consists of two main phases:

1. Moistening and mixing phase (wet): the raw material mixture is moistened with water to promote particle aggregation. Water acts as a binding agent, allowing the components to adhere to each other and form small agglomerates.
2. Drying and granule formation phase (dry): the mixture is subjected to rotary motion and drying. The heat reduces excess moisture, consolidating the granule structure and ensuring its final shape and mechanical resistance.

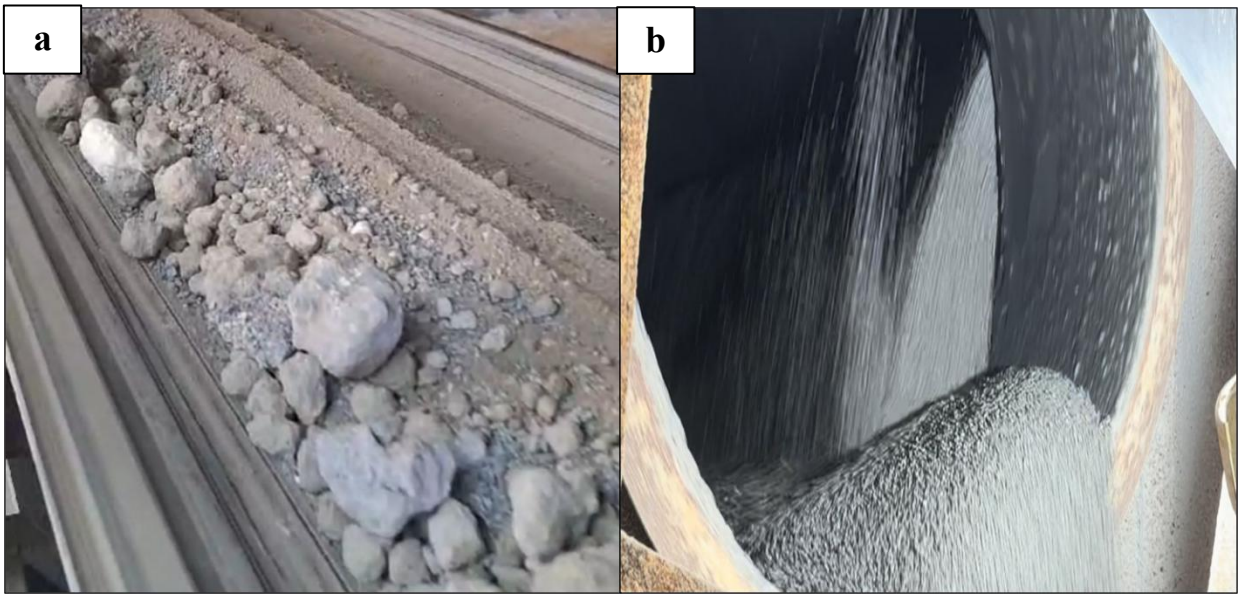


Figure 21. Mineral raw materials and ash on a conveyor belt (a) and granulator (b).

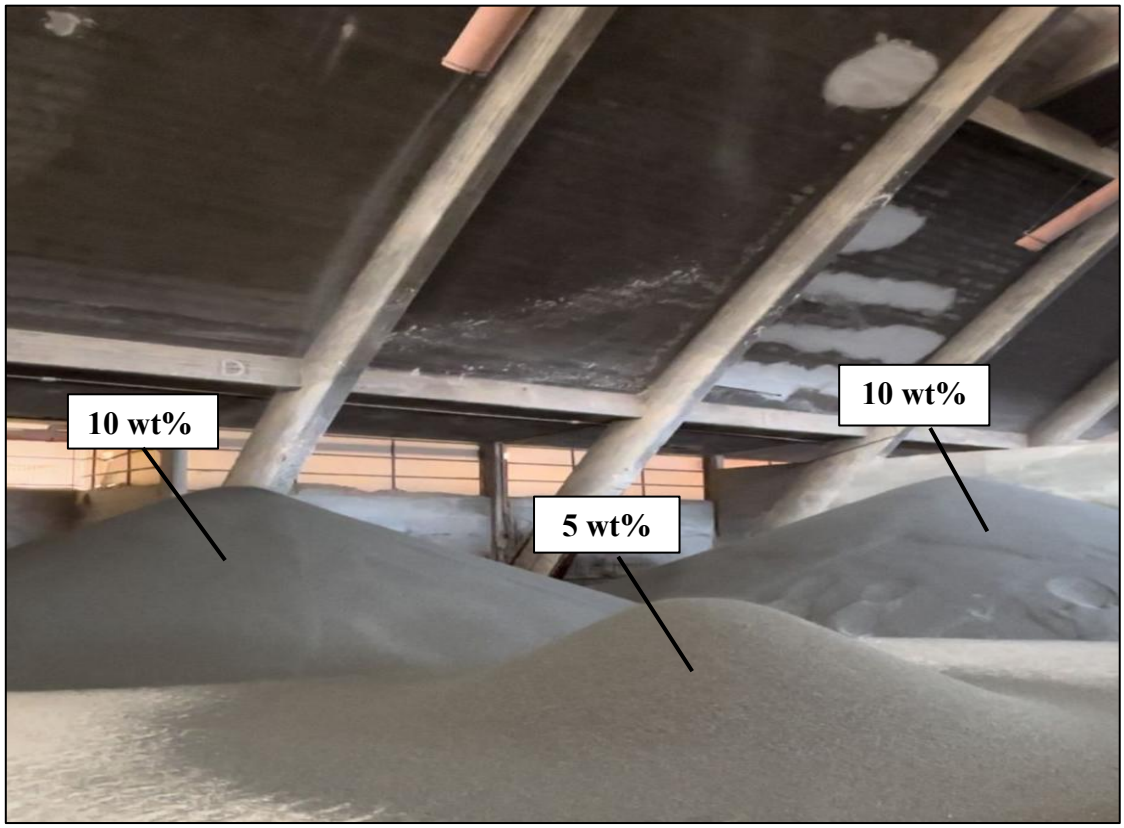


Figure 22. Total production of 250 tons of fertiliser formulation incorporating 5 wt% and 10 wt% of biomass ash.



Figure 23. finished granular fertiliser containing ashes.

The fertiliser granules obtained from the production process exhibited uniform consistency and a homogeneous particle distribution (Figures 22-23). However, the addition of fly ash influenced both the granulation phase and certain properties of the final fertiliser.

In particular, an increase in moisture content was observed: for the formulation containing 5 wt% ash, the moisture reached 5.8 %, while for the 10 wt% ash formulation, it increased to 7 %, compared to 5.5 % in the standard formulation.

The pH of the fertiliser also increased with ash addition: the 5 wt% ash formulation reached a pH of 5.5, whereas the 10 wt% ash formulation reached 5.8, compared to 4.5 in the standard mixture.

The addition of ash had a direct effect on granule compactness. In the formulation containing 5 wt% ash, granule compactness was comparable to that of the standard formulation, whereas in the formulation with 10 wt% ash, the granules exhibited a significantly reduced compactness. This difference can be attributed to the moisture content, which—as noted above—was very close to the standard 5.5 % in the 5 wt% substitution formulation, but significantly higher in the 10 wt% ash formulation.

This effect is likely attributable to the physical properties of the ash, whose hygroscopic nature may have altered particle adhesion during granule formation by promoting greater moisture absorption and retention compared with the conventional raw materials. The granulation process required approximately 3500 litres of water, which is essential for ensuring the formation of granules with an adequate structure.

An estimate of the nutrient contributions and the associated economic savings resulting from replacing part of the theoretical standard KCl addition (20 wt%) with an equivalent amount of biomass ash corresponding to 5 wt% and 10 wt%, respectively, in the two experimental fertiliser batches, is summarised in Table 17.

Table 17. Fertiliser production, KCl substitution, nutrient contributions (K, Mg, P, Ca), and associated economic savings for batches containing 5 wt% and 10 wt% biomass ash. Totals are also reported.

Batch	Fertiliser produced	KCl in conventional formulation	KCl substituted	K	Mg	P	Ca	Economic saving
Units	(t)			(kg)				(€)
5 % ash	100	20	5	668	345	136	1473	1850
10 % ash	150	30	15	2004	1036.5	409.5	4419	5550
Total	250	50	20	2672	1381.5	545.5	5892	7400

Notes: KCl substitution amounted to 25 % in the 5 wt% ash batch and 50 % in the 10 wt% ash batch. The nutrient contents (K, Mg, P, Ca) were calculated based on the oxide concentrations in the ash (Table 14), multiplied by the total amount of fertiliser produced in each batch. The economic saving (€) was calculated considering a conventional KCl price of €370 t^{-1} (TIMAC Agro private communication).

Although the proportion of ash used in this study was relatively low, the benefits achieved are by no means negligible. In particular, the partial substitution of KCl resulted in an economic saving of €1.850 in the 5 wt% ash batch and €5.550 in the 10 wt% ash batch, for a total reduction of €7.400. This is especially relevant in the fertiliser sector, where controlling production costs is essential to maintain the economic sustainability of agricultural activities, and any opportunity for optimisation provides a tangible advantage.

The incorporation of ash did not merely reduce the amount of conventional potassium chloride used but also provided a significant contribution of essential nutrients to the fertiliser. Specifically, by summing the values of K, Mg, P and Ca reported in Table 17, the cumulative nutrient content supplied by the ash amounted to 10491 kg. This corresponds to approximately 4.2 wt% of the total fertiliser produced (250 t), a notable outcome considering that the material used originates from a biomass residue that would otherwise have required disposal, being the final product of cogeneration plants exploiting the combustion of agro-forestry waste to produce thermal and electrical energy.

Furthermore, the valorisation of ash in fertiliser formulation avoided costs associated with its disposal. Assuming a typical European landfill fee of €100 t^{-1} (European Environment Agency, 2013), the 20 t of ash used in the 250 t of fertiliser translates into an additional estimated saving of approximately 2000 €. This aspect not only reinforces the economic efficiency of the strategy but also highlights its environmental value, transforming a potentially problematic waste into a valuable resource.

Overall, the partial substitution of KCl with biomass ash demonstrates that it is possible to integrate cost reduction, nutrient supply, and environmental sustainability. The adopted approach represents a concrete example of circular economy, generating a virtuous cycle of "*industrial symbiosis"* that valorises waste streams, enhances production efficiency, and provides tangible support to agriculture. Although only two incorporation levels were tested in this study, future work will explore a wider range of addition rates to identify the optimal balance between ash valorisation and the agronomic quality of the fertiliser. To further optimise the formulation and improve the quality of the final product, strategies to reduce the fertiliser's moisture content should be investigated, such as modifications to the granulation process or the addition of binding agents to enhance granule compactness. Additionally, the different ash integration percentages could be examined to achieve the best compromise between nutrient contribution, fertiliser stability, and reduction of conventional raw materials.

pH regulation also requires further study, including the potential use of corrective agents or adjustments to the fertiliser composition to attain the desired equilibrium. Finally, additional tests could be conducted to assess the agronomic effectiveness of the product, evaluating nutrient availability in the soil and its effects on crop growth.

This study represents a significant first step towards the use of biomass ashes in the mineral fertiliser industry, demonstrating their potential as a sustainable and alternative nutrient source, in line with circular economy principles and environmental impact reduction.

Section 7. Conclusions

7.1 Final remarks

Through a feasibility-oriented investigation various types of fly and bottom ashes generated from biomass combustion in Italian thermal power plants have been characterised to assess their potential application in the mineral fertiliser sector. A detailed analysis revealed significant variability in chemical and physical properties, influenced by numerous factors, including the type of plant, combustion operating conditions, the nature of the biomass used, as well as post-combustion storage and treatment methods. Despite these differences, all analysed ashes were found to be rich in essential plant nutrients, including K, Ca, Mg, P, Zn, Fe and Cu.

Chemical and mineralogical analyses revealed that fly ashes contain higher concentrations of nutrients compared to bottom ashes, with elevated levels of K_2O (up to 20 wt%) and CaO (up to 28 wt%), mainly present in water-soluble minerals such as sylvite (KCl), aphthitalite [$(K,Na)_3Na(SO_4)_2$], syngenite [$K_2Ca(SO_4)_2 \cdot H_2O$], and portlandite [$Ca(OH)_2$]. Moreover, fly ashes include several calcium-bearing minerals, such as calcite ($CaCO_3$), anhydrite ($CaSO_4$), and hydroxyapatite [$Ca_5(PO_4)_3(OH)$]. Minor mineral phases corresponding to oxides, including periclase (MgO) and zincite (ZnO), were also detected.

These characteristics suggest the potential use of fly ashes as fertilisers providing readily bioavailable macronutrients for plants. However, in certain types of ash, particularly those derived from the combustion of “wood waste” and “end of waste wood”, heavy metal concentrations exceed the limits set by the European Regulation 2019/1009, with notably high levels of Pb, Zn, Cd, As and Cu. Conversely, fly ashes originating from virgin wood and straw combustion exhibit significantly lower contaminant levels.

Water Leaching tests demonstrated a high solubilisation rate of fly ashes (ranging from 40.9% to 72.22%) and the formation of highly alkaline solutions (pH 12-14), which were found to be devoid of heavy metals in soluble form due to the strongly alkaline environment that hinders their mobility. The resulting eluates have the potential to replace synthetically produced potassium chloride and potassium sulphate in conventional fertiliser formulations.

Bottom ashes are characterised by high concentrations of SiO_2 (up to 58 wt%), CaO (up to 37 wt%), Al_2O_3 (up to 8 wt%), Fe_2O_3 (5 wt%), and MgO (up to 6 wt%), resulting in a dominant presence of silicate phases, with quartz detected in all samples. Various silicate minerals including leucite ($KAlSi_2O_6$) and cristobalite (SiO_2) were observed, alongside several calcium-based silicates, including akermanite ($Ca_2MgSi_2O_7$), hatrurite (Ca_3SiO_5), and merwinite [$Ca_3Mg(SiO_4)_2$]. Plagioclase

[$(Na,Ca)(Si,Al)_4O_8$] occurred in all samples, whereas other silicate phases, such as pyroxenes [$(Ca,Mg,Fe)_2Si_2O_6$], were detected depending on the sample. Several oxide phases, including hematite (Fe_2O_3), periclase (MgO), and rutile (TiO_2), were detected. Calcium-bearing minerals such as calcite ($CaCO_3$) — a common constituent in all samples — and hydroxyapatite [$Ca_5(PO_4)_3(OH)$] were also observed. Water-soluble minerals were found only in low concentrations in two samples, including Ca-bearing sulfates such as syngenite [$K_2Ca(SO_4)_2 \cdot H_2O$], gypsum ($CaSO_4 \cdot H_2O$), and the hydroxide portlandite [$Ca(OH)_2$].

Fewer exceedances of environmentally significant heavy metals—such as Zn, Pb, Cu, Cd, Cr, and Hg—and generally lower concentrations were observed in bottom ashes compared to fly ashes. This is attributed to the lower specific surface area of bottom ash, which limits its capacity to retain volatile heavy metals that, during combustion, tend to condense onto fine particles with higher specific surface area, such as those in fly ashes (particle size <0.063 mm), resulting in comparatively higher heavy metal concentrations in the latter.

Water leaching tests indicated that, despite exhibiting lower solubility (1.79%–7.43%) relative to fly ashes and releasing smaller quantities of nutrients, bottom ashes retain the potential to contribute to soil mineral enrichment. This capacity is attributable to their elevated concentration of alkaline elements (pH 9–11), which can facilitate pH correction and the enhancement of soil physicochemical properties, provided that appropriate treatments are applied to further mitigate heavy metal content and that a thorough assessment of the receiving soil is conducted.

The analysis of persistent organic compounds, including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs), identified only one instance of regulatory exceedance, observed in a fly ash sample collected from an electrostatic precipitator.

This finding highlights an additional critical issue that could be mitigated through specific flue gas purification treatments and a more stringent selection of biomass feedstocks to minimise the accumulation of such contaminants. Chemical and mineralogical analyses of the granulometric fractions of bottom ashes did not reveal systematic segregation of elements and mineral phases; however, variations in elemental concentrations were observed depending on sample origin and particle size. Notably, nutrients were the predominant component in each fraction, with relative proportions ranging from approximately 70 % to 90 %. Additionally, the only granulometric fractions that fully comply with both minimum and maximum regulatory limits across all fertiliser categories were those in the 0.063–0.125 mm and 0.125–0.25 mm ranges in two of the analysed samples (BaL and BaR). Therefore, granulometric separation proved to be an effective strategy for identifying particle size fractions free from contamination in these samples.

Furthermore, the multi-method characterisation of the analysed Italian biomass ashes enabled the identification of the materials most suitable for industrial trials at the Timac Agro Italia plant in Barletta (BT). Among the various types examined, the fly ash FaF, derived from flue gas desulphurisation processes of virgin plant biomass, was selected due to the high operational reliability of the source cogeneration plant, the substantial concentration of potentially bioavailable nutrients, and its relatively low heavy metal content compared with the other samples investigated.

The detailed chemical and mineralogical characterisation conducted in this study allowed the identification of upstream operational modifications at the cogeneration plant aimed at producing ash that is safe with respect to contaminants.

The chemical and mineralogical characterisation of the ash produced following the operational parameter adjustments at the plant (FaF-2024) revealed significant changes in the major oxides compared to the original ash, while still confirming a substantial contribution of K, Mg, P, and Ca, amounting to approximately 4.2 wt% of the final fertiliser. Mineralogical analyses further highlighted variation in the primary mineral phases of the original ash, with a marked increase in silicate phases and a significant reduction in chlorides. These interventions also resulted in a pronounced decrease in heavy metal concentrations, ensuring full compliance with European regulations on fertiliser constituents and enabling the production of a material with a stable, well-defined, and highly reliable chemical profile for agronomic applications.

Industrial trials confirmed the technical feasibility of integrating FaF-2024 ash into an NPK 30-20-50 formulation. However, the inclusion of ash induced certain modifications in the physico-chemical properties of the conventional product, including increased moisture content, elevated pH, and reduced granule compactness as the proportion of ash increased relative to the standard formulation. These effects can be primarily attributed to the hygroscopic nature of the ash and the high concentration of portlandite (21.4 wt%), derived from the hydrated lime used as a reagent in the in the flue gas desulphurisation processes within the source combustion system.

The valorisation of the ash generated a dual economic benefit, encompassing both the reduction in fertiliser production costs and the avoidance of disposal expenses for the cogeneration plant, resulting in a total economic gain of approximately €9,400.

Collectively, the results highlight the potential of biomass ashes as an alternative and sustainable nutrient source, demonstrating the possibility of combining cost reduction, production efficiency, and circular economy principles.

Finally, this study provides the first comprehensive mineralogical and chemical characterisation of biomass ashes from Italian biomass-fired power plants, integrating XRF, XRPD, ICP-MS, GC-MS, TG-DTA, FTIR, SEM–EDS, standardised water leaching tests, and particle size separation.

Quantitative Phase Analysis (QPA) using Rietveld refinement allowed the identification and quantification of both crystalline and amorphous phases, including key nutrient-bearing minerals that govern nutrient release, solubility, and potential contaminant mobility. In contrast to previous Italian studies, which focused primarily on general risk–benefit assessments or non-agronomic applications, this work assesses the direct suitability of biomass ashes as secondary feedstocks for fertiliser production. The results provide critical insights into nutrient content, contaminant distribution, and solubility, supporting strategies to maximise nutrient recovery while minimising landfill disposal.
By advancing the mineralogical and agronomic understanding of biomass ashes through Italian case studies, this research contributes to EU and national strategies for sustainable waste management and resource recovery, while broadening the scientific foundation for integrating underutilised secondary feedstocks into circular fertiliser value chains.

7.2 Future Perspectives

Considering the results obtained, several strategies emerge for the biomass ashes valorisation in the agricultural and environmental sectors. The main prospects include the selection of suitable and uncontaminated biomass sources, such as untreated wood. A second crucial aspect is the optimisation of combustion processes. More precise control over parameters such as temperature, oxygen supply, and flue gas treatment has been shown to influence the behaviour of trace elements and organic compounds during combustion. Specifically, higher combustion temperatures and effective flue gas purification can reduce the volatilisation of heavy metals and limit the formation of persistent organic pollutants, thereby improving the chemical quality of the resulting ash.
The potential reuse of ashes within fertiliser industry could be considered after reducing the heavy metals content through specific pre-treatments. Heavy metals such as Pb, Cd, Zn, Cu, and Cr can be extracted using various methods, including acid leaching with organic (*e.g.*, oxalic acid, $C_2H_2O_4$) or inorganic acids (HCl, H_2SO_4, HNO_3), chelating agents (*e.g.*, EDTA), and electrochemical techniques such as electrodialytic separation (EDS). The efficiency of heavy metal removal depends on the metals' binding environment and the leaching conditions, including redox potential, pH of the ash slurry, liquid-to-solid ratio, temperature, and leaching duration.
From an agronomic perspective, the targeted and differentiated use of ashes based on their chemical-mineralogical characteristics and soil requirements is essential. Previous studies have highlighted the potential for using biomass ashes with a high concentration of potassium and calcium to fertilise soils deficient in these elements, while ashes with high alkalinity could serve as effective amendments for acidic soils, such as forested areas subjected to intensive exploitation or nutrient-poor environments.

However, such applications must be accompanied by a thorough assessment of their compatibility with crops and potential issues related to the physicochemical properties of the ashes.

Even when ashes possess a significant nutrient content and comply with the contaminant safety criteria set by the European Fertilising Products Regulation (Regulation 2019/1009), their typically high alkalinity requires careful evaluation prior to direct application to soil. Excessive pH levels can disrupt soil chemical balance and adversely affect the activity of microorganisms essential for biogeochemical cycling and organic matter decomposition. In particular, populations of nitrogen-fixing bacteria and mycorrhizal fungi, which are highly sensitive to pH fluctuations, may decline, thereby compromising soil fertility and crop performance. Consequently, future research should prioritise strategies for pH adjustment prior to application. Furthermore, a critical aspect for the safe use of ashes in soils is the implementation of long-term environmental monitoring. Assessing the effects of ash application on soils and crops should rely on comprehensive studies designed to safeguard ecosystem integrity. Therefore, the targeted integration of ashes into balanced fertiliser matrices, as carried out in this study, ensures a high level of safety, being preceded by a quantitative and qualitative analysis of mineral speciation, necessary to accurately determine the chemical form of the nutrients, and by specific treatments aimed at minimising contaminants. This methodological approach allows for a thorough understanding of ash behaviour within biological and environmental ecosystems, the precise quantification of nutrient bioavailability for crops, and a rigorous assessment of compatibility with conventional raw materials used in the fertiliser industry. The synergy between accurate chemical and mineralogical characterisation, effective treatments, and the formulation of circular fertilisers represents the key to transforming a complex waste into a high-value secondary raw material, thereby contributing to intrinsically sustainable agriculture.

In the fertiliser sector, where controlling production costs is essential to ensure the economic sustainability of agriculture, every opportunity for optimisation represents tangible value. Although only two levels of ash incorporation were tested in a single type of conventional fertiliser in this study, future research could explore which types of mineral fertilisers are most suitable for integration with ashes and investigate strategies to mitigate potential disruptions in the granulation process caused, for example, by increased moisture content due to the hygroscopic properties of ashes, such as the addition of binding agents to improve granule compactness.

pH regulation also requires further investigation, including the possible application of corrective agents or adjustments to the fertiliser composition to achieve the desired balance. Additionally, further agronomic testing will be necessary to evaluate the efficacy of the product, monitoring nutrient availability in the soil and the corresponding effects on crop growth.

On a regulatory level, harmonisation of legislation at both European and national scales would be desirable to facilitate the adoption of biomass ashes as fertilisers or soil amendments while ensuring compliance with strict safety limits for potentially toxic elements. Establishing clearer and more uniform criteria would encourage their use while maintaining environmental and agronomic sustainability.

Biomass ashes represent a valuable resource for the agricultural sector and the circular economy, offering a potential contribution to reduce the use of conventional raw materials for the mineral fertilisers production. However, their utilisation must be carefully regulated, relying on innovative strategies for contaminant reduction and appropriate treatments to improve material quality. The future outlook for this valorisation will depend on the ability to integrate scientific research, technological innovation, and regulatory development, fostering the sustainable and responsible use of these secondary resources within a circular economy model.

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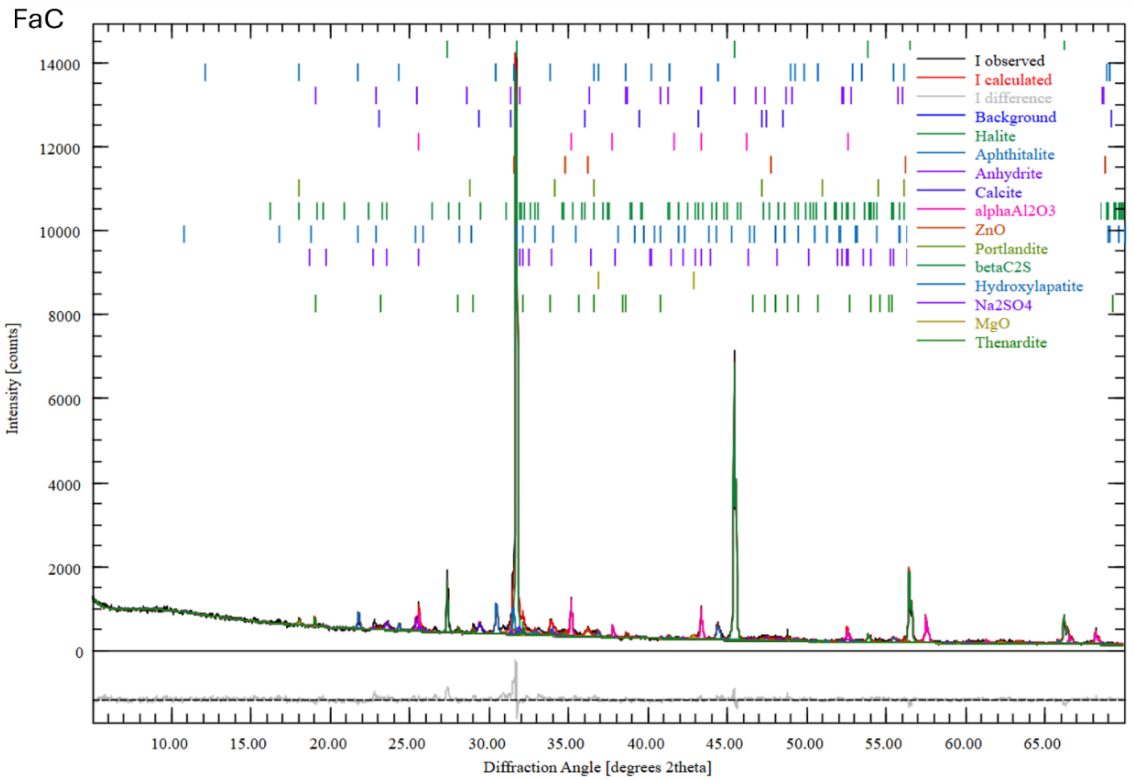
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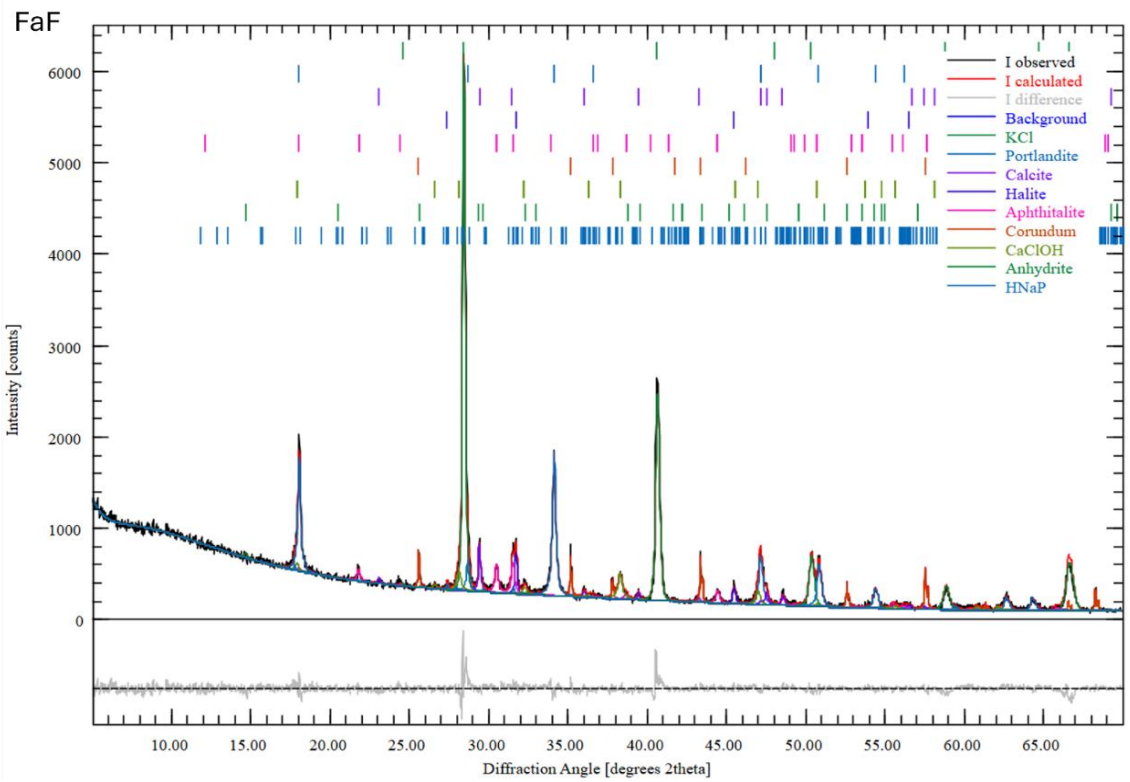
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Zörb, C., Senbayram, M., & Peiter, E. (2014). Potassium in agriculture – Status and perspectives. *Journal of Plant Physiology*, *171*(9), 656–669. https://doi.org/10.1016/j.jplph.2013.08.008

Appendix 1

Diagram outputs of Rietveld refinement from BGMN-Profex software





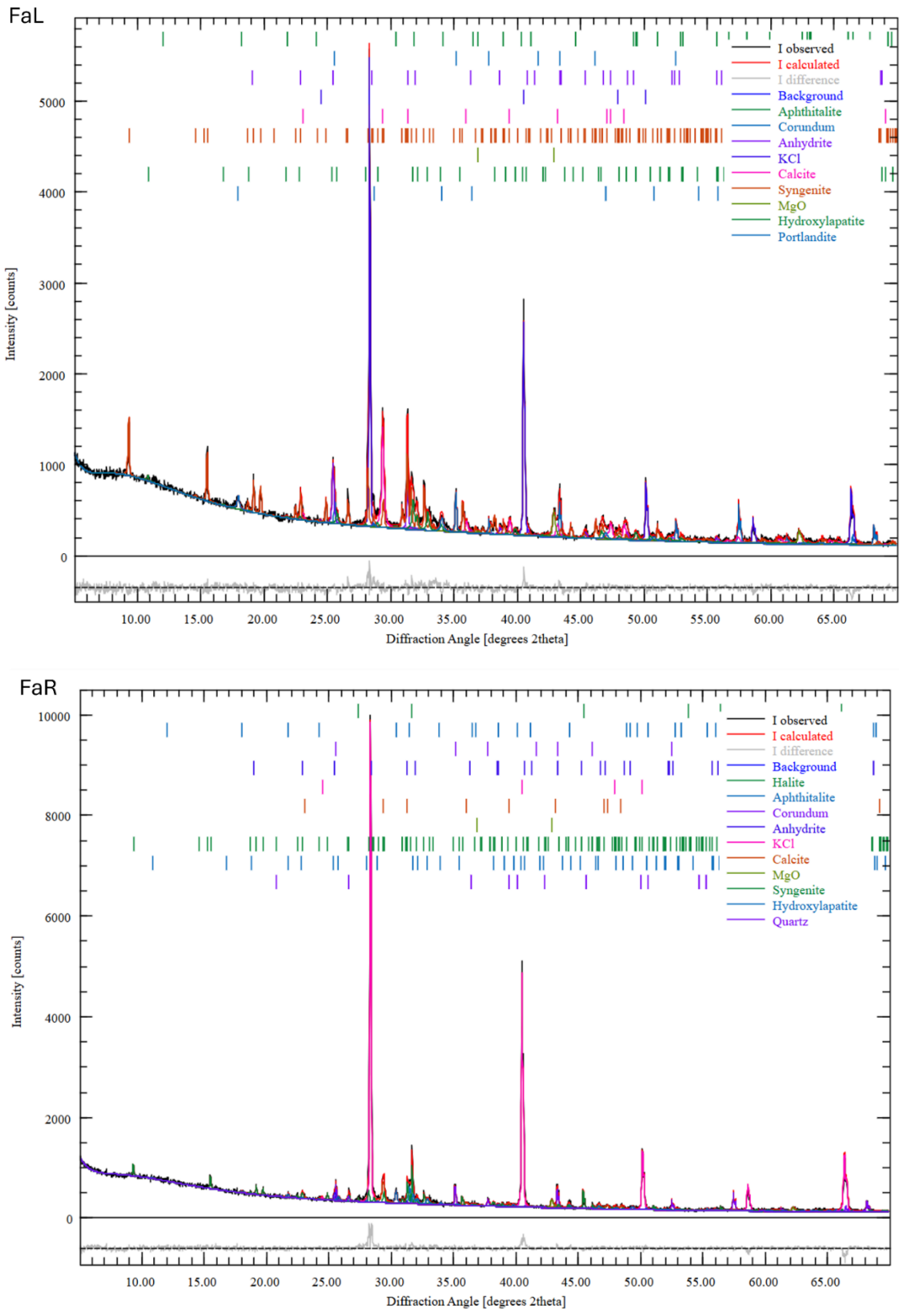
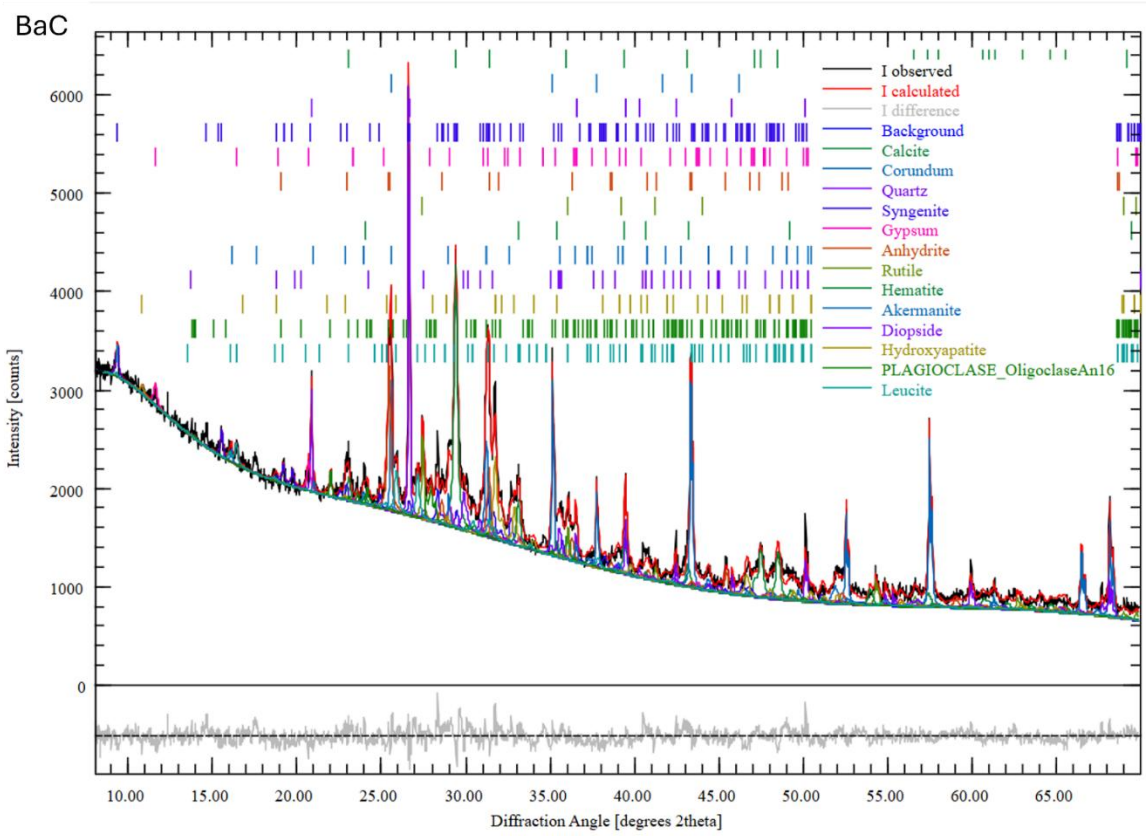
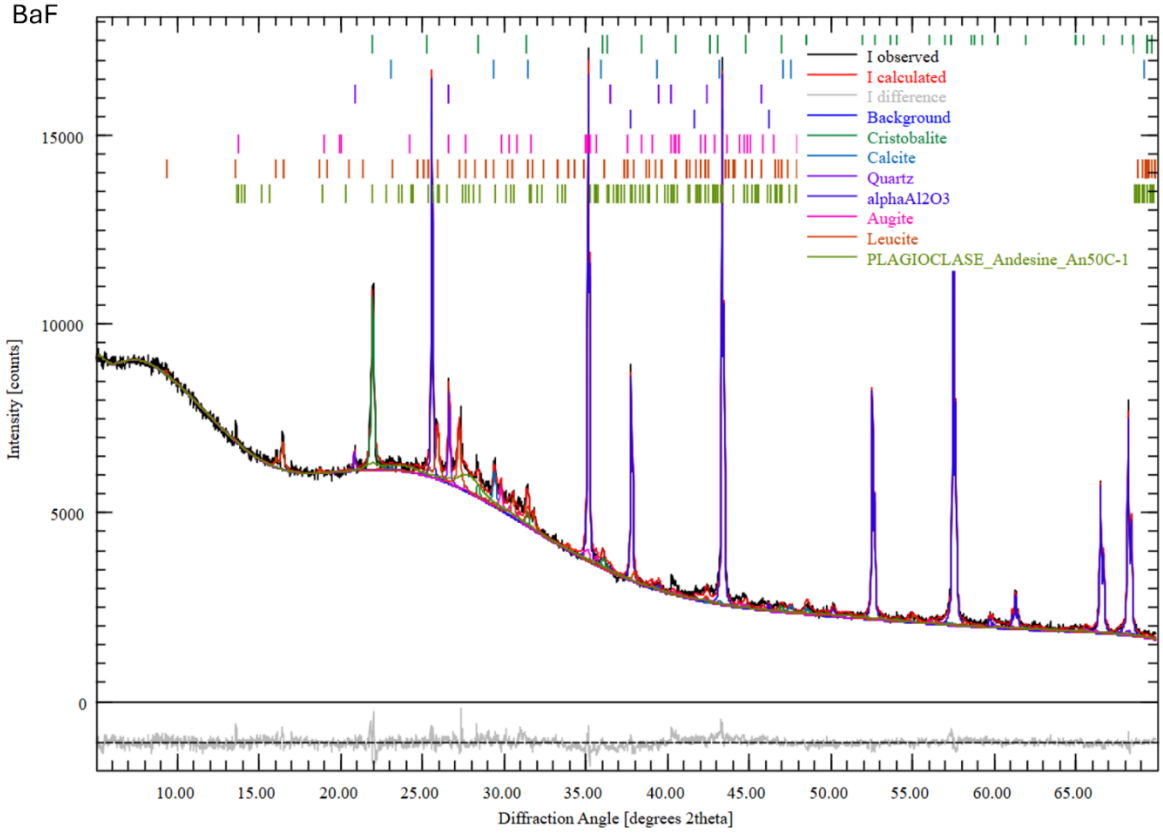


Figure A1.1 Diagram outputs of Rietveld refinements for bulk fly ashes (samples FaC, FaF, FaL, FaR).

BaC


I observed
I calculated
I difference
Background
Calcite
Corundum
Quartz
Syngenite
Gypsum
Anhydrite
Rutile
Hematite
Akermanite
Diopside
Hydroxyapatite
PLAGIOCLASE_OligoclaseAn16
Leucite
Intensity [counts]
Diffraction Angle [degrees 2theta]

BaF


I observed
I calculated
I difference
Background
Cristobalite
Calcite
Quartz
alphaAl2O3
Augite
Leucite
PLAGIOCLASE_Andesine_An50C-1
Intensity [counts]
Diffraction Angle [degrees 2theta]

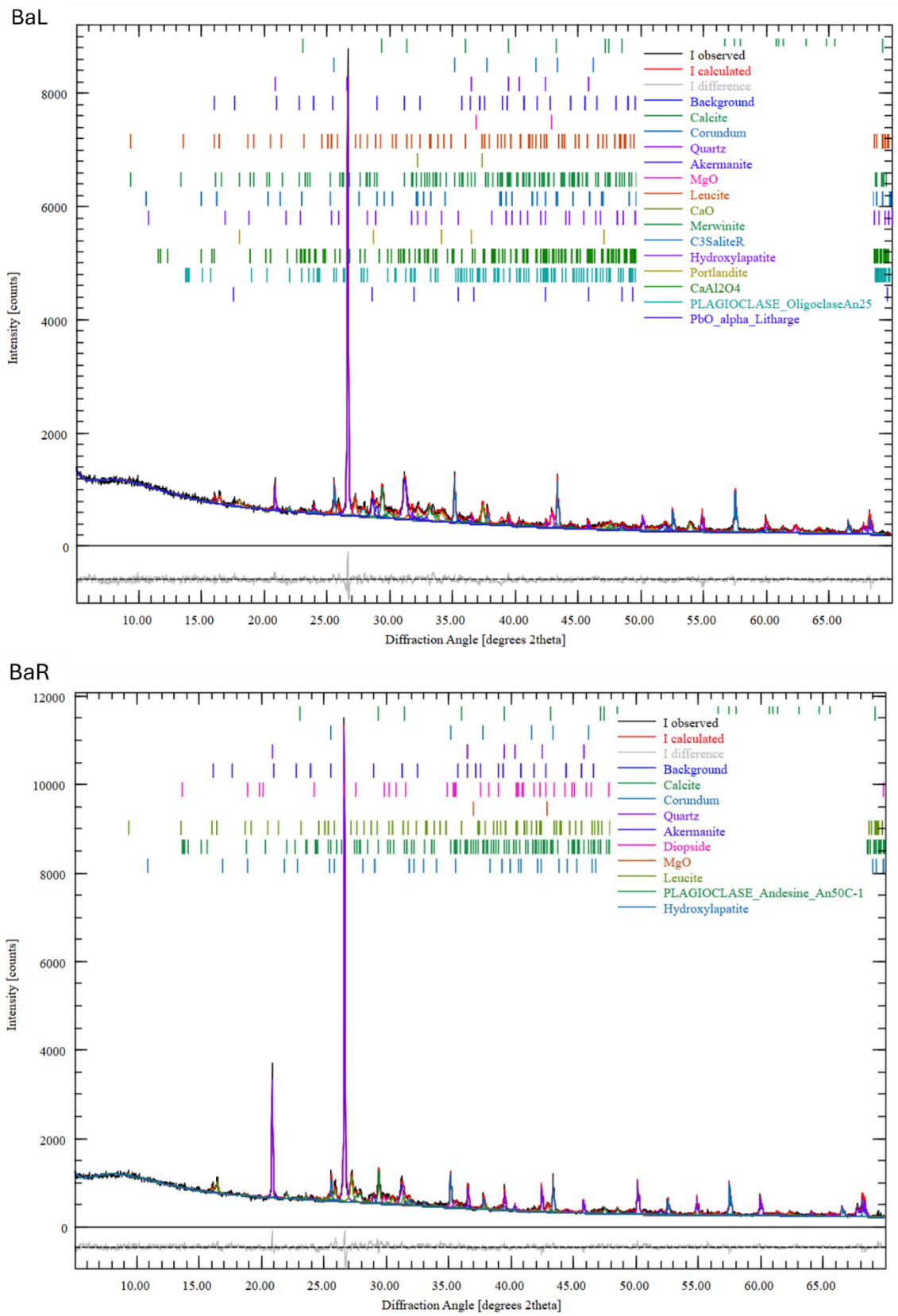


Figure A1.2 Diagram outputs of Rietveld refinements for bulk bottom ashes (samples BaC, BaF, BaL, BaR).

Appendix 2

Table A2.1. Elemental composition of different particle size for investigated ashes.

Particle size (mm)	Metals mg/kg	K	Ca	P	Mg	Na	Fe	B	Zn
< 0.063	BaC	20759	141778	7694	20402	7815	20008	383.21	10718
	BaL	25545	232514	6527	33068	2678	12048	195.69	459
	BaR	96172	65011	7999	7267	12401	18262	285.35	562
0.063-0.125	BaC	26666	127319	7419	18583	9871	21361	293.34	7219
	BaL	29601	165552	6440	25068	3395	14198	154.77	356
	BaR	14653	28505	7155	2938	3400	18976	159.15	329
0.125-0.25	BaC	26443	100640	6478	15143	10331	27869	233.52	5904
	BaL	36381	131651	6293	23301	3911	18326	119.45	236
	BaR	21553	73147	5852	11332	8708	20547	94.66	244
0.25-0.5	BaC	21327	71433	4690	11311	8667	21320	135.33	3799
	BaL	39055	135672	5791	24793	4389	17776	90.74	99
	BaR	26659	101783	4067	15174	10408	17868	60.56	130
>0.5	BaC	14503	26981	1448	2917	3393	13552	54.34	4377
	BaL	41773	135579	5996	26234	4917	18176	108.14	53
	BaR	27563	69985	4887	14981	3698	23564	68.7	110

Pb	Ti	V	Ba	Sb	Bi	Al	Si	Co	Cu	Mo	Mn
4047	3446	40	81.85	105.4	4.27	22105	13500	40	867	16.63	1866
129	1023	34	349.69	5.96	0.003	16180	14000	6	122	8.94	923
177	1105	45	385.4	10.06	0.003	24284	8000	8	163	21.93	1130
2828	6054	38	130.92	63.73	3.36	22767	11000	34	736	13.58	1496
78	1111	38	358.41	4.12	0.003	20563	11500	6	119	6.41	903
94	1273	42	342.81	5.87	0.003	25507	10500	8	144	12.55	900
3575	7427	40	292.2	49.18	3.98	24607	20500	35	677	13.89	1330
46	1296	47	386.5	3.3	0.003	27443	5500	8	141	4.96	997
47	1239	41	299.87	3.9	0.003	25762	5500	7	138	7.42	777
3794	8328	23	942.65	31.31	3.92	15159	11500	21	357	8.9	733
309	1253	42	338.96	2.02	0.003	25387	11500	7	149	3.51	894
49	1102	32	244	2.15	0.003	21643	21000	6	338	3.52	653
7063	3967	6	1302	34.79	2.42	3462	11500	8	198	7.58	274
18	1360	41	334.11	1.23	0.003	25684	14500	7	103	3.53	919
24	1086	36	240.08	2.09	0.003	24214	12000	7	97	4.86	701

Particle size (mm)	Metals mg/kg	Hg	Cr (Tot)	Cr VI	As	Cd	Ni
< 0.063	BaC	0.297	291	9	192	57	103
	BaL	<0.1	82	< 0.2	12	3	30
	BaR	0.12	107	1.5	20	1.9	45
0.063-0.125	BaC	0.249	224	5	111	44	95
	BaL	<0.1	76	< 0.2	9	1.9	29
	BaR	0.05	91	< 0.2	11	< 1	46
0.125-0.25	BaC	0.239	229	3.2	79	41	141
	BaL	<0.1	76	< 0.2	7	< 1	33
	BaR	<0.1	83	< 0.2	7	< 1	44
0.25-0.5	BaC	0.114	140	< 0.2	46	22	121
	BaL	<0.1	63	< 0.2	6	< 1	39
	BaR	<0.1	62	< 0.2	4	< 1	31
>0.5	BaC	0.121	75	< 0.2	50	13	65
	BaL	<0.1	60	< 0.2	3	< 1	29
	BaR	<0.1	86	< 0.2	5	< 1	54

Table A2.2 Mineralogical composition of different particle size for investigated ashes.

periclase	merwinite	leucite	hydroxyapatite	hematite	gypsum	calcite	anhydrite	akermanite	Mineral (wt%. 3σ)*	Particle size (mm)
1±0.3		-	6.6±1.1	1.3±0.3	2.4 ±0.6	16 ±1.2	2.9±0.4	8.7±0.7	BaC	<0.063
1.8±0.5	1.8±0.5	3.1±0.6	3.3±0.4	-	-	40.7±2.2	-	5.7± 0.7	BaL	
1.3±0.5	--	5.3±1.1	4.1±0.6	-	-	26.6±2.5	-	5.4±0.9	BaR	
1±0.4	-	-	5.1 ±1.5	1.5±0.4	1.5 ±0.6	12.8±1.4	1.8±0.8	7.5± 1.2	BaC	0.063-0.125
1.4±0.4	1.8±0.5	5.6±0.8	1.6±0.5	-	-	12.5±1.2	-	5± 0.8	BaL	
1±0.3	--	10.4±1.5	1.8±0.5	-	-	5.3±0.8	-	6.4±0.9	BaR	
-	-	4.7±0.9	6,.1±1.7	1.1±0.5	-	8.3±1	-	5.6 ± 0.9	BaC	0.125-0.5
1.1±0.4	2.9±0.5	7.2± 1.1	2.2±0.5	-	-	8.9±1.1	-	7.6± 1.3	BaL	
0.5±0.3	-	10.9±1.9	-	-	-	4±0.8	-	7±1.2	BaR	
-	-	0.8±0.5	-	0.8±0.2	-	8.7(±0.3)	-	1.5 ±0.5	BaC	>0.5
0.9±0.3	5.6±0.8	8.2±1.2	2.6±0.6	-	-	7.3(±1)	-	10.8± 1.3	BaL	
0.3±0.3	-	10.5±1.9	-	-	-	2.8(±0.7)	-	8.2±.9	BaR	

Particle size (mm)	Mineral (wt%)	amorph	feldspar	pyroxene	Ca-silicates	rutile	quartz
<0.063	BaC	48.2±3.3	4.5±0.6	3 ±0.6	-	1.2±0.3	4.2±0.6
	BaL	34.5±3.6	2.5±0.6	1.2±0.5	1±0.6	-	4.4±0.5
	BaR	38.8±5.6	7.1±1.2	4.4±0.9	-	-	7±1.2
0.063-0.125	BaC	49.4 ±4.8	6.4±0.8	3.4 ±0.8	-	1.2±0.4	8.4±0.8
	BaL	55.7±4.8	6±1	2.4±0.5	1.7±0.5	-	6.3±0.9
	BaR	45.1±5.1	7.8±1.2	4.5±0.9	-	-	17.7±1.8
0.125-0.5	BaC	53.6±4.2	4.1±0.9	4.0 ±0.9	-	1.7±0.5	10.8±0.9
	BaL	44.1±5.4	8±1.5	2.3±1.1	2.5±0.6	-	13.2±1.7
	BaR	38.6±9.6	11.9±6.3	4±1.2	-	-	23.1±3.0
>0.5	BaC	83.7±1.5	1.4±0.9	-	-	1.2±0.3	1.9±0.2
	BaL	36.6±4.8	10±1.6	3±0.8	1.1(±0.5)	-	13.9±1.3
	BaR	37.3±6.6	6.6±1.2	5.3±0.9	-	-	29±3

*Standard deviation calculated as 3σ

Appendix 3

Manuscript Submitted to an International Journal and Contributions to Conferences

Waste Management

Unveiling the Fertilizer Potential of Biomass Ashes from Italian Power Plants: Multi-Analytical and Mineralogical Characterization of Underexplored Secondary Feedstocks

--Manuscript Draft--

Manuscript Number:	
Article Type:	Full Length Article
Section/Category:	Recycling
Keywords:	Biomass Ash; Characterization; Quantitative Phase Analysis; Nutrient Valorization; Fertilizers
Corresponding Author:	Daniela Pinto, Ph.D. University of Bari Aldo Moro Bari, Daniela ITALY
First Author:	Daniela Pinto, Ph.D.
Order of Authors:	Daniela Pinto, Ph.D.
	Gianna Fornari
	Marina Clausi
	Daniel El Chami
Abstract:	This study provides a comprehensive multi-analytical characterization of biomass ashes from four Italian power plants to assess their suitability as secondary raw materials for fertilizers under current regulations. Using XRPD–Rietveld refinement, TG-DTA, FTIR, SEM-EDS, ICP-MS, and leaching analyses, it establishes direct links between mineral composition, nutrient release, and contaminant behavior. This phase-resolved approach offers a framework for evaluating the recovery and reuse potential of biomass ash in the Italian fertilizer industry. The ashes showed substantial compositional variability related to feedstock type, combustion technology, and post-combustion management. Fly ashes (FA) were rich in soluble alkali and alkaline-earth phases (e.g., KCl, NaCl, $Ca(OH)_2$), while bottom ashes (BA) consisted mainly of refractory silicates and carbonates (e.g., quartz, calcite). Leaching tests showed higher solubility and alkalinity in FA (up to 72% mass loss, pH 12–14) compared with BA (<7%, pH 9–11), confirming FA's potential as a fast-release nutrient source. Heavy metals such as Pb, Zn, and Cd were concentrated in FA from treated wood, while ashes from virgin biomass contained lower contaminant levels. Most organic pollutants were below EU limits, though one FA sample exceeded the dioxin threshold. Despite low Cd, As, Ni, and Cr concentrations, Zn and Pb surpassed European Fertilizing Products Regulation (EU 2019/1009) limits, highlighting the need for selective feedstock management before reuse. Overall, FA appears suitable as a nutrient-rich fertilizer precursor, and BA as a liming agent. Coupling quantitative phase identification with chemistry is essential for accurate risk assessment and valorization.

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Investigations on industrial wastes for the valorization of their mineral content in the fertilizer industry: preliminary results

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Keywords: minerals, waste, sustainable industry.

In the last decades, the fertilizer industry has been mainly based on the use of non-renewable resources used for plant nutrition. Minerals of commercial interest are removed from natural deposits causing significant social, environmental and economic costs (Bontoux & Bengtsson, 2016). In this perspective, there is an urgent need to implement sustainable methodologies for the preservation of these fundamental non-renewable environmental resources and, at the same time, to provide agricultural soils with the necessary supply of nutrients essential for healthy plant growth (Oliveira et al., 2012). The objective of this study is to offer new solutions for the recovery of industrial wastes thus reducing the environmental problems related to waste management and, at the same time, the excessive exploitation and use of non-renewable natural resources for the production of fertilizers. The research is conducted in collaboration with TIMAC AGRO Italia S.p.A., an Italian company of the French group Roullier, world leader in the production of fertilizers (Amin, 2014).

In this study different types of industrial wastes (i.e., industrial ashes and mineral processing wastes) are characterized from the chemical and mineralogical point of view using the following instrumentations: scanning electron microscopy with EDS microanalysis (SEM-EDS) for morphological, microstructural and microchemical analysis, fluorescence (XRF) for chemical characterization, diffraction (XRD) for mineralogical content, spectroscopy (FTIR) for the identification of functional groups and chemical bonds.

Preliminary investigations show the occurrence in the investigated materials of soil mineral nutrients essential for plant growth (i.e., K, P, Mg, Ca, Si, Fe, Cu, Zn, …) which can be included in new formulations of fertilizers after appropriate verification and eventual removal of potential harmful elements.

Amin N. (2014) - A multi-directional utilization of different ashes. RSC Advances, 4, 62769- 62788.

Bontoux L. & Bengtsson D. (2016) - Using scenarios to assess policy mixes for resource efficiency and eco-innovation in different Fiscal Policy frameworks. Sustainability, 8, 309.

Oliveira M.L., Ward C.R., Izquierdo M., Sampaio C.H., de Brum I.A., Kautzmann R.M., Sabedot S., Querol X. & Silva L.F.O. (2012) - Chemical composition and minerals in pyrite ash of an abandoned sulphuric acid production plant. Sci. Total Environ., 430, 34-47.

Comunicazione Poster

Vegetal biomass ashes as alternative activator in alkaline activated binders: characterization and feasibility study

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One of the main obstacles to industrial scale up of Alkaline Activate Binders (AABs) consists in the difficulty of handling high corrosive alkaline activating solutions for their preparation. Furthermore, the use of very expensive alkaline activating solutions (i.e. Na and K silicates) produced by the conventional chemical industry, badly affects the economic and environmental feasibility of AABs. In the perspective of reducing the environmental impact of AABs, it is useful to find alternative alkaline activators, as well as to implement new strategies for reducing the amount of activating solution during the preparation. Recent studies suggest that biomass ashes can be evaluated as interesting alternative activators owing to their high calcium, potassium and silicon content [e.g.1,2]. In this study, eight samples of vegetal biomass ashes, consisting of four fly ashes and four bottom ashes from different cogeneration plants producing electricity through the combustion of agro-forestry residues, were characterised from the chemical and mineralogical point of view to evaluate their suitability as alternative activators in the formulation of AABs.
Results show the occurrence of high proportions of K_2O, CaO, Na_2O in biomass fly ashes and their chemical and mineralogical composition indicate a good potential as alkaline activators. Bottom ashes samples show a high content of CaO and SiO_2, with significant amount of amorphous phase and several crystalline phases such as Ca, K-sulfates and -silicates; they can be evaluated both as solid precursors or a source for generating alkaline activating solutions.

Keywords: alkali activated binders, vegetal biomass ashes, alkaline solutions

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[2] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, *Fuel*, 105, 40-76 (2013).

Vegetal biomass ashes as a potential resource for sustainable production of mineral fertiliser: characterisation and feasibility study

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Keywords: fertilizer, circular economy, minerals.

Over the past few decades, the fertilizer industry has primarily relied on non-renewable resources for plant nutrition. Minerals of commercial interest such as phosphorite and potassium salts are removed from natural deposits causing significant environmental and economic costs (Van den Berg et al., 2016). Consequently, there is an urgent need to adopt sustainable methodologies that preserve these fundamentals non-renewable environmental resources while simultaneously supplying agricultural soils with the necessary nutrients for healthy plants growth. Recent studies suggest that vegetal biomass ashes i.e. the inorganic residue produced during the incineration of biomass for electricity production, have the potential to serve as a valuable source of essential plant nutrients thanks to their high concentration of potassium (K), phosphorus (P), magnesium (Mg), and calcium (Ca). Additionally, these ashes can be an effective soil amendment due to the presence of basic cations in the form of oxides, hydroxides, and carbonates (Vassilev et al., 2013, Zhai et al., 2021). In this perspective, this study aims to investigate the potential from a mineralogical and chemical point of view, of vegetal biomass ashes in order to recover elements and minerals useful for the growth of plants and, at the same time, to reduce the landfills disposal in accordance with the Circular Economy principles. In this study, eight samples of vegetal biomass ashes, consisting of four fly ashes and four bottom ashes from different cogeneration plants producing electricity through the combustion of agroforestry residues, were characterised from the chemical and mineralogical point of view to evaluate their potential as resource for sustainable production of mineral fertiliser. Results show high physical and chemical variability in both fly and bottom ashes from different agroforestry residues investigated. This variability is related to factors such as, the type of incinerator, the combustion temperature, and the type of ash (fly or bottom). However, results indicate a potential as a valuable fertilizer due to the occurrence in all samples investigated of high proportions of K_2O, CaO, MgO and relevant soluble mineral phases, especially in fly ash. Furthermore, investigations show the occurrence of basic cations in the form of oxides, hydroxides, and carbonates, which could be an excellent amendment to deal with soil acidity and compensate for the loss of nutrients.

Van den Berg M., Neumann K., van Vuuren D.P., Bouwman A.F., Kram T. & Bakkes J. (2016) - Exploring resource efficiency for energy, land and phosphorus use: Implications for resource scarcity and the global environment. Glob. Environ. Change, 36, 21- 34. https://doi.org/10.1016/j.gloenvcha.2015.09.016.

Vassilev S.V., Baxter D., Andersen L.K. & Vassileva C.G. (2013) - An overview of the composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification. Fuel, 105, 40-76. https://doi.org/10.1016/j.fuel.2012.09.041.

Zhai J., Burke I.T. & Stewart D.I. (2021) - Beneficial management of biomass combustion ashes. Renew. Sustain. Energy Rev., 151, 111555. https://doi.org/10.1016/j.rser.2021.111555.

Multi-methodical approach for a detailed characterization of cogeneration ashes and their valorisation in the fertilizer industry

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Keywords: by-products, ashes, fertilizer.

Various industries are paying growing attention to the importance of sustainability and environmental responsibility. This entails efforts to reduce waste, optimize resource usage, and minimize environmental impacts. Particularly, there is increasing interest in finding innovative ways to repurpose industrial by-products and waste materials, transforming them into valuable resources. This aligns with regulatory frameworks such as Directive 2008/98/EU, which promotes efficient waste management practices.

In the mineral fertilizer industry, there is a reliance on non-renewable mineral resources to produce fertilizers that support agricultural productivity. However, there is a growing recognition of the need to transition towards more sustainable practices by incorporating waste materials and implementing processes to transform them into valuable products.

One notable area of focus is the recovery and utilization of cogeneration ashes, which are generated from the incineration of biomass for electricity production. These ashes have been recognized for their potential as sources of essential plant nutrients, such as potassium, phosphorus, magnesium, and calcium. Additionally, due to the presence of basic cations in the form of oxides, hydroxides, and carbonates, these ashes can be an effective soil amendment (Freire et al., 2015; Maresca et al., 2017; Cruz et al., 2023).

From this perspective, this study aims to investigate the potential, from a mineralogical and chemical point of view, of cogeneration ashes in order to recover elements and minerals useful for plant growth and, at the same time, to reduce the landfills disposal in accordance with the principles of the Circular Economy.

In this study, eight samples of vegetal biomass ashes, comprising four fly ashes and four bottom ashes from different cogeneration plants, producing electricity through the combustion of agroforestry residues, were characterized using a multi- methodical approach. Various chemical, mineralogical, and microstructural analysis techniques, along with physical-chemical treatments, were applied to evaluate their content of phytoavailable components, occurrence of harmful substances, and viability as a sustainable resource for mineral fertilizer production.

Results reveal significant physical and chemical variability in fly and bottom ashes derived from various agroforestry residues. This variability is associated with factors such as the type of incinerator, combustion temperature, ash type and particle size of ashes. However, chemical analyses indicate the presence of substantial concentrations of K_2O, CaO, and MgO in all investigated samples, while leaching tests and mineralogical analysis reveal relevant water-soluble mineral phases that may be available to plants. Furthermore, investigations show the occurrence of basic cations in the form of oxides, hydroxides, and carbonates, which could be an excellent amendment to deal with soil acidity and compensate for the loss of nutrients.

Cruz N. et al. (2023) - Stabilization of biomass ash granules using accelerated carbonation to optimize the preparation of soil improvers. Waste Manage., 156, 297-306.

Freire M. et al. (2015) - Critical aspects of biomass ashes utilization in soils: Composition, leachability, PAH and PCDD/F. Waste Manage., 46, 304-315.

Maresca A. et al. (2017) - Recirculation of biomass ashes onto forest soils: ash composition, mineralogy and leaching properties. Waste Manage., 70, 127-138.

Cogeneration ashes from Italian biomass-fired power plants as raw materials for fertilizer industry: detailed multi-analytical characterization and feasibility study

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Numerous industries are increasingly emphasizing sustainability and environmental responsibility by focusing on waste reduction, resource optimization, and the repurposing of industrial by-products into valuable materials. Within the mineral fertilizer sector, there is a significant reliance on non-renewable mineral resources, crucial for enhancing agricultural productivity. The extraction of commercially valuable minerals, such as phosphorite—classified as Critical Raw Material (CRM) by the European Union—entails considerable social, environmental, and economic costs. In response to the growing demand for sustainable practices, there is growing interest in the shift toward using waste materials and developing processes to transform them into valuable products, addressing both resource depletion and environmental concerns.

One promising area of exploration is the recovery and utilization of cogeneration ashes generated from biomass incineration for electricity production within the fertilizer industry [1]. These ashes are recognized for their potential as sources of essential plant nutrients, including potassium, phosphorus, magnesium, and calcium. Furthermore, the presence of basic cations, in the forms of oxides, hydroxides, and carbonates, enhances their effectiveness as soil amendments [2].

This study aims to investigate the mineralogical and chemical properties of cogeneration ashes to recover nutrients beneficial for plant growth while simultaneously reducing landfill disposal in accordance with Circular Economy principles.

Eight samples of biomass ashes, comprising four fly ashes and four bottom ashes from various cogeneration plants distributed throughout Italy, were characterized using a multi-methodological approach. A variety of chemical, mineralogical, and microstructural analyses, along with physical-chemical treatments, were employed to assess their content of phytoavailable components, the presence of harmful substances, and their feasibility as sustainable resources for mineral fertilizer production.

The results demonstrate considerable physical and chemical variability in both fly and bottom ashes, influenced by factors such as the type of biomass utilized for combustion (virgin wood versus treated wood pellets), combustion temperature, and particle size. Chemical analyses reveal significant concentrations of essential plant nutrients, including K_2O, CaO, and MgO, across all samples. Additionally, leaching tests and mineralogical analyses identify relevant water-soluble mineral phases that may be bioavailable to plants. Furthermore, the implemented physico-chemical treatments effectively reduce heavy metal concentrations, bringing them below the thresholds established by the European Fertilizer Regulation 1009/2019, which delineates standards for the commercialization of fertilizer products.

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