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## Comprehensive Methods for Environmental Impact Assessment of Landfills and Novel Approaches for Sustainable Waste Management in Construction

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## **AUTHOR'S DECLARATION**

Except where specific reference is made to other sources, I certify that the work presented in the current PhD thesis is entirely my own effort. The work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged, and ethics procedures and guidelines have been followed.

**Hamza El Fadili**

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## **Abstract**

The proper management of solid waste for the reduction of its potential implications on the environment and human health is one of the most challenging issues faced worldwide due to the increase of public awareness and concern regarding protecting the environment. In the current thesis, comprehensive and detailed experimental studies were undertaken to evaluate the effects of landfilling activities on soils, water resources, and human health by taking the open dumpsite of *Benguerir* and the engineered landfill of *Oum Azza*, respectively as a case study. Then, some applications of dumped waste were deeply studied and several recycling methods were evaluated through the assessment of the effect of using discarded cigarette butts (CBs), Fly ash, and bottom ash in cementitious and geopolymer materials. The results highlighted through the use of several indicators (Geo-accumulation index, Pollution load index, Ecological risk indices, Nemerow pollution indice...), deterministic and probabilistic human risk assessment based on Montecarlo simulation, and statistical analysis (PCA, HCA) that landfilling can be seriously harmful to the soil, aquatic resources and human health. Especially, illegal landfilling in open dumpsites showed the highest potential for ecological and human health, nevertheless, they are not the only sources of pollution. It has been proven that regular landfills could have similar levels depending on the design, the collection systems for leachate and biogas, and the insulation systems. In addition, this research has discussed the Cigarette Butts (CBs) and incineration by-products pollution issues, potential recycling solutions, the results prove the possibility of their recycling in cementitious and geopolymer materials without compromising the physical, thermal and mechanical properties in comparison to conventional materials existing in the market. The prepared materials are recognized as a more environmentally friendly mixture in terms of reducing CO<sub>2</sub> emissions and could participate significantly in the achievement of sustainable development goals (SDGs) through keeping waste in use not in landfills.

**Keywords:** leachate, landfills, open dumpsite, Cigarette butts, fly ash, mortar, geopolymers, SDGs.

## Résumé

La gestion appropriée des déchets solides pour la réduction de leurs implications potentielles sur l'environnement et la santé humaine est l'une des questions cruciales et perplexes auxquelles le monde contemporain est confronté. Dans le présent travail de thèse nous avons mené des études expérimentales spatiaux-temporaires, sur deux sites de décharges, un site à ciel ouvert situé dans la décharge sauvage de Benguerir et environs (8 ha), et l'autre site est un centre d'enfouissement technique d'une décharge contrôlée, de 13 communes de la région Rabat- Salé- Témara- Bouznika et environs dénommée située dans la commune Oum Azza (Surface totale de 110 ha). Les études menées sont assez complètes et relativement bien détaillées et ayant pour objectifs principaux l'évaluation des procédés d'enfouissement et leurs impacts sur les sols, sur les ressources hydriques et sur la santé humaine grâce à l'utilisation de plusieurs indicateurs (indice de géo-accumulation, indice de charge polluante, indices de risque écologique, indice de pollution de Nemerow...), l'évaluation déterministe et probabiliste du risque humain basée sur la simulation de Montecarlo, et l'analyse statistique (corrélation, PCA, HCA). D'autre part, nous avons entrepris le volet du recyclage et de la valorisation, particulièrement pour certains types des déchets mis en décharge, ainsi nous avons entrepris des démarches de revalorisation des résidus des mégots de cigarettes, des cendres volantes et des mâchefers et nous avons réussi à les réutiliser et les intégrer dans les matériaux cimentaires et géopolymères sans qu'il y ait des effets de nocivité ou toxicités ou de régénérations de déchets secondaires, aussi les qualités eco-environnementales de ces nouveaux matériaux innovés ont été prouvées, confirmées et mis en évidence, Lors de notre étude on a montré que des décharges ordinaires, et induiraient à des impacts environnementaux comparables voire très inquiétants, lors des procédés d'enfouissements et ce en fonction de leur conception, des systèmes de collecte des lixiviats et des biogaz, et des systèmes d'isolation. Les résultats obtenus lors des études et analyses physico-chimiques et les caractérisations thermiques et mécaniques des matériaux cimentaires et géopolymères élaborés ont montré que leurs comportements structuraux, et leurs propriétés physiques, thermiques et mécaniques n'ont été ni compromises ni altérées. Les matériaux préparés sont reconnus comme nouveaux matériaux respectueux de l'environnement en termes de réduction des émissions de CO<sub>2</sub> et pourraient participer de manière significative à la réalisation des objectifs de développement durable en gardant les déchets en usage et non dans les décharges.

**Mots clés :** Lixiviat, Décharges, Décharges sauvages, Mégots de cigarettes, Cendres volantes, Mortier, Gestion des déchets.

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## **Abbreviations and Acronyms**

<b>AAMs</b>	<i>Alkaline Activation Materials</i>
<b>APHA</b>	<i>American Public Health Association</i>
<b>ASTM</b>	<i>American Society for Testing and Methods</i>
<b>BA</b>	<i>Bottom Ash</i>
<b>BOD</b>	<i>Biochemical Oxygen Demand</i>
<b>CAFs</b>	<i>Cellulose acetate fibers</i>
<b>CBE</b>	<i>Charge balance ions</i>
<b>CBs</b>	<i>Cigarette butts</i>
<b>CFs</b>	<i>Cigarette filters</i>
<b>COD</b>	<i>Chemical Oxygen Demand</i>
<b>CR</b>	<i>Carcinogenic Risk</i>
<b>DTPA</b>	<i>Diethylene Triamine Penta-acetic Acid</i>
<b>DW</b>	<i>Dry Weight</i>
<b>E.C</b>	<i>Electrical Conductivity</i>
<b>F.A</b>	<i>Fly Ash</i>
<b>EDS</b>	<i>Elemental Diffraction Spectrometer</i>
<b>EF</b>	<i>Enrichment Factor</i>
<b>EPA</b>	<i>Environmental Protection Agency</i>
<b>FTIR</b>	<i>Fourier-transform infrared spectroscopy</i>
<b>HCA</b>	<i>Hierarchical Clustering Analysis</i>
<b>HHR</b>	<i>Human Health Risk Assessment</i>
<b>HHRA</b>	<i>Human Health Risk Assessment</i>
<b>HI</b>	<i>Hazard Index</i>
<b>HQ</b>	<i>Hazard Quotient</i>
<b>ICP-AES</b>	<i>Inductively Coupled Plasma with Atomic Emission Spectroscopy</i>
<b>Igeo</b>	<i>Geo-Accumulation Index</i>
<b>ISWA</b>	<i>International Solid Waste Association</i>
<b>KR</b>	<i>Kelly's Ratio</i>
<b>K-S test</b>	<i>Kolmogorov-Smirnov test</i>
<b>LCA</b>	<i>Life cycle assessment</i>
<b>MCS</b>	<i>Montecarlo Simulation</i>

<b>Metal(oid)s</b>	<i>Metals and metalloids</i>
<b>MHR</b>	<i>Magnesium Hazard Ratio</i>
<b>MSAs</b>	<i>Multivariate Statistical Analyses</i>
<b>MSW</b>	<i>Municipal Solid Waste</i>
<b>N/A</b>	<i>Non-Available</i>
<b>NCR</b>	<i>Non-Carcinogenic Risk</i>
<b>PCA</b>	<i>Principal Component analysis</i>
<b>PERI</b>	<i>Potential Ecological Risk Index</i>
<b>PI</b>	<i>Permeability Index</i>
<b>PIN</b>	<i>Pollution Index Nemerow</i>
<b>PLI</b>	<i>Pollution Load Index</i>
<b>PTEs</b>	<i>Potentially Toxic Elements</i>
<b>O.M</b>	<i>Organic Matter</i>
<b>SAR</b>	<i>Sodium Adsorption Ratio</i>
<b>S.D</b>	<i>Standard Deviation</i>
<b>SDGs</b>	<i>Sustainable Development Goals.</i>
<b>SEM</b>	<i>Scanning Electron Microscopy</i>
<b>SSP</b>	<i>Soluble Sodium Percent</i>
<b>TCLP</b>	<i>Toxicity Characteristics Leaching Procedures</i>
<b>TDS</b>	<i>Total Dissolved Solids</i>
<b>TF</b>	<i>Total fraction</i>
<b>TMs</b>	<i>Total Cancer Risk</i>
<b>THI</b>	<i>Total Hazard Index</i>
<b>TMs</b>	<i>Total Trace Metal(oid)s</i>
<b>TSS</b>	<i>Total Suspended Solids</i>
<b>TTMs</b>	<i>Total trace metal(oid)s</i>
<b>UNEP</b>	<i>United Nations Environment Programme</i>
<b>USEPA</b>	<i>United States Environmental Protection Agency</i>
<b>WHO</b>	<i>World Health Organization</i>
<b>Wt%</b>	<i>Weight Percentage</i>
<b>XRD</b>	<i>X-ray diffraction</i>
<b>XRF</b>	<i>X-ray fluorescence</i>

## **General Introduction and problem statement**

The following section introduces the research background, rationale, research questions, objectives, approach, scope, and outlines the layout of this thesis into relevant chapters.

### **1. Background and problem statement**

Recent years have shown a dramatic increase in the generated quantity of waste and industrial pollutants worldwide, due to expressive economical and industrial growth. Regardless of the type of waste, its destination is generally landfilling with no further treatment. Therefore, how to deal with these issues become one of today's most urgent challenges (El Fadili et al., 2022). It is expected that the amount of waste will skyrocket increase by more than 50%, to reach 3.4 billion tons by 2025 (Kaza et al., 2018), according to the international solid waste association (ISWA), more than 40% of the generated waste across the world is improperly disposed of (Law & Ross, 2019).

The improper dumping of solid waste may endanger the environment and seriously threat every form of life in the neighborhood of MSW through the release of numerous dangerous pollutants, such as; Polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs) and heavy metal(oid)s (Arsenic, cadmium, zinc, lead, chromium, copper, iron... etc.) either from the leachate infiltration or as a fugitive emission. Therefore, the evaluation of contamination status around landfills and open dumpsites, their potential risk to human health and adjacent environment is merely important and must be continuously monitored during all stages of landfill exploitation.

As stated trace metal(oid)s (TMs) are one of the dangerous by-products which is typically originated from various anthropogenic activities, unlike many organic pollutants most of these substances are widely known for their toxicity to human beings, swift biological accumulation, and cannot be degraded biologically or chemically which enhance their persistence for a long period in the aquatic and terrestrial environment (Adelopo et al., 2018; Hussein et al., 2021; Varol, Gündüz, & Ras, 2021; S. Wang et al., 2022). Trace metal(oid)s are endocrine disruptors and the intake of soil contaminated with these harmful compounds may lead to severe carcinogenic and non-carcinogenic effects on receptors health if come into contact with them via different exposure pathways such as inhalation, dermal contact, ingestion, and via transfer along with the soil-food chain. For example, Pb and Cd can cause renal failure and damage the neurological system (Adimalla et al., 2020), but also can lead to the reduction of soil fertility and crop production (Fei et al., 2020; H. Jiang et al., 2020). Also, after their occurrence and accumulation in soils, removing TMs become costly and technically difficult (Varol et al.,

2021). Many previous studies were carried out and confirmed the contamination of soils and aquatic resources with trace metal(oid)s such as Cd, Pb, Cr, As due to the informal dumping and leakage of leachate (Elbl et al., 2018; Fadili et al., 2022; Hussein et al., 2021), without forgetting that the implementation of landfills in an agricultural area which may contribute to the increase of pollution degree as a result of the informal and excessive use of manure and fertilizers. Therefore, it is necessary to quantitatively examine the properties, and level and clarify the sources of metal(oid)s in these areas.

Given all these hazards, there are an increasing interest and several efforts have been drawn by scientists and stockholders worldwide to assess the environmental occurrence and fate of these dangerous elements and limit their harmfulness and adverse health consequence, therefore, stringent regulations and norms for waste disposal sites have been imposed in several countries (Thi et al., 2022).

For instance, with a footprint of 0.76 kg per capita per day it is estimated that approximately 7 million tons of waste are generated every year in Morocco, and most of them are discarded and illegally dumped in uncontrolled dumpsites without any treatment, according to the report of the Ministry of Energy Transition and Sustainable Development in Morocco there are more than 337 operated landfills in which only 16 are equipped with leachate collection and treatment system, factors such as cultural beliefs, lack of infrastructure, inadequately trained human and other logistics constraints have been highlighted as the main causes behind the current waste management situation. Assessing the status of trace metal(oid)s in soils and water resources is very necessary to ensure better management and develop sustainable policies to mitigate the current situation (Guan et al., 2018).

## **2. Research objectives**

The overcrowding of the population and industrial sector leads to an abnormal increase in the generated quantity of waste and therefore waste management service delivery become one of the important issues for scientists and governments worldwide, especially in developing countries where the majority of waste ends up at landfill sites due to financial and technical constraints. The amount of waste generated is expected to increase by more than 50 % to reach 3.4 billion tons by 2025 (Kaza et al., 2018). Morocco as the majority of developing countries faces this challenge. Although, the scarcity of studies regarding the heavy metal(oid)s contamination around landfills, has resulted in less attention focused on the removal of these pollutants. With the indiscriminate distribution of uncontrolled landfills and dumpsites in Morocco, significant volumes of waste are illegally dumped in uncontrolled dumpsites, causing major threats to human health and the environment (Fadili et al., 2022).

---

The current thesis aims to investigate the distribution of heavy metal(oid)s and pollutants in landfill leachate, soils, and water resources and the potential human and environmental effects of landfilling and to propose practical techniques to recycle some dumped wastes in construction applications. Therefore, the main objectives are:

- 1) Investigating the degree of metal(oid)s and other pollutants in leachate and leachate/wastes impacted soil and water and identifying the most significant pollutant in different types of landfills in Morocco.
- 2) Assessing the extent of pollution around Moroccan landfills and open dumpsites by taking Oum Azza and Benguerir as a case study.
- 3) Assessing the feasibility of recycling solutions in the construction field by taking some dangerous waste (cigarettes butts and incineration by-products) as a substitution for conventional materials in cementitious and geopolymer materials.

### **3. Significance of the research**

Determining the controlling factors of groundwater and soils quality can help decision-makers in preparing optimal management plans and drawing sustainable strategies for waste management:

- 1) Using innovative and comprehensive methods to evaluate the pollution degree around landfills and open dumpsites.
- 2) The research will develop and establish techniques to recycle CBs in cementitious and alkaline activation materials.
- 3) The research will develop and establish techniques to recycle fly ash and bottom ash in cementitious and alkaline activation materials.
- 4) The research will potentially reduce the pollution caused by littered CBs, and incineration by-products (fly and bottom ashes).

### **4. Thesis structure**

To meet the above objectives, a literature review of the existing body of knowledge was carried out (*first chapter*), divided into three sections. *The first one* deals with the issue of composition and structure, laws and regulations related to municipal and industrial wastes, and the main possible ways of valorization of waste. *The second section* presents an overview of the environmental effects of landfills and open dumpsites. Finally, the impact of some hazardous waste (Cigarette butts, Fly Ash, Bottom Ash) and the possible ways of their recycling and recovery was comprehensively reviewed.

**The second chapter** provides a comprehensive investigation about the soils pollution caused by the long-term effect of landfilling activities by taking the Oum azza landfill and Benguerir open dumpsite as a case study and using various pollution indices (geo-accumulation index, ecological risk, pollution load index, Nemerow pollution indicator), deterministic and probabilistic human risk assessment. Then, **the third chapter** discussed deeply the impact of the combination of landfilling and agricultural activities on water resources through the case study of Oum Azza using several indicators (leachate pollution index, Nemerow index, water quality index) and statistical tools. Then, assessing the possibility of using the impacted water for drinking and agricultural purposes was also assessed.

**The fourth chapter** describes the raw materials, testing methods used to produce eco-friendly cementitious mortars containing cigarette micro-fibers and reports the physical, chemical, thermal and microstructural characteristics of the prepared composite material in comparison to the reference mortar. The advantages of prepared mortars in terms of CO<sub>2</sub> emission and the achievement of SDGs were also described.

**The fifth chapter** presents experimental results of the effects of encapsulating cellulose acetate microfibers on the mechanical, thermal and environmental properties of metakaolin- fly ash geopolymers as a new solution to mitigate the cigarettes pollution, a comparison with conventional materials in terms of mechanical strength, thermal insulation, physical and mechanical properties was also undertaken in this chapter.

Finally, A general discussion and conclusion synthesizing the main results drawn from the current thesis are presented, and a set of recommendations and suggestions for future study were presented.

**Chapter 1: The landfilling impact and valorization options of dumped wastes**

## **Introduction:**

This first chapter of the current thesis is divided into three parts corresponding respectively to bibliographical synthesis on the composition, structure, laws, and regulations related to municipal and industrial wastes, and the main possible ways of recycling and valorization. The second section highlights the influence of landfills, open dumpsites, and the potential release of pollutants. While, the third section presents the impact of the selected hazardous waste such as Cigarette butts, Fly ash, Bottom ash and the possible ways for their recovery and recycling as discussed in the literature.

## **1.1 The problems related to waste management**

### **1.1.1 Definitions and general information on waste management**

Waste may be defined as any substance or object which is discarded and has great variations in composition. It can be classified as municipal solid waste, hazardous waste, sewage sludge, clinical waste, agricultural waste, construction and demolition waste, mines and quarry waste, fly ash, iron and steel slags, scrap tyres, industrial waste, and also commercial waste. Additionally, *The Law 28-00* relating to the management of waste and its elimination defines waste as "any residue resulting from a process of extraction, exploitation, transformation, production, consumption, use, control or filtration, and in general, any object or material abandoned or that the holder must eliminate in order not to harm public health, sanitation and the environment. In this context, this chapter reviews the existing body of knowledge about waste issues and management strategies followed to mitigate the pollution occurred in soils and water due to landfilling and other waste management methods in the waste management hierarchy (WMH). Through this review, gaps in knowledge, which form the basis for the aims and objectives of this research are identified.

Proper management of solid waste continues to be one of the most challenging environmental issues in the world and a perplexing task for authorities and stakeholders. The problems associated with the management of solid waste are complex due to the exponential increase in solid waste production (Hussein et al., 2021).

The main environmental impacts due to waste disposal can be summarized as:

- Soil quality degradation
- Water resources degradation
- Eutrophication
- Greenhouse effect and global warming
- Phytotoxicity and aquatic toxicity
- Ecological risks
- Human health risks (carcinogenic and non-carcinogenic risks)

### 1.1.2 Waste generation throughout the world

The rapidly growing of urbanization and industrial sector is strongly associated with a massive increase in the generated quantity of MSW (J. Liu et al., 2022). According to a recent study conducted by Kaza et al. (2018) the amount of waste will skyrocket increase by more than 50% by 2025, reaching roughly 3.4 billion tons. The international solid waste association (ISWA) stated that more than 40% of the generated quantity of waste worldwide is improperly disposed of and the most common disposal technique for MSW is landfilling and incineration (Law & Ross, 2019). **Fig.1-1** showed the evolution of the total mass of solid waste generated worldwide between 2010 and 2100, as clearly observed an exponential increase in the generated waste is expected, especially in developing countries. Given its threats to human health and the environment demonstrated in many previous studies (Bouzekri, El Fadili, et al., 2019; Fadili et al., 2022), an urgent intervention is required.

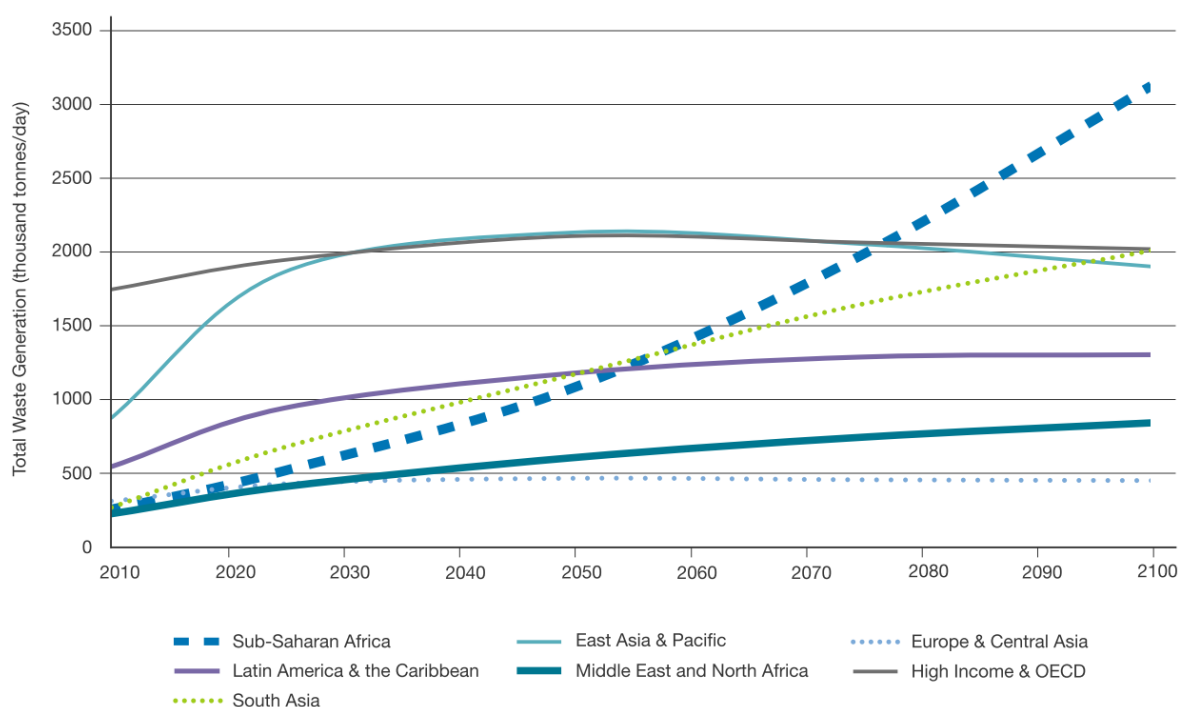


Figure 1-1. Evolution of the mass of solid waste generated worldwide 2010-2100 (thousand tones/day) (Kaza et al., 2018)

### 1.1.3 Waste composition

Undoubtedly, the composition of waste has direct implications for how it is collected and disposed of, it showed considerable variation among cities depending on consumer attitude, income level, and culture, among other things. As plotted in **Fig 1-2**, the results published by Kaza et al. (2018) confirmed that organic waste represents more than 65% of the African waste composition, although

the potential development will contribute to its decrease, it will still be the responsible behind the production of more than 50% of the total generated quantity.

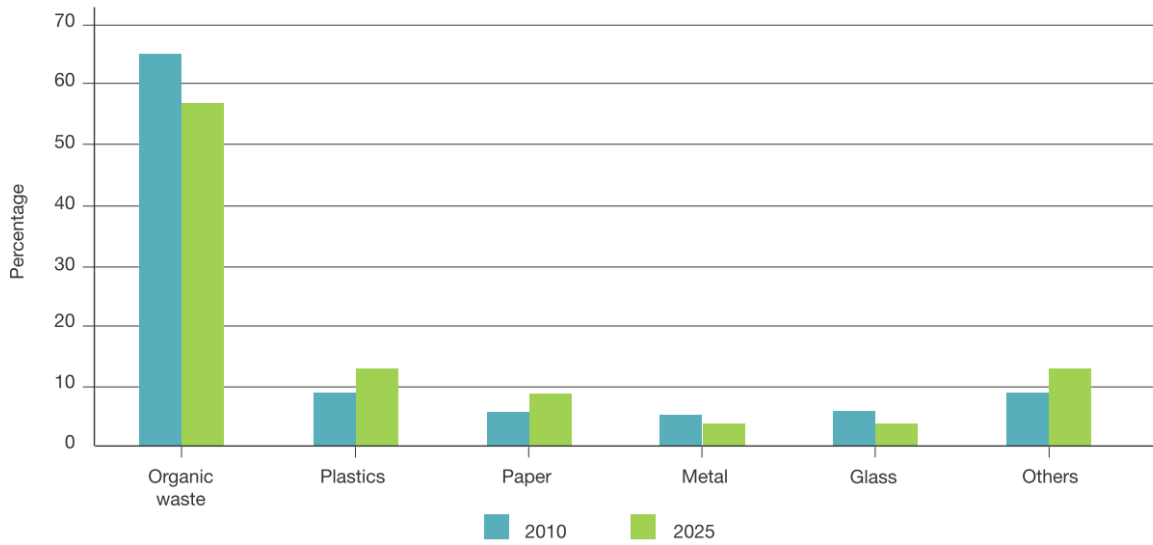


Figure 1-2. Changing composition of waste in African cities (Kaza et al., 2018)

In Morocco, the production of solid waste has increased dramatically with a ratio varying between 0.76 and 1, it depends mainly on the type of housing and standard of living. **The figure 1-3** showed the Moroccan municipal waste composition according to the statistics given by Ministry of environment and energetic transition, as clearly observed the waste in Morocco is like all developing countries are characterized by a high rate of organic matter ranging from 60% to 70%, the composition of waste reflected the dominance of organic fraction.

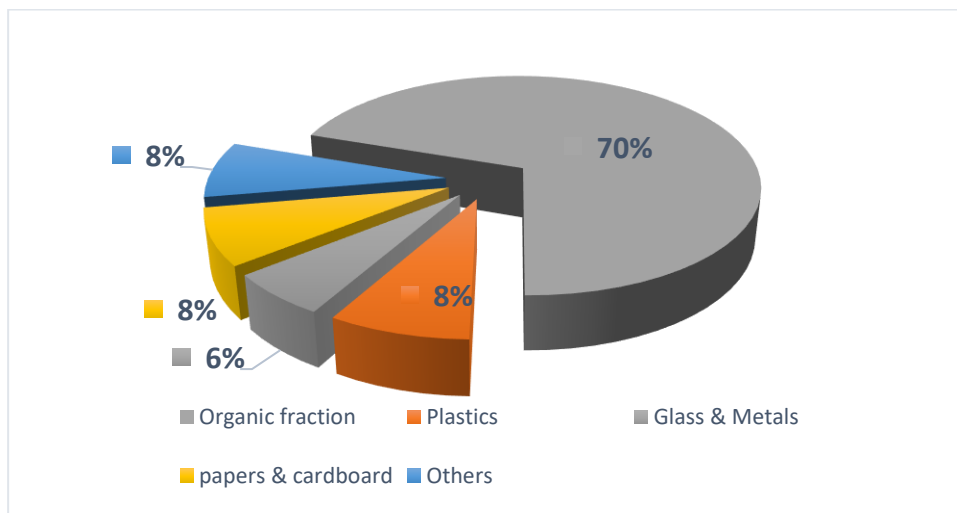


Figure 1-3. Waste composition in Morocco.

## 1.2 Legislative framework analysis of solid waste management in Morocco

Waste generation in Africa is projected to grow to reach 244 million tons per year by 2025. The rising concern about the impacts of landfilling and the mitigation of pollution menace led certain developed countries to implement strong waste control regulations that prescribe duties and sanctions, and a significant improvement has been achieved. Aware of this situation, Morocco has implemented strong regulations and policies aiming to:

- Encourage the reduction of waste production
- Using and recycling waste as a by-product in different sectors.
- Substitute illegal landfilling and uncontrolled waste disposal with engineered landfills.
- Reducing environmental and human beings impacts of improper waste landfilling.
- Management of leachate and gas emissions from landfilling
- Management of industrial waste/ by-products.

Fully aware of these issues, the Moroccan authorities have placed the agenda of sustainable management of waste among the national priorities and have adopted a progressive and integrated approach, through the development of an exhaustive and precise regulatory and normative framework. The main regulatory texts governing the field of waste management in Morocco are grouped in **Table 1-1**.

Table 1-1. The main regulatory text governing waste management in Morocco

Text	Comment
Dahir n° 1-06-153 of November 22, 2006 promulgating the law n° 28-00 relating to the management of waste and its elimination.	The purpose of this law is to prevent and protect human health, air, soil, landscapes, and the environment in general against the harmful effects of waste.
Decree No. 2-07-253 of July 18, 2008 on the classification of waste and the list of hazardous waste.	Pursuant to Articles 29 and 83 of Law No. 28-00, waste is inventoried and classified, according to its nature and origin, in a catalog called "Moroccan Catalogue of Waste".
Decree n° 2-14-85 of 28 rabii I 1436 (20 January 2015) relating to the management of hazardous waste.	The purpose of this decree is to establish: <ul style="list-style-type: none"> <li>• Organizational measures for the management of hazardous waste.</li> <li>• The authorizations for the treatment of the dangerous waste with a view to their elimination or</li> </ul>

	<p>their recovery, foreseen in article 29 of the law n° 28-00.</p> <ul style="list-style-type: none"><li>• The conditions and technical requirements for the collection, transport and storage of hazardous waste for disposal or recovery.</li></ul>
<p>Decree No. 2-09-139 of May 21, 2009, on the management of medical and pharmaceutical waste.</p>	<p>In application of articles 38 and 40 of the law n°28-00 mentioned, the present decree fixes the modalities of sorting, packing, collection, storage, transport, treatment and disposal of medical and pharmaceutical waste as well as the modalities of delivery of the authorization of collection and transport of these wastes.</p>
<p>Decree no. 2-09-284 of December 8, 2009, setting out the administrative procedures and technical requirements for controlled landfills.</p>	<p>This decree applies to controlled landfills of classes 1, 2 and 3 referred to in Article 48 of the aforementioned Law n°28-00.</p>
<p>Decree n° 2-09-538 of 5 rabii II 1431 (March 22, 2010) fixing the modalities of elaboration of the national master plan of hazardous waste management.</p>	<p>In application of the provisions of article 9 of the law n° 28.00 on waste management and disposal, the national master plan for hazardous waste management is established by the governmental authority in charge of of the environment.</p>
<p>Decree n° 2-12-172 of 12 jomada II 1433 fixing the technical prescriptions relating to the elimination the elimination and the processes of valorization of waste by incineration.</p>	<p>This decree establishes the technical requirements that must be taken into account in the development and operation of waste incineration facilities for disposal, the conditions and requirements to be met by facilities for the purpose of heat recovery or energy production. It also defines the environmental requirements for the management of residues resulting from waste incineration operations, as well as the modalities for the control of these facilities.</p>
<p>Decree No. 2-09-85 of September 6, 2011 on the collection, transportation and treatment of certain used oils.</p>	<p>The conditions for issuing the authorizations referred to in Article 29 of the above-mentioned law n° 28-00 for the specialized installations of waste oil treatment of the codes 13-02 and 13- 03 of the Moroccan catalogue of</p>

waste published by the above-mentioned decree n° 2-07-253 of 14 rejeb 1429 (July 18, 2008).

Order of the Minister of Energy Transition and The purpose of this order is to establish the specific Sustainable Development n°782-21 of 8 jomada I 1443 requirements for polychlorinated biphenyls (PCB) (December 13, 2021) establishing the special waste with respect to their collection transport, storage requirements of polychlorinated biphenyls (PCB) waste and treatment with a view to their disposal or disposal relating to their collection, transport, storage and or recovery.

treatment with a view to treatment with a view to their elimination or their recovery.

### 1.3 valorization options for dumped wastes

Several kinds of methods can be used to minimize the influence of waste on human beings and the adjacent environment. According to a recent study conducted by Kaza et al. (2018), the techniques used for waste management in Africa are summarized in **Fig.1-4**. By examining the graph, it is observed that disposing of waste in open dumpsites remains the most used solution for approximately 50% of the total generated quantity of MSW. Unfortunately, the recycling is less than 4%. The methods used for waste management on an international scale are discussed in this section:

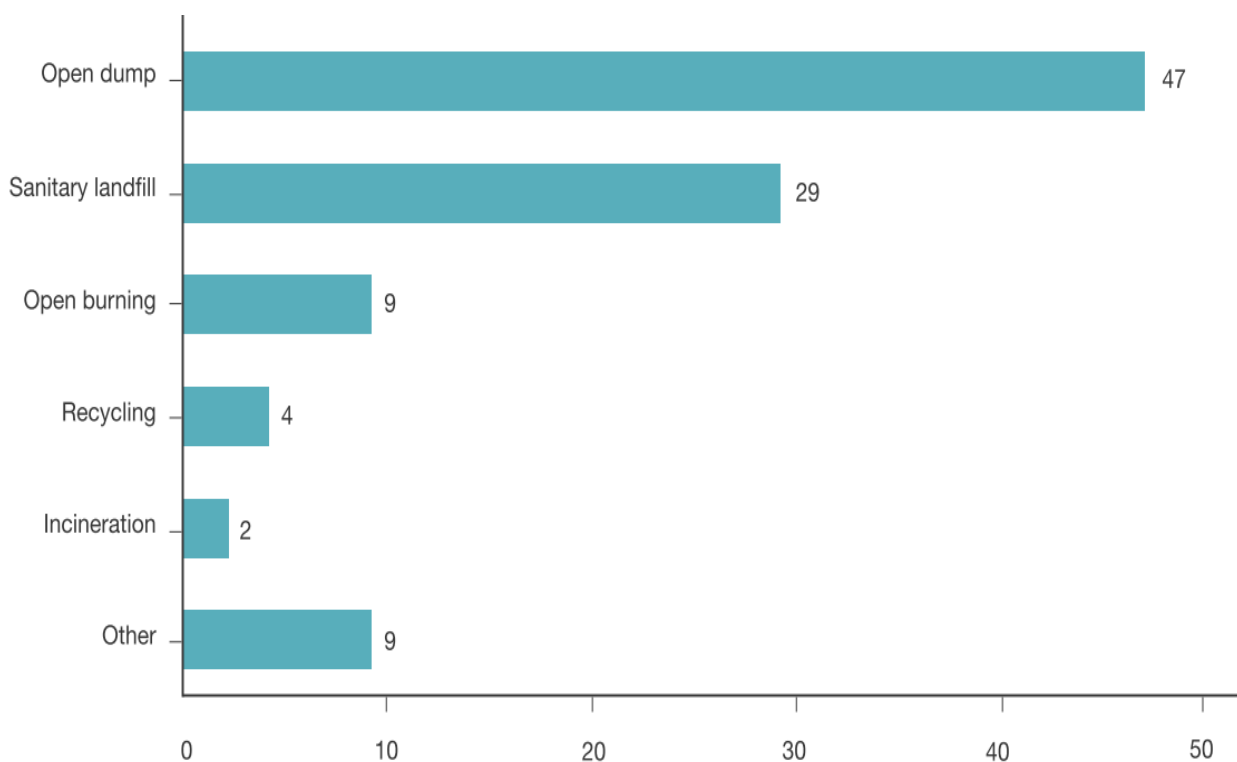


Figure 1-4. Methods of end-of-life MSW disposal in Africa (Kaza et al., 2018)

### 1.3.1 Incineration:

Incineration is a method of eliminating waste that is often collected without prior sorting, by burning it at high temperature (between 850 and 1000°C) in special furnaces adapted to its characteristics (composition, moisture content). The combustion must be carried out under optimal conditions and must be accompanied by an efficient treatment of the fumes.

The objective of waste incineration is to treat waste in a way that reduces its volume and hazardousness while capturing or destroying potentially harmful substances that are, or may be, released during incineration. Incineration processes can also provide a means to enable the recycling of energy (into thermal or electrical energy), mineral content, and/or chemical elements in the waste chemical content of the waste.

Unlike most other waste treatment methods, incineration is suitable for all kinds of MSW. On average, it reduces their mass by 70% and their volume by 90% (Rezaei et al., 2018). It ensures significant saving of fossil fuels (gas, oil, coal, etc.) and offers solutions to problems such as residual odors and leachate.

Although the partial depollution of the fumes emitted by the incineration plants, the process remains polluting and harmful to public health, through the emanation of toxic substances: dioxin, nitrogen oxides, sulfur oxides, heavy metals, etc. Even if the quantity of these substances is reduced, they can have carcinogenic consequences on human health. Furthermore, the incineration provides dangerous by-products such as fly ash and bottom ash which could contribute in the release of pollutants into the adjacent environment.

### 1.3.2 Anaerobic digestion/ biomethanation

Biomethanation (Anaerobic digestion) is the decomposition of organic matter under anaerobic conditions to generate methane and carbon dioxide as major by-products (Pujara et al., 2019). It is worth noting that the process allowed the generation of approximately 55-60% of methane which could be employed as a renewable energy source for various residential and industrial purposes. According to Ahsan (1999), a controlled anaerobic digester may produce 2-4 times more methane from 1 tone of MSW in 3 weeks, while the production of the same quantity in landfill requires 6-7 years. The net power generation potential (NPGP) from anaerobic digestion of MSW was calculated using the following equations:

$$\text{NPGP (kW)} = \text{P} \times \text{Q} \quad (1.1)$$

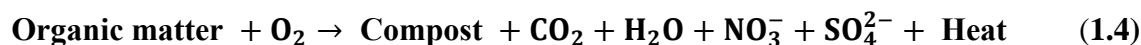
$$\text{P} = \text{X} \times \text{Y} \times \text{Z} \times \text{L} \times \text{W}_1 \times 10^3 \quad (1.2)$$

$$Q = W_2 \times CV \times h \quad (1.3)$$

Where, X is generated biogas (m<sup>3</sup>/kg of volatile solids/ day), Y is the efficiency of digester (%), Z is the total organic fraction (%), L is the organic biodegradable fraction (%), W<sub>1</sub> is daily total waste generated (tons), h is the conversion efficiency (%), W<sub>2</sub> is a constant obtained from (860×24)<sup>-1</sup>, CV is the calorific value of waste (kcal/m<sup>3</sup>). Based on the composition of Moroccan MSW is appeared that this technology could be a suitable solution for integrated management of generated wastes, especially that the anaerobic digestion process does not require any external source of energy, no odors and rodents' issues during the digestion; which make it one of the potential and viable alternatives.

### 1.3.3 Composting:

The composting is a process which converts the organic wastes (food, newspapers...) into fertilizers which can be further utilized in agricultural purposes. In this method, microorganisms i.e., bacteria, protozoa, algae and fungi biodegrade organic matter under controlled conditions, such as temperature, carbon to nitrogen ratio, pH, moisture, etc. The equation 1.4 below showed the aerobic decomposition of organic fraction during the composting process:



Several authors studied the possibility of transforming dumped MSW into biofertilizers with promising results as compared to conventional fertilizers existing in the market (Bohacz, 2018; Mendonça et al., 2017; Z. Zhang et al., 2019).

### 1.3.4 Recycling and Reuse

There is a large attempt towards the transformation of wastes into alternative resources used in various fields to avoid the harmful effect of their disposal in landfills. Recycling consists in collecting by selective sorting, transporting, and treating separately MSW (paper, cardboard, plastic, glass, aluminum, steel, wood, textiles, etc.) which have lost their usefulness in their present form, and to use the materials which compose them in the manufacture and sale of new valuable products. Recycling is therefore the use of materials from waste instead of virgin raw materials (Rivas-garcía et al., 2018). Generally, the recycling of waste into valuable products faced various challenges, including the societal acceptability of the application and the achievement of the technical properties similar to those exist already in the market. In 2015, The United Nations announced the 17 sustainable goals (SDGs) as a plan to promote social inclusion, economic growth, and environmental protection. The recycling and reuse of waste have a great potential to participate

effectively in the achievement of these SDGs. In this light, the incorporation of MSW and dangerous wastes in various applications has several economic and environmental benefits, including the control, management, and minimization of the huge amounts of wastes discarded annually throughout the world and keeping those materials in use not in landfills by transforming them into alternative resources.

### 1.3.5 Landfilling

According to recent research conducted by Kaza et al. (2018), it is expected that the amount of generated waste will skyrocket increase by more than 50%, reaching 3.4 billion tons by 2025. Unfortunately, more than 40% of the waste generated across the world will end up in dumpsites which are mostly located in Africa, Latin America, Asia, and other low- and middle-income countries according to the international solid waste association (Law & Ross, 2019). Based on the waste management hierarchy, the landfills disposal remains the least environmentally friendly waste option, until now landfilling of waste is very popular in Morocco like other developing countries worldwide. The **Fig.1-5** presented the possible emissions from landfills and open dumpsites.

There are several methods employed to dispose of municipal and industrial wastes on land. There are several kinds of landfills as discussed below:

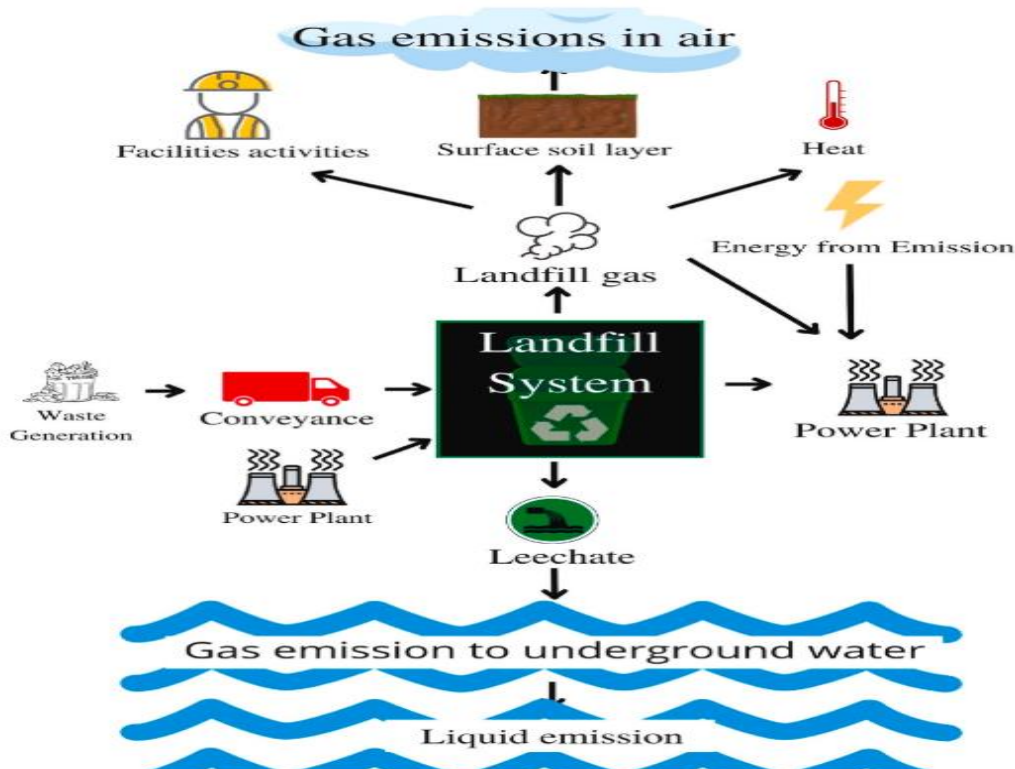


Figure 1-5. Emissions from landfills and open dumpsites (Yaashikaa et al., 2022)

### 1.3.5.1 Sanitary landfilling

The sanitary landfill is one of the approved methods for the safe disposal of solid wastes. Waste is deposited in an engineered, controlled facility, designed and operated to minimize impacts. Includes, e.g., liners, earth cover on top of it, leachate collection systems, and landfill gas recovery, etc. The gases produced by the anaerobic digestion of wastes inside the landfill, were recuperated, treated and further utilized for energy production.

### 1.3.5.2 Controlled disposal

Waste is deposited at a designated site, which has access control, cover and compaction, but no liners, leachate collection systems, etc.

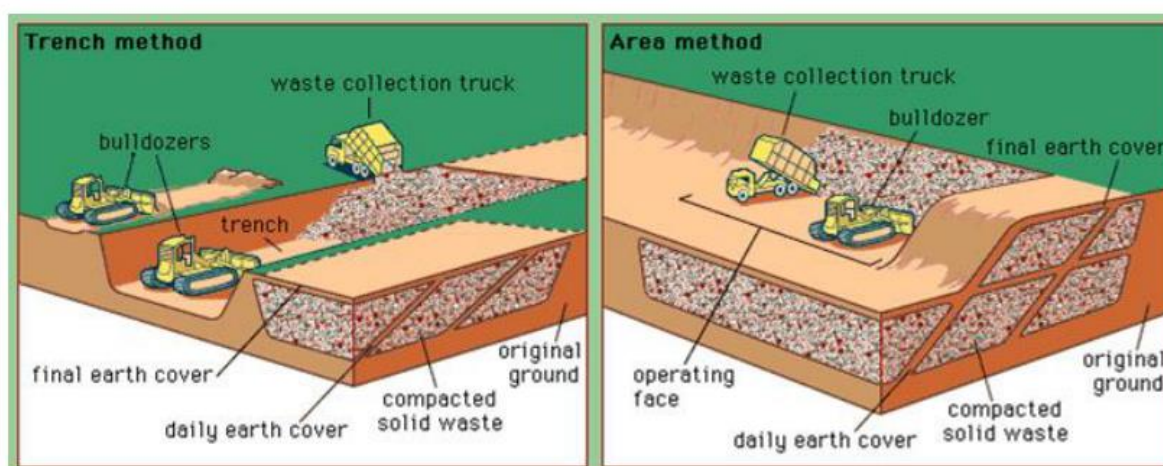


Figure 1-6. Controlled landfilling methodology.

### 1.3.5.3 Open dumpsites:

Uncontrolled dumping in open dumpsites is the most common type of waste disposal in most of the African countries, apart from the metro-cities, because it is considered a cheap way of getting rid of all kinds of solid waste, as shown in **Fig.1-7** waste is indiscriminately deposited at a designated site with either no, or at best very limited measures to control the operation and protect the surrounding environment. Most of the disposed waste will come in contact with ground and surface water (Akerlof, 1970). Leachate resulting from landfill sites and other solid waste disposal facilities will contact ground water and consequently pollute it. Therefore, this practice poses significant environmental and health risks due to toxic and greenhouse gases (GHGs) emission through direct combustion and/or decay of wastes, and the leakage of leachate loaded by heavy metal(oid)s. This type of landfill has harmful consequences for the environment and public health, such as the risk of fire and the proliferation of pathogens.



Figure 1-7. leachate leakage from the open dumpsite (Benguerir-Morocco).

## **1.4 Landfill leachate: Characteristics, regulatory limits, and treatment methods**

Leachate is a dangerous by-product effluent produced as a result of the decomposition of solid wastes and the rainwater seeping through layers of wastes (El Fadili et al., 2022). It is a heterogeneous mixture of organic and inorganic compounds and its physicochemical and microbiological composition depend on several factors including, the composition of dumped wastes, climate conditions, geological and physiological factors (Yaashikaa et al., 2022). Landfill leachate can cause severe human and environmental issues if it is managed unscientifically and discharged into the environment without proper treatment. It has been proved that this effluent consists of a myriad of pollutants including dissolved organic matter, heavy metal(oid)s, and salts (Talalaj, 2014; Tenodi et al., 2020).

Leachate management has become an alarming issue throughout the world because the migration of untreated leachate could significantly affect the quality of soils and water resources in its vicinity. In this context, the environmental concern and the possible scenarios of pollution via this effluent have been extensively discussed in the literature (Alam et al., 2020; Hussein et al., 2021; S. Singh et al., 2016).

### **1.4.1 Landfill leachate generation**

Leachate is the liquid effluent generated through the degradation of waste and the interaction between layers of waste and rainwater (Wijekoon et al., 2022). A combination of physical (evaporation, runoff, infiltration, percolation, precipitation), biological (acetogenesis, nitrification, methanogenesis) and chemical processes (dissolution, complexation, precipitation, oxidation) takes place to transform the waste materials into a wide variety of compounds which are then transferred

to percolating rainwater as presented in **Fig.1-8**. Landfill leachate is a highly polluted mixture of biodegradable and non-biodegradable toxic compounds.

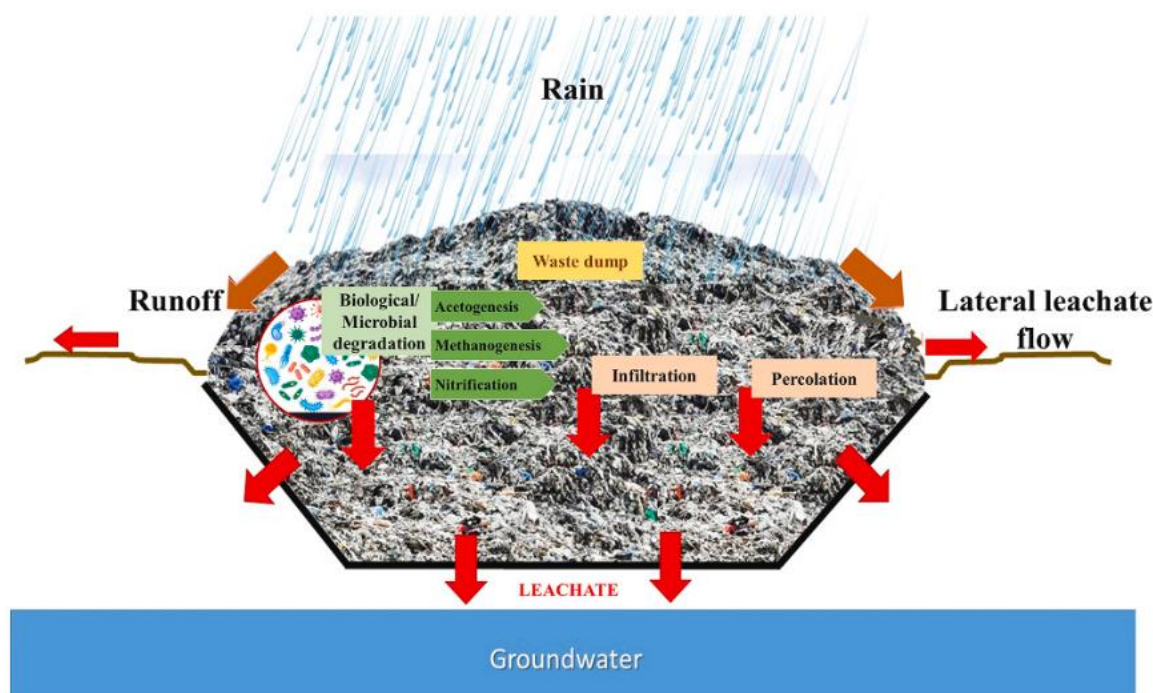


Figure 1-8. Conceptual model for leachate generation (Wijekoon et al., 2022)

## 1.4.2 Landfill leachate composition

The constituents of landfill leachate could be classified into four groups: inorganic macro components, xenobiotic organic components, dissolved organic matter, and metal(oid)s (Wijekoon et al., 2022).

### 1.4.2.1 Inorganic macro compounds

Ammonium ( $\text{NH}_4^+$ ),  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , Sodium ( $\text{Na}^+$ ), Potassium ( $\text{K}^+$ ), Calcium ( $\text{Ca}^{2+}$ ), Magnesium ( $\text{Mg}^{2+}$ ), hydrogen carbonate ( $\text{HCO}_3^-$ ) and Iron ( $\text{Fe}^{2+}$ ) are found among the most predominant inorganic components in landfill leachate. Based on the age of the landfill, the amount of inorganic macro-component varied widely.

### 1.4.2.2 Xenobiotic organic compounds (XOCs)

The concentration xenobiotic organic compounds, such as toluene, chlorinated aliphatics, benzene, phenols, halogenated hydrocarbons, and phthalates in landfill leachate are generally low, with less than 1 mg/L for each compound (Wijekoon et al., 2022). The main source of these pollutants in leachate are industrial chemical products, household, pesticides, and fertilizers. Their amount depends on several factors, including waste composition, landfill age, and technology. Many previous studies have comprehensively demonstrated the negative influence of xenobiotic organic

compounds (XOCs) on human health and the environment. For example, Adhikari & Khanal. (2015) conducted a qualitative study on landfill leachate from different ages of landfill sites in various countries and reported that monoaromatic hydrocarbons such as benzene, toluene; xylenes, and halogenated hydrocarbons have the most negative impact on human health and the adjacent environment.

#### 1.4.2.3 Dissolved organic matter (DOM)

DOM represent the fraction of organic matter that can pass through a 0.45  $\mu\text{m}$  filtration membrane (Wijekoon et al., 2022). Hydrophilic acids, VFA, amino acids are considered among the most dissolved organic matter present in landfill leachate.

#### 1.4.2.4 Heavy metal(oid)s

Various heavy metal(oid)s like Cd, As, Pb, Cr, Hg, and Cu which are naturally found in the soil or the waste materials, have been detected in the leachate of the active solid waste landfill (Talalaj & Biedka, 2016). The **table 1-2** below presents the source of heavy metal(oid)s in landfills according to the research conducted by Brignon et al. (2005).

Table 1-2. sources of heavy metal(oid)s in the landfill (Brignon et al., 2005).

Waste	Metal(oid)s
Used batteries	Cd Hg, Pb, Zn, Mn, Ni
Pigments et peintures	Cd, Hg, Pb, Zn, Mn, Cr, Cu, Fe
Metals and alloys	Cd, Pb, Zn, Mn, Ni, Cu
Plastics	Cd, Pb

#### 1.4.3 Impacts of metal(oid)s from landfill leachate

The pollution of soils and water resources by heavy metal(oid)s sourced from various anthropogenic activities (mining, landfilling, industry, etc.) and geogenic sources is of great concern due to the potential influence on human health and the environment.

The improper dumping of solid waste may endanger the environment and seriously threaten every form of life in the neighborhood of MSW through the release of numerous dangerous pollutants, such as Polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs) and metal(oid)s (cadmium, zinc, lead, chromium, copper, iron, arsenic...etc.) either from the leachate infiltration or as a fugitive emission. Heavy metal(oid)s are non-biodegradable, and can accumulate in the human body through ingestion, inhalation, dermal contact exposures (Karimian et al., 2021), and through the food chain, which could lead to severe influence on health.

As stated above trace metal(oid)s are one of the dangerous by-products of landfilling, unlike many organic pollutants most of these substances are widely known for their toxicity to human beings, swift biological accumulation, and cannot be degraded biologically or chemically which enhance their persistence for a long period in the aquatic and terrestrial environment (Adelopo et al., 2018; Hussein et al., 2021; Varol, Gündüz, & Ras, 2021; S. Wang et al., 2022). Trace metal(oid)s are endocrine disruptors and the intake of soil contaminated with these harmful compounds may lead to severe carcinogenic and non-carcinogenic effects on receptors health if come into contact with them via different exposure pathways such as inhalation, dermal contact, ingestion, and via transfer along with the soil-food chain.

Most of the implemented treatment processes of landfill leachate in Morocco were focused on organic compounds and ammonia removal due to the high concentration of these constituents in leachate. Therefore, less attention was given to the removal of heavy metals from landfill leachate. To further worsen the situation, most of the landfills do not even have any pollution control, neither leachate collection nor leachate treatment. Soil, as the primary recipient of solid wastes especially in unlined landfills or dumpsites, may accumulate contaminants aided by the capability of clay minerals and organic substances to bind them (Essien et al., 2019). Adsorbed metals in soil from wastes or leachate is a challenging issue as the metal(oid)s may not degrade in soil or permanently eliminated.

**Fig.1-9** denotes the fate of heavy metal(oid)s transport in a landfill environment. Their amount observed in leachate were probably emanated through leaching from indiscriminate dumping of waste with high metal contents by precipitation.

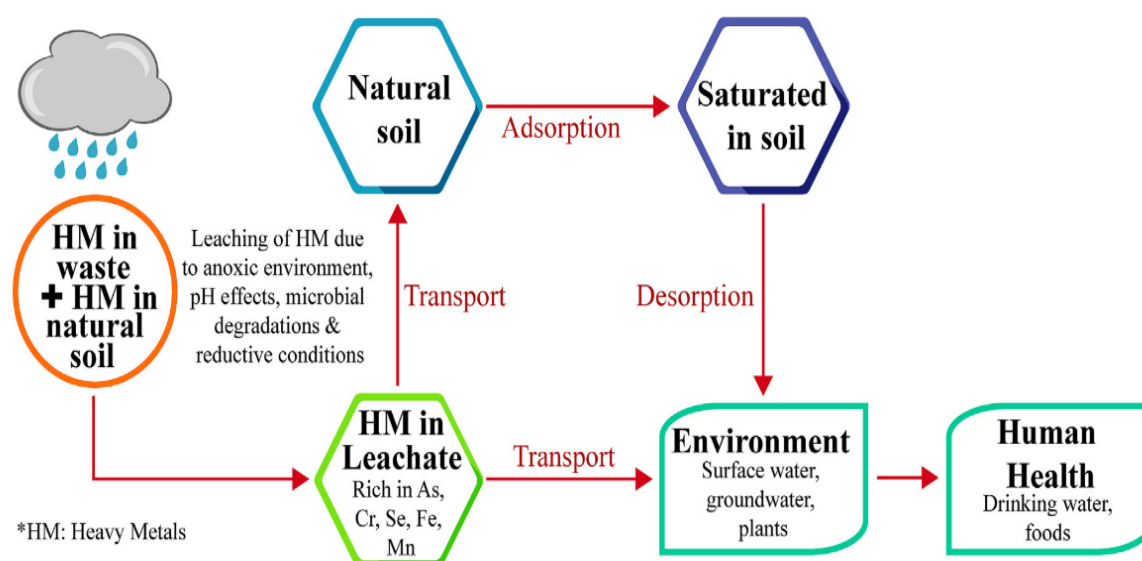


Figure 1-9. Flow of metal(oid)s fate in non-sanitary landfills (unlined and no leachate collection systems); (adapted from source: Hussein et al., 2021).

### 1.4.4 Treatment of leachate

Treatment of landfill leachate is a very challenging task based on the nature of leachate which is very complex. The characteristics of leachate may differ according to the wastes disposed, age of the landfill contents, degradation processes, hydrogeology, operational practice, as well as climatic conditions (Kurniawan et al., 2006; Zainol et al., 2012). Unlike industrial or agricultural wastewater, leachate from waste disposal sites is diverse. Landfill leachate is normally consisting organic contaminants, inorganic compounds, heavy metals, as well as contaminants of emerging concern (Krčmar et al., 2018). Thus, due to the heterogeneity characteristics, there are several technologies for the treatment of landfill leachate, including biological and physicochemical methods, and in some cases, combined treatment techniques. As shown in **Fig 1-10**.

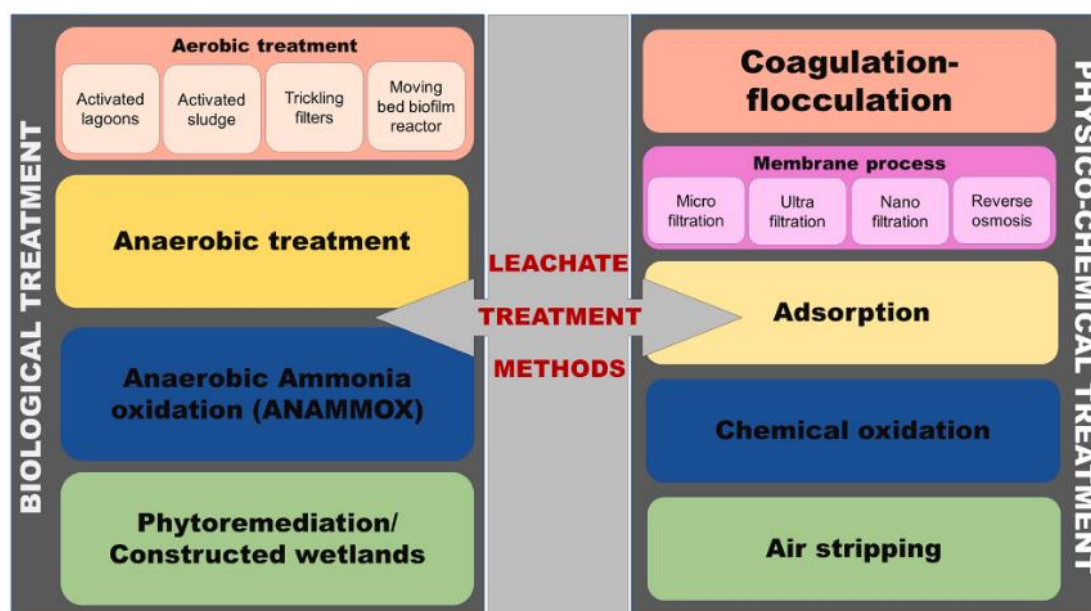


Figure 1-10. Schematic diagram of landfill leachate treatment methods (adapted from source: Wijekoon et al., 2022).

## 1.5 Soil and water pollution from landfills

### 1.5.1 The main heavy metals and metal(oid)s emitted by landfills

Heavy metal(oid)s are generally defined on the basis of their physicochemical and toxicological properties. Any naturally occurring metallic element with a density greater than  $5\text{g/cm}^3$  is referred to as a heavy metal or metallic trace element. The most toxic heavy metal(oid)s on human health are: lead, mercury, arsenic and cadmium. Other heavy metals such as copper, zinc, chromium, although necessary for the body in small quantities, can become toxic in larger doses. In the environmental sciences, the heavy metal(oid)s associated with the notions of pollution and toxicity

are generally arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg) (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn).

At high concentrations, heavy metal(oid)s create a huge environmental problem because they accumulate and are not biodegradable. Their presence in the environment results from natural causes (geogenic) and human activities (anthropogenic). Soils and water resources could be affected by landfilling practices through leachate mitigation and gaseous emissions. The migration of this pollution depends on several parameters.

### **1.5.2 Factors influencing metal(oid)s concentration in soils and water**

Certainly, it is important to highlight that some parameters such as clay content, organic matter, pH, CEC, and environmental factors, are necessary to assess the behavior of trace elements in soils and water. And therefore, a better choice of the potential remediation technique. Moreover, it has been demonstrated in some previous studies that soils and water characterization presents a determinant factor that controls the solubility and the availability of metal(oid)s (Gabarrón et al., 2017; Micó et al., 2006).

#### **1.5.2.1 pH**

The pH is a crucial factor that conditions the mobility of metal ions, as it influences the number of negative charges that can be put into solution. Generally speaking, when the pH increases, cations are less soluble and anions are more soluble, in addition, the increase in pH often induces the formation of precipitated species that can limit the solubility and bioavailability of all ionic species, Jung & Thornton. (1996) demonstrated that alkaline pH limits the passage of heavy metal(oid)s from the solid phase to the soil solution and then to the plants. Likewise, according to Sposito. (1989) (oid)elevated pH values increase the precipitation of metal(oid)s through the formation of insoluble carbonate. Also, according to some previous studies alkaline pH enhances the adsorption process of some metals such as Zn and Cu, and plays an important role in the precipitation of Pb (Serpaud et al., 1994).

#### **1.5.2.2 The cation exchange capacity (CEC)**

The CEC corresponds to the quantity of positive charges carried by the cations susceptible to be reversibly fixed on the negatively charged sites of some soil constituents.

#### **1.5.2.3 Organic matter**

The organic matter plays a very important role in the retention of heavy metals and organic pollutants, because it represents an important number of physico-chemical adsorption sites. At

constant pH, it will control their adsorption. Under these conditions, it is the distribution of heavy metals between the organic matter and the soil solution that determines the dissolved fraction of metals, and consequently the most mobile fraction.

### 1.5.2.4 CaCO<sub>3</sub> content

The total limestone is one of the inherited components of the soil, possibly slightly modifiable by massive and repeated contributions of basic amendments. The presence of limestone gives the soil specific characteristics in terms of physical and chemical behavior and influences its biological activity. Its absence results in a progressive acidification, more or less quickly according to the pedoclimatic context, that it is necessary to compensate by regular contributions of basic amendments (liming) (Zupančič et al., 2018).

## 1.6 Human health impact

Studies on exposures and health outcomes in workers, populations and organisms living near landfills and open dumpsites showed that there is definitive evidence of negative impacts on their health due to high exposures to bio-aerosols, volatile organic compounds, and metal(oid)s (Ahmad et al., 2021; Ravindra et al., 2015). Many previous studies showed that children and adults are likely to be exposed to carcinogenic and non-carcinogenic risks due to long time exposure to heavy metal(oid)s originated from landfilling practices (Arunbabu et al., 2017; El Fadili et al., 2022; Halder et al., 2022; A. Singh & Chandel, 2022; S. Singh et al., 2016). The **Fig 1-11** presented a schematic view of environmental and health impacts due to MSW based on a recent study published by Pujara et al. (2019).

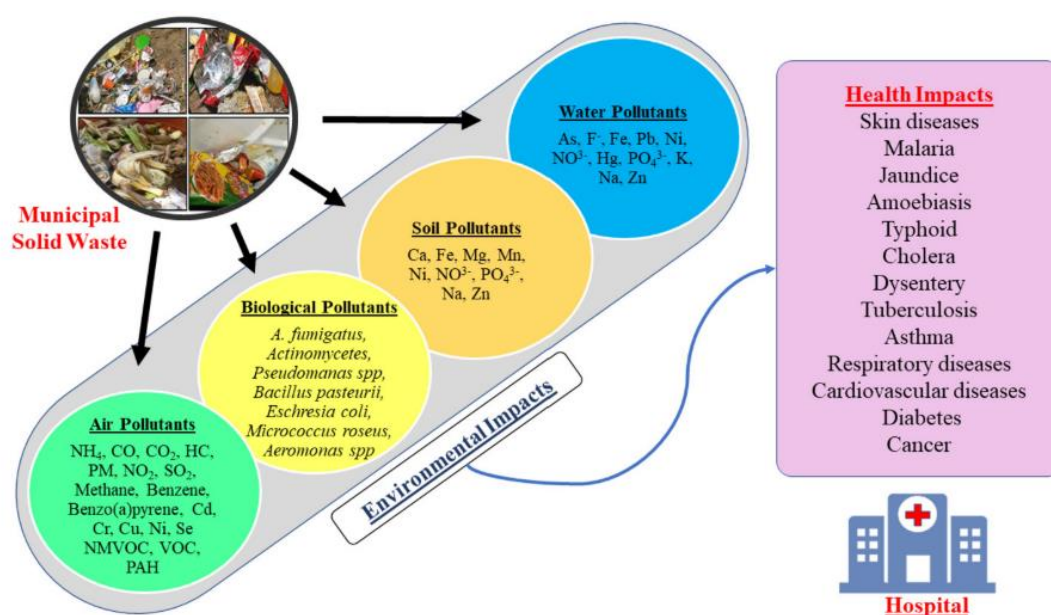


Figure 1-11. A schematic view of environmental and health impacts due to MSW (Pujara et al., 2019)

## **1.7 Impact of some heavy metals (Cadmium, Nickel, Lead, Chromium, Copper and Zinc) on the environment and public health**

The accumulation of heavy metal(oid)s presents a dangerous contaminant of environmental ecosystems and the food chain. Unlike many other pollutants, they are not biodegradable and can be bio-accumulated in living organisms and induce disturbances in their metabolism (Lei et al., 2022; Saber et al., 2014).

The impact of heavy metal(oid)s on health depends on their chemical species, their concentration, their bioavailability, their exposure time and their passage in the food chain. Some heavy metal(oid)s have no role in the human body and are considered as strict contaminants (toxic even at very low concentrations), such as mercury, lead and cadmium, others are essential but at low concentrations and are named (trace elements) like selenium and iron (Gao et al., 2018).

### **1.7.1 Cadmium (Cd)**

Environmental cadmium pollution has decreased since the 1980s, due to the removal of cadmium from paint pigments and the replacement of cadmium batteries by lithium batteries. But their pollution is still of concern, because cadmium is very toxic at low doses for human being and various living organisms (Amjad et al., 2017).

Cadmium is a very toxic element that has no known function in the body. Chronic exposure to cadmium can lead to obstruction of the lungs, kidney disease, cardiovascular disease, bone disease (osteoporosis) as well as cancers and growth retardation (Lienemann, 2005).

### **1.7.2 Nickel (Ni)**

Nickel detected in different environmental compartments (soil, air and water) may have a natural or anthropogenic sources. The natural sources of nickel are the alteration and erosion of rocks, sea salt and volcanoes. Anthropogenic sources include base metal production activities such as the mining and processing of nickel ores, gold and uranium mining, as well as the steel industry, the combustion of fossil fuels the production of nickel alloys and the recycling of metal waste, domestic and industrial wastewater sludge treatment plants and landfill leachate (Chaer et al., 2016).

Nickel is a trace element but, when the absorption is too important, it becomes a highly toxic element, especially for the respiratory system. Indeed, exposure to Ni associated with an increased risk of bronchopulmonary and nasal cavity cancer, lung fibrosis, asthma, chronic bronchitis, heart problems and allergic reactions such as skin rashes (Z. Ben Salem et al., 2014).

### **1.7.3 Lead (Pb)**

Lead is one of the most toxic contaminants in the environment because it is not biodegradable and has a geochemical half-life of about 7 centuries. The introduction of lead in certain paints as a pigment, and then in automotive gasoline, has resulted in a consequence of an even wider diffusion in the environment.

Lead causes the most poisoning among all metal(oid)s because it is toxic to the nervous system; in case of massive intoxication, the neurotoxic effect of lead can result in a convulsive encephalopathy that can lead to death. Furthermore, in cases of less severe intoxication, neurobehavioral disorders, and intellectual deterioration (Choe et al., 2003).

Lead is toxic to most vital organs. It causes lead poisoning, abdominal pain, high blood pressure, fatigue, muscle weakness, anemia, miscarriages behavioral problems, kidney problems, hearing loss, etc.

### **1.7.4 Chromium**

Chromium is a naturally occurring metallic element in the earth's crust that exist in small amounts in all types of rocks and soils. The main natural sources of chromium are: soil erosion, volcanic emissions, sea salt aerosols and dust from forest fires (Tariq et al., 2009).

More than 70% of the chromium in the environment comes from anthropogenic sources such as metal smelters, production of special stainless steels and alloys, refineries, tanneries, pulp and paper mill effluents, pigment and dye production (dyes, paints, cosmetics, ceramics, etc.), fungicide production, textiles and thermal power plant waste (Liu et al., 2016).

Most of the naturally occurring chromium is in the trivalent form (Chromium III), which is present in many vegetables, fruits, meats, seeds and yeast. It is an essential trace element for the carbohydrate metabolism in humans, its deficiency can affect insulin activity and cause heart problems, while those of anthropogenic origin are of hexavalent form (Chromium VI) highly toxic and carcinogenic (Choe et al., 2003).

### **1.7.5 Copper**

Copper is a stable metal and an excellent conductor of electricity and heat. It can be of natural or anthropogenic origin. Naturally, it can be the result of erosion and weathering of parent rocks, forest fires, sea spray and rotting vegetation. Of anthropic origin, it can be the result of mining or agricultural activity (pesticides), effluents from wastewater treatment plants and it is used in the manufacture of weapons materials, coins, electrical wires, plumbing pipes, paints, etc. (Ballabio et

al., 2018). It disturbs the environmental balance between living organisms by contaminating all the links of the trophic chains (Kouame et al., 2006).

Copper is an essential trace element for the growth of plants and animals. In humans, it is essential for the production of hemoglobin, a copper deficiency can lead to various health problems including anemia. On the other hand, a very high concentration of copper can be toxic and lead to deleterious effects such as deterioration of red blood cells, lungs, liver, pancreatic functions and even death. However, the current epidemiological data do not allow to conclude on the carcinogenicity of copper.

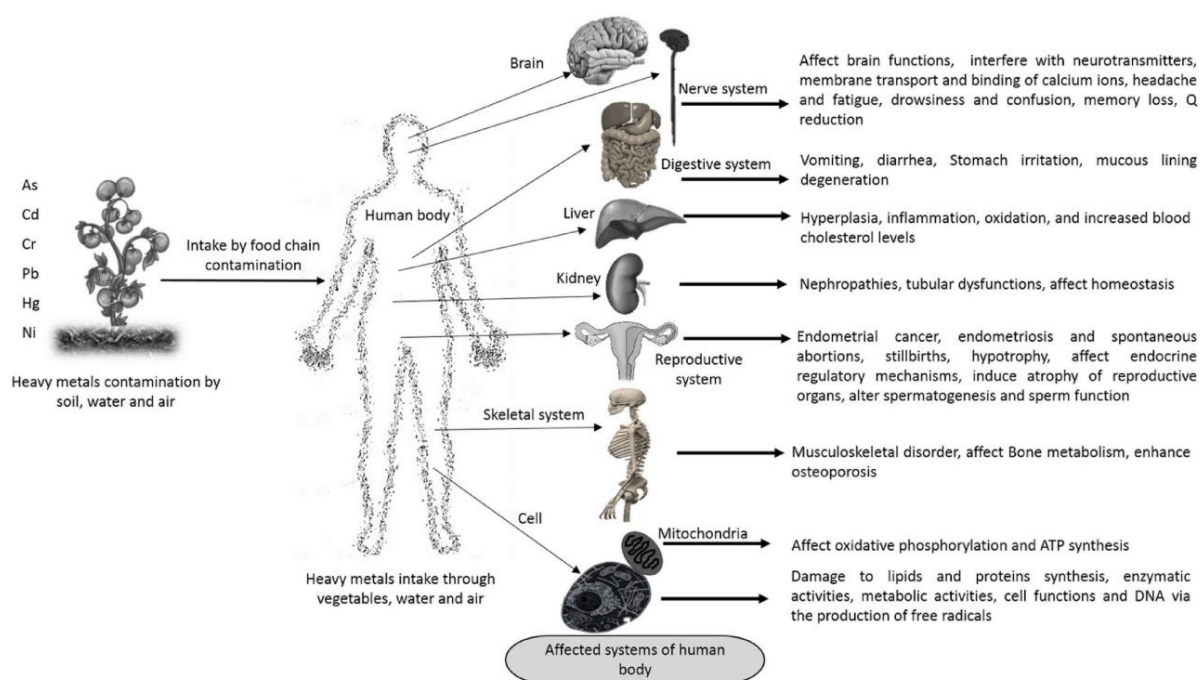


Figure 1-12. Health effects of heavy metal(oid)s on human health (S. Kumar et al., 2019)

### 1.7.6 Zinc

Zinc is one of the most abundant metals in the earth's crust and is naturally present in air, water, and soil. Zinc is found in varying concentrations in parent rocks, sea salt, volcanic eruptions, and forest fires. Anthropogenic emissions of zinc to the environment are from mining, waste incineration, fossil fuel combustion, and in the steel industry to protect steel from corrosion (Dumoulin et al., 2017). Zinc is an essential element for all forms of life, from the smallest micro-organism to the human being. A range of optimal zinc concentrations exists for every living organism, including humans (Bodjona et al., 2012).

Zinc is an essential trace element for human health, present in practically all cells of the living organism virtually every cell in the living body, including the adrenal glands skin, parts of the brain, the pancreas, the membranes of the eye, the prostate gland and sperm. Zinc plays an important role

in growth, immune response, neurological and reproductive functions. It is necessary for the functioning of about a hundred vital enzymatic processes in the body and has an influence on hormones. By Therefore, zinc deficiency is now recognized as a human health problem (Noulas et al., 2018). Zinc can become toxic at 150 to 450 mg/day. An excess of zinc in the body can lead to gastrointestinal problems and diarrhea, and cause symptoms associated with fever: chest pain, fever, nausea, cough tremors and difficulty of walking. To date, the carcinogenic potential of zinc has not been demonstrated (Kouame et al., 2006).

## 1.8 The Toxicity and Valorization Options of Cigarette Butts (CBs)

### 1.8.1 History and Generalities about Tobacco

Tobacco industry could be considered as one of the most prevalent industries, and contribute to high income of many countries. Yearly, six trillion cigarettes are produced and 5.8 trillion consumed by one billion smokers across the entire globe (Zafeiridou et al., 2018), contributing to the generation of approximately 1.3 tons of dangerous litter known widely as cigarette butts (CBs) (Mohajerani et al., 2016), which makes it one of the most abundant litter items on the planet (Rebischung et al., 2018). Moreover, as a result of population growth and the increasing uptake of smoking by young people year after year, it is estimated that the amount of cigarettes consumed will increase by more than 50%, to reach nine trillion by 2025. Based on the estimation published by the Tobacco atlas illustrated in **Fig 1-13**, China was the largest consumer and producer of cigarettes worldwide in 2016, approximately 2.35 cigarettes were consumed by Chinese people. The outcome which could be concluded from the figure is that cigarette production is expected to skyrocket, subsequently CBs litter.

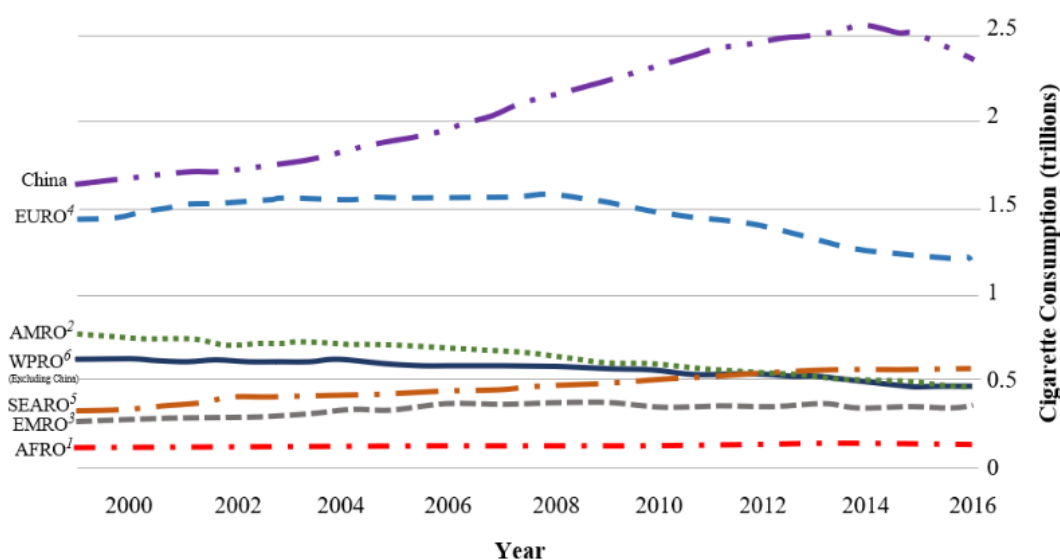


Figure 1-13. Global cigarette consumption by WHO region, 1999 – 2016, in trillions (adapted from The Tobacco Atlas (Kurmus, 2021); <sup>1</sup>Africa, <sup>2</sup>Americas, <sup>3</sup>Eastern Mediterranean, <sup>4</sup>European, <sup>5</sup>Southeast Asia, <sup>6</sup>Western Pacific

Most of these butts are discarded by smokers into the adjacent environment (Dobaradaran, Soleimani, et al., 2021). According to the cigarette butts pollution project in the USA, one-third to two-thirds of CBs littered by smokers into the environment (ocean, river, public roads...etc.). **Fig.1-14** presented the life cycle of discarded cigarette butte after its throw into the environment.

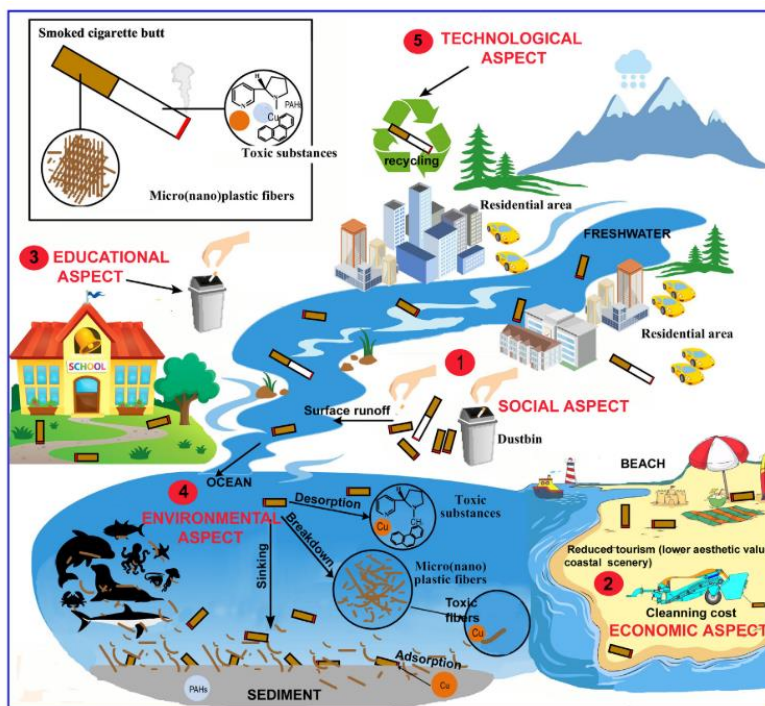


Figure 1-14. Life cycle of discarded cigarette butts (CBs) (Conradi & Sánchez-moyano, 2022)

## 1.8.2 Composition of Cigarette butts

As illustrated in **Fig.1-15** CBs consist of five main components: remaining tobacco, wrapping paper, ashes, additives and a filter made from cellulose acetate (Christina et al., 2019).

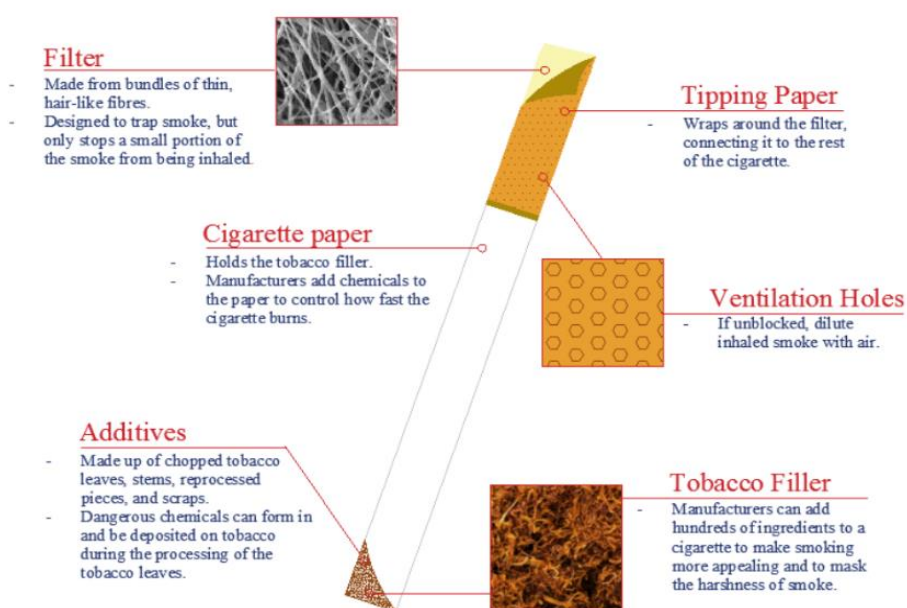


Figure 1-15. Physical structure of a cigarette with each component identified and described (Mohajerani et al., 2016)

Filters are composed of a synthetic plastic fiber commonly designed in a way to trap dangerous toxic compounds present in cigarettes during smoking process (Mohajerani et al., 2017; Novotny et al., 2009; Torkashvand et al., 2021). These filters are well known by its slow biodegradability (Kadir & Mohajerani, 2008; Mohajerani et al., 2016) and can take up to several years to biodegrade under normal conditions. Thus, it has sufficient time to release the entrapped contaminants into the environment (Yousefi et al., 2021).

### **1.8.2.1 Remaining tobacco and additives**

The discarded cigarettes discarded into the environment contain unburned tobacco after smoking. In other word, when a cigarette is discarded into the environment, unburned tobacco residue may remain in the cigarette butt and contribute to the release of toxic pollutants.



Figure 1-16. Remaining tobacco from cigarette butts (CBs)

### **1.8.2.2 Tripping paper**

The tripping paper is wrapped around the filter of the cigarette and contains small ventilation holes that allow fresh air to mix with the smoke. This tripping paper may take up to 5 months to biodegrade under normal conditions (Kurmus, 2021).



Figure 1-17. Tripping paper of cigarette butts

### 1.8.2.3 Filters

Cigarette filters are composed mainly of cellulose acetate, which is a naturally polymer of glucose ( $C_6H_7O_6$ ) derived from cotton linters and wood pulp (Kurmus & Mohajerani, 2021b), about 97% of the cigarette filters were composed of cellulose acetate, a modified natural polymer (Mohajerani et al., 2016). The molecular structure of cellulose acetate is presented in **Fig.1-18**. Cellulose acetate fibers take several years to degrade when discarded into the environment, because microorganisms do not accept cellulose acetate fibers as a source of food. Additionally, the remaining paper on the CBs inhibits the sunlight UV radiation reaching the fibers.

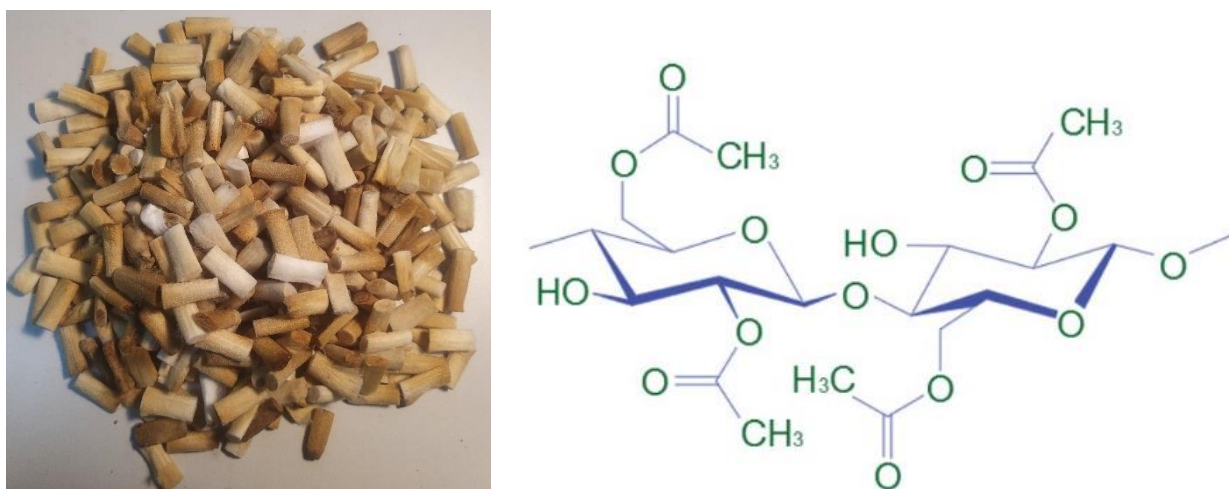


Figure 1-18. Molecular structure of cellulose acetate, which is used as a filter of cigarettes.

### 1.8.3 Toxicity of Cigarette butts (CBs)

Previous researches have already revealed that this small pollutant contains a myriad of toxicant and hazardous chemicals compounds (Torkashvand et al., 2020), such as nicotine (Dobaradaran, Soleimani, et al., 2021), polycyclic aromatic hydrocarbons (PAHs), formaldehyde, BTEX (Dobaradaran, Schmidt, Kaziur-Cegla, et al., 2021), phenol, heavy metal (oid)s (Dobaradaran et al., 2020), and other toxic compounds (Slaughter et al., 2011). Therefore, disposal of CBs is a very challenging issue because if not managed unscientifically and correctly disposed of, it could bring serious threat to the soil and aquatic resources quality (Christina et al., 2019; Slaughter et al., 2011). It is claimed that one single cigarette butt can contaminate up to 1000 liters of water and they might perhaps bio-accumulate in the wildlife and potentially the food chain. Although, until recently in the regulatory level, the Moroccan catalog of waste (decree 2-07-253) does not propose a specific entry for CBs, and is still considered as a municipal solid waste (MSW).

Hence, cigarette smoking is a serious threat to humans, it is estimated that every cigarette burned, the smoker receives roughly 1.4 - 2.2 mg of dangerous chemical compounds. A study conducted by

Yousefi et al. (2021) demonstrated that standard cigarette contains between 9 to 30 mg of nicotine, of which 0.5 – 2 mg is inhaled by the smoker.

Therefore, the toxicity of CBs influences detrimentally nervous, cardiovascular and reproductive systems. Slaughter et al., (2011) demonstrated that one discarded cigarette butt soaked in 1L of clean water for 96 h could reach the lethal concentration LD50 for test fish. The harmful effects of both active and passive smoking upon human health are well known and widely discussed in a good number of previous studies (Freire Lima et al., 2021; Mathers & Loncar, 2006). However, their possible damage on the environment and feasible solutions are still limited (Stigler-Granados et al., 2019).

The investigation of the possible leaching of heavy metals and metalloids from cigarette butts (CBs) in order to assess the influence on the adjacent environment was carried out by many authors. Akhbarizadeh et al. (2021) assessed the leaching of heavy metal(oid)s, including chromium (Cr), cadmium (Cd), arsenic (As), lead (Pb), iron (Fe), manganese (Mn), copper (Cu), mercury (Hg) and zinc (Zn) from cigarette butts (CBs) into deionized water (DW), tap water (TW), and seawater (SW) in different contact times from 60 min to 60 days. To understand how the pH level affects leaching behavior, a pH of 6.5, 7.5 and 8.3 was selected. The results reflected that the studied metal(oid)s have different leaching behaviors over time. Firstly, it is observed a clear relationship between the leaching amount of metal(oid)s and soaking time and the amount of leached metal(oid)s into DW, SW and TW exceeded the permissible limit of surface freshwater to maintain aquatic life.

#### **1.8.4 Research on Valorization of Cigarette Butts**

Unfortunately, landfilling and incineration are the two common disposal methods for cigarette butts in many countries around the world. Nevertheless, they are not efficient and inadequate due to the elevated cost and the possible release of gaseous pollutants. To this end, there are a large attempt by the scientific community to develop economically and environmentally sustainable solutions to recycle, and facing the blooming threat as well the huge quantities of CBs, by incorporating their different parts in various application (**Fig.1-19**), include recycling CBs as a corrosion inhibitor (X. Li et al., 2017; A. Singh et al., 2020; Zhao et al., 2010), production of cellulose pulp (d’Henri Teixeira et al., 2017), utilization as a sound absorbing material (Escobar & Maderuelo-Sanz, 2017; Maderuelo-Sanz et al., 2018), preparation of activated and charred carbon (Hamzah & Umar, 2017), the synthesis of superhydrophobic sorbent (Ifelebuegu et al., 2018; Ou et al., 2016), porous carbon (Matos et al., 2017). Also, incorporating cigarette butts in civil engineering construction materials has received a considerable interest. Mohajerani et al. conducted a comprehensive research based on adding CBs in fired clay bricks, asphalt concrete and fired clay brick (Kurmus, 2021; Md &

Abbas, 2021; Mohajerani et al., 2016, 2021). In addition, Girondi et al. (2020) presented a methodology to use cigarette butts as a fine powder in ceramic materials. The **Table 1-3** presented the characteristics and challenges ahead of CBs recycling reported in the literature.

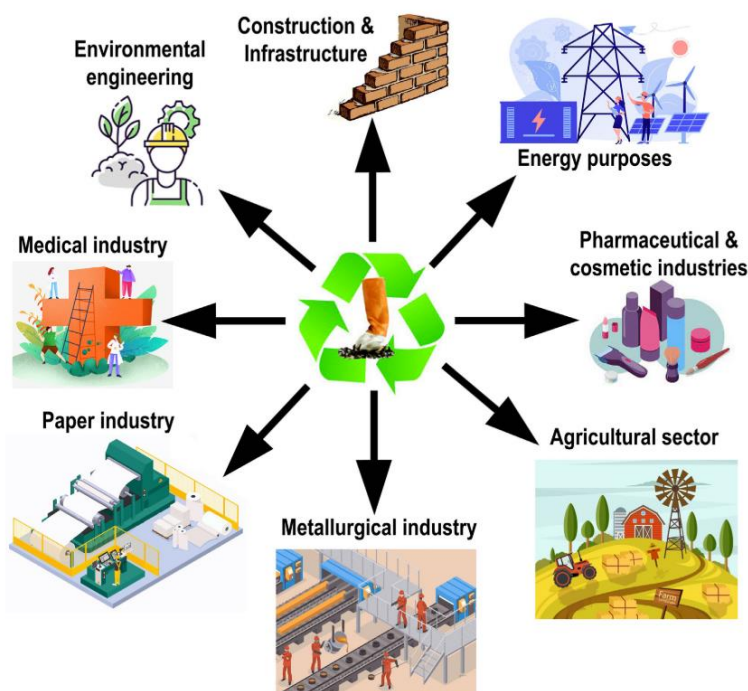


Figure 1-19. Recycling methods of discarded cigarette butts (CBs) according to the literature.

Table 1-3. The characteristics and challenges ahead of CBs recycling reported in the literature.

Recycling method	Process	Advantages	Challenges	References
<b>Gypsum composite for building applications</b>	1. CBs were submerged in water.	1. Recycling cigarette filters to produce eco-materials.	1. Washing cigarette filters leads to the production of wastewater.	(Romero-Gómez et al., 2022) (Morales-Segura et al., 2020)
	2. CBs were crushed into small fragments	2. The process does not require chemical addition.	2. The limited quantity recycled through this process in comparison to the amount of CBs discarded annually.	
	3. Incorporating crushed CBs in gypsum composite	3. Improving superficial hardness, mechanical strength, and density of gypsum composite.		
<b>Fired clay bricks</b>	1. The CBs were dried at 105 °C	1. Recycling cigarette butts (CBs) to produce fired clay bricks.	1. The limited quantity of recycled process in comparison to the production of CBs annually.	(Mohajerani et al., 2016) (Mohajerani et al., 2020)
	2. Crushing of the CBs and turned into the fine powder	2. The process does not require chemical addition.	2. The release of gaseous pollution	
	3. Produce fired clay bricks containing remaining tobacco			

<b>Production of selective adsorbent</b>	<ol style="list-style-type: none"> <li>1. Immersing 1.2 g of CBs in a solution containing a special quantity of: <math>\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}</math> or <math>\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}</math> or <math>\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}</math> and 20 mL acetic acid for 0.5 h</li> <li>2. drying the mixture at 333 K and carbonizing it (873 K; 3 h)</li> </ol>	<ol style="list-style-type: none"> <li>1. The obtained product was showed high adsorption rate.</li> <li>2. Adsorbent separating by magnet is possible.</li> </ol>	<ol style="list-style-type: none"> <li>1. The process require the addition of chemicals.</li> <li>2. The generation of wastewater.</li> <li>3. The emission of gases during the carbonizing process.</li> </ol>	<p>(Xiong et al., 2018)</p> <p>(S. Li et al., 2019)</p>
<b>Production of cigarette-derived functional carbon</b>	<ol style="list-style-type: none"> <li>1. Manually stripping to remove remained tobacco and impurities.</li> <li>2. Crushing CBs into a fluffy material and dried at 80 °C.</li> <li>3. Pyrolysis of CBs with <math>\text{K}_2\text{CO}_3</math> at 800 °C.</li> <li>4. Washing carbonized samples for several times by HCL and deionized water.</li> </ol>	<ol style="list-style-type: none"> <li>1. Re-using the discarded cigarette filters.</li> <li>2. Activated carbon obtained from the filter had high specific surface area.</li> <li>3. Final product had good ability on adsorption.</li> </ol>	<ol style="list-style-type: none"> <li>1. Some part of the CB is lost during the process of manufacturing activated carbon.</li> <li>2. Using washing process leads to wastewater production.</li> <li>3. The process require the use of chemical such as HCl.</li> <li>4. The emission of gases during the carbonizing process.</li> </ol>	<p>(Hamzah &amp; Umar, 2017)</p>
<b>Vector control by the chemicals extracted from CBs</b>	<ol style="list-style-type: none"> <li>1. Submerging CBs in distilled water</li> <li>2. The extraction of chemical trapped in water</li> </ol>	<ol style="list-style-type: none"> <li>1. No addition of chemicals to CBs.</li> </ol>	<ol style="list-style-type: none"> <li>1. No use of remaining filters after extracting the trapped materials.</li> <li>2. Effect of final product on organisms must be considered by further researches.</li> </ol>	<p>(Dieng et al., 2013)</p>

## 1.9 The Toxicity and valorization options of incineration residues

Fly ash and bottom ash constitute the two major by-products generated during the incineration process, and have become a significant environmental concern to ensure their disposal of adequately. **The fig.1-20** showed the appearance morphology of fly ash, bottom ash and crushed bottom ash, respectively.

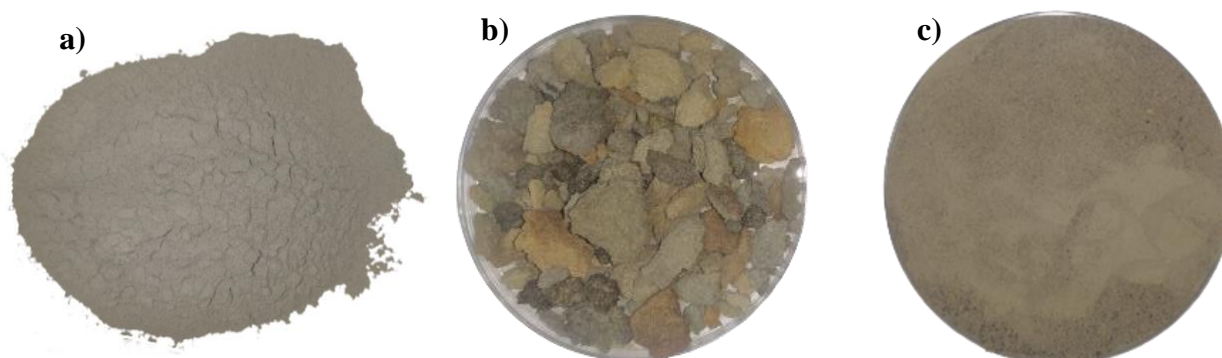


Figure 1-20. Appearance morphology; **a)** fly ash, **b)** bottom ash, **c)** crushed bottom ash.

The fly ashes are particles entrained by the combustion gases. Their proportion increases with the velocity of the gases leaving the layer of burning elements. They are collected in the hoppers under the boiler and in the dust collection system. They form a greyish powder in the granulometry varies from some  $\mu\text{m}$  to some hundreds of  $\mu\text{m}$ . It is worth noting that fly ash exhibits greater leaching due to its small particle size (Prabhakar et al., 2021).

The bottom ash has the appearance of a greyish gravel with a granulometry varying between 0 and 30 mm and which contains numerous metallic elements and glass fragments.

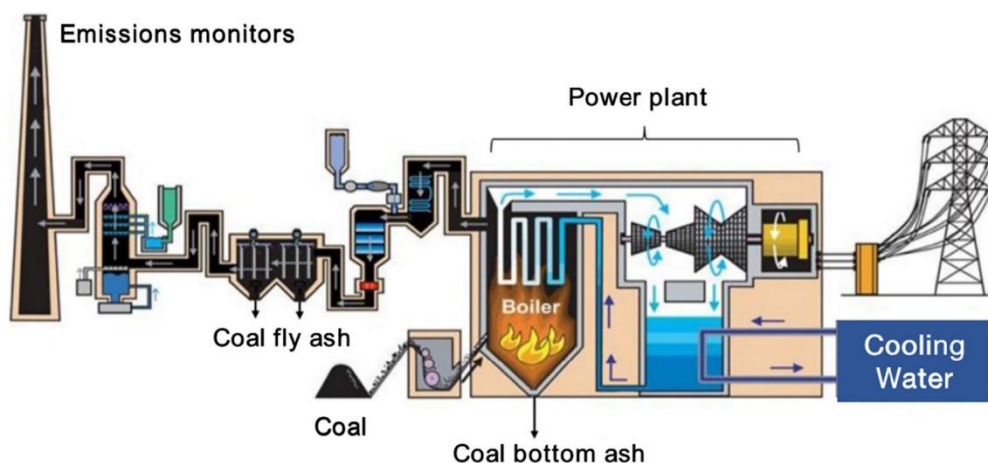


Figure 1-21. A schematic diagram of a typical coal-fired thermal power plant.

As observed in **Fig.1-21**, in a typical coal-fired power plant, BA consists of the minerals left over from combustion that settles on the walls and at the base of the boiler. On the other hand, FA is the fine residue, including ash, dust, soot, and cinders of combustion that enters the flue gas stream from the furnace upwards with gaseous byproducts.

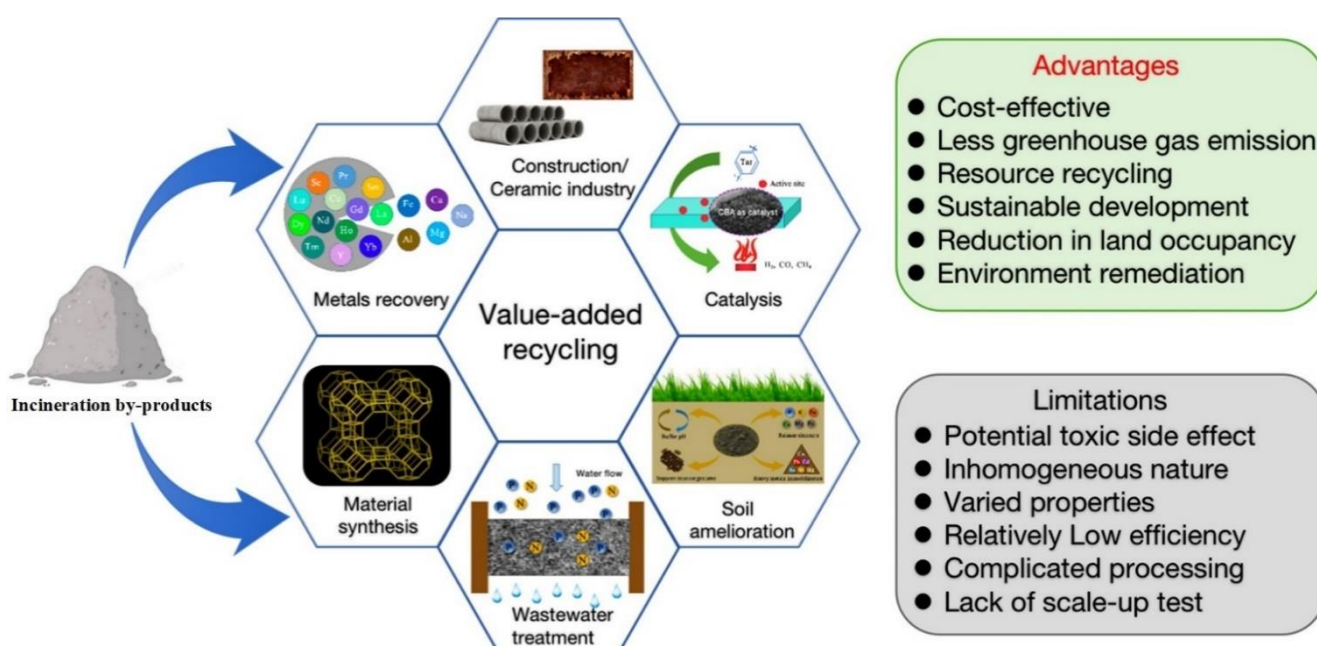


Figure 1-22. The existing applications of incinerated waste (H. Zhou et al., 2022).

Although the world is extensively moving towards renewable resources, at present the recycling technology for fly and bottom ashes is not mature, and they are mostly disposed of in situ landfills or in open piles, taking up a lot of land resources and harmful to the environment. Many previous studies have focused on the comprehensive utilization and environmental management of ashes. As shown in **Fig.1-22**, several works have been conducted to incorporate these by-products in several applications, including construction and ceramic industry, geopolymeric materials (Korniejenko et al., 2016; Ramagiri & Kar, 2021), wastewater treatment, soil amelioration, catalysis, metals recovery (H. Zhou et al., 2022).

The environmental and health impacts of the inadequate disposal of incineration by-products, contributed significantly in the increase of public awareness towards sustainable incineration industry through the transformation of ashes into wealth. Several solutions were proposed by the scientific community to keep these by-products in use and avoid their harmfulness. **Table 1-4** presented the advantages and limitations of each application according to the literature.

Table 1-4. The advantages and limitations ahead of incineration by-products recycling reported in the literature.

Recycling methods	Advantages	Limitations	References
<b>Ceramic industry</b>	<ol style="list-style-type: none"> <li>1. Ceramic production with incineration by-products provides great mechanical properties, resistance to water adsorption, and stability over time.</li> <li>2. Transformation of the chemical and physical properties of ashes by sintering leads to advantages over encapsulation techniques using cementitious binders.</li> </ol>	<ol style="list-style-type: none"> <li>1. Ceramic production requires elevated temperatures for firing which has associated costs.</li> <li>2. The iron oxides containing in BA have a negative effect on the thermal expansion coefficient of the product.</li> </ol>	<p>(S. Wang et al., 2014)</p> <p>(Q. Yuan et al., 2022)</p>
<b>Construction materials (cementitious and geopolymer materials)</b>	<ol style="list-style-type: none"> <li>1. Partial replacement of Portland cement feedstocks with ashes enhances the strength, durability, and micro-structural features of concrete.</li> <li>2. The promotion of cleaner production by reducing greenhouse gas emission and saving natural river sand during the concrete production process.</li> </ol>	<ol style="list-style-type: none"> <li>1. The properties of ashes varied, depending on the type and source of coal, along with their operating conditions.</li> <li>2. The concretes produced with the bottom ash are susceptible to water loss by bleeding in the fresh state.</li> </ol>	<p>(Korniejenko et al., 2016)</p> <p>(Wongsa et al., 2018)</p>
<b>Catalysis</b>	<ol style="list-style-type: none"> <li>1. ashes can be a bed catalyst due to the presence of silicon oxides.</li> <li>2. The cheap price of CBA can reduce the overall energy production cost price.</li> </ol>	<ol style="list-style-type: none"> <li>1. The large-scale application of CBA as a catalyst is still in its infancy.</li> <li>2. The generation of wastewater, and gases during the process</li> </ol>	<p>(W. Chen et al., 2022)</p> <p>(Czuma et al., 2022)</p>

<b>Soil amelioration</b>	1. CBA improves soil structure, buffers pH, and acts as a substrate for the propagation of microorganisms.	1. Lead to a rapid increase in soil pH if the CBA is used at inappropriate rates.	(Won et al., 2020)
	2. The release of several elements from CBA into the soil can benefit plant growth and crop yield.		(Manns & Martin, 2018)
	3. Heavy metal immobilization in contaminated soils can be achieved.		
<b>Materials synthesis</b>	1. Potential feedstocks used in many fields.	1. Most studies have been done to date that is restricted at the laboratory scale.	(Rashidi & Yusup, 2016)
		2. This option also consumes a large amount of reagent.	
<b>Wastewater treatment</b>	1. Easily modified by several modification methods to develop CBA-based adsorbents.	1. Powder-form of ashes is difficult to collect from contaminant water.	(Mushtaq et al., 2019)
			(S. Wang et al., 2005)

## 1.10 Discussion and conclusion

The huge volume of waste generated worldwide, the toxic content, and their persistence in the environment after usage, enhance the obligation to establish strategies for efficient disposal to prevent its harmful effect if managed improperly through landfilling and incineration, both techniques are inefficient and unsustainable due to economic and environmental concerns. Incineration by-products and discarded cigarette butts (CBs) are one of the dangerous wastes which attracted the attention of the scientific community and stockholders. This chapter reviewed the regulations governing waste management in Morocco, the leachate generation and severity and the impact of emissions from landfills and open dumpsites and the factors influencing on their availability and dangerousness on soils and water resources. Then, a summary review concerning the impact of incineration by-products and discarded cigarette butts (CBs) was highlighted based on previous works published in the literature. Finally, the possible technologies and methods on the valorization of these wastes and examined the viability of the research conducted was discussed as depicted in Tables 1-3 and 1-4. In summary, the following conclusions have been derived from this investigation:

- Landfills and open dumpsites lead to the emissions of dangerous elements, such as heavy metal(oid)s and a deeply control must be continuously conducted to avoid the propagation of pollution and the possible damages on human health and the whole ecosystem.
- The development of recycling and recovery methods is an urgent necessity for decisions makers and scientific community.

## **Chapter II: Ecotoxicological and pre-remedial risk assessment of heavy metal(oid)s in municipal solid wastes dumpsite impacted soil in Morocco**

### **(A case study in Benguerir and Oum Azza)**

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2- Long term impact of landfilling and intensive agriculture on the quality of soils and human health using PMF receptor model, PCA and MCS - *Under review.*

#### **Highlights:**

- Levels of Pb, Cd, Cu, Zn, Ni, As, Cr and Fe in soils and subsequent health risk were evaluated around the Benguerir' open dumpsite and Oum Azza landfill site.
- The concentrations of all examined metal(oid)s exceeded their geochemical background values.
- The pollution indices revealed a significant impact of the two landfills on the adjacent ecosystem.
- The human health risk was appraised using the deterministic method proposed by the USEPA, Monte Carlo simulation (MCS) and sensitivity analysis.
- Carcinogenic and non-carcinogenic health risk for children was higher compared to adults.
- Urgent intervention is required to avoid any potential health risk for population living near the studied area.

## **Chapter II: Ecotoxicological and pre-remedial risk assessment of heavy metals in municipal solid wastes dumpsite impacted soil in Morocco (A case study in Benguerir and Oum Azza)**

### **General Chapter Summary**

Studies related to heavy metal(oid)s pollution and subsequent health risk assessment adjacent to landfills and open dumpsites region is indispensable since these sites are a convergence point for hazardous elements which have adverse impacts on the soil and subsoil in the surrounding area with a threat to human health and ecosystem. In this view, assessing the spatial distribution of heavy metal(oid)s, and evaluating their associated hazards on public health in the areas surrounding open dumpsites and landfills in Morocco using pollution indicators, multivariate statistics, and potential human risk assessment through Monte Carlo simulation approach are the main objectives of the current work. Human and environmental impacts of unlined and engineered municipal solid waste landfills in two different districts located in Benguerir and Oum Azza, Morocco were chosen as a case study. The results of this investigation indicated that among 8 potentially toxic elements that were analyzed, As, Cd, Pb and Zn exhibited considerably high concentrations in examined surface soils and leachate. In addition, the average concentrations of Zn, Cd, Fe, Cu, Ni, Pb, As and Cr were well above the local geochemical background. This enrichment of soils by heavy metals and metalloids was confirmed through the analysis of available fractions using DTPA and  $\text{CaCl}_2$ . The application of pollution indices (Geo-accumulation index, Pollution Load Index and Nemerow indice) demonstrated a notable influence of landfilling on soils quality of its adjacent area with a significant ecological risk, especially for the open dumpsite of Benguerir. For example, a moderate to high contamination poly-metallic level was observed through the use of pollution load index (average value=1.84), owing especially to the enrichment of these soils by Cd and Pb. Multivariate statistical analysis showed that the examined metal(oid)s mainly originated from anthropogenic sources related to disposing of municipal solid wastes and agricultural activities. The deterministic and probabilistic risk assessment showed that the non-carcinogenic for all metal(oid)s and carcinogenic risk values were above the acceptable risk range and could threaten the health of the local community living near the landfill. This pre-remedial assessment provides useful tools and guidelines, to propose the appropriate remediation technique for this kind of open dumpsites and landfills.

**Keywords:** Trace metal(oid)s, Montecarlo simulation, human health risk assessment, soil pollution indices.

## **2.1 Introduction**

The fast-growing of industrial activities and unplanned urbanization is associated with an abnormal increase of the quantity of municipal solid wastes (MSW), and its proper management for building sustainable cities become one of the important political, environmental and social issues. Hence, numerous previous studies focus on better management of wastes practices by proposing sustainable approaches, such as: recycling and composting (Doaemo et al., 2021). However, landfilling remains the most commonly used solution worldwide (Kapelewska, Kotowska, Karpi, et al., 2019). Thus, the researchers around the world are seriously concerned about the possible effect of landfills.

Decomposition of wastes in landfills leads to the formation of several dangerous emissions, such as aerosols, leachate and gases (Kapelewska, Kotowska, Karpi, et al., 2019). Leachate is an unavoidable end product of landfilling, it is considered as one of the most challenging concerns resulting from improper waste management (Ward et al., 2005), as it may greatly influence the local ecosystem (e.g., water, soil, and human health) (Mor et al., 2006) through the release of a myriad of pollutants such as : Polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs) and heavy metal(oid)s ( cadmium, zinc, lead, chromium, copper, iron...etc.). For that reason, studies on the level of contaminations caused by open dumping sites especially due to the leachate migration are merely important.

Landfilling practice is unexceptional especially in developing countries like Morocco, where the unlined landfills in this country showed an alarming threat to the environment and human health. These sites (unlined landfills/uncontrolled landfills) are well known for the severe deterioration impacts on the human health and natural environment compared to sanitary and engineered landfills (Ali et al., 2019; Hussein et al., 2019; Mishra et al., 2019).

According to the report of the Ministry of Energy Transition and Sustainable Development in Morocco, the annual generation of wastes in this rapidly developing country are approximately 6.85 million tons, with a footprint of 0.76 kg per capita per day. Nonetheless, effective management of wastes remains an alarming challenge not only in Morocco but also for most developing and under-developed countries. Despite the existence of governmental policies, regulations, and numerous efforts of decision makers, the improper waste management is still a serious problem. There are more than 300 informal landfills where wastes are disposed of directly on the ground soil without insulation and protection systems. As stated above landfills are a common source of significant quantities of toxic elements, such as heavy metals, which can pose several impacts on its surrounding environment (Chantou et al., 2013). Unlike organic matter, these toxic pollutants are not biodegradable (Huang et al., 2007) and their residual time

in the soil can exceed thousands of years (C. Liu et al., 2013). Heavy metals can leach from the landfill if not managed appropriately, and can cause adverse effects to both human health and ecological sustainability (Oves et al., 2012; Wan et al., 2022).

In recent years, there have been published several studies about the contamination status of metals in the soils within the vicinity of landfills in many regions of the world (Ali et al., 2019; Doaemo et al., 2021; Essien et al., 2019; Kasassi et al., 2008; Kouame et al., 2006; Krčmar et al., 2018; Reyes-López et al., 2008; X. Wang et al., 2020). Due to gas emission (CO<sub>2</sub>, CH<sub>4</sub>...), and lack of any mechanism to treat generated leachate loaded by various contaminants. Nevertheless, to date there is no comprehensive study has been performed on the pollution status, human health and ecological risks associated with MSW dumpsites in most of Moroccan urban areas sufficient to measure the effectiveness of the MSW management plan and provide useful information for making decisions on adequate remediation solution of impacted soils. Also, based on available literature there are a few studies in which a comparison between the available and total fraction of heavy metals was carried out using DPTA (Rezapour et al., 2018) and most of the existing studies focus on comparing results with existing standards without taking into account the extent of pollution.

Thus, the main purposes of the current research are (1) to evaluate the extent of the total and available fractions of selected heavy metal(oid)s Pb, Zn, Ni, Cu, Cr, Cd, As and Fe in surface soils in the vicinity of two kinds of landfills (*Benguerir open dumpsite and Oum Azza landfill were chosen as a case study in the current investigation*), (2) assess the levels of soil contamination by comparing the background and control values of heavy metals in soil with the leachate/wastes impacted soil, (3) To examine the environmental impacts of the landfill area in more detail, specific indices; geo-accumulation index (I<sub>geo</sub>), pollution load index (PLI), enrichment factor (EF), potential ecological risk index (PERI), and Nemerow index (PIN) were performed. In addition, multivariate statistical analysis (correlation analysis, PCA, HCA) was performed to identify the feasible sources of heavy metals contamination and its spatial distribution. Also, the human health risks associated with the heavy metal(oid) pollutants, (*carcinogenic and non-carcinogenic risks*) were assessed using the Environmental Protection Agency' (USEPA) model and Monte Carlo simulation (MCS) approach. The results of this pre-remedial assessment provide insights into the state of the soil environment surrounding landfills, and present a supporting reference for future trace metal(oid)s studies at landfills of similar characteristics and invaluable tools and guidelines for decision-makers to design the appropriate approaches to deal with the huge quantities of waste generated.

## 2.2 Material and methods

For the purpose of the present study, the following methodological approach is followed.

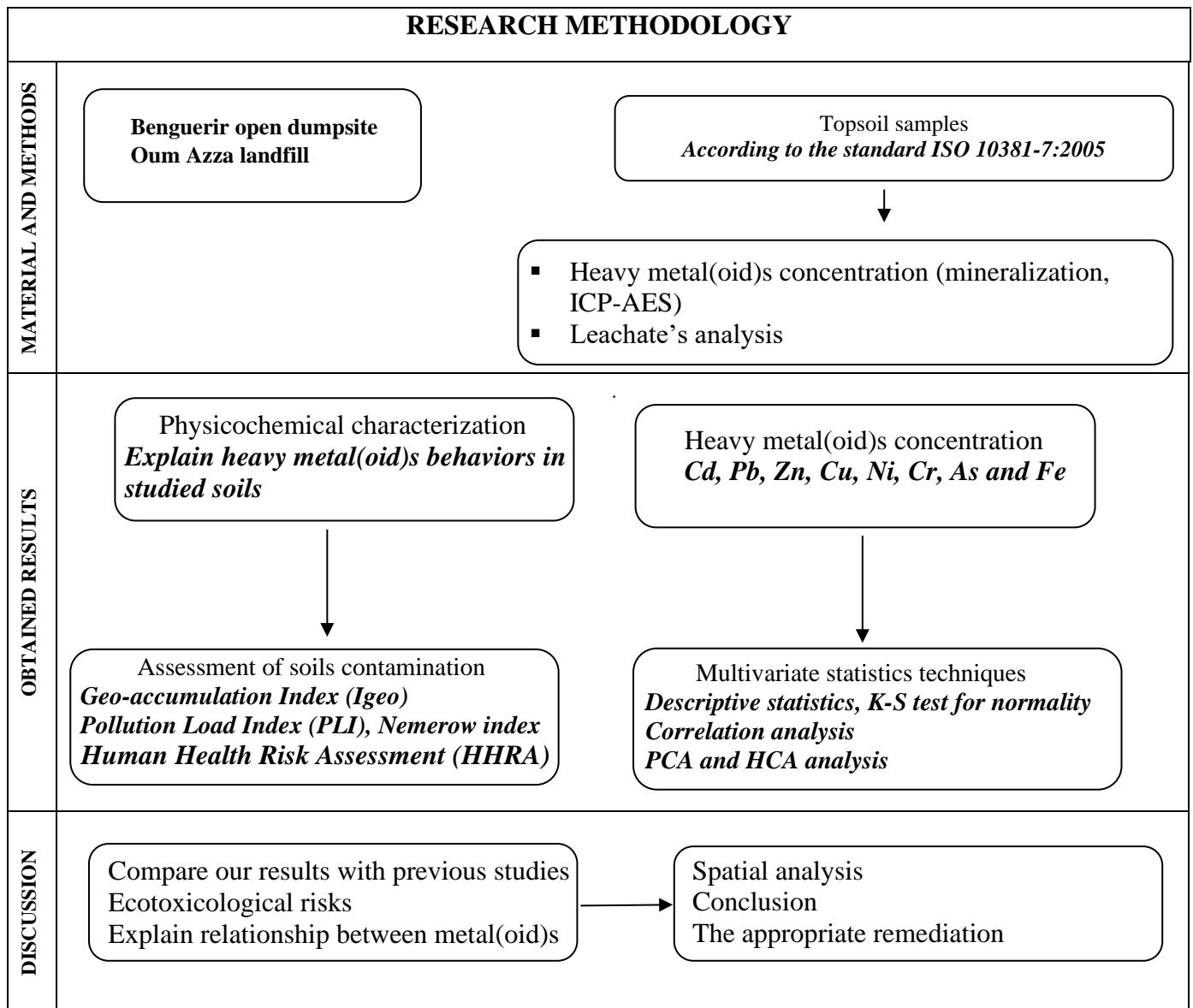


Figure 2-1. Methodological approach used in the current study

### 2.2.1 Study area

The examined study area is geographically located in the municipality of *Oum Azza* (33°52'50.87"N; 6°47'8.55"O) in the northwest region of central Morocco. Between 1994 and 2004, the population of the municipality increased from 8204 to 10530 inhabitants. The study area and its surrounding are characterized by the presence of one of the biggest Moroccan landfills for the disposal of 2100 tons solid waste per day and intense agricultural activities. The study area falls under arid regions with an annual average precipitation of 548 mm and an average temperature ranged from 7.6 and 28.1 °C, with the highest temperature in August and the lowest in January and a mean altitude of 170 m above sea level. The primary activity of

livelihood is agriculture. The geological and hydrogeological conditions in the study area are depicted in *Appendix A*.

The second study open dumpsite is located in *Benguerir city*, it lies in the longitude of  $7^{\circ} 54' 59.12'' O$  and latitude  $32^{\circ} 13' 56.92'' N$ , according to the UTM system, at an elevation of 450 m above the sea. This region has a semi-arid climate with a hot summer and a relatively dry winter, with average annual temperatures and rainfall of  $20^{\circ} C$  and 252 mm, respectively. The study area is characterized by average annual humidity rates varying between 47 and 54.4. it covers an area of about 8 Ha and it is 1.2 km far from the nearest residential area, it is surrounded by agricultural land with scattered houses, receives an average of 34 000 tons of wastes annually. The dumpsite is not equipped with a collector process and basin to stock leachate, waste was disposed of without being covered or protected, there was no insulation system to prevent leachate leakage. The deposition of waste on this site began in 1994 and will continue until the inauguration of a new sanitary landfill. In geological terms, the study area consists of clay, this impermeable layer plays an important role in protecting the aquifer from leachate infiltration. The topography of this landfill gently slopes towards the south-west to the north-east. As the dumps are not controlled, they have no leachate treatment plant, no degassing system and no barrier against windblown waste, furthermore environmentally damaging emissions escape freely into the environment. In particular, methane, a gas that is relevant to the greenhouse effect and 25 times more harmful than carbon dioxide, escapes freely into the atmosphere. On the other hand, after burial, the waste is not covered by soil or building materials, which explains the odors caused by the landfill. The location maps of the study area and geographic coordinates of examined samples in Oum Azza and Benguerir are presented in **Figures. 2-2** and **2-3**, respectively.

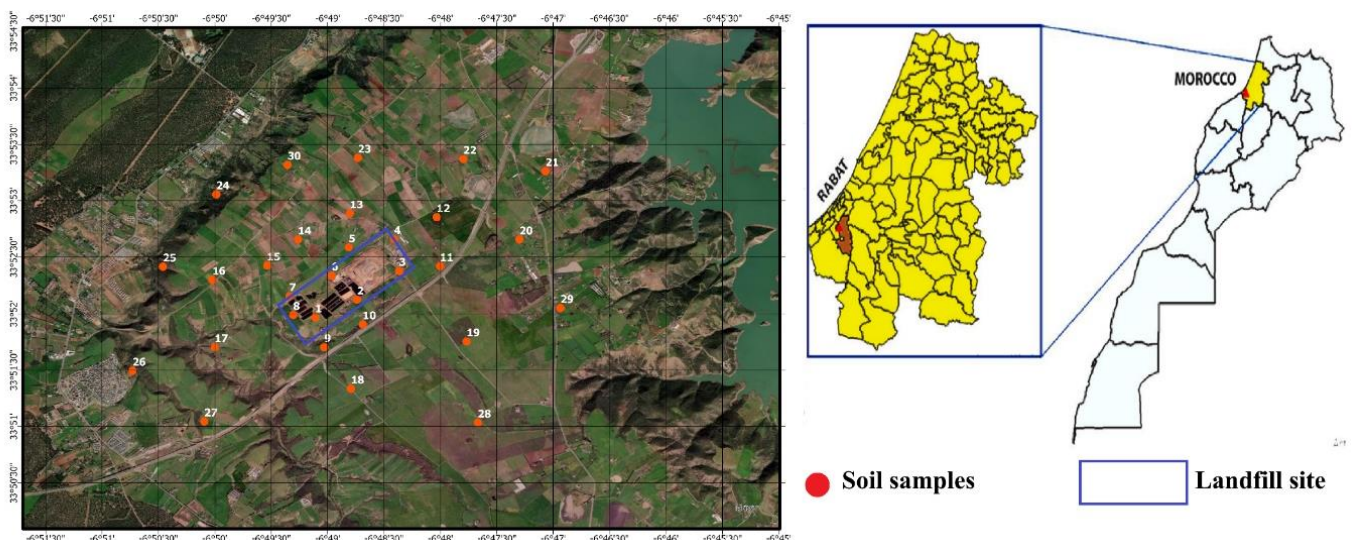


Figure 2-2. Study area map showing soils sampling location around Oum Azza landfill site, Morocco

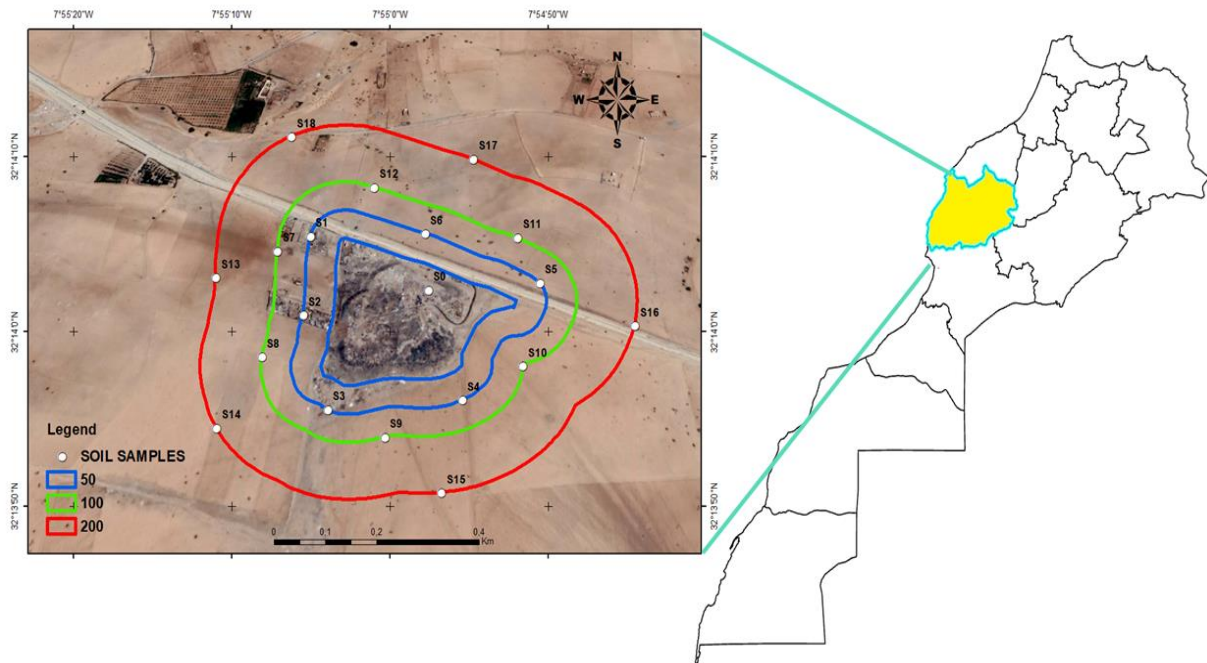


Figure 2-3. Study area map showing soils sampling location around Benguerir' open dumpsite, Morocco.



Figure 2-4. The configuration of the lining system of Oum Azza' landfill cells and lagoons.



Figure 2-5. Pictures showed the situation in Benguerir' open dumpsite, Morocco.

### **2.2.2 Sampling process and analysis of soil samples**

In order to assess the potential risks of trace metal(oid)s pollution in and around the selected study area due to the discharging of leachate from the examined landfills and the intensive use of pesticides and fertilizers. A total of 30 and 19 topsoil samples (5–20 cm depth from the surface) around Oum Azza landfill and Benguerir' open dumpsite, respectively were extensively collected using clean stainless-steel trowel. At each sampling site, 4 subsamples within a square of 1m<sup>2</sup> were collected and mixed thoroughly to obtain a representative composite soil sample (Varol,2021a). Then packed into clean polyethylene bags and transported immediately to the laboratory in ice-box for further analysis. During the sampling, the bulky debris, plant residues, and stones at each sampling point were removed manually (Essien et al., 2019). The depth (5–20 cm) was chosen because is very useful to assess the first receptor layer (recent material deposit), which can play an important role in the release of contaminated particles from the soil.

Once in the laboratory, the collected soil samples were air-dried at room temperature, then they were sorted through a 2-mm sieve using vibrating stainless sieves, Then, they were pulverized manually using a mortar and sieved through a 63 µm sieve. For determination of the total fraction of TMs (Cd, Ni, Cu, Zn, Fe, Pb, As, and Cr) content in soils and leachates, the finely powdered soil samples were subjected to wet digestion method using Aqua Regia (a mixture of hydrochloric acid (35%) and nitric acid (65%) in a molar ratio of 3:1) as described by the European standard NF EN ISO 13346 (AFNOR, 2000). Subsequently, 2 g of dried soil sample was digested with aqua regia using DK6 heating digester from VELP SCIENTIFICA until obtaining a high degree of clarity (Bouzekri et al., 2019). While, the bioavailable fraction for trace metal(oid)s was determined by mixing 10 g of examined soil samples with 20 ml of 0.01 CaCl<sub>2</sub> for Pb and 0.005 DTPA (diethylene triamine penta-acetic acid) for other metal(oid)s (Fadili et al., 2022), then the digested solution was filtered through Whatman No.42 filter paper and diluted to the required volume using ultrapure water. Metal(oid)s concentration was analyzed using an inductively coupled plasma- atomic emission spectrometer (ICP-AES, Brand Horiba Jobin Yvon, type Ultima Expert). Analyses were triplicated to guarantee the precision and maintain the quality of the extraction method (Essien et al., 2019), and only if the relative standard deviation (RSD) for three replicates of each sample was less than 5%, the measurement was retained and reported in the current paper.



Figure 2-6. Surface soil samples examined in the current thesis.

### 2.2.3 Quality assurance and quality control (QA/QC)

To avoid any source of contamination, all glassware and plastic vials were adequately washed and rinsed using 1 % nitric acid solution ( $\text{HNO}_3$ ) and ultrapure water. The maintain the quality and accuracy of the extraction method and analytical measurements were ensured with the use of certified reference material (CRM) (brand CARLO ERBA, Ref.505233), duplicates and method blanks. The recoveries of TMs in the CRM ranged between 98% and 99.5%. The limit of detection for all heavy metal(oid)s in calibrated method was 0.001 mg/kg.

### 2.2.4 Pollution indices

An integrated approach using different indicators and factors (Geo-accumulation index, Nemerow index, Enrichment factor and Pollution load index) were computed simultaneously for various sampling sites and metal(oid)s, in order to differentiate sources and status of pollution in a detailed way. Classification of all used indices are presented in **Table 2-1**. Uncontaminated local soil located at 3 km from the studied area with similar mineralogical and textural properties of examined soils, was collected and selected as lithogenic local background for each of the indices used in this paper, the concentration of metal(oid)s (mg/kg dw) at these stations is presented in **table 2-2**.

Table 2-1. grading methods of  $I_{\text{geo}}$ , PLI, PERI, PIN and EF.

Class	$I_{\text{geo}}$	PLI	PERI	EF
1	$I_{\text{geo}} \leq 0$ unpolluted	PLI < 0 low level	$\leq 150$ Low risk	EF $\leq 1$ no enrichment
2	$0 < I_{\text{geo}} < 1$ unpolluted to moderately polluted	$1 < \text{PLI} < 2$ moderate level	$150 < \text{PER} \leq 300$ Moderate risk	$1 < \text{EF} \leq 3$ minor enrichment
3	$1 < I_{\text{geo}} < 2$ moderately polluted to heavily polluted	$2 < \text{PLI} < 3$ High level	$300 < \text{PER} < 600$ Considerable risk	$3 < \text{EF} \leq 5$ moderate enrichment
4	$2 < I_{\text{geo}} < 3$ moderately polluted	PLI > 3 Extremely high level	$\geq 600$ High risk	$5 < \text{EF} \leq 10$ moderate to severe enrichment
5	$3 < I_{\text{geo}} < 4$ heavily polluted			$10 < \text{EF} \leq 25$ severe enrichment
6	$4 < I_{\text{geo}} < 5$ heavily polluted-extremely polluted			$25 < \text{EF} \leq 50$ very severe enrichment
7	$I_{\text{geo}} \geq 5$ Extremely polluted			EF > 50 extremely severe enrichment

Table 2-2. Concentrations of geochemical background soils in mg/ kg dry weight.

Metal(oid)s	Cd	Pb	As	Cr	Ni	Cu	Zn	Fe
Benguerir background	0.20	5.41	1.20	19.70	6.40	10.30	32.00	208.75
Oum azza background	0.30	9.50	2.50	12	14.30	3.50	26.50	6054.5

#### 2.2.4.1 Geo-accumulation index (Igeo)

The geo-accumulation index (Igeo) was proposed by Muller. (1969), and has been mainly used to measure and evaluate soil contamination by trace elements (Adimalla & Wang, 2018). The Geo-accumulation Index allows the assessment of contamination by comparing the current and background levels. According to Muller. (1969) this index is defined as follows:

$$I_{geo} = \log_2 [C_n / 1.5 B_n] \quad (2.1)$$

Where:  $C_n$  is the measured concentration of the element  $n$  in examined soil.  $B_n$  is the Geochemical background concentration value for the metal  $n$ , and 1.5 is the correction factor that permit to correct value variations due to lithogenic influences (Nekoeinia et al., 2016). Muller has defined seven classes of the geo-accumulation index (**Table 2-1**) ranging from uncontaminated to extremely contaminated ( $I_{geo} \geq 5$ ), respectively.

#### 2.2.4.2 Pollution load indice (PLI)

Pollution load index (PLI) integrates  $C_f$  values of all measured Trace metals and enables the assessment of the overall soil pollution at each site (Varol, Gündüz, & Ras, 2021). According to Tomlinson et al. (1980), the PLI is calculated as the geometric mean of  $C_f$  based on the following equation:

$$PLI = [C_{f_1} \times C_{f_2} \times C_{f_3} \times C_{f_4} \times \dots \times C_{f_n}]^{1/n} \quad (2.2)$$

Where:  $C_f$  (contamination factor) is applied to describe the level of contamination of a given toxic substance in the soil. According to (Hakanson, 1980) this parameter is computed by the following equation :  $C_f = \frac{C_{metal}}{C_{background}}$  , while  $n$  is the number of metals ( $n=8$ ).

#### 2.2.4.3 Nemerow index method (PIN)

The Nemerow was also employed in the current study, in order to conclude an overall about the degree of poly-metallic soil contamination, using the following equations:

$$P_i = \frac{C_i}{S_i} \quad (2.3)$$

$$PIN = \sqrt{\frac{\left(\frac{1}{n}\sum_{i=1}^n PI_i\right)^2 + [\max(PI)]^2}{2}} \quad (2.4)$$

where  $P_i$  is the single pollution index of metal (i) in the soil,  $C_i$  and  $S_i$  are the measured concentration and standard value of each metal (i), respectively. World Health Organization Guidelines for soils Quality is selected as the control standard for soil contamination.

#### 2.2.4.4 Enrichment factor (EF)

In order to evaluate comprehensively and distinct between geogenic and anthropogenic sources of TMs in the examined soil. The EF is calculated by normalization of metal concentration in the soil respect to the concentration of a reference element, using the following equation:

$$EF = \frac{(C_n/C_{ref})_{\text{Sample}}}{(C_n/C_{ref})_{\text{Background}}} \quad (2.5)$$

Where:  $C_n$  is the concentration of examined metal(oid) measured in every site,  $C_{ref}$  is the same concentration of the chosen reference metal. Fe was chosen as the reference metal due to its stability and abundance in soil (Varol et al., 2020). Chen et al. (2007) has defined six classes of Enrichment factor:  $EF < 1$ : no enrichment,  $3 < EF < 5$  : moderate enrichment,  $5 < EF < 10$  : moderate to severe enrichment,  $10 < EF < 25$ : severe enrichment,  $25 < EF < 50$ : very severe enrichment, and  $EF > 50$  means an extremely severe enrichment.

#### 2.2.4.5 Ecological risk assessment

Potential ecological risk factor ( $E_r$ ) and ecological risk index (PERI) were introduced by Hakanson (1980) to evaluate the potential single and multielement ecological risk based on the toxicity response and concentration of examined trace metals using the following equations:

$$E_r^i = T_r^i \times C_f^i \quad (2.6)$$

$$PERI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \times C_f^i \quad (2.7)$$

where  $T_r^i$  is the toxic-response factor of metal (i), they are 30, 10, 5, 5, 5, 2 and 1 for Cd, As, Cu, Pb, Ni, Cr and Zn, respectively (Varol et al., 2020). PERI enables the evaluation of the poly-metallic ecological threat at each sampling site by summing the  $E_r^i$  of every metal.

#### 2.2.5 human health risk appraisal using deterministic and probabilistic approach

Health risk due to the metals accumulation in examined soils is beneficial to assess the probability of negative health effects on local residents who are exposed to it. Generally speaking, soil with high level of contaminants may pose adverse health risks to the human beings through inhalation, dermal contact and accidental ingestion pathways. Therefore, in the current study, carcinogenic and non-carcinogenic risks were calculated for residential receptors

(children, adults, males) based on the method developed by the United States Environmental Protection Agency for the health risk appraisal (USEPA, 2005).

### 2.2.5.1 Exposure assessment

The assessment of long-time exposure was performed by calculating the Chronic Daily Intake (CDI: mg/kg/day) of each of the selected metals and considering the possible exposure routes mentioned above, using the below-stated Eqs. (8)-(10):

$$CDI_{\text{ing-soil}} = \left[ \frac{Ci \times \text{IngR} \times FC \times EF \times ED}{ABW \times AT} \right] \quad (2.8)$$

$$CDI_{\text{inh-soil}} = \left[ \frac{Ci \times \text{InhR} \times EF \times ED}{PEF \times ABW \times AT} \right] \quad (2.9)$$

$$CDI_{\text{der-soil}} = \left[ \frac{Ci \times SA \times FC \times AF \times ABS \times EF \times ED}{ABW \times AT} \right] \quad (2.10)$$

where,  $C_{\text{soil}}$  is the concentration of metals in soil ( $\text{mg} \cdot \text{kg}^{-1}$ ), IngR and InhR are the ingestion and inhalation rate, respectively, EF (exposure frequency, day/ year), BW: body weight, ED (Exposure duration, AT (average time,  $ED \cdot EF$ ), SA (skin surface area,  $\text{cm}^2$ ), AF (skin adherence factor,  $\text{mg}/\text{cm}^2/\text{day}$ ), ABS (Dermal absorption factor, unitless),  $FC = 10^{-6}$ , PEF (Particle emission factor,  $\text{m}^3/\text{kg}$ ), Variables and parameters of exposure applied in risk assessment calculation are summarized in **Table 2-3**.

Table 2-3. The values of factors that used in the probabilistic carcinogenic and non-carcinogenic risk assessment

Parameters	Symbol	Units	Children	Adults	Distribution	References
Heavy metal concentration	Csoil	mg/kg	Csoil $\pm$ SD	Csoil $\pm$ SD	Log-normal	This study
Ingestion rate	IngR	mg/day	200 $\pm$ 4	100 $\pm$ 1.7	Log-normal	(Fadili et al., 2022)
Inhalation rate	InhR	$\text{m}^3/\text{day}$	7.6 $\pm$ 2.39	20 $\pm$ 1.27	Log-normal	(Karimian et al., 2021)
Exposure frequency	EF	day/year	350 (180, 365)	350 (180, 365)	Triangular	(Karimian et al., 2021)
Exposure duration	ED	year	6 $\pm$ 2.39	30 $\pm$ 2.74	Log-normal	(Karimian et al., 2021)
Conversion factor	CF	kg/mg	$1 \times 10^{-6}$	$1 \times 10^{-6}$	Point	(Fadili et al., 2022)
Skin adherence factor	AF	$\text{mg}/\text{cm}^2/\text{day}$	0.2	0.07	Point	(Fadili et al., 2022)
Dermal absorption factor	ABS	unitless	$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	Point	(Fadili et al., 2022)
Exposed skin area	SA	$\text{cm}^2$	2800 $\pm$ 1171	5700 $\pm$ 440	Log-normal	(Karimian et al., 2021)
Particle emission factor	PE	$\text{m}^3/\text{kg}$	$1.36 \times 10^9$	$1.36 \times 10^9$	Point	(Fadili et al., 2022)
Average body weight	BW	kg	15 $\pm$ 1.5	70 $\pm$ 10.71	Log-normal	(Karimian et al., 2021)

### 2.2.5.2 Composite non-carcinogenic risk

In order to estimate the non-cancerous health risks associated with the measured Trace metals (TTMs), Hazard quotients was computed using the following equations:

$$HQ = \frac{CDI}{RfD} \quad (2.11)$$

$$HI = HQ_{ing} + HQ_{inh} + HQ_{derm} = \frac{CDI_{ing}}{RfD_{ing}} + \frac{CDI_{inh}}{RfD_{inh}} + \frac{CDI_{derm}}{RfD_{derm}} \quad (2.12)$$

$$THI = \sum_{j=1}^n HI_j \quad (2.13)$$

Hazard Quotient (HQ) is determined by calculating the ratio between CDI of potentially toxic elements in soil to the exposure reference dose (RfD) of a specific metal (mg/kg-day). The hazard index (HI) is the sum of HQs that represents the likely NCR induced by each metal, while the total hazard index (THI) measures overall health considering all TMs and various routes of contaminants penetration to human body.  $THI > 1$  indicates that metals exposure is likely to have adverse health effects; however,  $THI < 1$  indicates that there are no harmful health impacts (USEPA, 2005). Rfd were taken from the United States Integrated Risk Information System.

### 2.2.5.3 Composite carcinogenic risk

The cancer risk (CR) was calculated to determine the likelihood of cancer developing as a result of lifetime metal exposure. It worth nothing that Carcinogenic health risks were calculated for only Pb, Cd, Cr, Ni and As for which carcinogenic slope factors are available. The Cancer Risk (CR) was estimated using Eqs. (14)-(15)

$$ILCR (\text{Incremental Lifetime Cancer Risk}) = CDI \times CSF \quad (2.14)$$

$$TCR (\text{Total cancer risk}) = \sum CR (\text{ingestion} + \text{inhalation} + \text{dermal}) \quad (2.15)$$

The corresponding values of CSF including As, Ni, Pb, Cr and Cd are 1.5, 0.91, 0.0085, 0.5 and 6.3 mg/kg-day, respectively (Pirsahab et al., 2021). Then, the Total cancer risk (TCR) was computed by summing up the ILCR for all metals. If the CR and TCR are less than  $10^{-6}$ , the carcinogenic risk is considered insignificant or has no effect on the human body. While, values above  $10^{-4}$  suggest that there is a carcinogenic risk (Fadili et al., 2022). The reference values of RfD and CSF are shown in **Table 2-4**.

Table 2-4. Values of RfD (mg/kg/day) and CSF (per mg/kg/day) for examined metal(oid)s.

Parameters	Cd	Cr	As	Pb	Cu	Zn	Ni	Fe
<b>RfD for ingestion</b>	1.00E-03	3.00E-03	3.00E-04	3.50E-03	4.00E-02	3.00E-01	2.00E-02	7.00E-01
<b>RfD for dermal absorption</b>	1.00E-05	6.00E-05	1.23E-04	5.25E-04	1.20E-02	6.00E-02	5.40E-03	4.50E-02
<b>RfD for inhalation</b>	1.00E-05	2.86E-05	3.00E-04	3.50E-03	4.00E-02	3.00E-01	9.00E-05	2.20E-04
<b>CSF for ingestion</b>	3.80E+01	5.00E-01	1.50E+00	8.50E-03	-	-	8.40E-01	-
<b>CSF for dermal absorption</b>	3.80E+01	2.00E+00	3.66E+00	5.30E-04	-	-	8.40E-01	-
<b>CSF for inhalation</b>	6.30E+00	4.20E+01	1.51E+01	8.50E-03	-	-	8.40E-01	-

### 2.2.6 Montecarlo simulation & sensitivity analysis

There are numerous causes of variability and uncertainty when using the deterministic method for human risk appraisal. Variability and uncertainty of input parameters are attributed to the variation in values from person to person and the lack of complete understanding about a certain parameters. These limitations which could contribute to underestimate or overestimate the human risk (Rajasekhar et al., 2018). Hence, strengthening the understanding of the actual risk is required to conclude reliable outputs and allow decision-makers to take the right decision about mitigation measures. For these reasons Montecarlo simulation (what-if analysis) was conducted to calculate and simulate the human risk and minimize the uncertainty and variability of the deterministic approach with single-point variables (X. Gu et al., 2022). Meanwhile, the sensitivity analysis was employed to determine the most efficient input parameters in HHRA. Crystal Ball software version 11.1.2.4 (Oracle, USA) with  $10^4$  iterations and 95% confidence level was used to fit the probabilistic distribution of the THI and TCR considering the distribution of input variables presented in **Table 2-3** to obtain creditable risk outputs.

### 2.2.7 Statistical analyses

The data were first tested for normality using the Kolmogorov-Smirnov test ( $P < 0.05$ ). Because most of TTMs did not show normal distribution, the possible associations among them were assessed using non-parametric Spearman correlation test (Taati et al., 2020). The significance level is considered when  $p$  is  $< 0.05$ . In order to accomplish statistical analysis and obtain a reliable findings, all collected variables were subjected to normalization by computing their z-scores to avoid misclassification, because parameters have different units, it makes no sense to aggregate two values with distinct units (Jahin et al., 2020).

Multivariate statistical analyses (MSAs) including Factor Analysis (FA) was the most commonly used technique in environmental studies that involve the assessment of large datasets to ascertain sources of contamination (geogenic and/or anthropogenic). It is a dimension

reduction technique, widely used to transform complex data into many variables (PCs), and therefore make its interpretation easiest. The adequacy of the data for this analysis was done using Kaiser Meyer Olkin (KMO) and Bartlett's Sphericity tests (Fadili et al., 2022). In addition, HCA (Hierarchical Cluster Analysis) using Ward's method with squared Euclidean distance was also conducted to evaluate the effectiveness of assessment tools in grouping datasets, based on the similarities between examined variables. All statistical calculations used in the current thesis were performed using the statistical package for the social sciences (IBM SPSS software version 25.0) and XLSTAT software version 2014.5.03 from Addinsoft™.

## 2.3 Results and discussion

### 2.3.1 MSW composition

Waste samples were chosen from the studied landfills and collected in plastic bags, while the water content (moisture) of waste was carried out using the same procedure proposed by Ojuri et al. (2018). The hand-sorted of collected fresh waste, revealed that the composition of waste in Benguerir dumpsite (**Fig.2-7**) and Oum Azza landfill (**Fig.2-8**) was dominated by organic fraction (>65 %, composed mainly of food waste green waste, and other putrescible), followed by (>6 %) plastics, leather, and rubber (>6%), papers–cardboard (>6%), glass (>1.5%) and metals (1%). Like most developing countries, Moroccan waste is characterized by high moisture due to a high organic matter content. It should be noted that during our investigation, we observed the presence of a fairly large quantity of hazardous waste (e.g., electronic waste, tire waste, cigarette butts...) discarded around the open dumpsite of Benguerir without any treatment (**Fig.2-5**).

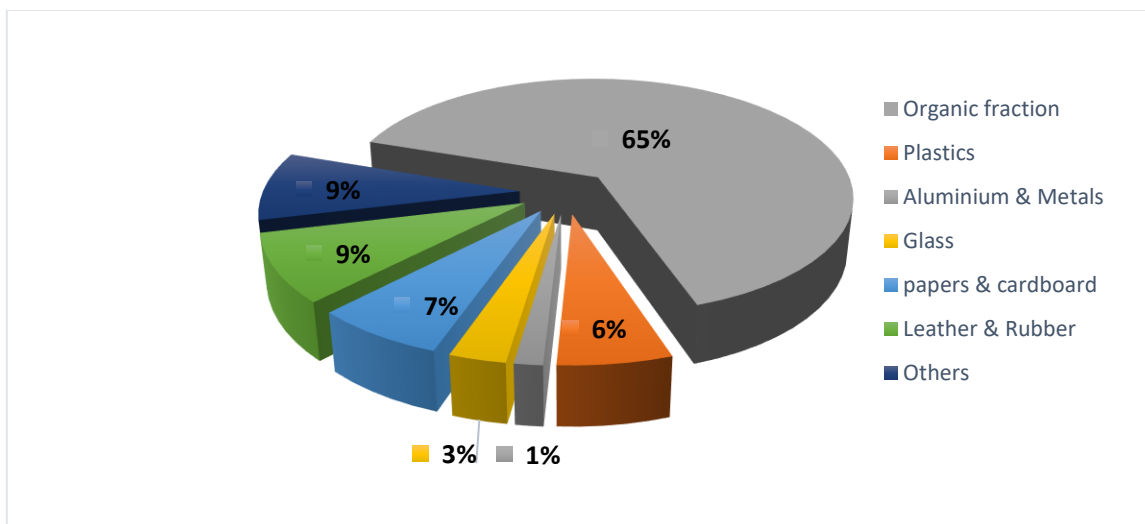


Figure 2-7. Municipal Solid Waste composition at Benguerir' open dumpsite.

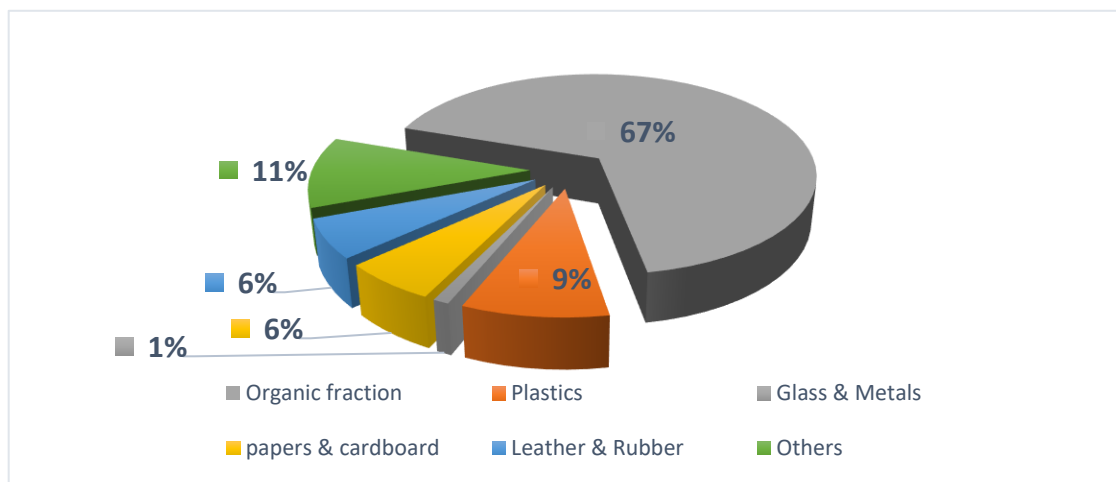


Figure 2-8. Municipal Solid Waste composition at Oum Azza' landfill.

## 2.3.2 Heavy metal(oid)s concentration in soil samples

### 2.3.2.1 Case study 1: Benguerir open dumpsite

The descriptive statistical results of the total and available fractions of heavy metal(oid)s (mg/kg dry weight) in the collected surface soils are presented in **Tables 2-5** and **Appendix B** respectively, including minimum, maximum, average, and standard deviation (*SD*). Across the sampling locations, the heavy metal(oid)s concentration impacted soil surrounding the landfill revealed large significant variation, as follows: 2.2–115.52 mg/kg for Pb, 2.50–54.50 mg/kg for Cu, 3.73–68.19 mg/kg for Cr, 7.92–190.50 mg/kg for Zn, 1.25–34.20 mg/kg for Ni, 0.36–6.80 mg/kg for Cd, As, 0.80–4.65 mg/kg for As and 0.22–0.85 g/kg for Fe. Furthermore, the mean values followed in the decreasing order of; Fe (406.27) > Zn (42.5) > Pb (22.01) > Cr (21.15) > Cu (13.32) > Ni (8.50) > As (3.02) > Cd (1.77).

Additionally, by comparing the average concentration of considered metal(oid)s with the reference value used in this study, it is observed that the amount of Pb, Cu, Cr, Zn, Ni, Cd, As, and Fe were 4.1, 1.3, 1.1, 1.3, 1.3, 8.8, 2.4 and 1.95 times higher, respectively, than their corresponding amounts measured for the control soil collected from ~3 km distance of the study area. Also, the high coefficient of variation reflected a fairly abnormal distribution of trace elements concentration around the dumpsite. Thus, the collected soils were seriously impacted by man-made activities connected with dumped wastes. It is noticeable that the concentrations of all metal(oid)s were found generally higher in examined soils collected from S0-S8 sites (**Fig.2-3**) compared to the other locations, suggesting that examined soils were locally impacted by TTMs, as well as the migration and distribution of these toxic elements around the landfill were not diffused widely, these findings were in accordance with physical and chemical

properties of soils discussed in our previous paper (Fadili et al., 2022), which enhanced the accumulation of metal(oid)s and limit their mobility.

Table 2-5. Descriptive statistics of heavy metals content around Benguerir open dumpsite (mg/ kg dw).

	Minimum	Maximum	Median	Mean	SD	K-S test
<b>Pb</b>	2.20	115.52	9.60	22.01	29.05	0.000
<b>Cu</b>	2.50	54.50	8.64	13.32	13.08	0.027
<b>Cr</b>	3.73	68.19	12.50	21.16	18.63	0.001
<b>Zn</b>	7.92	190.50	31.12	42.51	41.35	0.000
<b>Ni</b>	1.25	34.20	4.30	8.50	8.44	0.002
<b>Cd</b>	0.36	6.80	1.40	1.77	1.44	0.003
<b>As</b>	0.80	4.65	2.53	3.02	2.6	0.000
<b>Fe</b>	222.18	854.22	327.84	406.27	177.41	0.061

*SD: Standard deviation K-S test: Kolmogorov-Smirnov test*

The concentration of available metal(oid)s using DTPA for Pb, Cu, Cr, Zn, Ni, Cd, As, and Fe in the soils under the direct influence of the unformal landfill were found to be: 0.1–21.37, 0.1–10.29, 0.08–7.12, 0.98–23.52, 0.1–3.8, 0.09–1.35, 0.10–1.68 and 15.04–106.5 mg/kg, respectively. While, those of the geochemical background were, as follows: 0.08, 0.1, 0.06, 0.68, 0.1, 0.05, 0.09, and 13.57, respectively. Mismanagement practices of landfilling significantly increased all extractable–metal(oid)s regarding the background site in the decreasing order of Fe > As > Cd > Pb > Zn > Cr > Ni, which confirmed that studied soils were enriched by metal(oid)s, particularly in the stations with particular conditions (leakage of leachate, waste storage, open burning of tire waste...), similar results revealed the accumulation of metal(oid)s in the vicinity of MSW landfills under the influence of anthropogenic activities were discussed by Rezapour et al. (2018). Even with this redundancy, the results of this study have shown that soils within and around the dumpsite were below the permissible contamination level, set by the World Health Organization (WHO) as threshold values (in mg/kg dry weight), which are 2 for cadmium, 50 for Ni, 100 for lead and Cu, respectively, 150 for Cr, 300 for Zn, and 7000 for Fe (Essien et al., 2019). Heavy metal(oid)s concentration below recommended limits in surface soil might be related to continuous accumulation by plants and leaching down of metals into down soil profile (F. S. Tariq, 2021). However, only Cd and Pb with a proportion of 16.67% and 5.55%, respectively, were greater than their threshold values, which is consistent with previous works conducted by Rezapour et al. (2018) and Adamcová et al. (2017), who highlighted that the leakage of leachate from unformal landfills, was brought considerable enrichment of adjacent soils by Cd and Pb compared to other metals. For example, the highest concentration of Pb was observed in S0 (115.52 mg/kg) and S2 (80.20 mg/kg). Apparently, both of the samples are located near the dumpsite and are directly impacted by the leachate leakage.

The accumulation of metal(oid)s might lead to soil contamination and consequently their transfer to humans via the food chain.

### 2.3.2.2 Case study 2: Oum Azza landfill

A statistical summary of the measured metal(oid)s collected from the thirteen sampling sites is listed in **Table 2-6** and **Appendix C**. It is observed that the concentration of trace metal(oid)s varied significantly across the examined sampling sites, as follows (in  $\text{mg}\cdot\text{kg}^{-1}$  dw): 0.21–2.93 for Cd, 12.24–78.97 for Pb, 0.52–2.99 for As, 9.71–51.90 for Cr, 9.64–53.72 for Ni, 29.20–85.41 for Zn, and 5.67–6.58 g/kg for Fe. Among the detected TTMs, the average concentrations of Fe and Zn are the most, followed by Ni and Pb, and finally Cr, Cu, As, and Cd. Moreover, several TTMs (i.e., Pb, Cd, As, Cr, As, and Cu) had abnormal distribution in the studied area reflected by the observed high coefficient of variation (CV) values. The CV of total trace elements decreased in order; Cd (76.97%) > Pb (59.93%) > Cr (51.44%) > Cu (51.34%) > Ni (45.52%) > As (35.13%) > Zn (31.10%) > Fe (3.09%), the elevated coefficient of variation (CV) of these toxic elements implied that the anthropogenic activities in the study area have a significant effect on the spatial distribution and concentration of total trace metal(oid)s (TTMs) as stated previously by Kumar et al. (2022) and Islam et al. (2015) who explained this distribution as a result of anthropogenic activities which contributed to the enrichment of soils by these TTMs.

By comparing the average concentrations of TTMs with the background values, it is observed that the concentrations of Cd, Pb, As, Cr, Ni, Cu, Zn, and Fe were 2.96, 2.62, 2.91, 1.60, 1.78, 2.28, 1.85 and 1.02 times higher, respectively than their corresponding average background collected from ~ 5 km distance of the study area. More specifically, approximately 80%, 83%, 87%, 90%, 93%, 93%, 100%, and 100% of topsoil samples exceeded the corresponding geochemical background value for Cd, Cr, Cu, Ni, As, Fe, Zn, and Pb, respectively. Thus, local man-made activities including landfills, recycling center, the application of fertilizers and agrochemicals, traffic emissions, etc. brought a non-negligible amount of TTMs into the surface soils of the study area.

Table 2-6. Summary statistics of total metal(oid)s concentrations of surface soils in mg/ kg dry weight.

Metal(oid)s	Cd	Pb	As	Cr	Ni	Cu	Zn	Fe
<b>Minimum</b>	0.210	12.235	0.520	9.714	9.642	2.758	29.200	5671.500
<b>Maximum</b>	2.930	78.968	2.988	51.900	53.728	16.481	85.406	6583.000
<b>1st Quartile</b>	0.368	15.457	1.402	12.512	16.225	4.120	36.588	6072.500
<b>3rd Quartile</b>	0.929	25.198	2.182	23.625	31.519	11.114	63.193	6309.250
<b>Mean</b>	0.889	24.861	1.816	19.096	25.438	7.984	49.126	6183.317
<b>CV</b>	76.97%	59.93%	35.13%	51.44%	45.52%	51.34%	31.10%	3.09%
<b>K-S test</b>	<0.0001	<0.0001	0.050	<0.0001	0.009	0.033	0.026	0.050

*SD: standard deviation; CV: coefficient of variation; K-S test: Kolmogorov-Smirnov test.*

It is noticeable that the concentration of all metal(oid)s were found generally higher in examined soils collected from the sample sites, S1~S4, S6~S8, S10~S12, and S14~S15 were marked as the most polluted compared to other sites, suggesting that study soils were locally impacted by the synergic accumulation of toxic elements from the landfilling of municipal waste and the use of agricultural runoff. Overall, the Cd, Cu, Pb, and Zn concentrations decreased with increasing distance from the landfill, indicating that landfilling practices are the most important source of pollution in the study area.

The bioavailable fraction of metal(oid)s extracted using DTPA and CaCl<sub>2</sub> for Cd, Pb, As, Cr, Ni, Cu, Zn, and Fe were found to be; 0.03-0.44, 0.25-9.43, 0.013-0.42, 0.15-3.84, 0.25-2.64, 0.07-3.65, 0.84-3.61 and 19.10-73.25, respectively. While, those of the geochemical background were, as follows: 0.1, 0.035, 0.042, 0.10, 0.23, 0.07, 0.45, and 9.68, respectively. Thus, mismanagement of landfilling practices and agricultural activities significantly contributed to the increase of the extractable fraction of all metal(oid)s regarding the reference in the decreasing order of; Cd > Pb > As > Cu > Ni > Cr > Zn > Fe, indicating the high mobility and bioavailability of the majority of metal(oid)s across the study area (Liang et al., 2022).

### **2.3.2.3 Comparison of metal(oid)s concentrations**

A comparison between the measured metal(oid)s concentration in the collected surface soil samples from Benguerir' dumpsite and Oum Azza landfill with those from other dumpsites and sanitary landfill sites reported in previous studies around the world is presented in **Table 2-7**. The concentration of all selected metal(oid)s was found higher than those measured in Tunisian, Nigerian, and Greek landfills, respectively (Aydi, 2015; Essien et al., 2019; Kasassi et al., 2008). Similarly, the current findings were in accordance with those reported previously by Kouame et al. (2006) and Nhari et al. (2014). The difference in the concentration of metal(oid)s between the landfills suggests the influence of local conditions, such as the age of the dumpsite, climate, quantity of waste, etc., without forgetting that the operating system of the landfill remains the main factor behind the pollution level of soils.

The comparison between the measured TTMs concentrations in the examined surface soil samples with those from other agricultural sites highlighted that the amounts of As, Cr, Cu, and Pb were found below those measured in Harran Plain in Turkey (Varol et al., 2020), Isfahan city in Iran (Esmaili et al., 2014) and Benguerir in Morocco (Fadili et al., 2022). However, this difference is owing to the spatial heterogeneity in anthropogenic activities and soil properties in each region. It's important to note, that the comparison should take into account factors such as the type of soil, climate, and land use practices, among others.

Table 2-7. Comparison of metal(oid) concentrations with previous studies worldwide, and the WHO standard (mg/kg dry weight)

Station	Pb	Cu	Cr	Zn	Ni	Cd	Fe	Reference
Benguerir	2.20-115.52	2.50-54.50	3.73-68.19	7.92-190.50	1.25-34.20	0.36-6.80	222.18-854.22	This study
Oum Azza	12.23-78.96	2.75-16.48	9.71-51.90	29.20-85.41	9.64-53.72	0.21-2.93		This study
Moroccan landfill	62-656	1-11.5	52-76	63-68	47-62	N/A	N/A	(Nhari et al., 2014)
Ivoirian landfill	10.3-1500	20-369.7	27.7-125	18.6-1163.7	N/A	1-11.5	850-12500	(Kouame et al., 2006)
Tunisian landfill	1.8-13.2	0.1-1.7	34.4-109.9	7.6-76.8	4.6-39	0.3-1.2	N/A	(Aydi, 2015)
Greek landfill	3-93	8-356	4-172	6-344	6-64	0.5-19	N/A	(Kasassi et al., 2008)
Nigerian landfill	1.72-2.98	N/A	0.06-0.39	7.22-27.5	0.124-1.4	0.94-4.12	988.2-1411	(Essien et al., 2019)
WHO guidelines	100	100	150	300	50	2	7000	

N/A not available data

### 2.3.3 Pollution and ecological risk assessment of metal(oid)s

#### 2.3.3.1 Case study 1: Benguerir open dumpsite

To scale the pollution level in the area under investigation, the collected soils were evaluated using the geo-accumulation index based on their local geochemical background. Obtained results were summarized using a box plot diagram in **Fig.2-9-a**. The Igeo values for trace metals in sampling sites ranged widely from -2.99 to (Cr) to 4.50 (Cd), respectively. It can also be seen that the average Igeo values of the heavy metal(oid)s decrease in the following order: Cd (2.19) > Pb (0.56) > Fe (0.26) > Zn (-0.61) > Ni (-0.74) > Cu (-0.78) > Cr (1.03). According to the Igeo classifications given by Muller. (1969), Amongst the analyzed metals, it is observed that almost all sampling sites were considered as 'Unpolluted' by Cu, Zn, Ni, and Cr with Igeo values less than zero. Specifically, Cd and Pb were found to be the most contaminating metals, the pollution status dramatically ranged from "Moderately to Extremely polluted" and "Unpolluted to Moderately polluted" in different sampling sites by cadmium and lead, respectively. The above-mentioned results reflect an accumulation of metals originating from the bad exploitation of this dumpsite.

The enrichment factor (EF) was employed to identify the intensity of possible enrichment of soils by metals due to anthropogenic inputs, regarding collected reference soil samples (M. A. Hossen et al., 2021). The analysis of EFs results illustrated in **Fig.2-9-b** revealed minor enrichment by Zn, Ni, Cu, and Cr with an average value of less than one, and no significant differences were observed for these metals among the studied samples. On the contrary, Pb and Cd ranged from minor to severe enrichment according to the EF classification, elevated enrichment factors for all examined metals reflect strong effects of human inputs (Varol, Karakaya, et al., 2021) on the adjacent soils.

There are no industrial activities in the study area. Overall, soils under investigation were impacted and mainly enriched by metals originating from all kinds of waste dumped in the studied landfill. Also, it is remarkable that the values decrease considerably as one moves away from the landfill, confirming the limited mobility of metals and that the pollution is still concentrated in the first 100 meters.

PLI is another effective index employed to provide considerable details and allow the assessment of the poly-metallic contamination degree at each examined soil sample. The calculated PLI at each sampling site was presented in **Fig.2-10-a**. Obtained values of studied metals ranged from 0.51 to 5.66, with an average of 1.84. 11 samples (57.90 %) around the landfill ranged from moderately to extremely polluted by examined metals. Relatively higher PLI levels were observed among the sampling locations S0-S8 located in the first 100 m from the unformal landfill compared to other sites. Based on the results obtained using this index soil samples located at 200 m from the landfill were classified as unpolluted, with  $PLI < 1$  (PLI values varying from 0.63 to 0.96). Similar conclusions were highlighted by introducing the comprehensive PIN index for various sites and metals as shown in **Fig.2-10-b**. The soil pollution status nearby the landfill sites, was found to range from safe to heavily polluted by metals. Similar findings were reported by Rezapour et al. (2018) and Essien et al. (2019), who found higher pollution levels due to the leakage of leachate from uncontrolled municipal solid waste landfill in Iran and Nigeria, respectively. Indicating a strong impact of the landfills on its neighbors' soil quality.

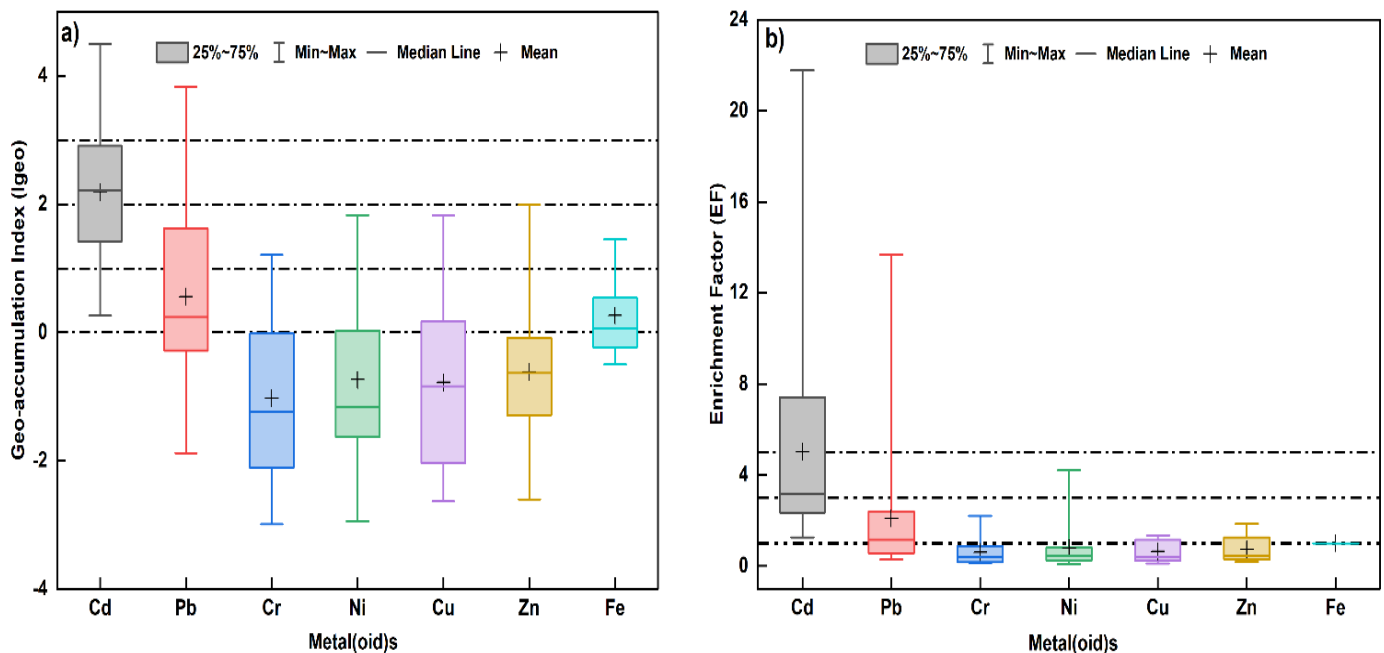


Figure 2-9. *a*) Geo-accumulation index, and *b*) Enrichment factor values for the total trace metal(oid)s in the surface soils Benguerir' open dumpsite.

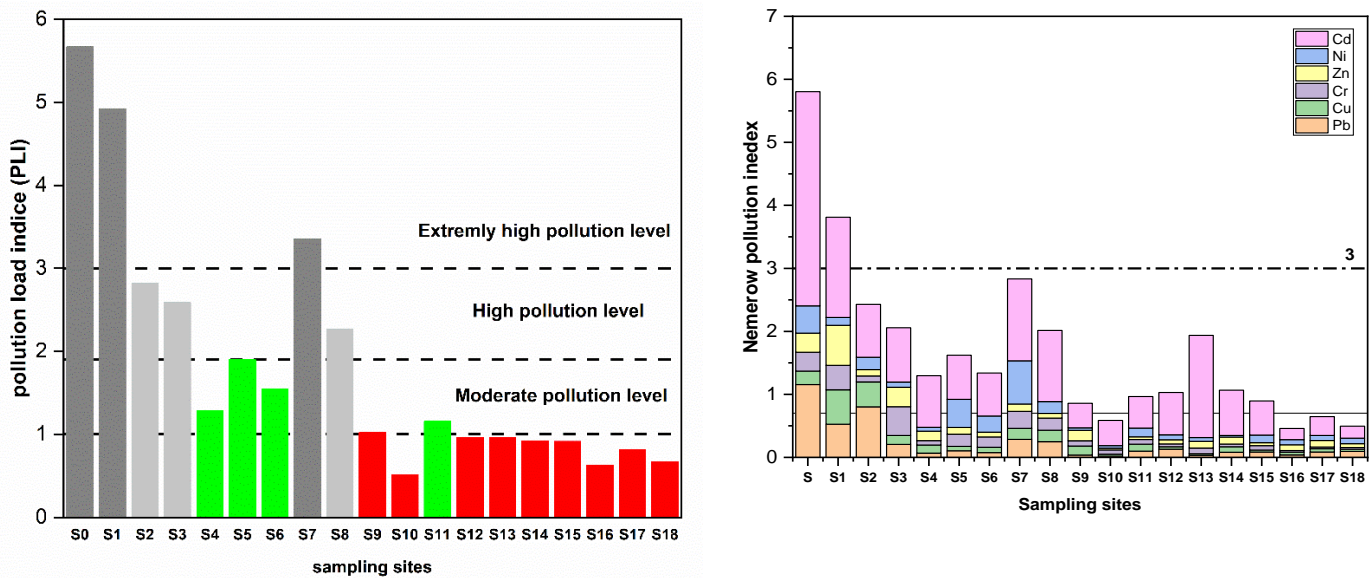


Figure 2-10. a) Pollution load index, and b) Nemerow index method values for the total trace metal(oid)s in the surface soils around Benguerir’ open dumpsite (from the left).

The individual ecological risk ( $E_i^r$ ) of each metal and Potential Ecological Risk Index values were employed to assess the potential hazard of the investigated landfill on its adjacent environment. The calculated values are presented in **Fig.2-11**. Zn, Cr, Cu, and Ni, showed a low potential ecological risk with  $E_i^r < 40$  in all studied samples. Conversely, Cd and Pb exhibited the highest  $E_i^r$  values in all examined soil samples. Concerning the potential ecological risk of trace elements was found to vary from 64.15 to 1161.52. Cd and Pb were the dominant contributors of PERI due to their abundance in collected soils and elevated toxicity. 14 samples ranged from moderate to high risk in the studied area based on the PERI classification (**Table 2-1**).

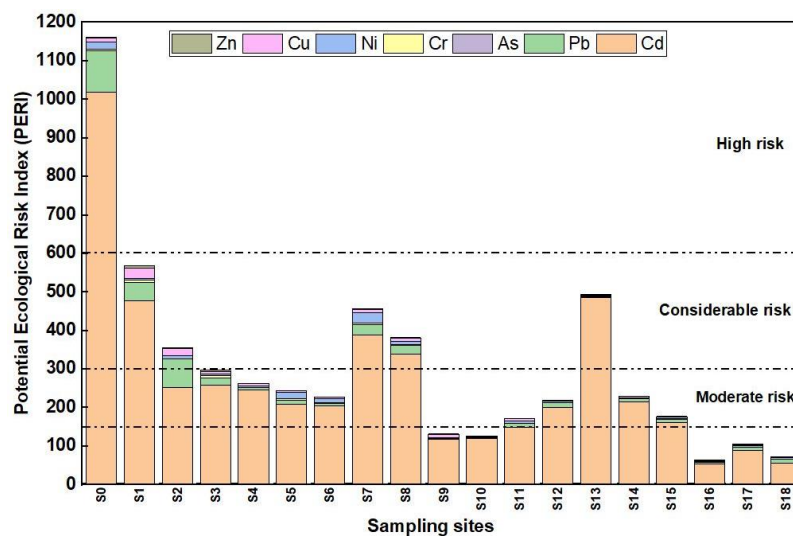


Figure 2-11. Potential Ecological Risk index (PERI) at each sampling site around Benguerir’ open dumpsite

These results suggested that the enrichment of Cd and Pb in studied soils contribute significantly to the high values of PERI which was higher than 312.49 reported by Iqbal et al.

(2019) previously. Above all, it is remarkable that the ecological risk values are very high in the first 100 m from the landfill, this is reflected that the migration and distribution of the toxic elements are still localized near the landfill and might pose a strong effect on public health and adjacent ecosystem. In summary, human activities should be kept at a safe distance from the landfill.

### 2.3.3.2 Case study 2: Oum Azza landfill

The Geo-accumulation Index (Igeo) was employed to analyze the contamination level in the area under investigation, the examined soils were assessed using the geo-accumulation index based on their local geochemical background. As shown in the box plot diagram (**Fig. 2-12-a**), the calculated values ranged widely across the sampling sites. The average values decreasing in the order of: As (0.84) > Cd (0.60) > Pb (0.59) > Cu (0.36) > Zn (0.21) > Ni (0.8) > Cr (-0.09) > Fe (-0.58). As, Cd and Pb exhibited the highest pollution level with an average value of 0.84, 0.60, and 0.59 respectively. Based on the Igeo classification given in **Table 2-1**, most of the sampling sites are uncontaminated to moderately polluted (Igeo less than 1). Only the samples located near the landfill, S1~S8 were found under moderate to heavily pollution by Cd, As, and Pb. In the same context, Taati et al. (2020) studied the agricultural soils of Arak industrial area (Iran) and also found that the surface soils were non-contaminated by Cu, Zn, and Ni with low Igeo values (less than 0). In contrast, As and Cd exhibited a moderate impact with an average Igeo of; 2.7 and 1.61, respectively. Shakil et al. (2023) and Adelopo et al. (2018) also reported an elevated level of geo-accumulation of Cd in surface soils around landfills and dumping sites, it is worth noting that exposure to higher levels of Cd could harm the kidneys, lungs and reproductive systems of adults, while it may impair learning, behavior, cognition and neuromotor skills.

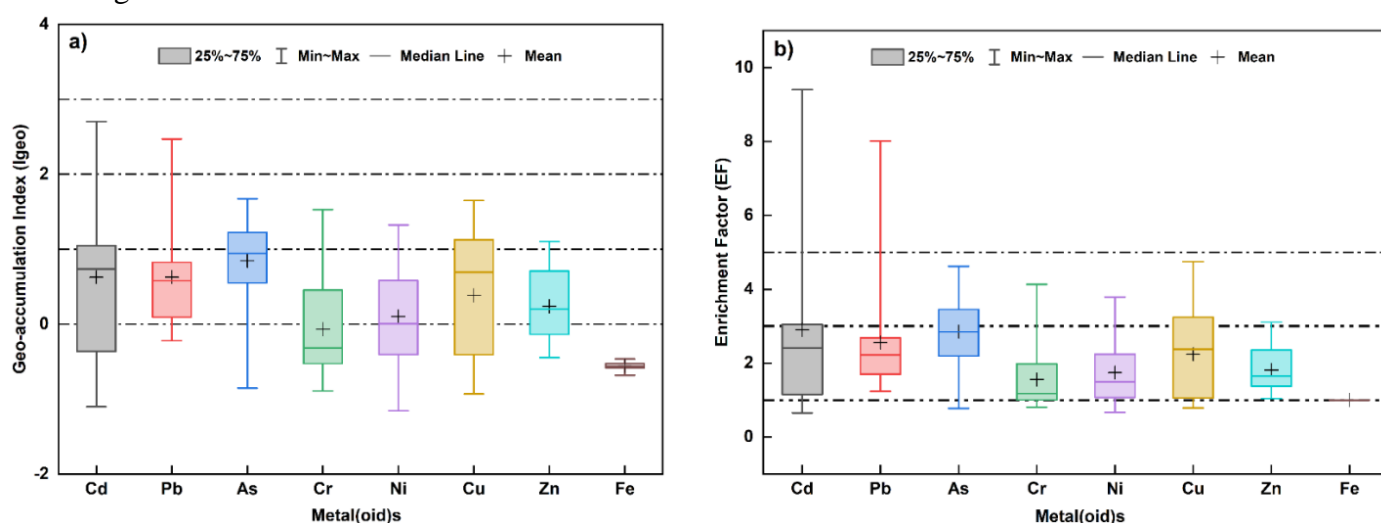


Figure 2-12. a) Geo-accumulation index, and b) Enrichment factor values for the total trace metal(oid)s in the surface soils around Oum Azza landfill.

The enrichment factors (EFs) of total trace metal(oid)s in surface soils have been calculated to differentiate elements originating from human activities and those from geogenic provenance and to assess the level of anthropogenic influence (Y. Jiang et al., 2017). As shown in **Fig.2-12-b**, the average EF values for Cd, Pb, As, Cr, Ni, Cu, and Zn were 2.84, 2.51, 2.80, 1.54, 1.72, 2.20, and 1.79, respectively, with the ranges of 0.65-9.40, 1.00-8.01, 0.78-4.62, 0.81-4.13, 0.67-3.78, 0.79-4.74 and 1.00-3.11, respectively. Based on the classification of EF depicted in **Table 2-1**, most of the samples are significantly enriched by the examined metal(oid)s in the studied soils with EF higher than one, and significant differences were observed among the studied samples, highlighting that an enrichment of surface soils by TTMs are likely to have occurred mainly from anthropogenic inputs. Amongst the examined metal(oid)s, Pb, Cd, As, and Cu displayed moderate enrichment which may be linked to the leakage of leachate from the landfill and the use of fertilizers and pesticides. Similarly, Adamcová et al. (2017) and Rezapour et al. (2018) found that the leakage from unformal landfills brought considerable enrichment of adjacent soils by Pb and Cd in comparison to other TTMs. Particularly, it is remarkable that the enrichment values decrease considerably as one moves away from the landfill, confirming the limited mobility of metals and that the pollution is still concentrated near the landfill.

Similarly, the poly-metallic pollution degree at each examined soil sample was assessed using the pollution load index as shown in **Fig 2-13-a**. The PLI values in the study area ranged from 1.02 to 3.39 with an average of 1.90. 40 % of the sampling displayed a PLI greater than 2, indicating overall that the area under investigation is moderately polluted with TTMs. The sample sites, S1~S4, S6~S8, S10~S12, and S14~S15 were marked as the most polluted compared to other sites, having PLI values ranging from 2.10 ~ 3.39. Cd, Pb, As and were mainly responsible for the major pollution in these sites. Contrary, moderate to lower soil pollution was observed for the rest of the examined sites.

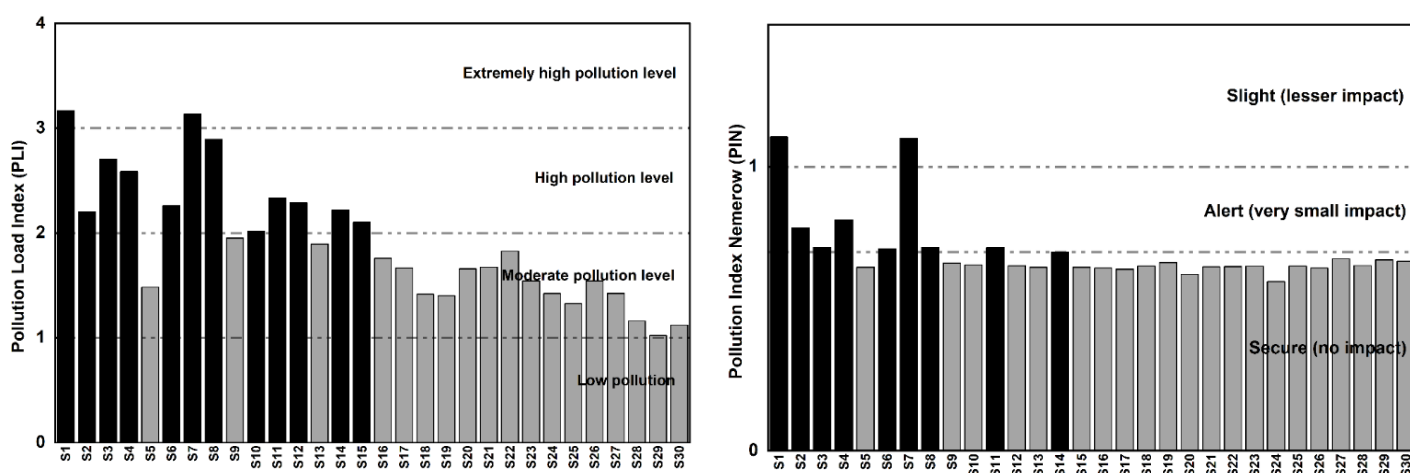


Figure 2-13. **a**) Pollution load index, and **b**) Nemerow index method values for the total trace metal(oid)s in the surface soils (from the left).

Likewise, similar findings were reported previously by Essien et al. (2019), and Rezapour et al. (2018) who reported a moderate to strong poly-metallic pollution level in agricultural soils in Nigerian and Iranian due to the elevated concentrations of toxic metal(oid)s like Cd, As, Pb and Cr owing to the leakage of leachate from an uncontrolled municipal solid waste landfill, respectively. Indicating a strong impact of the landfills on its neighbors' soil quality. In fact, the calculated indices reflected a moderate to strong influence due to the accumulation of TTMs originating from anthropogenic inputs, i.e., leachate leakage from the landfill, agricultural runoff, wastewater discharge, etc. However, the pollution level is still below the WHO and AFNOR guidelines, this is reflected by the low values found when introducing the Nemerow index based on the above-cited guidelines. The average PIN of each metal(oid) was in the order of; Ni (0.51) > Cd (0.44) > Pb (0.25) > Zn (0.16) > Cu (0.13) > As (0.07). As observed in Fig. 4-b, most of the examined soil samples did not show any impact due to the accumulation of TTMs (PIN<0.7), and only 30% (9 samples) indicated a very small to slight impact (0.7 <PIN< 2).

In this study, the individual ecological risk ( $Er_i$ ) of each metal(oid) and Potential Ecological Risk Index (PERI) values were introduced to evaluate the potential hazard of the accumulation of TTMs on its adjacent environment by combining the toxicity coefficient and soil geochemical background. The calculated values are illustrated in **Fig.2-14**. The results showed that the  $Er_i$  of TTMs in the surface soils of the study area was in the following order: Cd > As > Pb > Cu > Ni > Cr > Zn > Fe. Initially, Cu, Cr, Ni, and Zn showed a low potential ecological risk as their  $Er_i$  values were below 40 in all examined samples. Contrarily, Cd, Pb, and As displayed high ecological risk in almost all samples and were the dominant contributors in PERI, which is owing not only to their abundance in gathered soils but also their elevated toxicity factor in comparison to other metal(oid)s. Concerning the comprehensive ecological risk was found to vary greatly among the sampling sites, ranging from 50.54 to 411.66. 11 samples (36.37%) were higher than 150 as shown in **Fig.2-14**, suggesting a moderate ecological risk arising from the accumulation of TTMs. Remarkably, Cd, As, and Pb were the most responsible for the potential ecological risk, such observation has also been reported in previous work conducted by Iqbal et al. (2019), Varol et al. (2021) and Karimian et al. (2021) on agricultural soils under various anthropogenic stressors, In Irak, Turkey, and Iran, respectively. In contrary to our PERI results, very high values were reported in our previous study examining agricultural soils located near an open dumpsite in Benguerir (Morocco) (Fadili et al., 2022). This indicates that the problem of soil contamination tends to be similar in the future if the increase of metal(oid)s continues in the same way. In particular, Cd, Pb, and As.

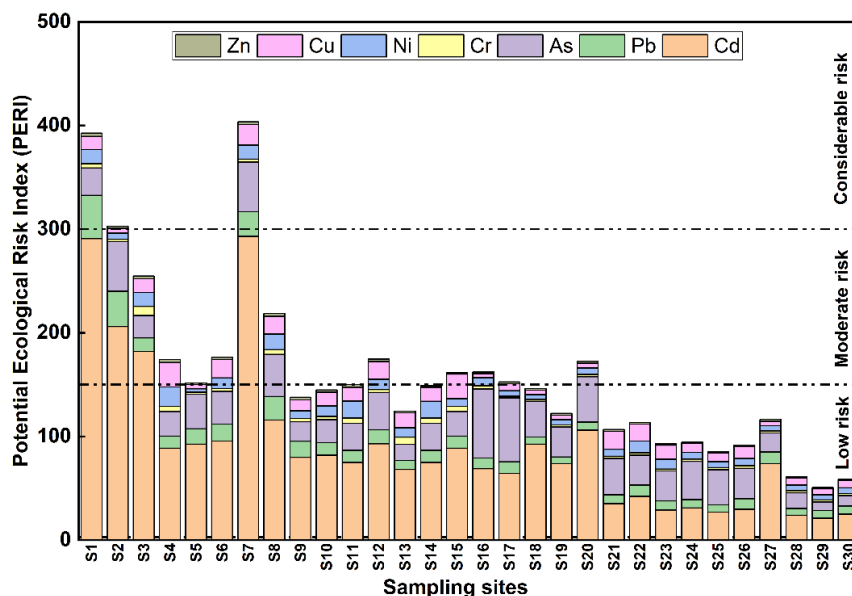


Figure 2-14. Potential Ecological Risk index (PERI) at each sampling site around Oum Azza landfill.

### 2.3.4 Multivariate statistical analysis:

Results of normality using the Kolmogorov-Smirnov showed that the data are not normally distributed as shown in **Tables 2-8** and **2-9**, respectively, this heterogeneous distribution is probably due to the effect of the landfill and agricultural activities which caused an increase in the concentration of metal(oid)s around the sampling sites, to confirm these results, Spearman's correlation, PCA and HCA were performed.

#### 2.3.4.1 Case Study 1: Benguerir' open dumpsite

- **Spearman's correlation matrix :**

Since the studied metal(oid)s were non-normally distributed as can be shown using the K-S test, a non-parametric Spearman correlation analysis was applied between variables. Correlation coefficient values close to or greater than 0.5 are considered significant. Obtained results are given in **Table 2-8**. According to the correlation coefficient results, a significant positive correlation was revealed between PTEs, suggesting a specific association among them at the studied dumpsite, which confirms the results discussed previously in this work. In addition, Pb was correlated with Cu ( $r=0.705$ ,  $P<0.01$ ), Ni ( $r=0.731$ ,  $P<0.01$ ), As ( $r=0.671$ ,  $P<0.05$ ), and Cd ( $r=0.537$ ,  $P<0.05$ ). We notice that in some previous studies, it has been demonstrated that when we have a significant positive correlation between studied metals, means that they have the same source and/or mutual behavior during transport from the source of pollution to impacted soils (Essien et al., 2019; Suresh et al., 2011). On the other hand, the results showed that Cr, Zn, Cd, and Cu were positively correlated with each other, with  $r>0.537$ , which indicates that the bad practices used to manage MSW in this landfill remain the major source of metals accumulation in this investigation, as the majority of metal(oid)s are correlated

with each other, and their average concentration exceeds the geochemical background as mentioned before. The absence of a linear correlation between Fe and other metal(oid)s indicates that its source is quite different.

Table 2-8. Spearman's correlation coefficients for heavy metal(oid)s in the soil samples of Benguerir open dumpsite.

Variables	Pb	Cu	Cr	Zn	Ni	Cd	Fe	As
<b>Pb</b>	<b>1</b>							
<b>Cu</b>	<b>0.705 **</b>	<b>1</b>						
<b>Cr</b>	<b>0.561 *</b>	<b>0.633 **</b>	<b>1</b>					
<b>Zn</b>	0.285	<b>0.614 **</b>	<b>0.521 *</b>	<b>1</b>				
<b>Ni</b>	<b>0.731 **</b>	<b>0.463 *</b>	<b>0.587 **</b>	0.047	<b>1</b>			
<b>Cd</b>	<b>0.537 *</b>	<b>0.549 *</b>	<b>0.756 **</b>	<b>0.563 *</b>	0.370	<b>1</b>		
<b>Fe</b>	0.358	0.140	0.254	-0.018	0.244	0.340	<b>1</b>	
<b>As</b>	<b>0.671*</b>	<b>0.493*</b>	<b>0.821**</b>	0.135	0.248	0.120	0.165	<b>1</b>

\*Significance level  $\alpha=0.05$       \*\*significance level  $\alpha=0.01$

#### • PCA and cluster analysis :

The monitored data were assessed statistically using PCA to identify the probable sources of pollution in the study area. Firstly, the KMO score (0.614) and Bartlett's sphericity test value ( $p < 0.0001$ ) indicated the accuracy of the examined datasets for PCA analysis. The observed factor loadings, the percentage of cumulative, and the variance explained by the factors are displayed in **Tables 2-9**, respectively. In the current thesis, PCs with eigenvalues higher than one was only retained.

Table 2-9. Rotated component matrix for soil total trace metal(oid)s in Benguerir's landfill.

	<b>F1</b>	<b>F2</b>	<b>F3</b>	<b>F4</b>
<b>Pb</b>	<b>0.839</b>	0.155	-0.374	-0.251
<b>Cu</b>	<b>0.860</b>	-0.381	-0.072	0.149
<b>As</b>	<b>0.756</b>	0.105	<b>-0.240</b>	-0.172
<b>Cr</b>	<b>0.792</b>	0.182	<b>0.481</b>	0.198
<b>Zn</b>	<b>0.815</b>	-0.270	<b>0.451</b>	-0.083
<b>Ni</b>	<b>0.441</b>	<b>0.727</b>	-0.215	<b>0.463</b>
<b>Cd</b>	<b>0.772</b>	<b>0.405</b>	-0.087	-0.414
<b>Fe</b>	<b>0.546</b>	-0.660	-0.388	0.199
<b>Eigenvalues</b>	3.825	1.403	0.785	0.556
<b>Variability (%)</b>	54.648	20.047	11.208	7.944
<b>Cumulative %</b>	54.648	74.696	85.903	93.847

Extraction method: Principal component analysis, PCA loadings  $>0.4$  are shown in bold.

The two first PCs contribute to 74.696 % of the total variance with an eigenvalue superior to 1 (3.82 for F1 and 1.40 for F2), the PC1 and PC2 account for 54.65% and 20.04% of the total variance, respectively. The first component (PC1) was significantly correlated with Pb, Cd, Cu, Cr, and Zn with a loading value of more than 0.772, and moderately correlated with Ni, and Fe. The PC1 can be defined as an anthropogenic component, due to the presence of Cd and Pb strongly loaded in this group, and characterized by EF values greater than 1, confirming that

metals were mainly derived from the input of waste disposing and agricultural activities nearby the landfill, these elements are commonly found in batteries, pesticides, pigments, WEEE...etc. On the other hand, the Ni factor loads in the first and second components were 0.441 and 0.727, respectively, it therefore, has complex resources and is controlled by geogenic and anthropogenic factors.

For further understanding of the interaction between heavy metal concentrations, Hierarchical cluster analysis (HCA) using Ward's method with squared Euclidean distance as a segmentation technique was employed to sort studied data into similar groups, for better understanding the relationship between variables among sampling sites. The obtained dendrograms for soils are displayed in (Fig.2-15).

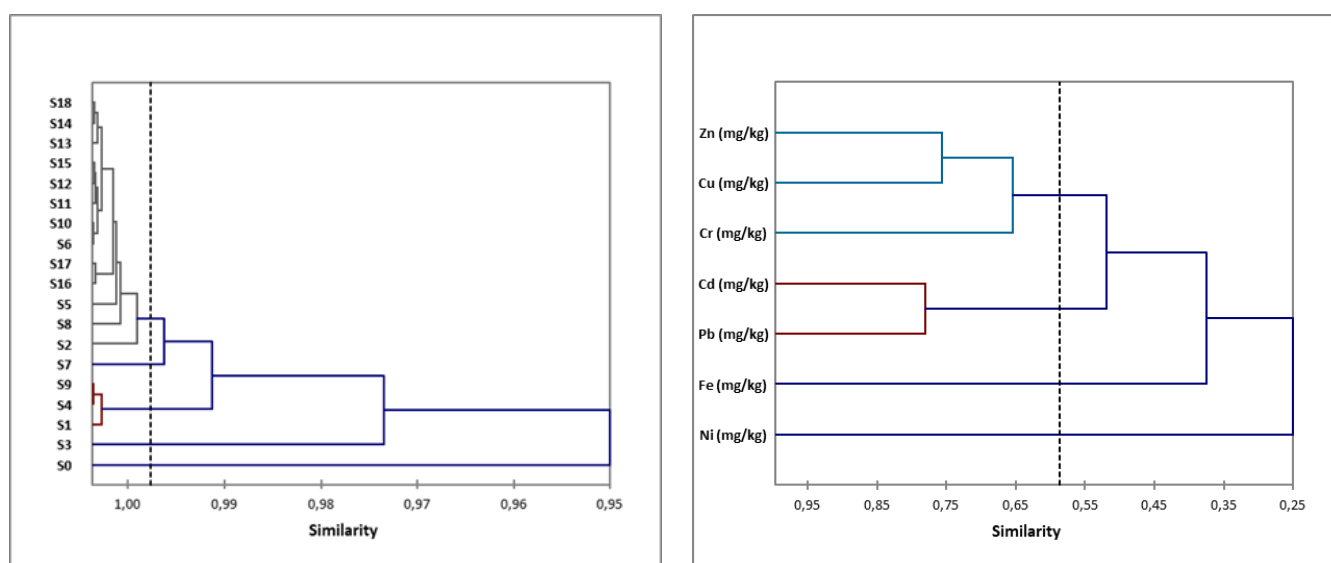


Figure 2-15. Dendrogram of studied variables: *a*) Sampling stations *b*) Heavy metal(oid)s. (Distance metrics are based on the Euclidean distance single linkage method).

HCA for all soil samples suggests they can be classified into three statistically significant clusters based on their similarities (Fig.2-15-a), that illustrate clearly the complexity of the study area. Cluster 1 includes station S0 located in the landfill, whereas, the second cluster contained all soils located in the first 100m from the solid waste dumpsite, and the third cluster includes all other sites, which does not pose a great threat to the surrounding ecosystem, obtained results confirmed the above discussed findings in this research, indicated that pollution of soils decreased gradually, with the distance from the pollution source (open dumpsite activities). Concerning the second dendrogram produced for metals in Fig.2-15-b, the obtained 3 clusters were in accordance with the results discussed in the current investigation. The first cluster contains Pb and Cd which were identified as high contaminants derived mainly from anthropogenic sources (disposing practices ...). Cluster 2 includes Zn, Cu, and Cr indicating that these metals were derived from similar and mixed sources, without reaching the threat level

on the surrounding ecosystem ( $E^r_i < 0$ ). While, the third and Fourth Clusters include Ni and Fe, respectively, which are derived mainly from lithogenic sources. PCA and HCA revealed that anthropogenic activities have a great influence on heavy metal(oid)s concentration in the vicinity of the studied area.

### 2.3.4.2 Case study 2: Oum Azza landfill

- **Spearman's correlation matrix:**

Since the observed data were not normally distributed based on the Kolmogorov-Smirnov test, the correlation between examined metal(oid)s were conducted using Spearman correlation coefficients. As shown in **Table 2-10**, The results showed a strong correlation coefficient among all investigated metal(oid)s ( $P < 0.01$ ), and therefore the application of PCA is of ultimate importance (Kapelewska, Kotowska, Karpińska, et al., 2019).

Table 2-10. Spearman's correlation coefficients for heavy metal(oid)s in the soil samples of Oum Azza landfill.

Variables	Pb	Cu	As	Cr	Zn	Ni	Cd	Fe
<b>Pb (mg/kg)</b>	<b>1</b>							
<b>Cu (mg/kg)</b>	<b>0.838</b>	<b>1</b>						
<b>As (mg/kg)</b>	<b>0.589</b>	<b>0.563</b>	<b>1</b>					
<b>Cr (mg/kg)</b>	0.315	0.154	-0.152	<b>1</b>				
<b>Zn (mg/kg)</b>	<b>0.386</b>	0.340	0.138	<b>0.661</b>	<b>1</b>			
<b>Ni (mg/kg)</b>	0.200	0.170	0.073	<b>0.461</b>	<b>0.702</b>	<b>1</b>		
<b>Cd (mg/kg)</b>	<b>0.690</b>	<b>0.637</b>	0.347	<b>0.460</b>	<b>0.705</b>	<b>0.462</b>	<b>1</b>	
<b>Fe (mg/kg)</b>	0.129	0.178	-0.276	0.048	0.125	-0.024	0.137	<b>1</b>

\*Significance level  $\alpha=0.05$       \*\*significance level  $\alpha=0.01$

- **PCA and Cluster Analysis**

Principal component analysis was introduced in the current study to identify the possible sources of pollution in the study area. Firstly, The Kaiser-Meyer-Olkin (KMO) score (0.657) and Bartlett's sphericity test value ( $p < 0.0001$ ) indicated the accuracy of the examined samples for PCA.

Table 2-11. Rotated component matrix for soil total trace metal(oid)s around Oum Azza landfill.

	F1	F2	F3	F4
<b>Cd</b>	<b>0.823</b>	<b>0.417</b>	0.146	0.191
<b>Pb</b>	<b>0.765</b>	<b>0.484</b>	0.220	0.028
<b>As</b>	<b>0.477</b>	<b>0.713</b>	-0.340	-0.165
<b>Cr</b>	<b>0.579</b>	-0.596	-0.055	0.502
<b>Ni</b>	<b>0.796</b>	-0.464	-0.101	-0.119
<b>Cu</b>	<b>0.595</b>	-0.504	-0.313	-0.451
<b>Zn</b>	<b>0.892</b>	-0.019	0.056	0.004
<b>Fe</b>	0.132	-0.174	<b>0.929</b>	-0.233
<b>Eigenvalue</b>	3.627	1.771	1.163	0.588
<b>% of variance</b>	45.331	22.132	14.540	7.348
<b>Cumulative %</b>	45.331	67.463	82.003	89.351

Extraction method: Principal component analysis, PCA loadings  $>0.4$  are shown in bold.

The first three-components contribute to 82 % of the total variance (45.33% for F1, 22.13 % for F2, and 14.54 % for F3) with an eigenvalue superior to 1 (3.81 for F1, 1.53 for F2, and 1.20 for F3). The first component PC1 explains 47.57 % of the total cumulative variance and was significantly correlated with all examined trace metal(oid)s with a loading value superior than  $> 0.477$  except for Fe ( $F=0.132$ ). The first component could be defined as an anthropogenic component and confirmed that a non-negligible amount of examined trace metal(oid)s were originated mainly from the anthropogenic activities in the study area, the PC2 demonstrated positive loadings of Cd, Pb, and As suggesting that they were mainly the result of anthropogenic sources as confirmed by the highest EF values, while the PC3 showed a strong positive loading with Fe confirming the geogenic source was the main factor behind the elevated concentration of Fe in the study area.

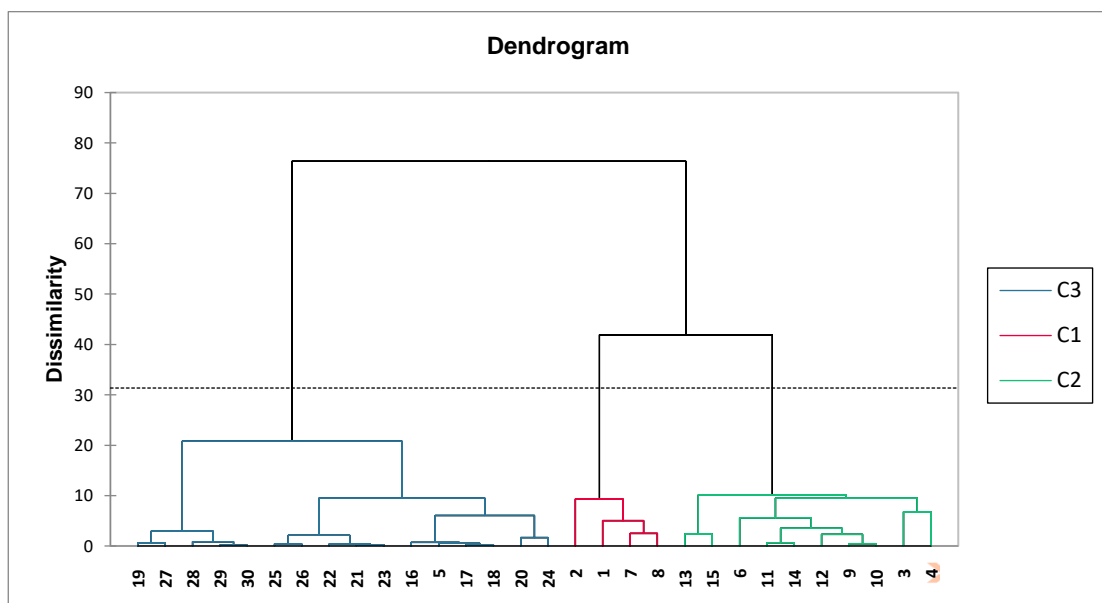


Figure 2-16. Dendrogram of studied variables: **a**) Sampling stations **b**) Heavy metal(oid)s. (Distance metrics are based on the Euclidean distance single linkage method)

As shown in **Fig.2-16**, Hierarchical Clustering Analysis (HCA) suggests that the sampling locations could be classified into three statistically significant clusters based on their similarities, confirming the complexity of the pollution sources in the study area. As discussed in the previous sections, several sources of pollution have contributed to soil pollution around the two landfills, particularly in Oum Azza. The region is known for its intense agricultural activity and heavy road traffic on the highway, which have both contributed to the problem. For these reasons, evaluating the potential risks to human health for the local population is essential in order to make informed decisions regarding this alarming situation.

### 2.3.5 human health risk assessment

#### 2.3.5.1 Case study 1: Benguerir' open dumpsite

- **Deterministic non-carcinogenic human health risk**

The non-carcinogenic risk and hazard quotient values were evaluated for the local communities using the minimum, average and maximum values measured for the examined metal(oid)s considering three possible pathways of contamination on both children and adults are depicted in **Table 2-12**. It should be pointed out that among all the investigated routes, the average daily dose (ADD) through ingestion exposure was the main pathway for all metal(oid)s. The hazard quotient (HQs) of all examined elements for both age groups decreased in the following order: ingestion > dermal > inhalation. In addition, similar to the findings obtained by Rezapour et al. (2018) and Essien et al. (2019), who reported that Cd, As and Pb were the metal(oid)s with the greater hazard quotient for both adults and children in regard to other metal(oid)s because of their high content in soils, and lower RfD. However, until now the HQs values of all metal(oid)s in adjacent soils to the landfill were lower than 1 which is considered as the acceptable non-carcinogenic level according to the USEPA, such data illustrate that the average daily intake has no negative health effects on the surrounding populations in terms of individual heavy metal(oid)s.

However, the total hazard index (THI) was approximately ten times higher for children (max THI = 1.14) than for adults (max value THI = 0.12). Because children were the most vulnerable group to environmental contaminants due to their lower immunology and sensitivity (Mallongi, Astuti, et al., 2021; Varol & Tokatli, 2023; X. Wang et al., 2022). It is also worth noting that other heavy metal(oid)s is not considered in this study, e.g., Hg, and might contribute to the increase of estimated risk posed by these activities.

- **Deterministic carcinogenic human health risk**

The carcinogenic risk posed by the accumulation of TTMs in surface soils was calculated considering the multi-pathways exposure to As, Pb, Cd, Ni, and Cr for which slope factor (SF) was available according to the EPA (USEPA, 2005) as shown in **Table 2-13**. The obtained values for both children and adults exposed to the metal(oid)s through different pathways decreased in the order of: ingestion > dermal > inhalation. Concerning the carcinogenetic impact, the average calculated total cancer risk (TCR) values due to the exposure to all metal(oid)s were 4.05E-04 and 4.42E-05 for children and adults, respectively. Therefore, the cumulative carcinogenic risk for both age groups was higher than the acceptable limit of  $10^{-6}$ . In addition, the average value for children was observed to be higher than the maximum allowable limit ( $10^{-4}$ ) considered as a threshold value by the USEPA, which reflects that the

multi-pathways exposure to TTMs had a significant cancer risk. The carcinogenic risk is much higher compared to other similar studies carried out in Turkey (Varol, Gündüz, & Ras, 2021) and Saudi Arabia (Ali et al., 2019), indicating that the continuity of the accumulation of metal(oid)s, may worsen the situation in the future, and therefore corrective actions are urgently required.

- **The Monte Carlo simulation (MCS)**

Various reasons could participate to an overdetermination or underdetermination of the calculated human health risk using deterministic method, including body weight, metal(oid)s concentration, exposure duration, exposure frequency, etc. To overcome these limitations, Montecarlo simulation (what-if-analysis) was employed in the present thesis. Histograms and tornado sensitivity diagrams for simulating Total hazard index (THI) and Total cancer risk (TCR) for children and adults due to long-term exposure to metal(oid)s are presented in **Figs.2-17 and 2-18**, respectively. The probability estimation revealed that there was an equivalence between the calculated NCR for both deterministic and simulated 50th percentile. As shown in Table 2-12, the mean value for adults (0.04) and children (0.36) were compared with the 50th percentile of the non-carcinogenic distribution obtained through the probabilistic approach (0.036 for adults and 0.32 for children). According to the probability analysis, the likelihood of children experiencing adverse health effects was found to be higher compared to that of adults. The 95th for children was 0, while for adults it was 0.067, which supports earlier findings (Rajasekhar et al., 2018; Q. Yang et al., 2022) suggesting that children are more vulnerable compared to other age groups.

Based on the probability distribution shown in **Fig. 2-18**, it can be observed that the accumulation of TTMs in surface soils poses a significant carcinogenic risk to both children and adults. The 5th percentile and average values indicate that for children, the risk ranges between  $3.03E-4$  and  $5.89E-4$ , while for adults, the risk ranges between  $3.34E-5$  and  $6.88E-5$ . Both age groups exceed the acceptable value of  $1E-06$  by almost 300 and 34 times for children and adults. This suggests that almost 95% of the population living in the study area faced cancer risks if corrective actions are not taken as soon as possible. In addition, the 95th percentile of TCR values for children and adults were approximately 10 and 1.2 times higher than the threshold value ( $10E-4$ ).

- **Sensitivity and uncertainty analysis**

Sensitivity analysis was introduced in the current thesis to highlight the most effective parameters influenced in the carcinogenic and non-carcinogenic risks are presented as tornado plots in **Fig.2-17 (c-d)** and **Fig.18 (c-d)**. The results showed that the concentration of Cr, Pb,

As and the exposure frequency were the most significant factors in the carcinogenic risk for adults, with a positive variability of 28%, 20.3%, 19.7% and 13.8%, respectively. Likewise, the same parameters were the most significant on the calculated THI (**Fig.2-17-d**) with a variability of 28.7%, 24.8%, 22.6% and 14.3% for Cr, Pb, As and EF, respectively. Body weight (BW) was an insignificant parameter in the simulated total hazard index (THI) with a total variability of -15.3% and -6.7% for adults and children, respectively. In other words, the increase in BW can significantly reduce potential health risks (Pasupuleti et al., 2022).

The tornado plots in **Figure 18 (c-d)** revealed that Ni, EF, and Cr were the most sensitive factors with a contribution of 59.8%, 15.8%, and 15.2% for children and 54.8%, 14.8%, and 13.3% for adults regarding carcinogenic risks. Pasupuleti et al. (2022) also conducted a sensitivity analysis, showing that the concentration of metal(oid)s and exposure frequency were the most significant factor in both NCR and CR, while body weight was the most insignificant parameter. In addition, Ni had the highest contribution to the carcinogenicity risk among the contaminants studied, indicating the need for strict control measures.

Table 2-12. Non-carcinogenic risks posed to adults and children by each element and exposure pathway around Benguerir' landfill

Metal(oid)s	level	Conce (mg/kg)	Children						HI Total Pahway	Adults						HI Total Pathway
			Oral ingestion		Dermal exposure		Inhalation			Oral ingestion		Dermal exposure		nhalation		
			ADD	HQ	ADD	HQ	ADD	HQ		ADD	HQ	ADD	HQ	ADD	HQ	
<b>Pb</b> (mg/kg)	Min	2.20	2.81E-05	8.04E-03	7.88E-08	1.50E-04	7.55E-10	2.14E-07	8.19E-03	3.01E-06	8.61E-04	1.22E-08	2.33E-05	4.43E-10	1.26E-07	8.84E-04
	Max	115.52	1.48E-03	4.22E-01	4.14E-06	7.88E-03	3.96E-08	1.13E-05	4.30E-01	1.58E-04	4.52E-02	6.42E-07	1.22E-03	2.33E-08	6.61E-06	4.64E-02
	Mean	22.01	2.81E-04	8.04E-02	7.88E-07	1.50E-03	7.55E-09	2.15E-06	8.19E-02	3.02E-05	8.61E-03	1.22E-07	2.33E-04	4.43E-09	1.26E-06	8.85E-03
<b>Cu</b> (mg/kg)	Min	2.50	3.20E-05	7.99E-04	8.95E-08	7.46E-06	8.58E-10	2.14E-08	8.07E-04	3.42E-06	8.56E-05	1.39E-08	1.16E-06	5.04E-10	1.26E-08	8.68E-05
	Max	54.50	6.97E-04	1.74E-02	1.95E-06	1.63E-04	1.87E-08	4.68E-07	1.76E-02	7.47E-05	1.87E-03	3.03E-07	2.53E-05	1.10E-08	2.74E-07	1.89E-03
	Mean	13.32	1.70E-04	4.26E-03	4.77E-07	3.97E-05	4.57E-09	1.14E-07	4.30E-03	1.82E-05	4.56E-04	7.41E-08	6.17E-06	2.68E-09	6.71E-08	4.62E-04
<b>Cr</b> (mg/kg)	Min	3.73	4.77E-05	1.59E-02	1.34E-07	2.23E-03	1.28E-09	4.48E-05	1.82E-02	5.11E-06	1.70E-03	2.07E-08	3.46E-04	7.51E-10	2.63E-05	2.08E-03
	Max	68.19	8.72E-04	2.91E-01	2.44E-06	4.07E-02	2.34E-08	8.18E-04	3.32E-01	9.34E-05	3.11E-02	3.79E-07	6.32E-03	1.37E-08	4.80E-04	3.79E-02
	Mean	21.16	2.71E-04	9.02E-02	7.58E-07	1.26E-02	7.26E-09	2.54E-04	1.03E-01	2.90E-05	9.66E-03	1.18E-07	1.96E-03	4.26E-09	1.49E-04	1.18E-02
<b>Zn</b> (mg/kg)	Min	7.92	1.01E-04	3.38E-04	2.84E-07	4.73E-06	2.72E-09	9.06E-09	3.42E-04	1.08E-05	3.62E-05	4.40E-08	7.34E-07	1.60E-09	5.32E-09	3.69E-05
	Max	190.50	2.44E-03	8.12E-03	6.82E-06	1.14E-04	6.54E-08	2.18E-07	8.23E-03	2.61E-04	8.70E-04	1.06E-06	1.77E-05	3.84E-08	1.28E-07	8.88E-04
	Mean	42.51	5.44E-04	1.81E-03	1.52E-06	2.54E-05	1.46E-08	4.86E-08	1.84E-03	5.82E-05	1.94E-04	2.36E-07	3.94E-06	8.56E-09	2.85E-08	1.98E-04
<b>Ni</b> (mg/kg)	Min	1.25	1.60E-05	7.99E-04	4.47E-08	8.29E-06	4.29E-10	4.77E-06	8.12E-04	1.71E-06	8.56E-05	6.95E-09	1.29E-06	2.52E-10	2.80E-06	8.97E-05
	Max	34.20	4.37E-04	2.19E-02	1.22E-06	2.27E-04	1.17E-08	1.30E-04	2.22E-02	4.68E-05	2.34E-03	1.90E-07	3.52E-05	6.89E-09	7.66E-05	2.45E-03
	Mean	8.50	1.09E-04	5.43E-03	3.04E-07	5.64E-05	2.92E-09	3.24E-05	5.52E-03	1.16E-05	5.82E-04	4.73E-08	8.75E-06	1.71E-09	1.90E-05	6.10E-04
<b>Cd</b> (mg/kg)	Min	0.36	4.60E-06	4.60E-03	1.29E-08	1.29E-03	1.24E-10	1.24E-05	5.90E-03	4.93E-07	4.93E-04	2.00E-09	2.00E-04	7.25E-11	7.25E-06	7.01E-04
	Max	6.80	8.69E-05	8.69E-02	2.43E-07	2.43E-02	2.33E-09	2.33E-04	1.12E-01	9.32E-06	9.32E-03	3.78E-08	3.78E-03	1.37E-09	1.37E-04	1.32E-02
	Mean	1.77	2.26E-05	2.26E-02	6.34E-08	6.34E-03	6.07E-10	6.07E-05	2.90E-02	2.42E-06	2.42E-03	9.84E-09	9.84E-04	3.57E-10	3.57E-05	3.44E-03
<b>As</b> (mg/kg)	Min	0.80	1.02E-05	3.41E-02	2.86E-08	2.33E-04	2.75E-10	9.15E-07	3.43E-02	1.10E-06	3.65E-03	4.45E-09	3.62E-05	1.61E-10	5.37E-07	3.69E-03
	Max	4.65	5.95E-05	1.98E-01	1.66E-07	1.35E-03	1.60E-09	5.32E-06	2.00E-01	6.37E-06	2.12E-02	2.59E-08	2.10E-04	9.37E-10	3.12E-06	2.14E-02
	Mean	3.02	3.86E-05	1.29E-01	1.08E-07	8.79E-04	1.04E-09	3.45E-06	1.30E-01	4.14E-06	1.38E-02	1.68E-08	1.37E-04	6.08E-10	2.03E-06	1.39E-02
<b>Fe</b> (mg/kg)	Min	222.18	2.84E-03	4.06E-03	7.95E-06	1.77E-04	7.62E-08	3.47E-04	4.58E-03	3.04E-04	4.35E-04	1.24E-06	2.75E-05	4.48E-08	2.03E-04	6.66E-04
	Max	854.22	1.09E-02	1.56E-02	3.06E-05	6.80E-04	2.93E-07	1.33E-03	1.76E-02	1.17E-03	1.67E-03	4.75E-06	1.06E-04	1.72E-07	7.82E-04	2.56E-03
	Mean	406.27	5.19E-03	7.42E-03	1.45E-05	3.23E-04	1.39E-07	6.34E-04	8.38E-03	5.57E-04	7.95E-04	2.26E-06	5.02E-05	8.18E-08	3.72E-04	1.22E-03
HI for min. values (TTMs)			6.86E-02		4.09E-03		4.10E-04		<b>7.31E-02</b>	7.35E-03		6.36E-04		2.40E-04		<b>8.23E-03</b>
HI for max. values (TTMs)			1.06E+00		7.54E-02		2.53E-03		<b>1.14E+00</b>	1.14E-01		1.17E-02		1.49E-03		<b>1.27E-01</b>
HI for mean. Values (TTMs)			3.41E-01		2.18E-02		9.86E-04		<b>3.64E-01</b>	3.65E-02		3.38E-03		5.79E-04		<b>4.05E-02</b>

Table 2-13. Carcinogenic risks posed to adults and children by each element and exposure pathway around Benguerir' landfill

metal(oid)s	level	conce (mg/kg)	Children				Adults			
			Oral ingestion	Dermal exposure	Inhalation	TCR total pathways	Oral ingestion	Dermal exposure	Inhalation	TCR total pathways
<b>Pb</b> (mg/kg)	Min	2.20	2.39E-07	6.69E-10	5.35E-07	7.75E-07	2.56E-08	1.04E-10	1.86E-11	2.24E-07
	Max	115.52	1.26E-05	3.52E-08	1.43E-07	1.27E-05	1.35E-06	5.46E-09	9.77E-10	1.35E-06
	Mean	22.01	2.39E-06	6.70E-09	1.01E-06	3.41E-06	2.56E-07	1.04E-09	1.86E-10	2.58E-07
<b>Cr</b> (mg/kg)	Min	3.73	2.38E-05	2.67E-07	5.38E-08	2.42E-05	2.55E-06	4.15E-08	3.16E-08	2.63E-06
	Max	68.19	4.36E-04	4.88E-06	9.83E-07	4.42E-04	4.67E-05	7.58E-07	5.77E-07	4.80E-05
	Mean	21.16	1.35E-04	1.52E-06	3.05E-07	1.37E-04	1.45E-05	2.35E-07	1.79E-07	1.49E-05
<b>Ni</b> (mg/kg)	Min	1.25	2.72E-05	1.90E-06	3.60E-10	2.91E-05	2.91E-06	2.95E-07	2.12E-10	3.21E-06
	Max	34.20	7.43E-04	5.20E-05	9.86E-09	7.95E-04	7.96E-05	8.08E-06	5.79E-09	8.77E-05
	Mean	8.50	1.85E-04	1.29E-05	2.45E-09	1.98E-04	1.98E-05	2.01E-06	1.44E-09	2.18E-05
<b>Cd</b> (mg/kg)	Min	0.36	1.75E-06	4.90E-09	7.78E-10	1.75E-06	1.87E-07	7.61E-10	4.57E-10	1.89E-07
	Max	6.80	3.30E-05	9.25E-08	1.47E-08	3.31E-05	3.54E-06	1.44E-08	8.63E-09	3.56E-06
	Mean	1.77	8.60E-06	2.41E-08	3.83E-09	8.63E-06	9.21E-07	3.74E-09	2.25E-09	9.27E-07
<b>As</b> (mg/kg)	Min	0.80	1.53E-05	1.05E-07	4.15E-09	1.55E-05	1.64E-06	1.63E-08	2.43E-09	1.66E-06
	Max	4.65	8.92E-05	6.09E-07	2.41E-08	8.98E-05	9.55E-06	9.47E-08	1.41E-08	9.66E-06
	Mean	3.02	5.79E-05	3.96E-07	1.56E-08	5.83E-05	6.21E-06	6.15E-08	9.19E-09	6.28E-06
Cumulative carcinogenic risk for min. values (TTMs)			6.83E-05	2.28E-06	5.94E-07	<b>7.12E-05</b>	7.32E-06	3.54E-07	3.47E-08	<b>7.91E-06</b>
Cumulative carcinogenic risk for max values (TTMs)			1.31E-03	5.77E-05	1.17E-06	<b>1.37E-03</b>	1.41E-04	8.96E-06	6.06E-07	<b>1.50E-04</b>
Cumulative carcinogenic risk for mean. values (TTMs)			3.89E-04	1.49E-05	1.34E-06	<b>4.05E-04</b>	4.17E-05	2.31E-06	1.92E-07	<b>4.42E-05</b>

Note: E is the abbreviation of exponent, which means the index based on 10.

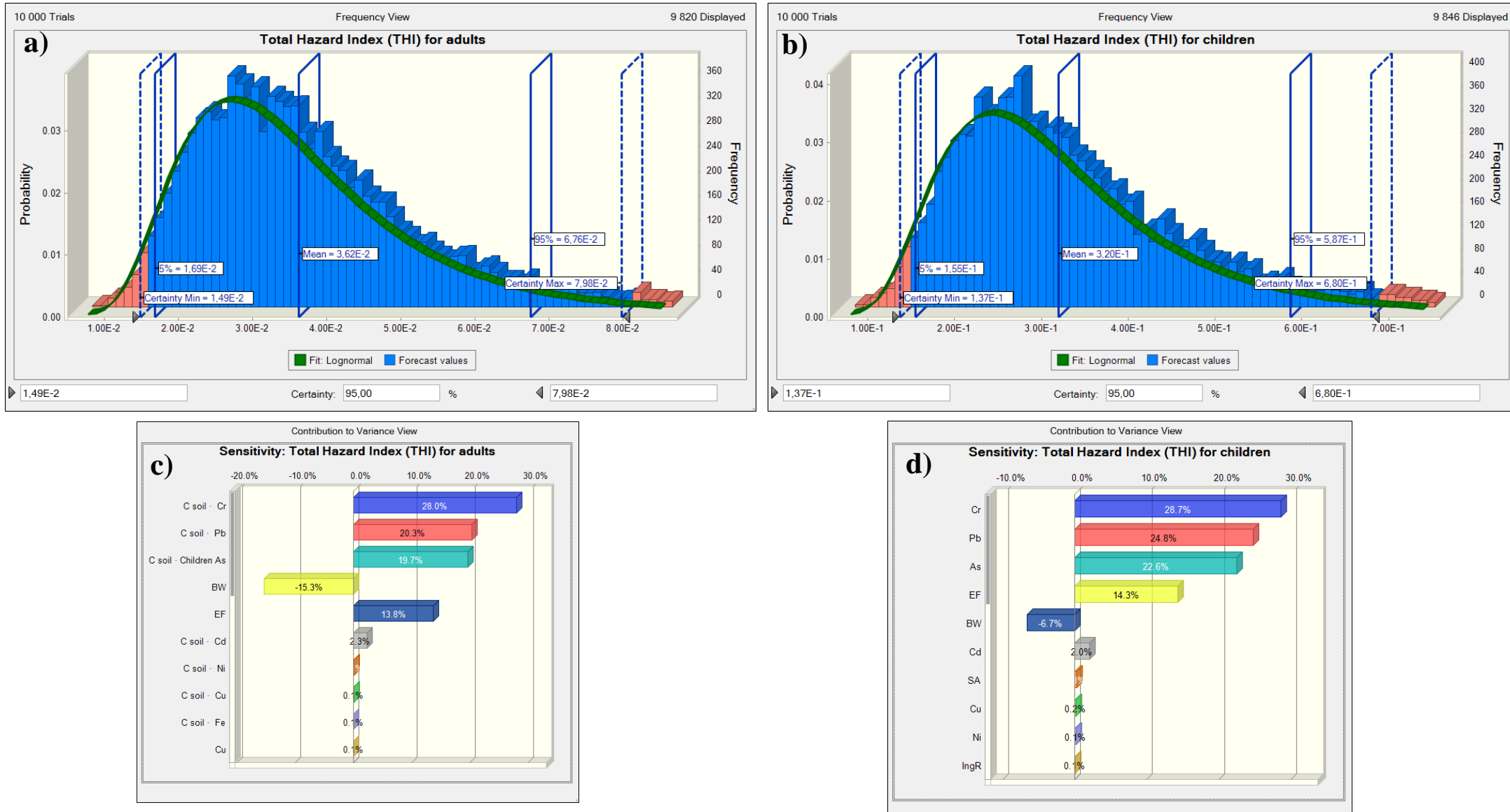


Figure 2-17. Simulated total hazard index (THI) for the considered age groups in the examined surface soil around Benguerir dumpsite: **a)** THI for adults; **b)** THI for children; **c)** sensitivity diagram for adults; **d)** sensitivity diagram for children.

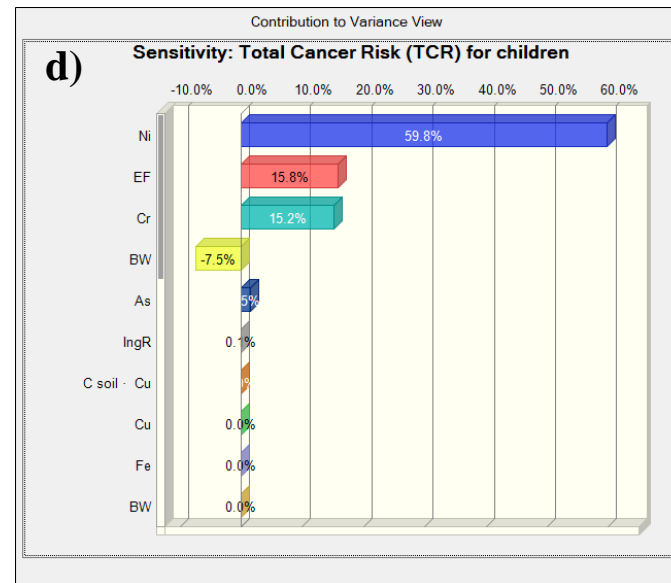
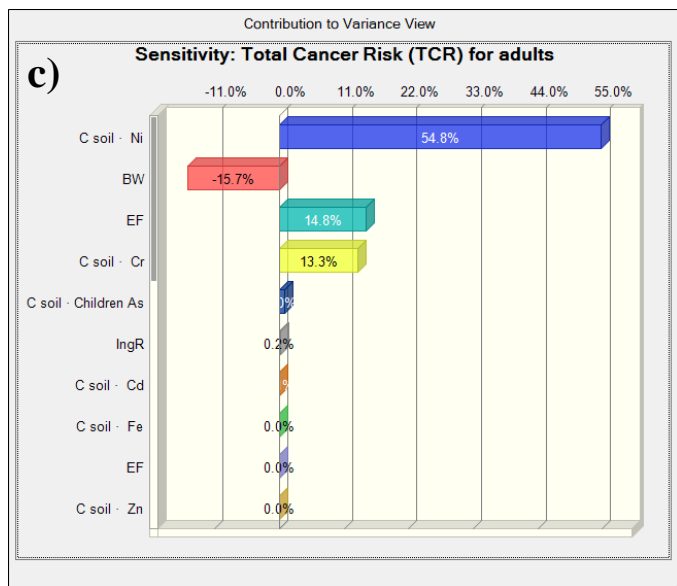
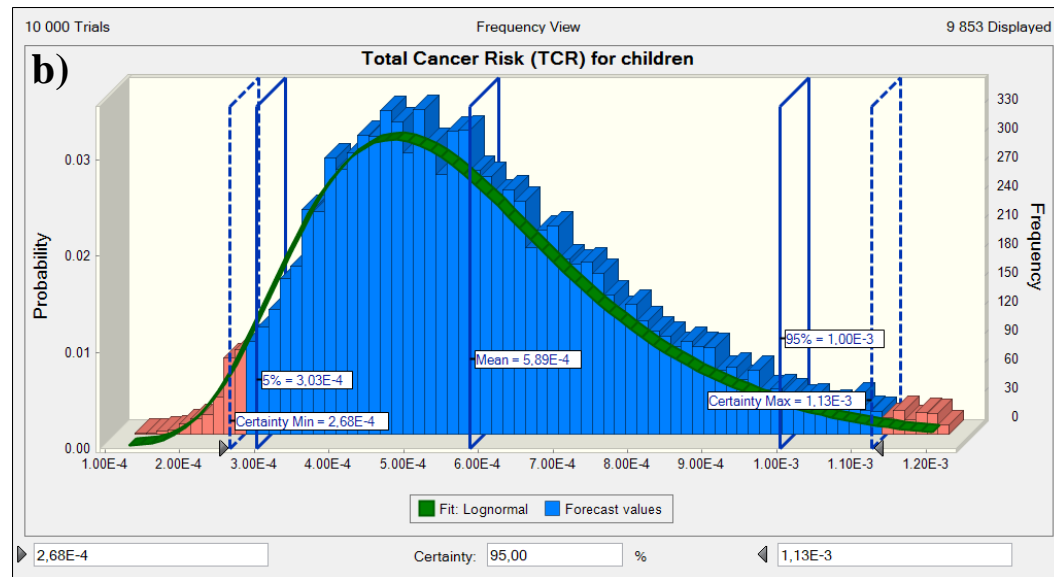
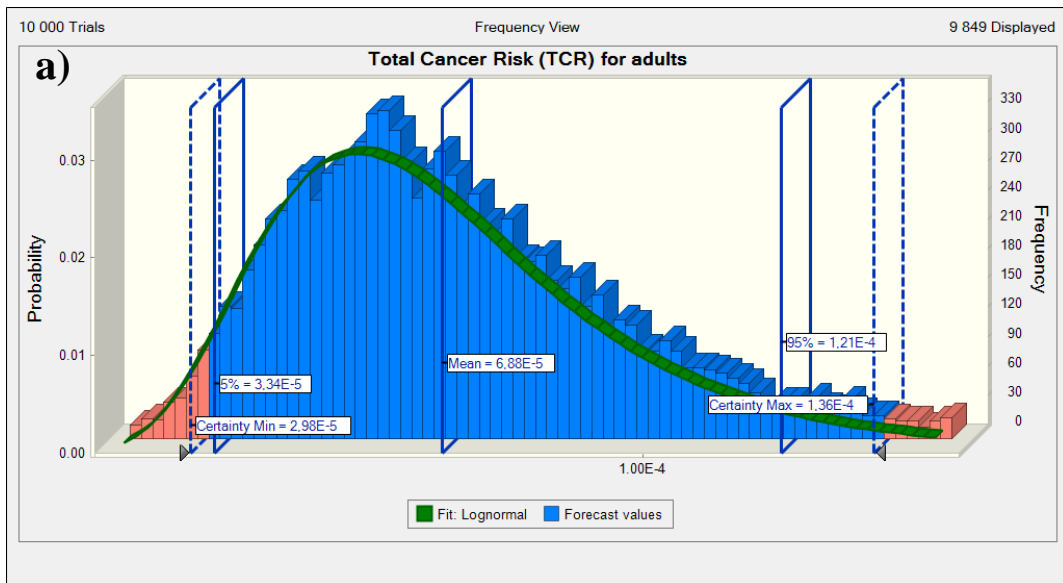


Figure 2-18. Simulated total carcinogenic risk (TCR) for the considered age groups in the examined surface soil around Benguerir dumpsite: **a)** TCR for adults; **b)** TCR for children; **c)** sensitivity diagram for adults; **d)** sensitivity diagram for children

### 2.3.5.2 Case study 2: Oum Azza landfill

- **Deterministic non-carcinogenic human health risk**

The composite non-carcinogenic health risk was assessed for the local communities (children and adults) living in the study area using the minimum, average and maximum values measured for the examined TTMs considering ingestion, inhalation, and dermal absorption pathways of contamination are summarized in **Table 2-14**. As clearly shown the non-carcinogenic impact on human health expressed in terms of HQs, HIs, and THIs values for ingestion pathway were found to be higher in comparison to other considered routes of exposure, which is consistent with similar previous studies that reported that ingestion is the main pathway could pose the highest non-carcinogenic risk adverse on the health of children and adults living in the impacted area (Essien et al., 2019; Fadili et al., 2022). In addition, Pb, Cd and As exhibited the highest hazard index (HI) in regard to other metal(oid)s for both age groups (children and adults) owing to their elevated contents in surface soils and lower reference dose (RfD). It should be pointed out that it was found that for all trace metal(oid)s, HQs, HIs, and THs for children were higher for all exposure pathways than for adults. For example, the average total hazard index (THI) was approximately ten times higher for children (THI = 0.425) than for adults (THI = 0.043). Because children were the most vulnerable group to environmental contaminants due to their lower immunology and sensitivity (Mallongi, Astuti, et al., 2021; Varol & Tokatlı, 2023; X. Wang et al., 2022). However, until now the hazard index was less than the acceptable limit of 1 in all examined soil samples, suggesting that the exposure to metal(oid)s through multi-pathways was still acceptable for people living around the study area. However, the continuous accumulation of metal(oid)s concentration could initiate a whole chain of adverse dangerous effects on human health in the future, especially since other metals are not considered in the present investigation, e.g., Hg and Co which also could be brought a non-negligible influence on the human health.

- **Deterministic carcinogenic human health risk**

The carcinogenic risk posed by the accumulation of TTMs in surface soils was calculated considering the multi-pathways exposure to As, Pb, Cd, Ni, and Cr for which slope factor (SF) was available according to the EPA (USEPA, 2005). Based on the results summarized in **table 2-15**, the CR and TCR risks for both age groups (children and adults) pointed out that ingestion was found as the principal pathway for carcinogenic risk for all metal(oid)s, followed by dermal contact and inhalation, respectively. Concerning the carcinogenetic impact, the average calculated total cancer risk (TCR) values due to the exposure to all metal(oid)s were 7.60E-04 and 8.32E-05 for children and adults, respectively. Thus, the calculated carcinogenic for both

age groups were higher than the acceptable limit of  $10^{-6}$ , at the same time, the average value for children was observed to be higher than the threshold value of  $10^{-4}$ , which reflects that the multi-pathways exposure to TTMs had a significant cancer risk. And therefore, the residents of the study area are all exposed to cancer implications emanating from the exposure to metal(oid)s. It is pointed out that the measured TCR values were found much higher compared to other similar studies carried out in Turkey (Varol & Tokatlı, 2023) and Saudi Arabia (Ali et al., 2019) and in the same range as what was reported in India (Pirsaheb et al., 2021).

- **The Monte Carlo simulation (MCS)**

Several reasons could lead to an overdetermination or underdetermination of the above-calculated human health risk including body weight, metal(oid)s concentration, exposure duration, exposure frequency, etc. To overcome these limitations Montecarlo simulation (what-if-analysis) was introduced in the present paper. Histograms and tornado sensitivity diagrams for simulating Total hazard index (THI) and Total cancer risk (TCR) for children and adults due to long-term exposure to metal(oid)s are depicted in **Figs.2-19** and **2-20**, respectively. From the probability estimation, it is observed that the 50<sup>th</sup> percentile was equivalent to the NCR calculated through the deterministic method. By comparing the average value for both children (0.425) and adults (0.368) through the deterministic approach (**Table 2-14**) and the 50<sup>th</sup> percentile of risk distribution from the probabilistic approach (i.e., 0.368 for children and 0.045 for adults), it is clearly observed that the findings are nearly the same. From the probability estimation, it is observed that children had higher probability to have non-carcinogenic adverse health than adults, with a 95<sup>th</sup> percentile of 0.542 in regard to 0.067 for adults. Which is in agreement with previous studies (Rajasekhar et al., 2018; Q. Yang et al., 2022) indicating that children were the most sensitive groups in the studied exposed population.

As depicted in **Fig.2-20**, the probability distribution of total carcinogenic risks, showed that the 5<sup>th</sup> percentile and mean values due to the accumulation of TTMs in surface soils ranged between  $3.07E-4$ ,  $6.20E-4$  for children and  $3.40E-5$ ,  $7.23E-5$  for adults, both age groups exceed the acceptable value of  $1E-06$  by almost 307 and 34 times for children and adults, respectively. This implies that almost 95% of the population living in the study area faced cancer risks if corrective actions are not taken as soon as possible, particularly for children. Meanwhile, the 95<sup>th</sup> percentile of TCR values for children and adults were approximately 11 and 1.3 times higher than the threshold value ( $10E-4$ ).

- **Sensitivity and uncertainty analysis**

Sensitivity analysis was also employed in the current paper to highlight the most effective parameters in the calculated total hazard index (THI) and Total cancer risk (TCR) due to the

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long-term exposure to TTMs, the obtained results are presented as tornado plots in **Fig.19 (c-d) and Fig.20 (c-d)**. Our findings showed that the exposure frequency (EF) was the most significant factor, with the highest positive variability of 32.5%, followed by Pb (14.4%), Cr (13.6%), As (8.3%), and Cd (0.8%) for the adults, similarly EF, Pb, Cr, As and Cd were the most significant parameters for children with a variability of 36.5%, 21.8%, 15.8%, 6.3%, and 0.9% respectively. Body weight (BW) was the most insignificant parameter in the estimated total hazard index (THI) with a total variability of -34% and -16.90% for adults and children, respectively. In other words, the increase in BW can significantly reduce potential health risks (Pasupuleti et al., 2022).

The tornado plots of carcinogenic risk indicated that EF, Ni, and Cr were the most sensitive risk factors comprising a contribution of 12.4%, 68.3%, and 4% for adults and 13.7%, 73.6%, and 5.6% for children. Likewise, Pasupuleti et al. (2022) conducted a sensitivity analysis and reported that the concentration of metal(oid)s was the most significant factor in the NCR and CR, and body weight was the most insignificant among the parameters. Ni had the highest contribution in carcinogenicity risk among the studied contaminants and thus required the strictest control.

### **2.3.5.3 Comparison and Summary**

The calculated and simulated human risks reflect that landfilling activities and open dumpsites could have a non-negligible adverse effect on human health in terms of both carcinogenic and non-carcinogenic risks. This investigation highlights the urgent need for policymakers to enforce regulations and strategies to limit pollution. Even controlled landfills can have harmful effects due to leachate spillage, so it is essential to ensure rigorous quality control of the sealing system, especially the HDPE geomembrane. Ignoring the long-term effects of landfill liner system degradation can lead to a severe underestimation of a landfill's environmental impact. Sun et al. (2019) investigated the long-term behavior of HDPE geomembranes under field conditions, using analytical and mechanical tests, as well as the geo-electric leak location method. The study's findings showed that HDPE geomembranes have a service life of approximately eight years in landfill operations. After this period, the hydraulic performance of the liner system significantly deteriorates. These results serve as a reminder of the need to take action to control the aging process of HDPE geomembranes in landfill environments to prolong their service life. Additionally, the findings highlight the importance of considering the long-term emissions of landfills and the impact of secondary waste disposal when conducting a comprehensive life cycle assessment of landfills.

Table 2-14. Non-carcinogenic risks posed to adults and children by each element and exposure pathway around Oum Azza landfill.

Metal(oid)s	level	conce (mg/kg)	Children						HI Total Pahway	Adults						HI Total Pathway
			Oral ingestion		Dermal exposure		Inhalation			Oral ingestion		Dermal exposure		Inhalation		
			ADD	HQ	ADD	HQ	ADD	HQ		ADD	HQ	ADD	HQ	ADD	HQ	
<b>Pb</b> (mg/kg)	Min	12.24	1.56E-04	4.47E-02	4.38E-07	8.34E-04	4.20E-09	1.19E-06	4.55E-02	1.68E-05	4.79E-03	6.80E-08	1.30E-04	2.46E-09	7.00E-07	4.92E-03
	Max	78.97	1.01E-03	2.88E-01	2.83E-06	5.38E-03	2.71E-08	7.70E-06	2.94E-01	1.08E-04	3.09E-02	4.39E-07	8.37E-04	1.59E-08	4.52E-06	3.17E-02
	Mean	24.86	3.18E-04	9.08E-02	8.90E-07	1.70E-03	8.53E-09	2.42E-06	9.25E-02	3.41E-05	9.73E-03	1.38E-07	2.63E-04	5.01E-09	1.42E-06	1.00E-02
<b>Cu</b> (mg/kg)	Min	2.76	3.53E-05	8.82E-04	9.87E-08	8.23E-06	9.46E-10	2.37E-08	8.90E-04	3.78E-06	9.45E-05	1.53E-08	1.28E-06	5.56E-10	1.39E-08	9.57E-05
	Max	16.48	2.11E-04	5.27E-03	5.90E-07	4.92E-05	5.66E-09	1.41E-07	5.32E-03	2.26E-05	5.64E-04	9.17E-08	7.64E-06	3.32E-09	8.30E-08	5.72E-04
	Mean	4.10	5.24E-05	1.31E-03	1.47E-07	1.22E-05	1.41E-09	3.52E-08	1.32E-03	5.62E-06	1.40E-04	2.28E-08	1.90E-06	8.26E-10	2.06E-08	1.42E-04
<b>Cr</b> (mg/kg)	Min	9.71	1.24E-04	4.14E-02	3.48E-07	5.80E-03	3.33E-09	1.17E-04	4.73E-02	1.33E-05	4.44E-03	5.40E-08	9.00E-04	1.96E-09	6.84E-05	5.40E-03
	Max	51.90	6.64E-04	2.21E-01	1.86E-06	3.10E-02	1.78E-08	6.23E-04	2.53E-01	7.11E-05	2.37E-02	2.89E-07	4.81E-03	1.05E-08	3.66E-04	2.89E-02
	Mean	19.10	2.44E-04	8.14E-02	6.84E-07	1.14E-02	6.55E-09	2.29E-04	9.30E-02	2.62E-05	8.72E-03	1.06E-07	1.77E-03	3.85E-09	1.35E-04	1.06E-02
<b>Zn</b> (mg/kg)	Min	29.20	3.73E-04	1.24E-03	1.05E-06	1.74E-05	1.00E-08	3.34E-08	1.26E-03	4.00E-05	1.33E-04	1.62E-07	2.71E-06	5.88E-09	1.96E-08	1.36E-04
	Max	85.41	1.09E-03	3.64E-03	3.06E-06	5.10E-05	2.93E-08	9.77E-08	3.69E-03	1.17E-04	3.90E-04	4.75E-07	7.92E-06	1.72E-08	5.74E-08	3.98E-04
	Mean	49.13	6.28E-04	2.09E-03	1.76E-06	2.93E-05	1.69E-08	5.62E-08	2.12E-03	6.73E-05	2.24E-04	2.73E-07	4.55E-06	9.90E-09	3.30E-08	2.29E-04
<b>Ni</b> (mg/kg)	Min	9.64	1.23E-04	6.16E-03	3.45E-07	6.39E-05	3.31E-09	3.68E-05	6.26E-03	1.32E-05	6.60E-04	5.36E-08	9.93E-06	1.94E-09	2.16E-05	6.92E-04
	Max	53.73	6.87E-04	3.43E-02	1.92E-06	3.56E-04	1.84E-08	2.05E-04	3.49E-02	7.36E-05	3.68E-03	2.99E-07	5.53E-05	1.08E-08	1.20E-04	3.86E-03
	Mean	25.44	3.25E-04	1.63E-02	9.11E-07	1.69E-04	8.73E-09	9.70E-05	1.65E-02	3.48E-05	1.74E-03	1.41E-07	2.62E-05	5.12E-09	5.69E-05	1.83E-03
<b>Cd</b> (mg/kg)	Min	0.21	2.68E-06	2.68E-03	7.52E-09	7.52E-04	7.21E-11	7.21E-06	3.44E-03	2.88E-07	2.88E-04	1.17E-09	1.17E-04	4.23E-11	4.23E-06	4.09E-04
	Max	2.93	3.75E-05	3.75E-02	1.05E-07	1.05E-02	1.01E-09	1.01E-04	4.81E-02	4.01E-06	4.01E-03	1.63E-08	1.63E-03	5.90E-10	5.90E-05	5.70E-03
	Mean	0.89	1.14E-05	1.14E-02	3.18E-08	3.18E-03	3.05E-10	3.05E-05	1.46E-02	1.22E-06	1.22E-03	4.94E-09	4.94E-04	1.79E-10	1.79E-05	1.73E-03
<b>As</b> (mg/kg)	Min	0.52	6.65E-06	2.22E-02	1.86E-08	1.51E-04	1.78E-10	5.95E-07	2.23E-02	7.12E-07	2.37E-03	2.89E-09	2.35E-05	1.05E-10	3.49E-07	2.40E-03
	Max	2.99	3.82E-05	1.27E-01	1.07E-07	8.70E-04	1.03E-09	3.42E-06	1.28E-01	4.09E-06	1.36E-02	1.66E-08	1.35E-04	6.02E-10	2.01E-06	1.38E-02
	Mean	1.81	2.31E-05	7.71E-02	6.48E-08	5.27E-04	6.21E-10	2.07E-06	7.77E-02	2.48E-06	8.26E-03	1.01E-08	8.18E-05	3.65E-10	1.22E-06	8.35E-03
<b>Fe</b> (mg/kg)	Min	5671.50	7.25E-02	1.04E-01	2.03E-04	4.51E-03	1.95E-06	8.85E-03	1.17E-01	7.77E-03	1.11E-02	3.15E-05	7.01E-04	1.14E-06	5.19E-03	1.70E-02
	Max	6583.00	8.42E-02	1.20E-01	2.36E-04	5.24E-03	2.26E-06	1.03E-02	1.36E-01	9.02E-03	1.29E-02	3.66E-05	8.14E-04	1.33E-06	6.03E-03	1.97E-02
	Mean	6183.32	7.91E-02	1.13E-01	2.21E-04	4.92E-03	2.12E-06	9.64E-03	1.28E-01	8.47E-03	1.21E-02	3.44E-05	7.64E-04	1.25E-06	5.66E-03	1.85E-02
THI for min. values (TTMs)				2.23E-01	1.21E-02		9.01E-03		<b>2.44E-01</b>	2.15E-02		1.86E-03		5.29E-03		<b>2.86E-02</b>
THI for max. values (TTMs)				8.38E-01	5.34E-02		1.12E-02		<b>9.03E-01</b>	7.61E-02		8.16E-03		6.58E-03		<b>9.09E-02</b>
THI for mean. Values (TTMs)				3.93E-01	2.19E-02		1.00E-02		<b>4.25E-01</b>	3.39E-02		3.32E-03		5.87E-03		<b>4.31E-02</b>

Table 2-15. Carcinogenic risks posed to adults and children by each element and exposure pathway around Oum Azza landfill.

Metal(oid)s	level	conce (mg/kg)	Children				Adults			
			Oral ingestion	Dermal exposure	Inhalation	TCR total pathways	Oral ingestion	Dermal exposure	Inhalation	TCR total pathways
Pb (mg/kg)	Min	12.24	1.33E-06	3.72E-09	3.71E-07	1.70E-06	1.42E-07	5.78E-10	1.04E-10	1.24E-06
	Max	78.97	8.58E-06	2.40E-08	2.25E-07	8.83E-06	9.19E-07	3.73E-09	6.68E-10	9.24E-07
	Mean	24.86	2.70E-06	7.57E-09	2.64E-06	5.35E-06	2.89E-07	1.18E-09	2.10E-10	2.91E-07
Cr (mg/kg)	Min	9.71	6.21E-05	6.96E-07	1.40E-07	6.29E-05	6.65E-06	1.08E-07	8.22E-08	6.84E-06
	Max	51.90	3.32E-04	3.72E-06	7.48E-07	3.36E-04	3.55E-05	5.77E-07	4.39E-07	3.66E-05
	Mean	19.10	1.22E-04	1.37E-06	2.75E-07	1.24E-04	1.31E-05	2.12E-07	1.62E-07	1.35E-05
Ni (mg/kg)	Min	9.64	2.10E-04	1.47E-05	2.78E-09	2.24E-04	2.25E-05	2.28E-06	1.63E-09	2.47E-05
	Max	53.73	1.17E-03	8.17E-05	1.55E-08	1.25E-03	1.25E-04	1.27E-05	9.09E-09	1.38E-04
	Mean	25.44	5.53E-04	3.87E-05	7.33E-09	5.92E-04	5.92E-05	6.01E-06	4.30E-09	6.53E-05
Cd (mg/kg)	Min	0.21	1.02E-06	2.86E-09	4.54E-10	1.02E-06	1.09E-07	4.44E-10	2.67E-10	1.10E-07
	Max	2.93	1.42E-05	3.99E-08	6.33E-09	1.43E-05	1.53E-06	6.19E-09	3.72E-09	1.54E-06
	Mean	0.89	4.32E-06	1.21E-08	1.92E-09	4.33E-06	4.63E-07	1.88E-09	1.13E-09	4.66E-07
As (mg/kg)	Min	0.52	9.97E-06	6.81E-08	2.69E-09	1.00E-05	1.07E-06	1.06E-08	1.58E-09	1.08E-06
	Max	2.99	5.73E-05	3.92E-07	1.55E-08	5.77E-05	6.14E-06	6.08E-08	9.09E-09	6.21E-06
	Mean	1.81	3.47E-05	2.37E-07	9.38E-09	3.50E-05	3.72E-06	3.68E-08	5.51E-09	3.76E-06
Cumulative carcinogenic risk for min. values			2.84E-04	1.54E-05	5.17E-07	<b>3.00E-04</b>	3.04E-05	2.40E-06	8.58E-08	<b>3.40E-05</b>
Cumulative carcinogenic risk for max values			1.58E-03	8.59E-05	1.01E-06	<b>1.67E-03</b>	1.69E-04	1.33E-05	4.62E-07	<b>1.83E-04</b>
Cumulative carcinogenic risk for mean. values			7.17E-04	4.03E-05	2.94E-06	<b>7.60E-04</b>	7.68E-05	6.27E-06	1.73E-07	<b>8.32E-05</b>

Note: E is the abbreviation of exponent, which means the index based on 10.

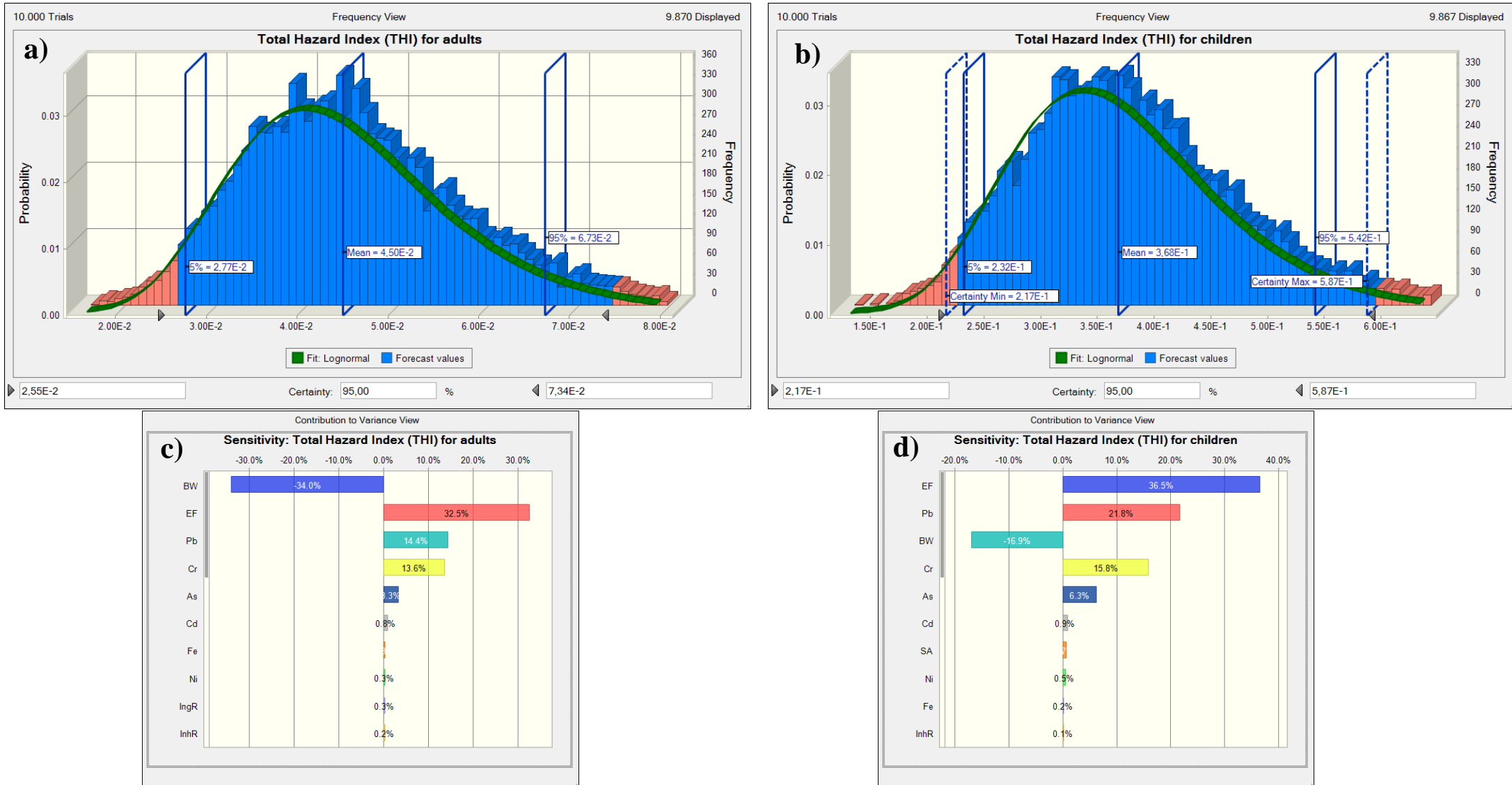


Figure 2-19. Simulated total hazard index (THI) for the considered age groups in the examined surface soil around Oum Azza landfill: **a)** THI for adults; **b)** THI for children; **c)** sensitivity diagram for adults; **d)** sensitivity diagram for children.

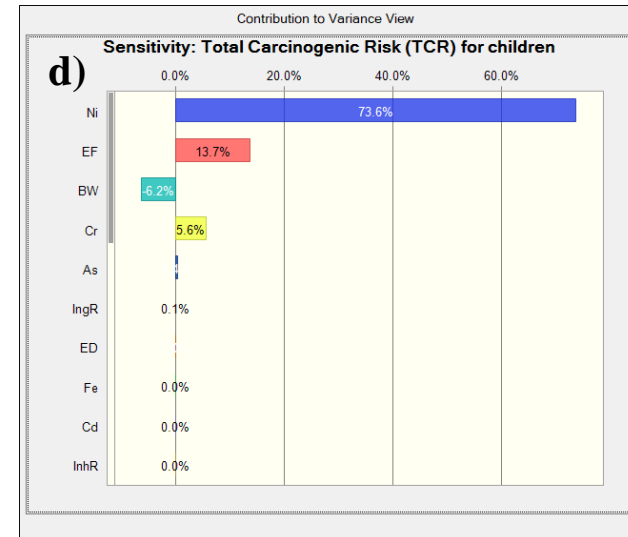
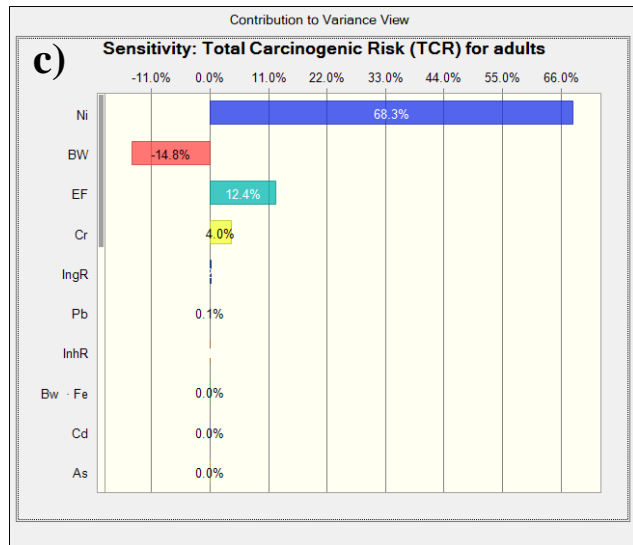
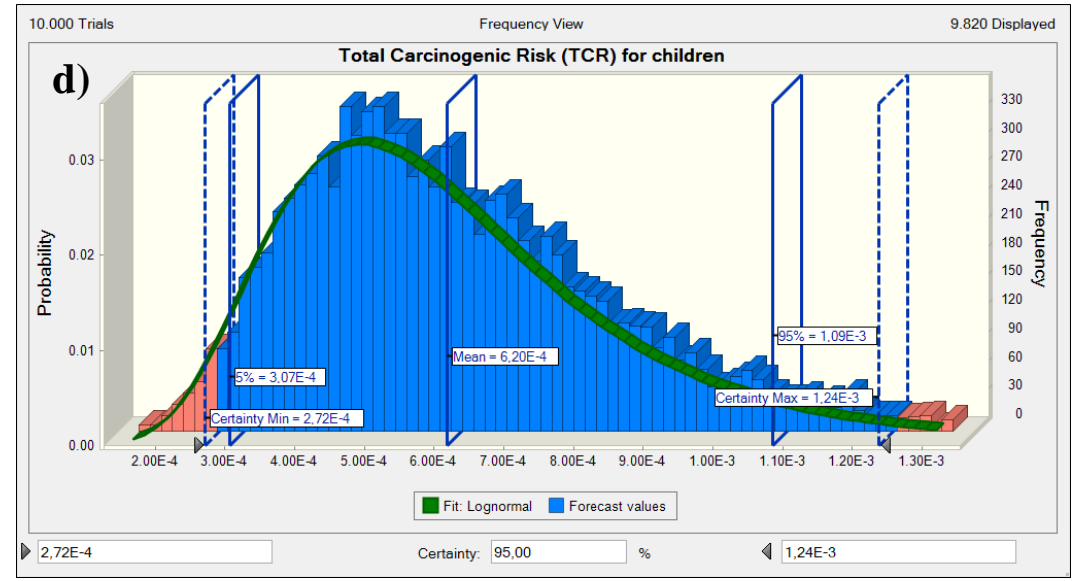
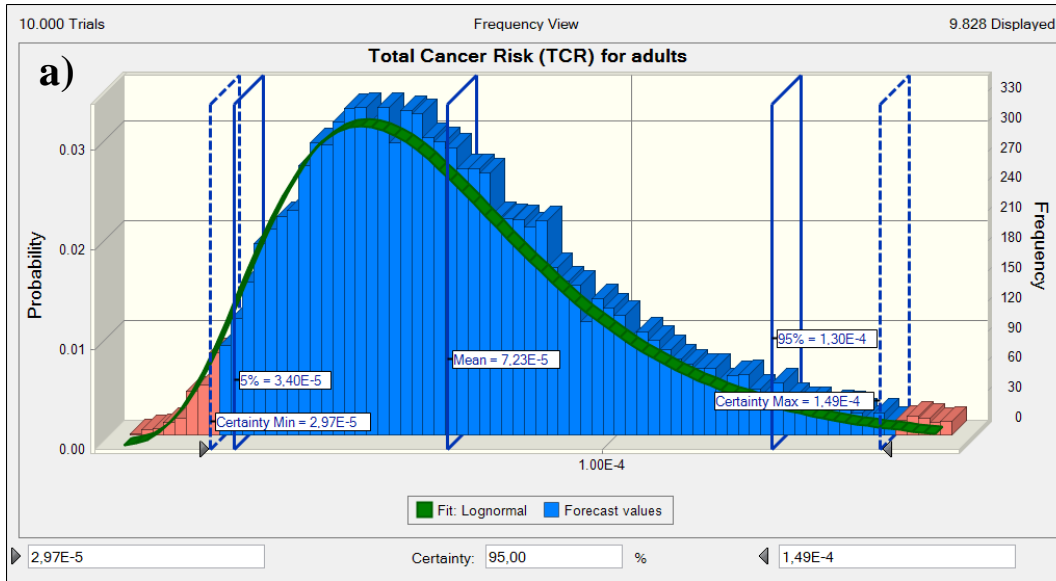


Figure 2-20. Simulated total carcinogenic risk (TCR) for the considered age groups in the examined surface soil around Oum Azza landfill: **a)** TCR for adults; **b)** TCR for children; **c)** sensitivity diagram for adults; **d)** sensitivity diagram for children

## **2.4 Conclusion**

In this study, PCA, HCA, pollution indices, deterministic and probabilistic HHR assessment were combined to comprehensively assess the source contribution, contamination degree, ecological risk and human health of 8 typical metal(oid)s in surface soils around Oum Azza landfill (2100 tons/day) and Benguerir' open dumpsite (90 tons/day). The concentration of examined metal(oid)s (Pb, Cd, Cr, Zn, Fe, Ni, As and Cu) exceed the geochemical reference, as well as the pollution indices showed that the soils in the vicinity of the landfills were significantly impacted by metal(oid)s, especially Cd, As and Pb, with a high ecological risk. In other words, the obtained results reflected that landfilling activities and intensive agriculture contributed significantly to the accumulation of total and available fractions of trace metal(oid)s around the study area, most of metal(oid)s were found above their corresponding background values. The assessment of the non-carcinogenicity and carcinogenicity risks indicated that both children and adults faced a high probability of adverse health. The findings suggest that both landfills and open dumpsites could have a detrimental effect on the quality of soils in the study area, and effective measures and targeting policies should be taken urgently to reduce the continuous spread of contaminants and the increase health risks in these regions.

### **Chapter III: A comprehensive health risk assessment and groundwater quality for irrigation and drinking purposes around municipal solid waste sanitary landfill: (A case study in Oum Azza)**

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#### **Highlights:**

- The variation of physicochemical parameters and heavy metal(oid)s content of groundwater and leachate were comprehensively monitored around Oum Azza' landfill.
- The severity of leachate was appraised using leachate pollution index (LPI)
- Concentrations of all examined parameters exceeded their permissible values established by the WHO.
- Various indices (WQI, PIN...) reflects a significant impact of landfill and agriculture on water resources in the studied area.
- Most groundwater samples became unsuitable for irrigation and drinking purposes.
- Carcinogenic and non-carcinogenic health risk were evaluated using the USEPA model.
- The human health risk is still within acceptable level.
- Urgent intervention is required to prevent leachate leakage from the landfill and minimize the use of manure and fertilizers.

## Chapter III: A comprehensive health risk assessment and groundwater quality for irrigation and drinking purposes around municipal solid waste sanitary landfill: (A case study in Benguerir and Oum Azza)

### Graphical abstract

The figure 3.1 showed the summary view of the present chapter

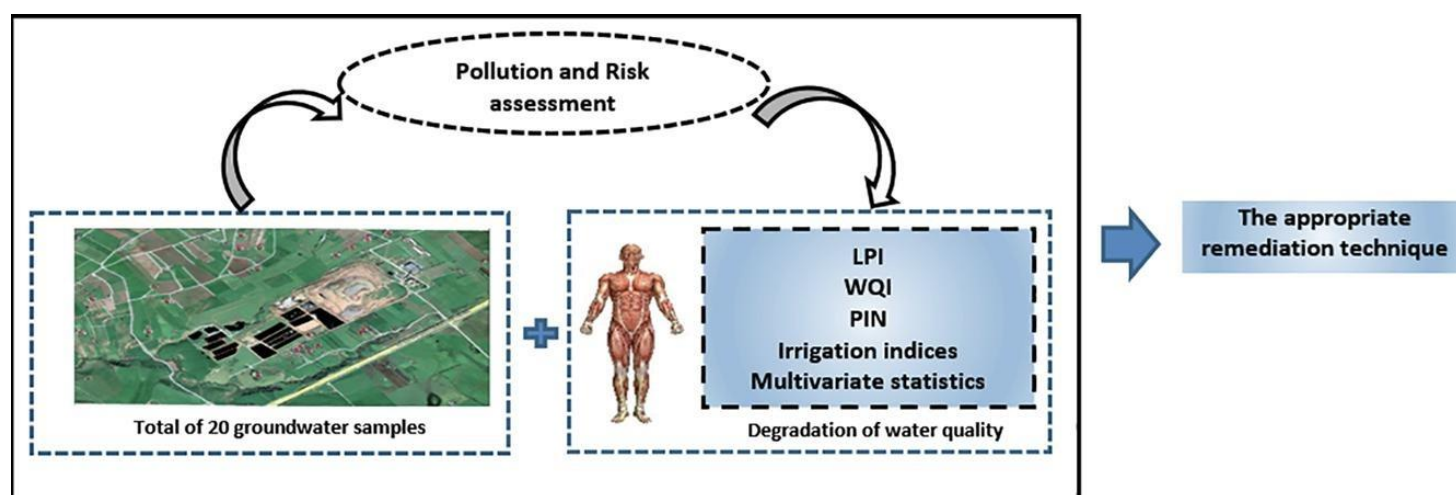


Figure 3-1. Graphical abstract of the chapter.

### General summary

The proper management of municipal solid waste for the reduction of its potential impacts on the environment is one of the most challenging issues faced by the world. In this study, a comprehensive characterization of leachate and groundwater was carried out surrounding the Oum Azza sanitary landfill in Morocco to assess their potential risks to human health. The groundwater quality was analysed using quality indices and chemometric expertise. For this purpose, spatiotemporal variation of sixteen (16) physico-chemical parameters and nine (9) heavy metals (Cd, Pb, Ni, Cu, Cr, Hg, Ni, Zn, and Fe) in groundwater and leachate were studied. Experimental data showed elevated leachate contamination potential (LPI=29.14) surpassed the permissible limits for discharge of leachate. Besides, the application of WQI (27.47-214.58), Nemerow index (0.72-6.17), irrigation quality indices (SAR, MHR, %Na, KI, and PI), and spatial distribution revealed the unsuitability of most of the groundwater samples in vicinity of the landfill area for drinking and irrigation purposes. However, the carcinogenic and non-carcinogenic risks are still within acceptable limits for residential receptors. The multivariate statistical (PCA and HCA) analysis suggested that the deterioration of groundwater quality was mainly originated from anthropogenic sources related to landfill leachate. This study proved an alarming threat of the

groundwater in vicinity of the sanitary landfills due to leachate pollution. It is important to note that despite the fact that the landfill is a sanitary landfill and provided with liners, leachate contamination potential is inevitable. Thus, it is important to continuously monitor the groundwater quality surrounding the landfill. The study also recommended emphasizing on the status and conditions of geomembrane used in the landfill liner systems to prevent leachate percolation into the groundwater.

**Keywords:** Sanitary landfill, Water quality index, Leachate pollution index, Groundwater quality, irrigation indices, Nemerow pollution indice, Human health risk.

### 3.1 Introduction

Water is undoubtedly the most precious resource for human wellbeing. Unfortunately, water is extensively wasted and polluted by both natural and anthropogenic activities. The enormous economic and industrial growth are often accompanied by urbanization and population growth. As a consequence, the quantity of municipal solid waste (MSW) produced in the last few decades has increased significantly throughout the world (Somani et al., 2019), despite the development of waste management practices including incineration, composting, and recycling (Aziz et al., 2021; Baghanam et al., 2020; Fadili et al., 2022). The disposal of waste in landfills is still one of the widely used methods for municipal solid waste management (Chidichimo et al., 2020; Kapelewska, Kotowska, Karpi, et al., 2019). As a result, mitigation of negative environmental impacts of landfilling has become one of the most challenging issues of the world (Akoto et al., 2021).

The decomposition by-products of solid wastes and the rainwater seeping through layers of wastes produce landfill leachate. It is a heterogeneous mixture of organic and inorganic compounds and its physicochemical and microbiological composition depend on several parameters including climate conditions and the composition of municipal waste. Landfill leachate can cause severe environmental and human health issues if it is discharged to the environment without proper treatment. It has been demonstrated that leachate consists of a myriad of pollutants including dissolved organic matter, heavy metals and salts (Przydatek & Kanownik, 2019; Talalaj & Biedka, 2016; Tenodi et al., 2020). The leachate management has become a burning issue throughout the world because the untreated leachate could significantly affect the quality of ground-and surface waters in its vicinity. In this context, the environmental concern and the possible scenarios of water pollution, migration of leachate pollution have been extensively discussed in the literature (Alam

et al., 2020; Bellezoni et al., 2014; Najafi Saleh et al., 2020; Przydatek & Kanownik, 2019; Rathod et al., 2013; S. Singh et al., 2016; Talalaj & Biedka, 2016; Tenodi et al., 2020).

Like many other countries in the world, Morocco, is not exempt from groundwater contamination by leachate because of poor solid waste management strategies. According to the Moroccan Ministry of Energy, Mines and Environment, the estimated solid waste generation in Morocco is up to 7 million tons per year, with a footprint of 0.76 kg per capita per day, and the most common disposal destinations are landfills. There are about 300 open dump sites and 16 engineered landfills around major cities in Morocco and the open dumpsites have been constructed without proper mechanisms to collect and to treat leachate. Despite the strong legislation and policymakers' interest towards adoption of the national household waste program (NHWP), and construction of sanitary landfills, there is no strict guidelines for waste disposal due to technical and financial constraints. As a result, negative impacts on the environment by dumpsites are becoming acute in larger cities because the disposal facilities available are less than the quantity generated.

The mismanagement of local landfills exacerbates the undesirable long-term impact on soils and water resources. A few studies have been conducted to investigate the potential impact of waste around landfills in Morocco (Chofqi et al., 2004; Gamar et al., 2018; Smahi et al., 2013), and they observed considerable negative environmental impacts of landfilling practices. However, most of the previous studies have focused on assessing and comparing the experimental data with existing water quality standards (National and international) without explaining in detail the causes behind the revealed pollution, assessing the potential human risks on the community living adjacent to these landfills and concluding an overall idea about the use of polluted water for drinking and agriculture, compared to other research conducted worldwide (Baghanam et al., 2020; Kapelewska et al., 2019; Tenodi et al., 2020).

In this regard, the current research is focused on assessing the pollution occurring in shallow groundwaters and its possible risks to human health associated with landfilling activities of MSW. This chapter discusses and delineate the impacts of an existing sanitary landfill in Oum Azza and an open dumpsite in Benguerir on the surrounding environment with emphasis on the waste mismanagement issues in landfills and open dumps which could lead to the pollution of aquatic resources. A comprehensive quantification of the environmental impact by landfills is required for decision-makers to enforce their vision about landfill management practices and propose feasible recommendations to improve the current situation. The main objectives of the chapter are: *1*) characterizing the MSW leachate of Oum Azza landfill and Benguerir Open dumpsite, and

evaluate its severity using the leachate pollution index (LPI); **2)** assessing the groundwater quality in the vicinity of studied landfills; **3)** estimating the contamination of groundwater by landfill leachate, based on the calculation of Nemerow pollution index and Water Quality Index; **4)** classify the impacted sources based on their impact level using chemometrics expertise; **5)** evaluate the possible carcinogenic and non-carcinogenic risks on the community living near the study area using deterministic method from EPA and Montecarlo simulation; **6)** propose recommendations to ensure good monitoring and to prevent the extension of groundwater pollution.

## **3.2 Material and methods**

### **3.2.1 Description of the Study area**

The Oum Azza landfill is the largest non-hazardous and inert waste sanitary landfill in North Africa, with a total area of 110 hectares located in the commune of Oum Azza. It is situated approximately 20 km from Rabat, the capital of Morocco. The average altitude is approximately 170 m above mean sea level and the annual precipitation is around 548 mm with rainfall concentrated between October to May, with a peak in December. The average minimum and maximum temperatures recorded over the last 10 years at the Rabat station are respectively around 7.6 °C and 28.1 °C. The maximum temperature is often recorded in August and the minimum in January. The average potential evaporation is about 1600 mm/year. The prevailing winds are from the West, and occasionally from the Northwest and Southwest. Since its inauguration in 2007, the Oum Azza landfill receives an average of about 2100 tons of waste per day, characterized by high organic matter fraction (67 %, composed mainly of food waste green waste, and other putrescible), followed by (9%) plastics, papers–cardboard (6%), glass (0.5%), metals (0.5%), wood and textiles (6%), others (11%).

The areas surrounding the landfill are characterized by the presence of intense agriculture, cattle and sheep breeding. There is an aquifer with a water table depth ranging from 6 to 24 m from the soil surface. After reception and sorting of waste arrived at the facility, waste is stored in cells equipped with a HDPE membrane sealing system, biogas collection network, leachate treatment by activated sludge followed by reverse osmosis treatment. In geological terms, the studied site has mixed lithological, clay lithology with a permeability of less than  $10^{-6}$  m/s in the North. It has calcarenites formations in the South. More details about the geological and hydrogeological conditions in the study area are depicted in supplementary materials. The location of the study area and geographic coordinates of collected samples is shown in **Fig. 3-2**.

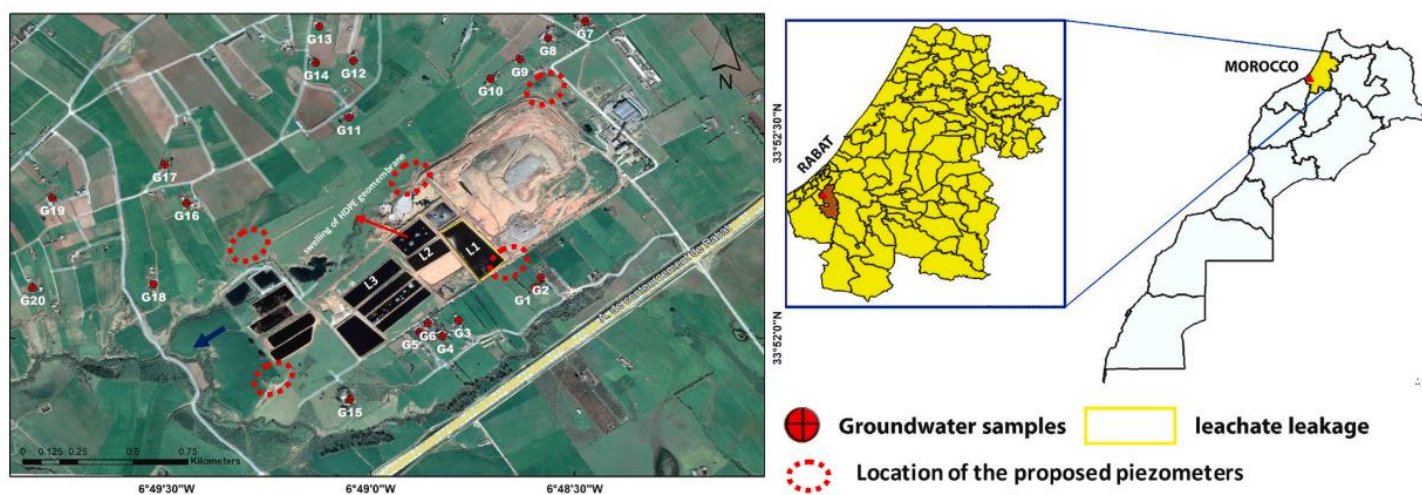


Figure 3-2. Study area map showing groundwater sampling location around Oum Azza landfill site.

### 3.2.2 Sampling methodology

The current study required the collection of well-distributed water quality data in both space and time to evaluate the possible environmental impact of Oum Azza landfill on its surrounding water bodies. Field sampling were performed during the dry (June) and the wet climate seasons (December) in 2021. Water samples were collected in pre-cleaned polyethylene bottles from 20 dug-wells in the vicinity of the landfill which are commonly used for agricultural and drinking purposes. The samples for trace metal(oid)s analysis were collected separately and preserved by adding few drops of 7 M nitric acid. All the leachate samples were collected according to the ISO 5667-10 standard method (Tenodi et al., 2020). All water and leachate samples were brought to the laboratory immediately using a refrigerator box at 4°C. The groundwater and leachate samples were labelled as G and L, respectively (*see fig. 3-2*).

### 3.2.3 Chemicals and reagents

All glassware and plasticware used in the current study were autoclaved and then rinsed thoroughly using 1 % nitric acid solution and finally with distilled water (Taati et al., 2020; Yijing et al., 2020). The sampling bottles were filled with the samples leaving no space to prevent any contact with air. All tests were conducted using the standard procedures for water and wastewater examination recommended by the American Public Health Association (APHA, 2005) in an accredited CNRST Laboratories (Rabat, Morocco). The experimental data presented in the manuscript are the average of three replicates.

### 3.2.4 Physical and chemical analysis

Sixteen (16) water quality parameters and nine (9) heavy metal(oid)s were analysed in the study. Temperature, pH, total dissolved solids (TDS), electrical conductivity (EC), and

dissolved oxygen (DO) concentration were measured *in-situ* using a portable multi-parameter analyser (Aquared AQUALINK). The TDS/EC ratio was within acceptable limits (0.6 - 0.8) confirming the reliability of the analytical results. Biochemical oxygen demand (BOD<sub>5</sub>) was carried out with respirometric method (BOD Sensor, VELP SCIENTIFICA), while COD was measured by the dichromate oxidation method. The total phosphate (TP) and ortho phosphate (OP) were determined as described previously by Kapelewska et al. (2019). The ammoniacal nitrogen content was determined by the Kjeldahl method (Khawla & Mohamed, 2020). The concentration of major cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>), and anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>) were analysed by ion-exchange chromatography. The reliability of the results has been controlled based on the calculation of the charge balance error as described by the equation 3.1

$$\text{CBE}(\%) = 100 \times \left( \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \right) \quad (3.1)$$

where, the sum of amount of anions and cations values are expressed in meq/l. If the CBE is less than  $\pm 5\%$ , the measurement is valid, and was reported in the current work (All calculated ionic balance for study samples were performed using *Diagrammes software*).

Finally, the concentrations of heavy metal(oid)s Cu, Pb, Cd, Ni, Hg, As, Zn, Cr, and Fe were determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Ultima Expert - Horiba Jobin Yvon) after wet digestion using aqua-regia (Bouzekri, Laarbi, et al., 2019). The detection limits of metals are 0.10  $\mu\text{g/l}$ . All the experiments were triplicated to ascertain the precision and maintain the quality of the extraction method (Essien et al., 2019). If the relative standard deviation (RSD) for each measure was less than 5%, the measurement was retained, and the average value was reported.

### 3.2.5 Assessment methods

A set of various pollution indicators (Leachate pollution index, Nemerow pollution indices and Water quality index) were used to assess the toxicity of leachate and the suitability of nearby groundwater for agricultural and drinking purposes.

#### 3.2.5.1 Leachate pollution index (LPI) calculation

The leachate pollution index (LPI) is a straightforward and meaningful tool for quantifying and evaluating the potential threat of produced landfill leachate on their surrounding environment. It was formulated using the DELPHI method (D. Kumar & Alappat, 2005) and calculated using the eighteen (18) important parameters into a single value that is easy to interpret and gives a clear idea to decision-makers in order to choose the appropriate treatment technique for the leachate (Eq. 3.2).

$$\mathbf{LPI} = \sum_{i=0}^n \mathbf{w}_i \mathbf{p}_i \quad (3.2)$$

In a case of having less than eighteen 18 leachate parameters, LPI could be assessed using the available parameters as described in the Eq. 3.3.

$$\mathbf{LPI} = \frac{\sum_{i=1}^n \mathbf{w}_i \mathbf{p}_i}{\sum \mathbf{w}_i} \quad (3.3)$$

where:  $w_i$  is the assigned relative weight of each parameter, the choice of  $w_i$  based on the level of pollutant significance.

$P_i$  = the sub-index score of the  $i^{\text{th}}$  parameter.

$n$  = number of leachate parameters considered in calculating LPI

### 3.2.5.2 Water quality index (WQI) :

The water quality index (WQI) is known to be the most convenient tool widely used throughout the world (Adimalla & Li, 2018; Nong et al., 2020; Seifi et al., 2020; Verma et al., 2020; Wu et al., 2018) to assess the groundwater quality. The overall quality of water for drinking purposes based on the influence of each individual parameter. The following three steps are involved to calculate WQI: (a) weights ( $w_i$ ) are assigned to each water quality parameter involved; (b) computing the relative weight ( $W_i$ ) as given by the Eq. 3.4; (c) calculate the quality rating scale (Eq. 3.5)

$$\mathbf{W}_i = \frac{\mathbf{w}_i}{\sum_{i=1}^n \mathbf{w}_i} \quad (3.4)$$

$$\mathbf{Q}_i = \left( \frac{\mathbf{C}_i}{\mathbf{S}_i} \right) \times 100 \quad (3.5)$$

where:  $Q_i$ : the pollution index for the  $i^{\text{th}}$  parameter,  $C_i$ : the monitoring value of the parameter (i), and  $S_i$ : the standard value of the same parameter (i). The standard for parameters in the presented case study was derived from relevant national and international legislation, the standard World Health Organisation guidelines for drinking water quality. When the WHO standards were not available, the Moroccan drinking water standards were applied. The WQI is given Eq 3.6.

$$\mathbf{WQI} = \mathbf{W}_i \times \mathbf{Q}_i \quad (3.6)$$

### 3.2.5.3 Nemerow Pollution Index:

Similar to WQI, this comprehensive index indicates its usefulness as an assessment tool in some previous studies in order to understand and evaluate the pollution levels of groundwater under

the impact of municipal solid waste landfills (Han et al., 2016; Jie et al., 2012; Tenodi et al., 2020).

$$PIN = \sqrt{\frac{P_{i\text{avg}}^2 + P_{i\text{max}}^2}{2}} \quad (3.7)$$

where:  $Q_i=P_i$ ,  $P_{\text{avg}}$ : the average value of  $P_i$  for all samples, and  $P_{\text{max}}$  is the maximum value for the same samples. The grading method for PIN and WQI indices were summarized in **Table 3-1**.

Table 3-1. Grading method for WQI and Nemerow index.

Class	WQI	PIN
1	WQI < 50 <b>Best Quality</b>	$PI \leq 0.7$ <b>secure (No impact)</b>
2	$50 \leq WQI < 100$ <b>Good Quality</b>	$0.7 < PI \leq 1$ <b>alert (Very small impact)</b>
3	$100 \leq WQI < 200$ <b>Acceptable Quality</b>	$1 < PI \leq 2$ <b>slight (Lesser impact)</b>
4	$200 \leq WQI < 300$ <b>Threatened Quality</b>	$2 < PI \leq 3$ <b>moderate (Medium impact)</b>
5	WQI > 300 <b>Unsuitable for drinking</b>	$PI > 3$ <b>heavy impact</b>

#### 3.2.5.4 Irrigation water quality

Quality of water used for irrigation is a crucial parameter to ensure soil quality and crop improvement. The quality of water used in irrigation might affect both soil physical conditions and crop yields. To this end, several indices were calculated and interpreted to reveal the suitability of water under investigation for irrigation.

- **Sodium adsorption ratio (SAR)**

Introduced by the United States Salinity Laboratory (USSL) to study the sodium hazard and it is formulated as (Richard, 1954):

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}} \quad (3.8)$$

- **Soluble Sodium Percent (SSP)**

High amounts of sodium could profoundly influence plant growth and therefore, it is necessary to calculate sodium percentage using the following equation (Wilcox, 1955).

$$\%Na = \frac{Na^+}{(Ca^{2+} + Mg^{2+} + Na^+)} \times 100 \quad (3.9)$$

- **Magnesium hazard ratio (MHR)**

MHR was calculated using the following equation (Szabolcs & Darab, 1964).

$$MHR = \frac{Mg^{2+}}{(Ca^{2+} + Mg^{2+})} \times 100 \quad (3.10)$$

A harmful influence on soils appears when  $MHR > 50$

- **Permeability Index (PI)**

The soil permeability hazard is evaluated according to the following equation (Doneen, 1962)

$$PI = \frac{(Na^+ + \sqrt{HCO_3^-})}{(Ca^{2+} + Mg^{2+} + Na^+)} \times 100 \quad (3.11)$$

- **Kelly's Ratio (KR)**

KR is calculated according to the following equation and a harmful influence on soils appears when  $KR > 1$  (Szabolcs & Darab, 1964).

$$KR = \frac{Na^+}{Ca^{2+} + Mg^{2+}} \quad (3.12)$$

All ionic concentrations are expressed in meq/l.

### 3.2.6 Statistical analyses

Kolmogorov-Smirnov test ( $< 0.05$ ) was carried out to check the normality and homogeneity distribution of the parameters. Since the experimental data were found not normality distributed, non-parametric Spearman's correlation was used to investigate significant connections between involved pollutants, to identify their feasible sources (Taati et al., 2020). The significance level is considered when p is less than 0.05. In order to accomplish statistical analysis and obtain a reliable findings, all collected variables were subjected to normalization by computing their z-scores, Because parameters have different units, it makes no sense to aggregate two values with distinct units (Jahin et al., 2020).

Multivariate statistical analyses (MSAs) including factor analysis (FA) was also extensively employed to explore the possible sources of pollution (Baghanam et al., 2020; A. Hossen et al., 2021; Wdowczyk & Szymańska-Pulikowska, 2021a). It is a dimension reduction technique, widely used to transform complex data into PCs, and therefore make its interpretation easy. The verification of the adequacy of the data for this analyse, Kaiser Meyer Olkin (KMO) and Bartlett's Sphericity tests were performed on the parameter correlation matrix. In the presented study factor loadings higher than 0.7 were taken into consideration. Readers are directed to the

following paper (Abdi & Williams, 2010) to learn more details about PCA. HCA (Hierarchical Cluster Analysis) was also conducted to evaluate the effectiveness of assessment tools in grouping datasets, based on their chemical composition. All statistical calculations were performed using the statistical package for the social sciences (IBM SPSS software version 25.0) and Minitab 19.1.

### 3.2.7 Human health risk assessment

Potential non-carcinogenic and carcinogenic health risks for the community near the landfill (adults and children) from metals exposure in groundwater through ingestion and dermal contact were evaluated using the approach proposed by the USEPA. (2005).

#### 3.2.7.1 Exposure assessment

Chronic daily intake (mg/kg/day) for both groups (adults and children) was evaluated using the following equations

$$CDI_{\text{ingest}} = \left[ \frac{Ci \times \text{IngR} \times FC \times EF \times ED}{ABW \times AT} \right] \quad (3.13)$$

$$CDI_{\text{dermal}} = \left[ \frac{Ci \times SA \times FC \times AF \times ABS \times EF \times ED}{ABW \times AT} \right] \quad (3.14)$$

Where: CDI is the chronic daily intake of metals in mg/kg/day, Ci is the concentration of metal i, ED is the exposure duration (years), IngR is the daily ingestion of metal in mg/day, EF is the exposure frequency (350 days/year), ABW is the average body weight, the other parameters and their corresponding values are summarized in table SM1, as described by Varol et al. (2021).

#### 3.2.7.2 Non-carcinogenic risk assessment

Hazard quotients were computed to assess the individual non-carcinogenic health risks associated with seven TTMs in the water (Varol, Karakaya, et al., 2021), it is equal the ratio of CDI to the reference dose of each metal. Total Hazard Index (THI) is computed by aggregating the HQ for each metal. The equations below were used to calculate the above-mentioned health risk indices.

$$HQ = \frac{CDI}{RfD} \quad (3.15)$$

$$THI = \Sigma(HQ_{\text{ingestion}} + HQ_{\text{dermal}}) \quad (3.16)$$

According to USEPA. (2005),  $THI > 1$ , indicate that there are likely adverse health effects from metals exposure; however, when  $THI < 1$ , there is no adverse health effects (Varol, Gündüz, & Sünbül, 2021a)

### 3.2.7.3 Carcinogenic risk assessment

Exposure of humans to trace metals is a leading source of cancer. To this end, the potential carcinogenic risk was evaluated using the following equations as prescribed by USEPA. (2005)

$$(Cancer\ Risk)\ CR = CDI \times CSF \quad (3.17)$$

$$(Lifetime\ cancer\ risk)\ LCR = \sum CR (ingestion + inhalation + dermal) \quad (3.18)$$

Where: CSF is the cancer slope factor (mg/kg/day), carcinogenic health risks were calculated only for Pb, As, Cr and Cd which have CSF among the studied metals. The corresponding values of CSF are 0.0085, 1.5, 0.5 and 0.38 for Pb, As, Cr and Cd, respectively.

## 3.3 Results and Discussion

### 3.3.1 Results of leachate characterization

The descriptive statistical analysis of monitored physicochemical parameters of leachate samples during dry and wet seasons, and a comparison of its potential of pollution with other landfills sites from previous studies were shown in **Tables 3.2** and **3.3**. It should be noted that samples were collected randomly from three sites (Fig.3-2) and the mean value was reported. Leachate composition varies strongly among landfills depending on waste composition, landfilling techniques, ambient temperature, and age of dumped waste (Kjeldsen et al., 2010).

#### 3.3.1.1 pH, Temperature, TSS, and Turbidity

The raw leachate is characterized by an unpleasant odour due to the presence of hydrogen sulphide and ammonia. The dark colour caused by the oxidation of ferrous to ferric which forms ferric hydroxide colloids and complexes with fulvic and humic compounds (Shadi et al., 2020; Shehzad et al., 2016). Elevated turbidity (avg. 2260 NTU) was also recorded in the collected leachate. The decrease of measured values during wet season could be mainly attributed to the dilution of leachate by rainfall during this period which is consistent with the previous findings found high values of most recorded parameters in dry season compared to wet period (Baghanam et al., 2020; Mishra et al., 2019).

The temperature ranged from 17.5°C to 24.5°C reflecting a good environmental conditions for biological and chemical reactions (Mishra et al., 2019). The pH values ranged from 7.5 to 8.0 and was in accordance with previous research (Baghanam et al., 2020; Rana & Ganguly, 2018). It indicates that the landfill could be classified as intermediate to mature phase due to the long period of exploitation. The alkaline pH values for leachate and considering the stages discussed

in the literature (Wijekoon et al., 2022) reflects the decrease in the free volatile fatty acids (FVA) (Hussein et al., 2019). The high EC values in leachate (17470 - 20590  $\mu\text{S}/\text{cm}$ ) is directly attributed to high load of anions and cations marked by high values of TDS (13946 - 16150 mg/l). High conductivity value in the leachate has a significant impact on groundwater movement within the soil layers and facilitating the leaching of contaminants into the aquifer system (Mishra et al., 2019).

### **3.3.1.2 Biochemical oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD) and Dissolved Oxygen (DO)**

The BOD<sub>5</sub>/COD ratio is commonly applied to provide information regarding the biodegradability of landfill leachate (Abunama et al., 2021). In the current study, BOD was fluctuated between 3100 and 5500 mg/l with a mean value of 4,300 mg/l and the COD values ranged between 11000 mg/l and 14000 mg/l with an average of 12,500 mg/l, indicating high organic matter in dumped wastes surpassed the permissible limits of BOD and COD leachate discharge which are 100 and 500mg/l respectively.

The ratio BOD<sub>5</sub>/COD ranges from 0.47-0.62. This indicates that majority of organic compound is biodegradable which is typical to landfills in developing countries. They are characterized by wastes with high organic matter (nearly 65%) compared to other constituents. Slightly low values of dissolved oxygen (DO) were mainly due to the consumption of oxygen by bacteria in the process of organic matter contained in the waste. It also explains the bad odours emanating from the landfill leachate.

### **3.3.1.3 Inorganic Components**

Ammonia-nitrogen (AN) is one of the most abundant form of nitrogen present in leachate (Wdowczyk & Szymańska-Pulikowska, 2021b). It is a major pollutant toxic to organisms (Arunbabu et al., 2017) which releases as a result of protein decomposition. Several researchers have suggested that  $\text{NH}_4^+$  do not decrease with time and during all stages of refuse decomposition (Kjeldsen et al., 2010). For this reason, it is widely used as a significant pollution indicator of contamination by leachate. The concentration of ammonia nitrogen was very high in the collected leachate, ranged from 1960 to 2815 in both dry and wet seasons, respectively. The  $\text{NH}_4^+$ /TKN ratio, which represents the degree of ammonification, thus indicate the residence time of the leachate in the storage basins, was found higher (average=0.51), reflecting that the leachate treatment and production rate are not adapted, and therefore the leachate remains in the basins for a long time without any treatment.

#### 3.3.1.4 Metal(oid)s concentration in landfill leachate

Heavy metal(oid)s concentration ranged greatly through the studied leachate, Fe and Zn were the most abundant dissolved trace metals in the leachate in terms of average concentrations, whereas As and Hg were the least abundant. The concentration of metals decreased in the following order: Fe > Zn > Ni > Cr > Cu > Pb > Cd > As > Hg. There is no significant seasonal variation observed among heavy metals in leachate. The main sources of heavy metals depend on the composition of dumped waste in the landfill (e.g., refused batteries, WEEE, plastics, glass, ceramics, other metallic items) (Abunama et al., 2021), which still constant during the year. The above outcome is consistent with leachate samples taken from landfills with similar conditions (Abd El-Salam & Abu-Zuid, 2015; Hussein et al., 2019). All measured metals were found within the permissible limits for leachate discharge established by the Moroccan standards (in mg/l) in both seasons, which are 0.05 for Hg, 0.1 for As, 0.2 for cadmium, 2 total chromium, 5 for Zn and 0.5 for Cu, Ni and Pb, respectively. Only Fe was above this limit (3 mg/l) with average concentration of 9.56 mg/l, which attributed to the dumping of metal scrap (Hussein et al., 2019).

The reason for the low concentrations of other heavy metals in the leachate is not the lack of heavy metals present in the waste, but the alkaline pH in methanogenic stage, contribute to the reduction of heavy metal solubility and therefore, their concentration in landfill leachate (Barlaz et al., 2002; S. Singh et al., 2016; Wijekoon et al., 2022).

#### 3.3.1.5 Calculation of leachate pollution index Leachate (LPI)

From the univariate analysis of parameters discussed above, a primitive view about the severity of leachate in the study area is generated. However, it's hard to get a broad picture of how much leachate is polluting the water. In this way, the use of comprehensive indicators is required to reduce data dimensionality. As a result, LPI was calculated based on the available 15 parameters monitored. TCB, cyanide, and phenolic compounds were not measured due to the lack of equipment, The evaluated results were presented in **Table 3-2**. The LPI for the dry season (30.21) was relatively higher than that of the wet season (28.06), due to the dilution effect by rainwater (Negi et al., 2020), as can be seen lower concentrations of investigated pollutants were observed in this period. However, calculated in both seasons LPI values were found above the LPI for standard leachate discharge requirements which is fixed in 5.596 for example in Malaysia (Hussein et al., 2019). The high LPI values obtained in this study indicate that leachate is not mature and stabilized, and are still undergoing decomposition (Naveen et al., 2017), these findings are directly attributable to elevated amounts of most of the computed parameters,

especially BOD, COD, NTK and AN, without forgetting the significant contribution of metals in the cumulative pollution rating (*wipi*), even if its low concentration in raw leachate.

By comparing the leachate quality of the studied landfill with recent similar studies from landfills have different characteristics (size, quantity of waste, kind of insulation, the method of collecting leachate and age) as is shown in **Table 3-3**. Similar findings were obtained, translating the hazardous nature of leachate in developing countries due to the heterogeneity of waste dumped in these landfills. It is obvious from the results, that the leachate from the studied landfill has the capacity to contaminate and pose detrimental effects on its surrounding ecosystem, if encounter soil and water resources. It is evident that the choice of effective leachate treatment method largely depends on the characteristics of generated leachate. The calculated LPI for treated leachate is 5.71 and the values of most parameters become consistent with the Moroccan standards for direct discharge in water and soil (Table 3-3), indicate that its discharge will not pose a toxic risk to adjacent water resources. However, the adopted treatment technique is not suitable in regard to the treatment capacity provided compared to generated leachate. Therefore, the quantity of leachate stored in basins and lagoons reached more than 80.000 m<sup>3</sup> (calculated using COVADIS software) and still increases exponentially leading to overflow of leachate during the rainy period. Besides, some problems concerning liner system were also revealed during field investigation like the swelling of HDPE geomembrane.

Table 3-2. Leachate pollution index (LPI) calculation.

N°	Index	Parameter	Significance	Pollutant weight (wi)	Pollutant concentration			Sub-index value (pi)			Cumulative pollution rating (pi*wi)		
					DS	WS	AT	DS	WS	AT	DS	WS	AT
1	LPI organic (LPIor)	COD	3.963	0.062	14000.00	11000.00	350.00	90	80	15	5.580	4.960	0.93
2		BOD5	3.902	0.061	5500.00	3100.00	90.00	60	52	8	3.660	3.172	0.488
3		TCB	3.289	0.052	---	---	---	---	---	---	---	---	---
4		Phenolic compounds	3.627	0.057	---	---	---	---	---	---	---	---	---
5	LPI inorganic (LPIin)	PH	3.509	0.055	8.00	7.60	8.30	5	5	3	0.275	0.248	0.165
6		TKN	3.367	0.053	5060.00	4372.00	27.50	100	100	5	5.300	5.300	0.265
7		TDS	3.196	0.050	16150.00	13946.00	350.00	40	35	4	2.000	1.750	0.2
8		Ammonia nitrogen (AN)	3.250	0.051	2815.00	1960.00	50.00	100	100	5	5.100	5.100	0.255
9		Chlorides (Cl <sup>-</sup> )	3.078	0.048	2400.00	1710.00	150.00	15	10	4	0.720	0.480	0.192
10		Total chromium (Cr)	4.057	0.064	0.60	0.50	0.08	6	5	5	0.384	0.320	0.32
11		Lead (Pb)	4.019	0.063	0.10	0.07	0.02	5	5	5	0.315	0.315	0.315
12		Cyanide (CN <sup>-</sup> )	3.694	0.058	---	---	---	---	---	---	---	---	---
13	LPI heavy metals (LPIhm)	Mercury (Hg)	3.923	0.062	0.001	BDL	BDL	5	5	5	0.310	0.310	0.31
14		Zinc (Zn)	3.585	0.056	2.85	2.03	0.20	5	5	5	0.280	0.280	0.28
15		Nickel (Ni)	3.321	0.052	1.03	0.70	0.05	7	6	5	0.364	0.312	0.26
16		Arsenic (As)	3.885	0.061	0.002	BDL	BDL	5	5	5	0.000	0.000	0.305
17		Copper (Cu)	3.170	0.050	0.45	0.32	0.10	7	6	5	0.350	0.300	0.25
18		Total iron (Fe)	2.830	0.045	9.87	9.25	4.80	5	5	5	0.225	0.225	0.225
		<b>Sum of available parameters</b>		0.833							24.863	23.072	4.760
		<b>LPI calculation</b>									<b>30.21</b>	<b>28.06</b>	<b>5.71</b>

DS: dry season, WT: wet season, AT: after treatment (biological treatment and Inverse osmosis).

Table 3-3. Comparison of LPI of Oum Azza landfill with previous studies worldwide.

N°.	Location	Source	LPI	Reference
1	Rabat, <i>Morocco</i>	Active landfill	28.77	Curent study
	Rabat, <i>Morocco</i>	After treatment	5.71	Current study
3	Brahmapuram, Kochi, <i>India</i>	Active landfill	31.99	(D. Kumar & Alappat, 2005)
	Chandigarh, <i>India</i>	Active landfill	33.18	(Mor et al., 2018)
4	Ulu Maasop landfill, <i>Malysia</i>	Closed landfill	15.28	(Hussein et al., 2019)
	kk1, <i>Malysia</i>	Active landfill	13.89	(Hussein et al., 2019)

### 3.3.2 Assessment of the quality of groundwater

The experimental data of the physical and chemical characteristics of sampled groundwater and potential sources of their pollution is discussed in this section. A statistical summary of the water quality parameters recorded at 20 sampling sites during wet and dry seasons are shown in **Tables 3.4** and **3.5**. Moreover, the detailed results for both seasons were reported in **Appendix D**. It is noteworthy to mention that an obvious difference in the groundwater among the studied sites was observed, demonstrated by elevated standard deviation values likely due to the variability source of these elements reflecting the possible impact by anthropogenic activities such as the pollutants released from the investigated landfill and agricultural activities. The pH is an essential parameter affecting the solubility of metals in water. The pH values of the groundwater varied from 6.85 to 7.9 with an average value of 7.22 in dry season and from 6.5 to 7.8 with an average value of 7.21 during the wet season, without observing significant seasonal variation. More than 75% of the samples have a pH above 7. The results reflected the slightly alkaline properties of water, probably coming from the geology nature of the aquifers of the study area (Adimalla & Qian, 2019). This could be confirmed with the presence of bicarbonates. Nevertheless, pH values for all samples are within the range set by the WHO and Moroccan standards (6.5-8.5).

Electrical Conductivity (EC) is one of the most important parameters to assess the water quality. It is directly related to the concentration of dissolved salts in water. EC values fluctuated widely among the water samples around the landfill. It varied between a minimum of 592  $\mu\text{S}/\text{cm}$  and a maximum of 5032  $\mu\text{S}/\text{cm}$  (standard deviation 2,405  $\mu\text{S}/\text{cm}$ ) signifying a medium to strong mineralization of the study area. Moreover, it is noted that EC values were relatively much higher in the southern side of the study area at locations G1 to G6 compared to other sites, with nearly 20% of samples classified as saline with  $\text{EC} > 3000$  (Brindha & Kavitha, 2015) which

appears to depend on increasing of ions contents. This is confirmed by the elevated amount of TDS in these stations (TDS was oscillated from 386 to 3,221 mg/l with a mean value of 1185 mg/l in wet period, from 424 to 3232 mg/l with a mean value of 1199 in dry season) and the strong correlation between them. Values of TDS and EC were found above the permissible limit set by Moroccan and WHO standards (500mg/l, and 2,500  $\mu$ S/cm, respectively) in many samples in both seasons. The measured values in dry season were higher than that of the wet season, mainly due to the increase of the density of dissolved inorganic ions in groundwater, attributed to the decrease precipitation and increase of evapotranspiration in this period. These high EC and TDS values are an indication of landfill effect on nearby water quality (Alam et al., 2021). The possible differences in geographical characteristics may also contribute to the revealed variation (Şener et al., 2017).

COD determines the total amount of organic pollutants present in water (Rana et al., 2016) and the biochemical oxygen demand is an indicator of the biodegradable fraction of organic matter. The chemical oxygen demand (COD) value of the groundwater samples ranged from 6 to 84 mg O<sub>2</sub>/l (avg. 26.25 mg (O<sub>2</sub>)/l) during the wet season and from 9 to 67 mg/l (avg. 18.6 mg (O<sub>2</sub>)/l) in the dry season, respectively. This distribution was like that of BOD<sub>5</sub> as can be seen in Tables SM2 and SM3. Based on spatial analysis of COD and BOD<sub>5</sub> both parameters showed a large variation among sampling sites. A major part of the study area was marked mainly by high BOD<sub>5</sub> and COD levels during both seasons. Similarly, Mishra et al. (2019) reported elevated BOD<sub>5</sub> and DCO amounts in groundwater around *Ramna MSW landfill site* in India due to the infiltration of leachate.

Ammoniacal nitrogen which is amongst one of the most used indicators of possible contamination was varied greatly with values ranged from below detection limit (0.05) to 4.25 mg/l. The reported values exceeding the recommended standards (0.5 mg/l) in many samples. The main reason behind that may be the migration of organic pollutants from the leachate and their release into the surrounding ecosystem, which probably enters to the nearest groundwater. Various sources could be responsible for the release of orthophosphate (OP) (e.g., garden waste, fertilizer from the surrounding field, the breakdown of food, and other types of waste) (Mishra et al., 2019; Raju et al., 2009). However, OP had the smallest influence on groundwater with average concentration below the threshold limit (5 mg/l) in all samples. Phosphates normally bind to soil particles through adsorption and leach into the aquifer only when the soil sorption capacity is surpassed (Tirkey et al., 2017). The results of this study are in agreement with other studies (Kapelewska, Kotowska, Karpi, et al., 2019) confirming that the phosphates (OP and

TP) cannot be used as an indicator of possible pollution of the aquifer by unsanitary dumpsite and leachate leakage. The  $\text{NO}_3^-$  was ranged between 2.80 –12.30 mg/l with an average value of 7.23 mg/l in wet season and 2.9 –14 mg/l with an average value of 8 mg/l in the dry period, without exceeding the permissible limit (50 mg/l) in any samples reflecting a moderate nitrate impact. High level of nitrate is very harmful and can be the reason of illness recognized as a blue baby syndrome.

Table 3-4. Descriptive statistics of physicochemical parameters of samples collected in dry season (n=20).

Parameter	Mean	Min	Max	LQ	HQ	SD	% of samples > WHO limits	WHO guidelines
<b>pH</b>	7.22	6.85	7.80	7.03	7.38	0.26	0%	6.5-8.5
<b>EC</b>	1821.40	685.00	5032.00	880.00	2396.50	1198.12	25%	2500
<b>Turbidity</b>	4.60	1.00	10.00	2.00	7.00	2.84	35%	5
<b>BOD<sub>5</sub></b>	2.40	1.00	8.00	1.00	2.25	2.35	15%	5
<b>COD</b>	26.25	6.00	84.00	7.00	49.00	28.92	35%	10
<b>TDS</b>	1199.96	424.00	3232.24	576.50	1613.75	793.67	30%	1500
<b>NO<sub>3</sub><sup>-</sup></b>	8.04	2.90	14.00	5.74	10.38	3.21	0%	50
<b>OP</b>	0.99	BDL	1.78	0.60	1.48	0.63	0%	3
<b>NH<sub>4</sub><sup>+</sup></b>	1.20	BDL	4.25	0.17	2.44	1.57	30%	0.5

*LQ: lower quartile, HQ: higher quartile, SD: standard deviation, BDL: Below detection limit.*

*All the values are in mg/l except, pH, EC ( $\mu\text{s}/\text{cm}$ ) and Turbidity (NTU).*

Table 3-5. Descriptive statistics of physicochemical parameters of samples collected in wet season(n=20).

Parameter	Mean	Min	Max	LQ	HQ	SD	% of samples > WHO limits	WHO guidelines
<b>pH</b>	7.21	6.50	7.80	6.94	7.45	0.35	0%	6.5-8.5
<b>EC</b>	1594.95	592.00	4712.00	802.75	2115.25	1146.46	20%	2500
<b>Turbidity</b>	3.80	1.00	8.00	2.00	5.00	1.96	20%	5
<b>BOD<sub>5</sub></b>	2.65	1.00	10.00	1.00	3.25	2.80	15%	5
<b>COD</b>	18.60	6.00	67.00	6.00	21.25	18.34	45%	10
<b>TDS</b>	1185.52	386.00	3221.24	565.06	1603.61	795.42	25%	1500
<b>NO<sub>3</sub><sup>-</sup></b>	7.34	2.80	12.30	5.11	9.75	2.97	0%	50
<b>OP</b>	0.67	BDL	1.30	0.22	1.06	0.47	0%	3
<b>NH<sub>4</sub><sup>+</sup></b>	0.71	BDL	3.60	0.00	1.24	1.02	30%	0.5

*All the values are in mg/l except, pH, EC ( $\mu\text{s}/\text{cm}$ ) and Turbidity (NTU).*

### 3.3.3 Major cations and anions

The average concentration of ionic species was in the order of  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$  and  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$  for cations and anions as presented in **Table 3-6 and Appendix D**. By comparing the results obtained in both seasons, higher concentrations for all major ions were measured in the dry period. However, no seasonal change was found in the anion ascendancy pattern. Chloride is known as an index of to trace movement of contamination of water by landfilling activities. The measured  $\text{Cl}^-$  was characterized by high concentrations fluctuated from 115.62 mg/l (G11) to 1328.21 mg/l (G1), with an average value of 453.41 mg/l. Chloride levels recorded in this study were higher than previous studies (Adimalla & Li, 2018; Devi et al., 2021; Tirkey et al., 2017) where 50 % of groundwater samples were above the acceptable limit (250 mg/l). Only sample taken from G1 was found higher than the permissible limit (> 1000 mg/l). Geogenic sources e.g., weathering of rocks (Devi et al., 2021) is the principal source of high levels of chloride in water, without forgetting the influence of various anthropogenic activities, such as the leaching of landfill leachate from topsoil, and excessive use of manure and chemical fertilizers (Akoto et al., 2021).

Sulphate concentration was observed between 50.6 (G7) and 492 (G1) mg/l. The permissible limit for sulphate as given according to WHO is 500 mg/l. None of the samples exceeded the acceptable limit. Sulphate concentration in groundwater usually remains low due to reducing conditions in the aquifers which inhibits sulphide oxidation. The calcium and magnesium concentrations in the groundwater ranged between 56.28 and 375.40 mg/l, and 11.03 and 210.40 mg/l with average values of 157.44 mg/l and 57.65 mg/l, respectively. About 30% of groundwater samples are exceeded the maximum permissible limits (WHO, 2011).

Table 3-6. Descriptive statistics of major ions content in studied wells (n=20).

Parameter	Mean	Min	Max	LQ	HQ	SD	% Of samples > WHO limits	WHO 4 <sup>th</sup> ed. guidelines
$\text{Ca}^{2+}$	157.44	56.28	375.40	75.25	237.81	111.04	20%	300
$\text{Mg}^{2+}$	57.65	11.03	210.40	15.59	85.45	62.29	40%	30
$\text{Na}^+$	135.37	50.89	356.50	121.42	200.31	72.59	15%	200
$\text{K}^+$	6.67	1.29	32.46	2.795	7.33	6.63	5%	12
$\text{SO}_4^{2-}$	138.02	50.60	492.00	62.50	123.00	121.76	0%	400
$\text{HCO}_3^-$	234.45	92.70	421.52	110.60	317.04	105.70	65%	200*
$\text{Cl}^-$	453.41	115.62	1368.21	116.98	540.38	376.12	35%	400

All the values are in mg/l, The presented results are the average of values measured in both seasons.

Concerning other ions, it was observed that reported concentrations presents a great heterogeneity translated by the elevated values of the standard deviation as can be seen in **Table 3-6**.

The Piper diagram is extensively used for a better understanding of hydrochemistry. It's useful for determining the hydrogeochemical types of water by defining the dominating cations and anions that influence the area's hydrochemistry (Khanoranga & Khalid, 2019). As shown in **Fig.3-3**, the hydro-chemical evolution, and the variation of ionic composition of groundwater, among the studied wells was carried out by plotting major ions data the average values of the anions and cations in both seasons on the Piper trilinear diagram. The result of the present study showed that water of the studied sites permits to distinguish the dominance of  $\text{SO}_4^{2-}$ -Cl-Ca-Mg facies includes most investigated stations 16 samples, G1 to G6, G16 to G20 and G7 to G10 which are characterized by elevated amounts of chloride, calcium, and sulfate. The second group contained only 5 samples indicated the facies  $\text{SO}_4^{2-}$ -Cl- $\text{Na}^+$ . This reflects that various anthropogenic source, such as the use of different fertilizers, and wastewater brought non-negligible changes to the studied water resources.

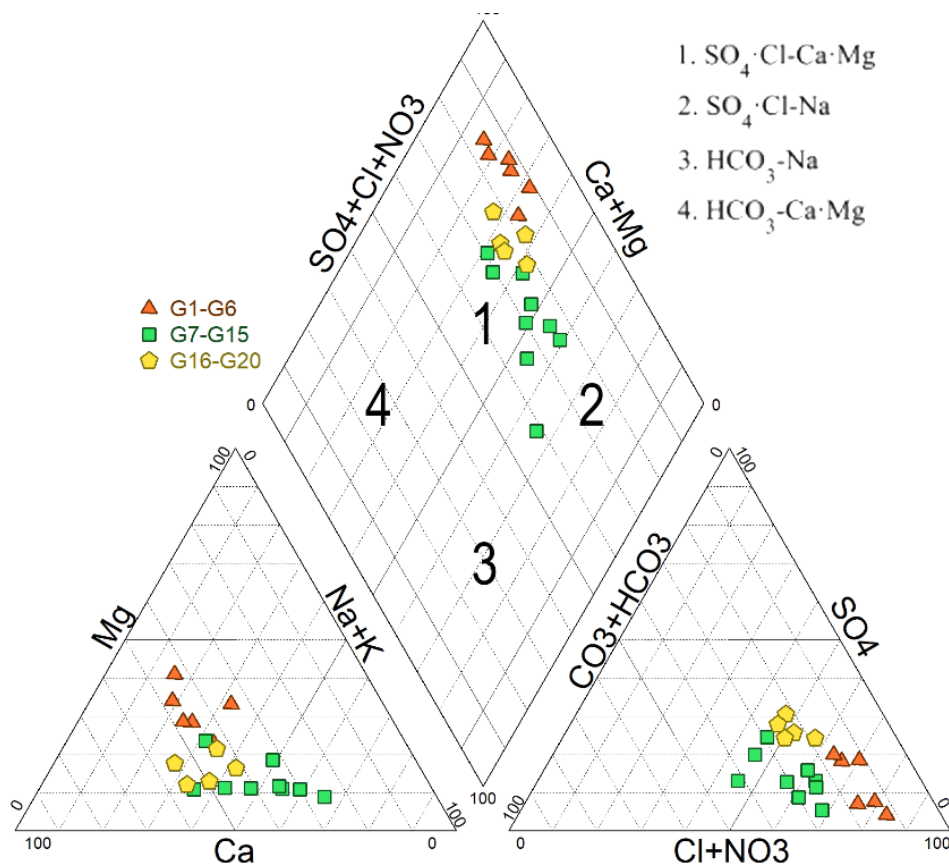


Figure 3-3. Piper diagram showing the classification of water hydro-facies, Oum Azza landfill.

### 3.3.4 Trace metal(oid)s

The concentration of trace metals measured in the collected water samples around the study site is presented in **Table 3-7** and **Appendix D**. The average concentration of selected metals in water follows the decreasing order of Fe > Zn > Cu > Ni > As > Cr > Pb > Cd > Hg. Fortunately, the maximum concentrations of Cu, Cr, Zn, Hg, total As and Fe were less than the WHO standard for drinking water (WHO, 2011). Adsorption of heavy metals on soils (Bradl, 2004) could be responsible of low concentration (Baghanam et al., 2020). However, the increase of As and Cd in certain sampling (G1-G6 and G7-G12) was notable and could reflect not only the leaching of metals-containing solid waste from the landfill site, but also the extensive use of fertilizer in agriculture which represent the principal source of survive for the population in this region. Spatially, higher concentration levels were observed in the monitoring wells with a shorter distance from the landfill. For example, lead, cadmium, and nickel has been found in many samples (G1 to G6) exceeds their permissible limit set by the World Health Organization (WHO) as threshold values (in mg/l) which are 0.003 for Cd, 0.02 for Ni, and 0.01 for Pb, respectively. These results reflected anthropogenic activities (e.g., landfill exploitation, agricultural activities) could be the main reason behind the non-negligible amount of heavy metal pollution which might pose a risk to human. Therefore, is crucial to assess risks of metal pollution by calculating the possible carcinogenic and non-carcinogenic human risk associated with ingestion of water for both children and adults using the method proposed by the Environmental Protection Agency (EPA).

Table 3-7.Descriptive statistics of heavy metal(oid)s content in studied wells (n=20).

Parameter	Mean	Min	Max	LQ	HQ	SD	% Of samples > WHO limits	Moroccan guidelines	WHO 4 <sup>th</sup> ed. guidelines
<b>Pb</b>	7.11	2.26	15.70	4.59	9.11	3.78	20%	10	10
<b>Cd</b>	2.40	0.26	5.80	1.17	3.52	1.54	35%	10	3
<b>Cu</b>	7.54	0.20	18.00	1.58	12.50	6.13	0%	----	2000
<b>Cr</b>	3.52	0.20	11.25	0.38	7.34	3.86	0%	50	50
<b>Zn</b>	34.19	0.56	140.00	2.25	61.00	37.10	0%	----	3000
<b>Ni</b>	11.27	0.78	22.50	3.22	18.43	7.61	15%	20	20
<b>As</b>	4.22	0.25	9.41	0.77	7.16	3.17	0%	----	10
<b>Fe</b>	35.55	1.20	162.40	3.21	70.04	47.28	0%	----	300

All the values are in µg/l, The presented results are the average of values measured in both seasons.

The above sections highlight the severity of leachate generated in the landfill containing high inorganic nutrients, organic matter (BOD, COD), and metals that could be responsible for revealed groundwater pollution through leaching and runoff. Especially, wells situated near the landfill are considered vulnerable to possible pollution from the landfill in case of leakage problems. This hypothesis is supported by the higher pollutant's concentration revealed in these sites and the presence of permeable geological formation (saturated calcarenite). The possible scenario of migration of pollutants from leachate basins to adjacent wells was illustrated in Fig.3-4 and confirmed by interpreting the flow direction using the piezometric map prepared by the prepared by the company that manages the landfill.

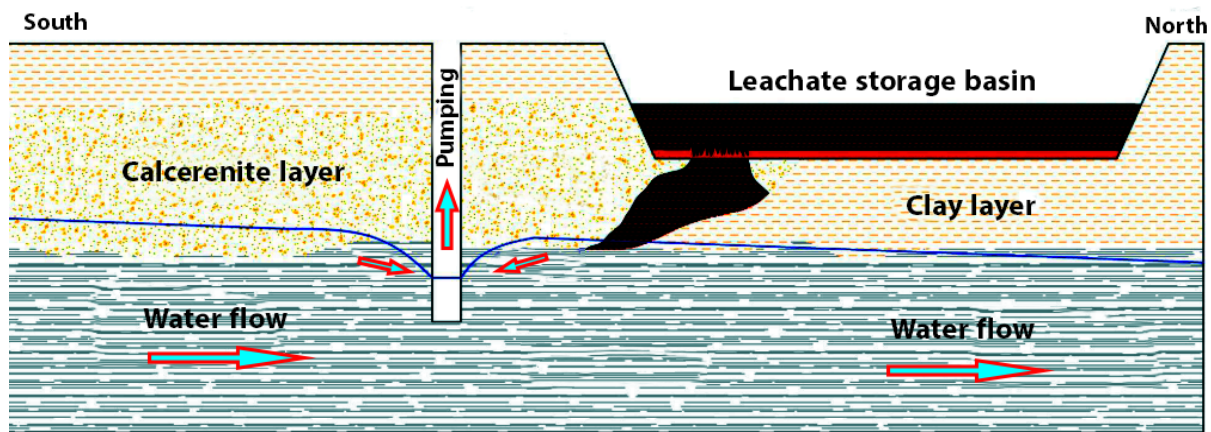


Figure 3-4. Probable pollution track of leachate from landfill, which drains to the nearby wells (G1-G6).

### 3.3.5 Groundwater quality assessment using the WQI and PIN

As discussed above almost all the parameters were higher compared to their permissible level. However, it is not easy to obtain a general view on the level of water quality based only on the interpretation of a large number of separate parameters (Han et al., 2016). For this reason, WQI and PIN were calculated to provide a general idea about the overall water quality in this region, in both dry and wet seasons, and assess the status of water quality for drinking purposes. Fourteen (14) parameters namely, pH,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , COD, Pb, Cd, Cu, Cr, As and Fe were taken into account to compute the above indicators and selection of these parameters was justified based on previous studies (Khan & Umar, 2019; Krčmar et al., 2018; Naveen et al., 2017; S. Singh et al., 2016; Talalaj & Biedka, 2016; Uddin et al., 2021; Varol, 2020). Firstly, the weight values for each water quality parameter were established according to their relative importance in the overall quality of water for drinking purposes to produce WQI values at each sampling station (**Table 3-8**). Nutrients and trace metals which have important

effects on water quality especially for drinking purposes were given the highest weight of 5 (Şener et al., 2017). Then, the relative weights ( $W_i$ ) were computed for each parameter using Equation.3.4. Mercury was excluded from the calculations because its concentration was below the detection limit in all the samples.

Table 3-8. Weights of parameters required to calculate WQI.

Pollutants	WHO guidelines (2011)	Weight (wi)	Relative weight ( $W_i$ )
<b>pH</b>	6.5-8.5	4	0.0741
<b>Ca<sup>2+</sup></b>	300	2	0.0370
<b>Mg<sup>2+</sup></b>	30	2	0.0370
<b>Na<sup>+</sup></b>	200	2	0.0370
<b>Cl<sup>-</sup></b>	250	3	0.0556
<b>HCO<sub>3</sub><sup>-</sup></b>	200*	3	0.0556
<b>SO<sub>4</sub><sup>2-</sup></b>	250	4	0.0741
<b>COD</b>	10	4	0.0741
<b>Pb</b>	0.01	5	0.0926
<b>Cd</b>	0.003	5	0.0926
<b>Cu</b>	2	5	0.0926
<b>Cr</b>	0.05	5	0.0926
<b>As</b>	0.01	5	0.0926
<b>Fe</b>	0.3	5	0.0926

\* The acceptable value set by the BIS standard.

Descriptive statistics of calculated indicators were reported in **Table 3-9** and represented graphically using Boxplots (**Fig.3-5**), also distribution maps of both calculated indexes were drawn using Geographic Information System (GIS) techniques as depicted in **Fig.3-6**.

Table 3-9. Obtained values for the selected groundwater quality indices for drinking purposes.

Index	Period	Mean	Min	Max	SD
<b>WQI</b>	Dry season	80.19	29.21	214.58	59.01
	Wet season	74.52	27.47	201.63	50.75
<b>Nemerow index (PI)</b>	Dry season	2.17	0.75	6.19	2.01
	Wet season	1.83	0.72	5.23	1.44

The outcome showed significant variation of groundwater quality among the studied wells, with values ranged from 27.46 to 201.63 (avg. 74.52) in wet season, and from 29.21 to 214.58 (avg.

80.19) in dry the period. According to the water quality index (WQI) groundwater was categorized as “best quality” to “threatened quality” range for both seasons. According to the grading method (Table 2-1), groundwater was sorted into 3 categories corresponding to different levels of the suitability for use as drinking water, as follows. Approximately 40% of the total groundwater samples belong to excellent category with WQI less than 50, 35% fell under the good water category, 20% still acceptable for drinking purposes, and only one sample collected from well G1 fell under the threatened quality in both seasons ( $WQI > 200$ ). Similarly, the Nemerow index has a heterogeneous spatial distribution in the study area (avg.  $SD = 1.73$ ) and follow the same trend and fluctuated from very small to heavy impact, with values from 2.17 to 6.19 and from 1.83 to 5.23 in dry and wet seasons, respectively. It was noted that PIN, suggest intensive anthropogenic activity contributed to the deterioration of water quality. This hypothesis is mainly due to impurities of municipal wastes and/or agricultural activities discharge.

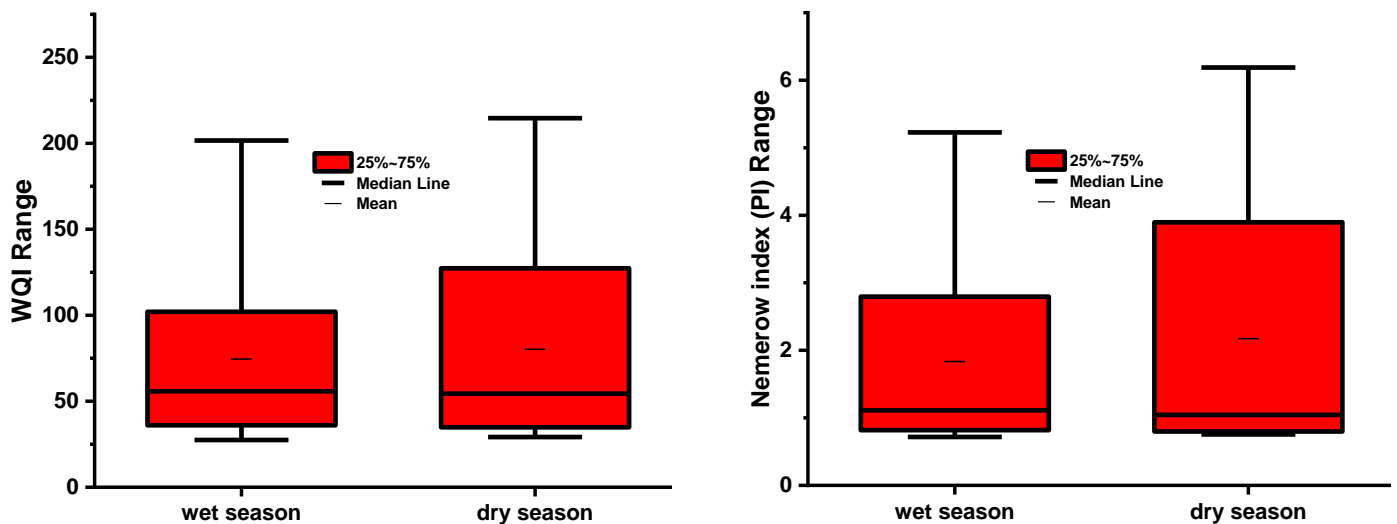


Figure 3-5. The distribution of water quality indices in dry and wet seasons shown by box-plots: a) WQI, b) PIN.

The present interpretation was completed with the use of Geostatistical analysis (Inverse Distance Weighted). It was possible to organize and present obtained data on maps, to generate a general overview about the spatial distribution quality of groundwater resources in the study area. In summary, both calculated indexes (WQI and PI) showing a deterioration in water quality of the most of studied area during both seasons. Perhaps, it was not surprising that a notable decreasing of water quality was observed when approaching to the landfill compared to other sites. Because most of the physical and chemical parameters showing the highest concentration in these samples and exceeded their permissible limits as discussed in the above

sections. This may indicate that leakage and seeping of leachate as illustrated in Fig.3-4 has a greater effect on water regarding other sources like agricultural activities, and geogenic inputs, as demonstrated in previous works (Kapelewska, Kotowska, Karpi, et al., 2019; Krčmar et al., 2018; Nagarajan et al., 2012; Reyes-López et al., 2008).

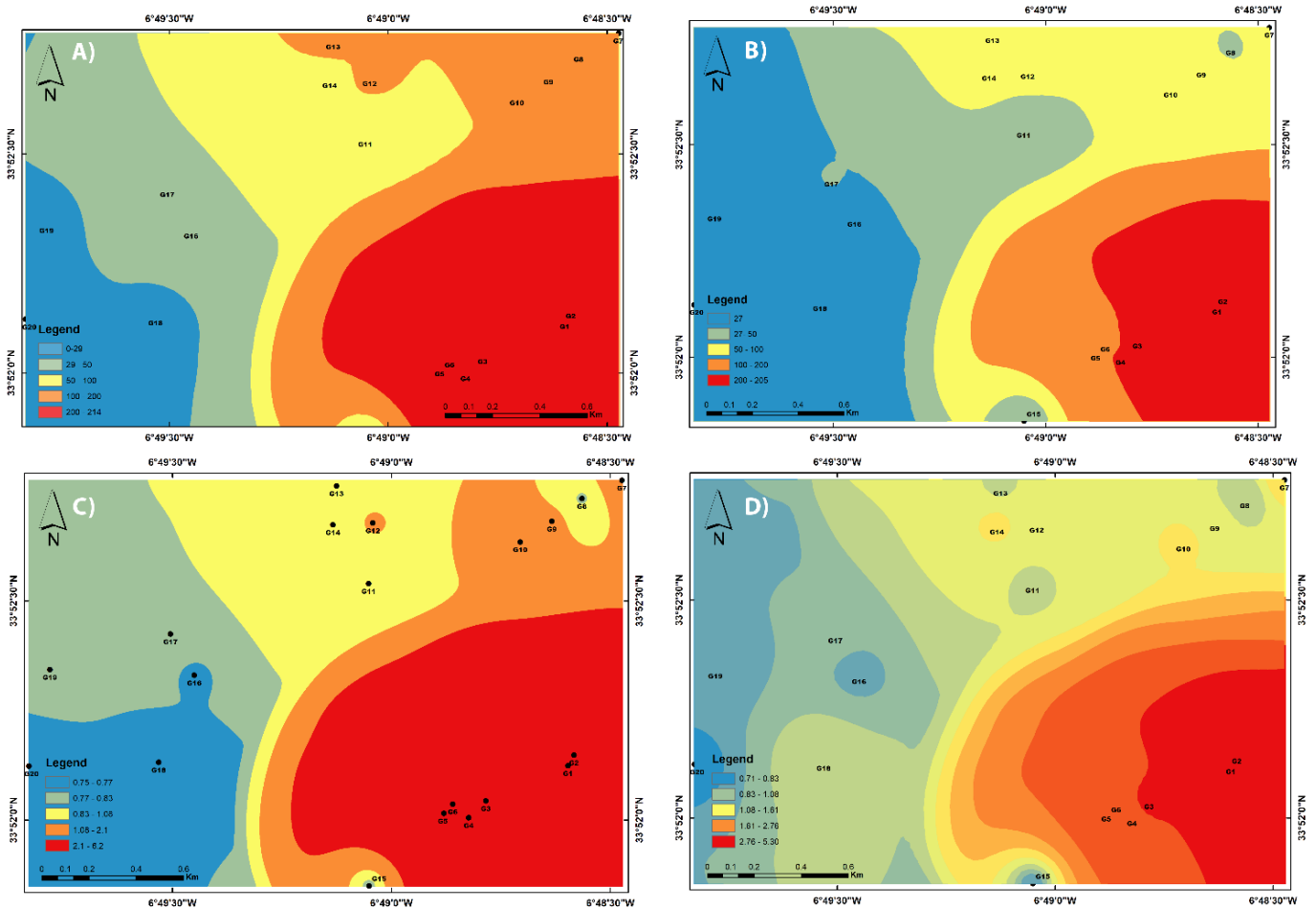


Figure 3-6. Spatial distribution maps of water quality indices by IDW method; a) WQI in DS, b) WQI in WS, c) PIN in DS and d) PIN in WS.

### 3.3.6 Evaluation of groundwater suitability for irrigation

Groundwater represents a vital resource for the agriculture sector in the study area. In this view, it is mandatory to assess the quality of irrigation water in the study zone. A mixture of parameters influences the quality of irrigation water including pH, temperature, alkalinity, and salinity (Zhou et al., 2020). To this end, Wilcox's diagram, and multiple indices (SAR, MHR, %Na, KI, and PI) were calculated to assess the accuracy of analysed water for irrigation based on their anionic and cationic composition. The suitability of water for irrigation widely depends on its chemical composition (Brindha & Kavitha, 2015). A statistical summary of calculated indices was reported in Table 3-10.

Table 3-10. Obtained values for the selected groundwater quality indices for irrigation purposes.

Indices	Min	Max	LQ	HQ	Mean	SD
<b>MHR</b>	16.889	49.33	23.79	36.85	30.43	9.43
<b>PI</b>	21.617	81.71	38.26	61.06	50.53	16.71
<b>%Na<sup>+</sup></b>	15.50	65.30	30.24	46.59	37.58	13.43
<b>KR</b>	0.174	1.84	0.42	0.86	0.68	0.43
<b>SAR</b>	1.791	8.16	2.34	5.14	3.74	1.68
<b>RSC</b>	-26.779	-0.927	-9.88	-2.66	-6.68	6.28

The pH values were within the range recommended for agricultural purposes (6.5-8.5). The measured heavy metal(oid)s values were less than the limit set by the Moroccan irrigation standards ( $\mu\text{g/l}$ ), which are 100 for As, 10 for Cd, 50 for Pb, 5000 for Zn, 1000 for Cu and 100 for Fe  $\mu\text{g/l}$ . In the case of TDS, 5 samples (G1, G2, G3, G4 and G6) were found above the tolerated limit according to the United Nations Food and Agriculture Organization (Alam et al., 2020). It has been demonstrated previously that elevated EC could negatively impact the suitability of water for all agricultural purposes due to the increase of salinity, as well as, high sodium amounts lead to the formation of alkaline soil (Tran et al., 2021). Furthermore, high levels of sodium in irrigation water inhibit growth, reduce crop yield, and influence negatively on as discussed by Kurunc et al. (2020).

Sodium is a crucial chemical element in irrigation water. However, when present in excess in regard to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , it could contribute significantly to the reduction of soil permeability, as a result of saturation of soil cation exchange complexes (Tran et al., 2021). For this reason, SAR was calculated, it was found ranged from 1.8 to 8.2 with an average value of 3.7. Based on this indice, all samples could be used in irrigation under natural conditions ( $\text{SAR} < 10$ ). However, the confirmation of suitability of the studied water requires its comparison with their measured electrical conductivity. The relationship between EC and SAR was plotted on the Riverside diagram to evaluate the combined effect of sodium and salinity. As shown in **Fig.3-7**, two groups were observed, the first one includes nearly 75% of samples that fall in the C3S1, C4S1 classes, indicating waters with low sodium hazard, and medium (C3) to high (C4) salinity. Whereas the second group containing 25% of groundwater samples (G1, G2, G3, G4 and G6) characterized by high salinity ( $> 2,250 \mu\text{s/cm}$ ) reflecting that the use of these samples for irrigation is restricted and can significantly affect the soil structure if used without any treatment.

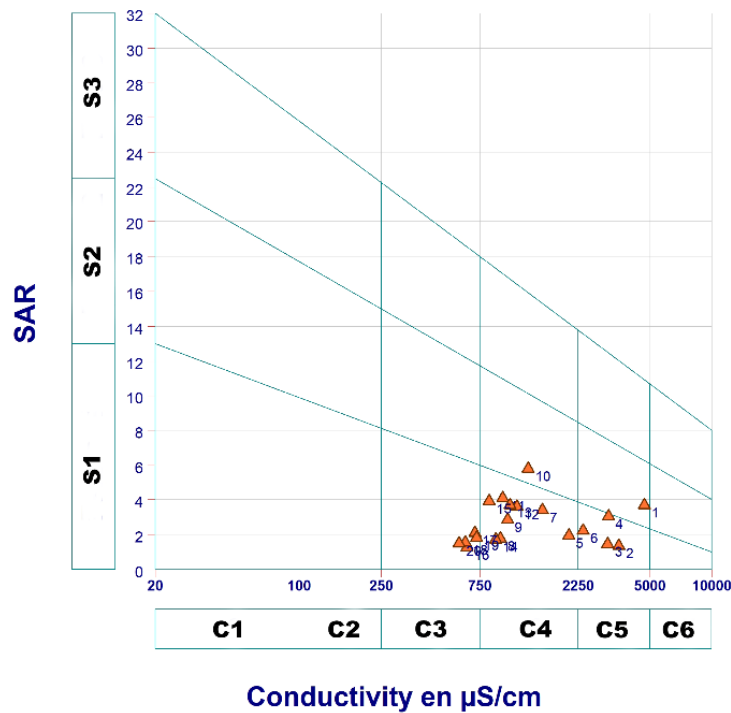


Figure 3-7. Suitability of groundwater for irrigation using Riverside diagram.

In the same context, Wilcox’s graphic (Wilcox, 1955) (**Fig.3-8**), permits the classification of water quality for irrigation, as 25% excellent, 40% good, 5% permissible, 10% doubtful and 20% unsuitable. In other words, almost one in six samples is found with elevated salinity that could impact the agricultural activities, the main reason behind these results is the elevated EC values because sodium percentage was found below 60% in all samples, which is considered the permissible limit (Y. Zhou et al., 2020).

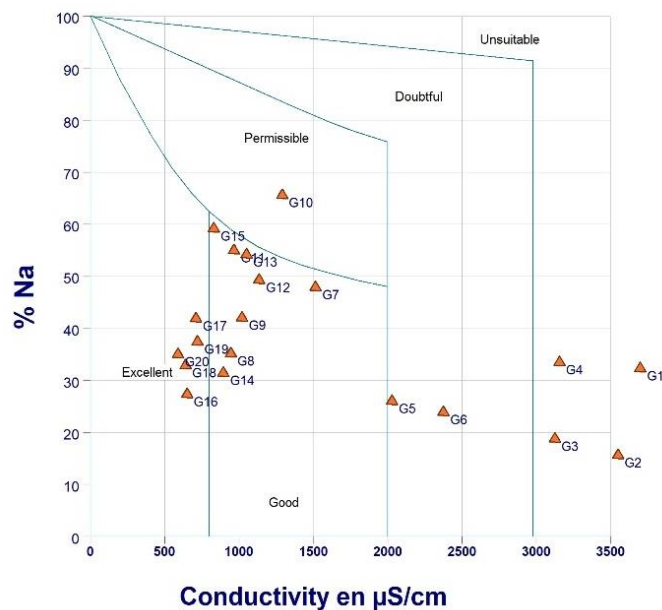


Figure 3-8. Suitability of groundwater for irrigation using Wilcox diagram.

Permeability index was performed to check the equilibrium between bicarbonates, sodium, and alkaline earths ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). PI index was found to be ranging between 21.62 and 81.71 as given in Table 10. About 30 % of the samples was unsuitable for irrigation based on Doneen's diagram showing irrigation water classes based on Permeability Index ( $\text{PI}>60$ ) due to the increase of  $\text{Na}^+$  in these sites reflecting that long-term irrigation will affect soil permeability which prevent water from reaching the leaves and branches of plants (Y. Zhou et al., 2020). Therefore, a possible treatment by the addition of gypsum is required before irrigation.

The safe MHR limit is 50, above which the water is unfit for irrigation (Brindha & Kavitha, 2015). In the current work measured MHR was within the acceptable level and indicate that amount of magnesium maintains a state of equilibrium level with calcium in the study wells, and does not pose any threat, for intended usage for irrigation. Similarly, RSC was acceptable and reflecting an equilibrium between bicarbonates and alkaline earths. Finally, Kelly's ratio (KR) evaluated groundwater quality for irrigation purposes by comparing the concentrations of  $\text{Na}^+$  to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Chidambaram et al., 2022). ranged from 0.17 to 1.84 with a mean value of 0.68, 16 out of 20 water samples are suits for irrigation. According to the results of this index, with KR less than one (Vijai & Khan, 2021). It is concluded by combining between calculated irrigation indices, that most of samples are not consistent with the recommended standard, mainly because of elevated EC values, and moderate concentration of calcium and magnesium.

### 3.3.7 Multivariate statistical analysis

Since the studied datasets were non-normally distributed as illustrated using the K-S test, a non-parametric Spearman correlation was performed to examine the interrelationship between variables, as is shown in **Table 3-11**. The relationships among HMs were examined using the Spearman correlation matrix (Table SM 5). The obtained results showed a strong positive correlation between all investigated metals ( $r>0.5$ ;  $P<0.01$ ), suggesting specific association among them and/ or mutual behaviour during the transport from the pollution source (Suresh et al., 2011; Varol et al., 2020). High positive correlations among variables means that they have the same source and mutual dependence. The EC showed significant positive correlations with TDS,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  reflecting the contribution of these ions in water salinity.

Overall, strong significant correlation was observed among all physico-chemical parameters, translated by the predominance of highly significant ( $p=0.001$ ) correlation coefficients, which justified the necessity of applying PCA in this study (Kapelewska, Kotowska, Karpi, et al., 2019).

### 3.3.7.1 PCA

PCA/FA are the most common statistical method used in environmental studies, applied to sorting of groundwater samples based on their possible sources of pollution. The KMO score (0.94) and Bartlett's sphericity test value ( $p < 0.001$ ) indicated the accuracy of the analytical datasets for PCA. The observed factor loadings and the percentage of cumulative and variance explained by the factors were presented in **Appendix D**.

The PCA/FA with varimax rotation identified 2 varifactors (VF), representing about 82.56 % of the total variance (the PC1 and PC2 account for 76.02% and 6.54%, respectively) with an eigenvalue greater than 1 (17.84 for F1 and 1.50 for F2). The first factor had strong positive loadings ( $>0.7$ ) on all parameters and accounted for 76.02% of the total variance (Table 11). Significance correlations were revealed with inorganic parameters ( $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ), and organic pollutants (COD,  $\text{BOD}_5$ ), such findings indicate the dominance of anthropogenic impact in all samples (Krčmar et al., 2018). It suggests that the studied site is under influence of the landfill leachate and probably by agriculture due to the extensive use of fertilizers and manure and probably less influenced by wastewater from domestic activities having regard to the absence of a sanitation system. To this end, the projection of PCA is promising to conclude a general overview about the impact level of anthropogenic activities in each site.

Biplots for principal component analysis was performed by the projection of samples on 2D factorial F1-F2 using varimax rotation, to ensure a reliable visualisation of PCA results, **Fig.3-9**, allowed us to extract a clear picture of the grouping of collected samples, spatiotemporal discrimination was clearly observed, and three homogeneous groups (Circled by a dashed line) was revealed. The wells namely G1, G2, G3, G4, G5 and G6 were strongly correlated with higher factor scores, implying that these sites are the most impacted in the study area and required emergency intervention, since the higher factor score reflect the higher influence caused by anthropogenic activities around the landfill as demonstrated previously by Baghanam et al. (2020) and Kapelewska et al. (2019).

Table 3-11. Spearman's correlation coefficients between parameters in groundwater samples around MSW landfill.

Parameters	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	EC	pH	BOD <sub>5</sub>	COD	TDS	NO <sub>3</sub> <sup>-</sup>	OP	NH <sub>4</sub> <sup>+</sup>
Ca <sup>2+</sup>	1														
Mg <sup>2+</sup>	<b>0.85***</b>	1													
Na <sup>+</sup>	0.48	<b>0.53**</b>	1												
K <sup>+</sup>	<b>0.68***</b>	<b>0.78***</b>	<b>0.70***</b>	1											
SO <sub>4</sub> <sup>2-</sup>	0.31	0.38	-0.04	0.42	1										
HCO <sub>3</sub> <sup>-</sup>	<b>0.67***</b>	<b>0.74***</b>	<b>0.75***</b>	<b>0.78***</b>	0.23	1									
CL <sup>-</sup>	<b>0.85***</b>	<b>0.83***</b>	<b>0.76***</b>	<b>0.80***</b>	0.14	<b>0.85***</b>	1								
EC	<b>0.82***</b>	<b>0.84***</b>	<b>0.78***</b>	<b>0.85***</b>	0.27	<b>0.91***</b>	<b>0.96***</b>	1							
pH	<b>0.47**</b>	<b>0.59***</b>	0.43	<b>0.46*</b>	0.25	<b>0.55**</b>	<b>0.62**</b>	<b>0.61**</b>	1						
BOD <sub>5</sub>	<b>0.88***</b>	<b>0.84***</b>	<b>0.53*</b>	<b>0.73***</b>	0.39	<b>0.72***</b>	<b>0.86***</b>	<b>0.86***</b>	<b>0.72**</b>	1					
COD	<b>0.70***</b>	<b>0.67**</b>	0.25	<b>0.55**</b>	<b>0.49*</b>	<b>0.47***</b>	<b>0.54*</b>	<b>0.60**</b>	<b>0.50*</b>	<b>0.73***</b>	1				
TDS	<b>0.86***</b>	<b>0.87***</b>	<b>0.77***</b>	<b>0.84***</b>	0.27	<b>0.90***</b>	<b>0.97***</b>	<b>0.99***</b>	<b>0.59**</b>	<b>0.87***</b>	<b>0.60***</b>	1			
NO <sub>3</sub> <sup>-</sup>	<b>0.77***</b>	<b>0.74***</b>	<b>0.70***</b>	<b>0.76***</b>	0.06	<b>0.72***</b>	<b>0.88***</b>	<b>0.87***</b>	<b>0.56**</b>	<b>0.80***</b>	<b>0.69***</b>	<b>0.87***</b>	1		
OP	<b>0.57***</b>	<b>0.64**</b>	<b>0.75***</b>	<b>0.76***</b>	0.20	<b>0.77***</b>	<b>0.78***</b>	<b>0.83***</b>	<b>0.55**</b>	<b>0.60**</b>	<b>0.49*</b>	<b>0.80***</b>	<b>0.72***</b>	1	
NH <sub>4</sub> <sup>+</sup>	<b>0.73***</b>	<b>0.71***</b>	<b>0.79***</b>	<b>0.76***</b>	0.18	<b>0.89***</b>	<b>0.91***</b>	<b>0.94***</b>	<b>0.63**</b>	<b>0.81***</b>	<b>0.62**</b>	<b>0.92***</b>	<b>0.87***</b>	<b>0.82***</b>	1
Pb	<b>0.70***</b>	<b>0.61**</b>	<b>0.47*</b>	<b>0.62***</b>	0.36	<b>0.63**</b>	<b>0.79***</b>	<b>0.79***</b>	<b>0.63**</b>	<b>0.82***</b>	<b>0.65**</b>	<b>0.78***</b>	<b>0.72***</b>	<b>0.67**</b>	<b>0.78***</b>
Cd	<b>0.72***</b>	<b>0.72***</b>	<b>0.64**</b>	<b>0.80***</b>	<b>0.46*</b>	<b>0.85***</b>	<b>0.74***</b>	<b>0.81***</b>	0.30	<b>0.68***</b>	0.44	<b>0.82***</b>	<b>0.53**</b>	<b>0.71***</b>	<b>0.73***</b>
Cu	<b>0.62**</b>	<b>0.56**</b>	<b>0.65**</b>	<b>0.74***</b>	0.21	<b>0.77***</b>	<b>0.75***</b>	<b>0.80***</b>	0.37	<b>0.61**</b>	0.44	<b>0.77***</b>	<b>0.64**</b>	<b>0.65**</b>	<b>0.75***</b>
Cr	<b>0.81***</b>	<b>0.69***</b>	<b>0.67**</b>	<b>0.68***</b>	0.09	<b>0.77***</b>	<b>0.91***</b>	<b>0.86***</b>	<b>0.59**</b>	<b>0.85***</b>	<b>0.61**</b>	<b>0.87***</b>	<b>0.85***</b>	<b>0.72***</b>	<b>0.89***</b>
Zn	<b>0.80***</b>	<b>0.72***</b>	<b>0.63**</b>	<b>0.65***</b>	0.12	<b>0.80***</b>	<b>0.89***</b>	<b>0.86***</b>	<b>0.60**</b>	<b>0.85***</b>	<b>0.60**</b>	<b>0.86***</b>	<b>0.77***</b>	<b>0.60***</b>	<b>0.87***</b>
Ni	<b>0.70***</b>	<b>0.66***</b>	<b>0.47*</b>	<b>0.62***</b>	0.41	<b>0.69***</b>	<b>0.71***</b>	<b>0.74***</b>	<b>0.47*</b>	<b>0.63**</b>	<b>0.57**</b>	<b>0.74***</b>	<b>0.56**</b>	<b>0.75***</b>	<b>0.66**</b>
As	<b>0.75***</b>	<b>0.70***</b>	<b>0.46*</b>	<b>0.69***</b>	0.42	<b>0.73***</b>	<b>0.74***</b>	<b>0.73***</b>	0.35	<b>0.64**</b>	<b>0.55*</b>	<b>0.75***</b>	<b>0.53**</b>	<b>0.68***</b>	<b>0.70***</b>
Fe	<b>0.86***</b>	<b>0.73***</b>	<b>0.55**</b>	<b>0.66**</b>	0.32	<b>0.67**</b>	<b>0.87***</b>	<b>0.87***</b>	<b>0.59**</b>	<b>0.87***</b>	<b>0.59**</b>	<b>0.86***</b>	<b>0.76***</b>	<b>0.57**</b>	<b>0.77***</b>

\*Significance level  $\alpha=0.05$     \*\*significance level  $\alpha=0.01$     \*\*\*significance level  $\alpha=0.001$

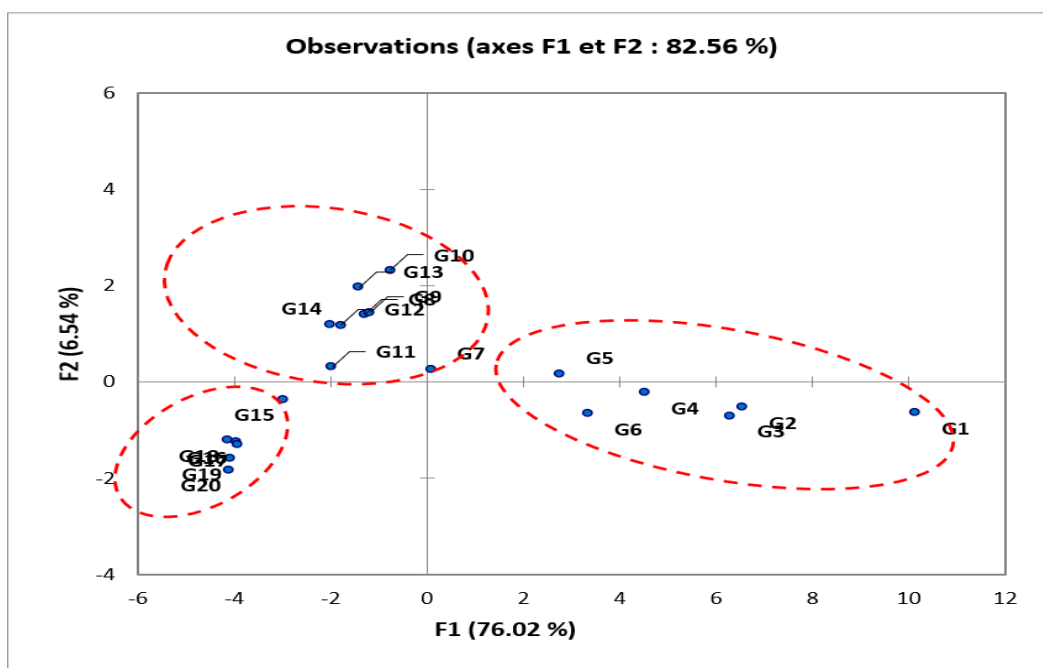


Figure 3-9. Biplots for Principal component analysis reflecting the relationship between study samples.

### 3.3.7.2 Hierarchical cluster analysis (HCA)

Hierarchical cluster analysis (HCA) as a segmentation technique was carried out using Ward's algorithm and Squared Euclidean linkage to classify studied sites into similar groups known as clusters based on the relationship between variables among sampling sites. A lesser distance between samples indicates a higher degree of similarity. The obtained dendrograms in both seasons were displayed in (Fig.3-10). The dendrogram suggests that the 20 sampling wells, could be classified into three statistically significant clusters based on the concentrations of the analyzed parameters. However, each cluster was distributed in a geographically limited area, and a same pattern was observed in both seasons (Fig.10-a and b) without revealing notable differences. The first cluster includes 6 sampling locations (G1, G2, G3, G4, G5 and G6). The experimental data of groundwater analysis in these samples indicated the maximum values characterized by high loading of both organic and inorganic pollutants, which could be mainly attributable to the influence of MSW landfill site, anthropogenic and domestic activities, respectively. The second cluster consists of 8 sampling points (from G7 to G13) located in the northern edge of the studied area having moderate pollution level. The cluster is characterized by high inorganic loading, associated mainly with agricultural activities and less impacted by the MSW landfill. The third cluster includes 6 samples (G15-G20), where low pollution level influence was observed, and as stated earlier all examined parameters in these sites were still within the permissible values for agricultural and drinking purposes.

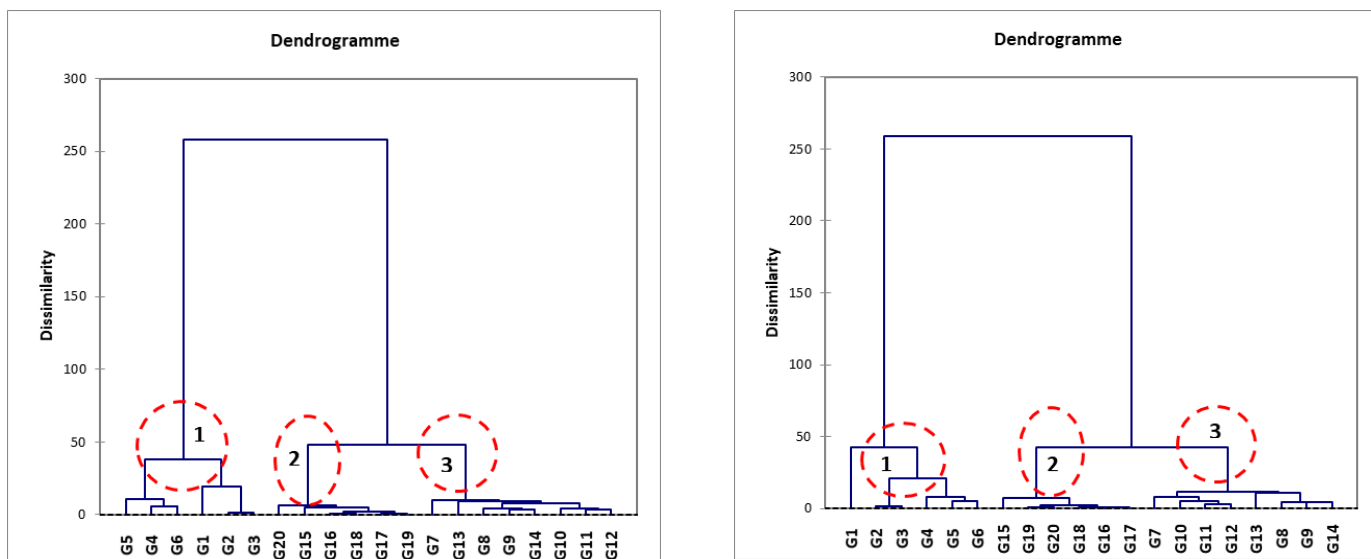


Figure 3-10. Hierarchical clustering analysis (Ward's Method) showing the relevant association among samples at MSW sites during dry and wet seasons. (*Distance metrics are based on the Euclidean distance single linkage method*).

Overall, results obtained using PCA, HCA and pollution indicators (WQI, PIN) were the same, implying the admissibility of such indices to revealed and assess the status of pollution. They could be used as a time saving and cost-effective methods to orient any further clean-up intervention based on the recorded level of pollution in each site.

### 3.3.8 Human health risk assessment

The non-carcinogenic risks to children and adults posed by trace metals through different routes are shown in **table 3-12**. Minimum, average and maximum concentrations of TTMs were used to conclude an overall about the human risk range in the study area.

The HQs for water ingestion on both adults and children were higher than dermal contact, which is consistent with previous studies that reported that among the exposure pathway the ingestion route has the highest adverse influence on health (Tokatlı & Varol, 2021; Varol, Karakaya, et al., 2021). However, the hazard index was less than the acceptable limit of 1 in all examined water samples, suggesting that the exposure of metals through multi-pathways was still acceptable for people living near the study area. The maximum estimated THIs were  $7.38 \times 10^{-4}$  and  $8.96 \times 10^{-6}$  for children and adults, respectively. As expected, similar to previous similar works performed by Ma et al. (2018) and Mallongi et al. (2021) children were more vulnerable to contaminants compared to adults due to their sensitivity and lower immunology (Mallongi, Dwi, et al., 2021). The contribution rates of different metals were similar for both age groups, and decreasing in the following order of, As > Cd > Pb > Cr > Ni > Zn > Cu, this outcome is logical considering the toxicity levels of these metals. For example, As and Cd (mg/kg/day) have the lowest reference dose among these metals (0.0003 and 0.0005 for As and Cd, respectively).

The carcinogenic risk was estimated for As, Pb, Cd and Cr based on their CSF given by the USEPA. As depicted in **table 3-13**, the calculated carcinogenic for both age groups were within or below the acceptable range of  $10^{-4}$  to  $10^{-6}$  as shown in Table 15. These results reflected that As, Pb, Cd and Cr in the studied water bodies did not pose any carcinogenic health risks to the local residents. Similarly to our findings, Varol et al. (2021b) and Jahin et al. (2020) were found an acceptable carcinogenic risk around agricultural area.

For instance, the population living in the surrounding of the landfill were unlikely exposed to carcinogenic and non-carcinogenic risk due to metals exposure. However, more attention should be paid to the anthropogenic activities adjacent to the study area which might lead to the accumulation of metals in water and soils.

### **3.4 Conclusion, recommendations, and future challenges**

In this study, groundwater quality around the biggest Moroccan sanitary landfill and its suitability for agricultural and drinking use was assessed based on their physicochemical compositions using pollution indices, statistical analysis and the deterministic and probabilistic human risk assessment.

The results indicated that almost all investigated parameters exceeded the corresponding limits set by the WHO and Moroccan standards. The WQI, PIN, hydrochemical facies, and irrigation indices indicating that water was not suitable for drinking and agricultural uses. Chemometric analysis (PCA, HCA) classified the studied site in three zones, and reflected that the studied landfill has a significant negative impact. In addition, intensive use of pesticides and fertilizers significantly contributed in the propagation of revealed pollution discussed in this work. The obtained findings highlight the need for the development of an appropriate intervention to limit the propagation of pollution and prevent water quality for drinking and agricultural use. As conclusion, several recommendations can be made. The leachate treatment approach is urgently required to limit the huge quantity of leachate (more than  $80.000\text{ m}^3$ ). It must be emphasized the use of geomembrane in the landfill liner systems to prevent leachate percolation into the groundwater. The installation of new piezometers is highly recommended for monitoring the groundwater quality.

Table 3-12. Non-carcinogenic risk and cumulative risk for different exposure routes on both children and adults.

Metal(oid)s	level	conce (mg/l)	Children				Adults			
			Oral ingestion		Dermal exposure		Oral ingestion		Dermal exposure	
			CDI	HQ	CDI	HQ	CDI	HQ	CDI	HQ
<b>Pb (mg/l)</b>	Min	0.0023	7.22E-08	2.06E-05	8.09E-11	1.54E-07	3.10E-09	8.85E-07	1.26E-11	2.39E-08
	Mean	0.0071	2.27E-07	6.49E-05	2.55E-10	4.85E-07	9.74E-09	2.78E-06	3.96E-11	7.53E-08
	Max	0.0157	5.02E-07	1.43E-04	5.62E-10	1.07E-06	2.15E-08	6.14E-06	8.73E-11	1.66E-07
<b>Cu (mg/l)</b>	Min	0.0002	6.39E-09	1.60E-07	7.16E-12	1.79E-10	2.74E-10	6.85E-09	1.11E-12	2.78E-11
	Mean	0.0075	2.41E-07	6.03E-06	2.70E-10	6.75E-09	1.03E-08	2.58E-07	4.20E-11	1.05E-09
	Max	0.0180	5.75E-07	1.44E-05	6.44E-10	1.61E-08	2.47E-08	6.16E-07	1.00E-10	2.50E-09
<b>Cr (mg/l)</b>	Min	0.0002	6.39E-09	2.13E-06	7.16E-12	2.50E-07	2.74E-10	9.13E-08	1.11E-12	3.89E-08
	Mean	0.0035	1.12E-07	3.75E-05	1.26E-10	4.40E-06	4.82E-09	1.61E-06	1.96E-11	6.84E-07
	Max	0.0113	3.60E-07	1.20E-04	4.03E-10	1.41E-05	1.54E-08	5.14E-06	6.26E-11	2.19E-06
<b>Zn (mg/l)</b>	Min	0.0006	1.79E-08	5.97E-08	2.00E-11	6.68E-11	7.67E-10	2.56E-09	3.11E-12	1.04E-11
	Mean	0.0342	1.09E-06	3.64E-06	1.22E-09	4.08E-09	4.68E-08	1.56E-07	1.90E-10	6.34E-10
	Max	0.1400	4.47E-06	1.49E-05	5.01E-09	1.67E-08	1.92E-07	6.39E-07	7.79E-10	2.60E-09
<b>Ni (mg/l)</b>	Min	0.0008	2.49E-08	1.25E-06	2.79E-11	1.36E-09	1.07E-09	5.34E-08	4.34E-12	2.11E-10
	Mean	0.0113	3.60E-07	1.80E-05	4.03E-10	1.96E-08	1.54E-08	7.72E-07	6.27E-11	3.04E-09
	Max	0.0225	7.19E-07	3.60E-05	8.05E-10	3.91E-08	3.08E-08	1.54E-06	1.25E-10	6.07E-09
<b>Cd (mg/l)</b>	Min	0.0003	8.31E-09	1.66E-05	9.31E-12	1.86E-08	3.56E-10	1.02E-07	1.45E-12	2.89E-09
	Mean	0.0024	7.68E-08	1.54E-04	8.60E-11	1.72E-07	3.29E-09	9.40E-07	1.34E-11	2.67E-08
	Max	0.0058	1.85E-07	3.71E-04	2.08E-10	4.15E-07	7.95E-09	2.27E-06	3.23E-11	6.45E-08
<b>As (mg/l)</b>	Min	0.0003	7.99E-09	2.66E-05	8.95E-12	1.28E-11	3.42E-10	9.78E-08	1.39E-12	1.99E-12
	Mean	0.0042	1.35E-07	4.49E-04	1.51E-10	2.16E-10	5.78E-09	1.65E-06	2.34E-11	3.35E-11
	Max	0.0094	3.01E-07	1.00E-03	3.37E-10	4.81E-10	1.29E-08	3.68E-06	5.23E-11	7.48E-11
Cumulative <b>CDI</b> for min. values			1.44E-07		1.61E-10		6.18E-09		2.51E-11	
Cumulative <b>CDI</b> for max. values			2.25E-06		2.51E-09		9.62E-08		3.91E-10	
Cumulative <b>CDI</b> for mean. values			7.12E-06		7.97E-09		3.05E-07		1.24E-09	
THQ for min. values			6.75E-05		4.25E-07		1.24E-06		6.60E-08	
THQ for mean. values			7.33E-04		5.09E-06		8.17E-06		7.91E-07	
THQ for max. values			1.70E-03		1.56E-05		2.00E-05		2.43E-06	
<b>THI for max. values</b>					<b>7.38E-04</b>				<b>8.96E-06</b>	

Table 3-13. Carcinogenic risk and cumulative risk for different exposure routes on both children and adults.

Metal(oid)s	level	conce (mg/l)	Children			Adults		
			Oral ingestion	Dermal exposure	LCR	Oral ingestion	Dermal exposure	LCR
<b>Pb (mg/L)</b>	Min	0.0023	6.14E-10	6.88E-13	6.15E-10	2.63E-11	1.07E-13	2.64E-11
	Mean	0.0071	1.93E-09	2.16E-12	1.93E-09	8.28E-11	3.36E-13	8.31E-11
	Max	0.0157	4.27E-09	4.78E-12	4.27E-09	1.83E-10	7.42E-13	1.84E-10
<b>As (mg/L)</b>	Min	0.0003	1.20E-08	1.34E-11	1.20E-08	5.14E-10	2.09E-12	5.16E-10
	Mean	0.0042	2.02E-07	2.26E-10	2.02E-07	8.66E-09	3.52E-11	8.70E-09
	Max	0.0094	4.51E-07	5.05E-10	4.52E-07	1.93E-08	7.85E-11	1.94E-08
<b>Cr (mg/L)</b>	Min	0.0002	3.20E-09	3.58E-12	3.20E-09	1.37E-10	5.56E-13	1.38E-10
	Mean	0.0035	5.62E-08	6.30E-11	5.63E-08	2.41E-09	9.78E-12	2.42E-09
	Max	0.0113	1.80E-07	2.01E-10	1.80E-07	7.71E-09	3.13E-11	7.74E-09
<b>Cd (mg/L)</b>	Min	0.0003	3.16E-09	3.54E-12	3.16E-09	1.35E-10	5.49E-13	1.36E-10
	Mean	0.0024	2.92E-08	3.27E-11	2.92E-08	1.25E-09	5.08E-12	1.26E-09
	Max	0.0058	7.04E-08	7.89E-11	7.05E-08	3.02E-09	1.23E-11	3.03E-09
Cumulative carcinogenic risk for min. values			1.90E-08	2.12E-11	<b>1.90E-08</b>	8.12E-10	3.30E-12	<b>8.16E-10</b>
Cumulative carcinogenic risk for mean values			2.89E-07	3.24E-10	<b>2.90E-07</b>	1.24E-08	5.04E-11	<b>1.25E-08</b>
Cumulative carcinogenic risk for max. values			7.06E-07	7.90E-10	<b>7.06E-07</b>	3.02E-08	1.23E-10	<b>3.04E-08</b>

Note: E is the abbreviation of exponent, which means the index based on 10

## Chapter IV: Determination of properties and environmental impact due to the inclusion of cigarettes fibers in cementitious mortars: a new solution to mitigate the CBs pollution

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### Highlights:

- cellulose acetate microfibrils (CAFs) were used in the elaboration of cementitious mortars for the first time.
- It was observed that the prepared mortars, exhibited satisfactory mechanical and physical properties.
- A notable improvement of thermal insulation was achieved when adding CAFs as a substitution of sand.
- Elaborated mortars will contribute to the solving of the environmental impacts associated with cigarette butts.
- The prepared mortars could be used as insulating building materials.

## **Chapter IV: Determination of properties and environmental impact due to the inclusion of cigarettes fibers in cementitious mortars: a new solution to mitigate the CBs pollution**

### **General summary**

Cigarette butts generated are one of the major sources of total solid waste production and lead to environmental issues. This article has the objective of evaluating the effects of cellulose acetate microfibers (CAFs) sourced from discarded cigarette filters (CFs) as fiber-reinforcement on the physico-mechanical properties and thermal conductivity of cementitious materials. To do so, mortar samples were prepared using different incorporated quantities of fibers (0.5, 1, 1.5, 2, 2.5, and 5% compared to the quantity of sand added to the mixture) and subjected to different tests to characterize the influence of CAFs on the microstructure of elaborated materials, considering the changes in workability time, compressive strength, flexural strength, density, water absorption, and microstructural analysis. Furthermore, the life cycle assessment (LCA) of mortar mixes in terms of CO<sub>2</sub> emissions is made. The results revealed that the increasing percentages of CAFs reduced the dry density and compressive strength, by approximately 1.62% – 51% and 37– 69.64% respectively, also a notable enhancement of insulation characteristics by about 5-47.5% was achieved. Microstructure analysis confirmed the experimental investigation and revealed that adding more than 1% of fibers resulted in a significantly low unit weight with greater entrapped air content. The studies prove the possibility of recycling cigarette butts for insulating cementitious matrix. In addition, applying mortar containing acetate cellulose fibers is recognized as a more environmentally friendly mixture in terms of reducing CO<sub>2</sub> emissions and could participate significantly in the achievement of SDGs.

**Keywords:** Cement Mortar, Cigarette butts, cellulose acetate, life cycle assessment, CO<sub>2</sub> emissions, SDGs

**Abbreviations:** **CBs** (Cigarette butts): discarded part of the cigarette; **CFs**: Cigarette filters; **CAFs** (Cellulose acetate microfibers): the main constituent of CFs

## **4.1 Introduction**

Recent years have shown a dramatic increase in the generated quantity of waste and industrial pollutants worldwide, due to expressive economical and industrial growth. Regardless of the type of waste, its destination is generally landfilling with no further treatment. Therefore, how to deal with these issues become one of today's most urgent challenges (Bouzekri, Laarbi, et al., 2019; El Fadili et al., 2022; Fadili et al., 2022).

The tobacco industry could be considered one of the most prevalent industries, and contribute to high income in many countries. Yearly, six trillion cigarettes are produced and 5.8 trillion are consumed by one billion smokers across the entire globe (Zafeiridou et al., 2018), contributing to the generation of approximately 1.3 tons of dangerous litter known widely as cigarette butts (CBs) (Mohajerani et al., 2016), which makes it one of the most abundant litter items on the planet (Rebischung et al., 2018). Moreover, as a result of population growth and the increasing uptake of smoking by young people year after year, it is estimated that the amount of cigarettes consumed will increase by more than 50%, to reach nine trillion by 2025, and most of their butts are discarded by smokers into the adjacent environment (Dobaradaran, Soleimani, et al., 2021). For example, according to the cigarette butt pollution project in the USA, one-third to two-thirds of CBs end up in nature (ocean, river, public roads...etc.).

CBs consist of four main components: remaining tobacco, wrapping paper, ashes, and a filter made from cellulose acetate (Christina et al., 2019). Filters are composed of synthetic plastic fiber commonly designed in a way to trap dangerous toxic compounds present in cigarettes during the smoking process (Mohajerani et al., 2016, 2017; Torkashvand et al., 2021). These filters are well known for their slow biodegradability (Mohajerani et al., 2016; Romero-Gómez et al., 2022) and can take up to thousand of years to biodegrade under normal conditions. Thus, it has sufficient time to release the entrapped contaminants into the environment (Yousefi et al., 2021).

Previous works have already revealed that this small pollutant contains a myriad of toxicant and hazardous chemicals compounds (Torkashvand et al., 2020), such as nicotine (Dobaradaran, Soleimani, et al., 2021), polycyclic aromatic hydrocarbons (PAHs), formaldehyde, BTEX (Dobaradaran, Schmidt, Kaziur-Cegla, et al., 2021), phenol, heavy metals (Dobaradaran et al., 2020) and other toxic compounds (Slaughter et al., 2011). Therefore, the disposal of CBs is a very challenging issue because if not managed unscientifically and correctly disposed of, it could bring a serious threat to the soil and the quality of aquatic resources (Christina et al., 2019; Dobaradaran et al., 2019). It is claimed that one single cigarette butt can contaminate up to 1000 liters of water and they might perhaps bio-accumulate in the wildlife and potentially the food chain. Although,

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until recently at the regulatory level, the Moroccan catalog of waste does not propose a specific entry for CBs, and is still considered as a municipal solid waste (MSW).

The harmful effects of both active and passive smoking on human health are well-known and widely discussed in a good number of previous studies (Freire Lima et al., 2021). However, their possible damage on the environment and feasible solutions are still limited.

Unfortunately, landfilling and incineration are the two common disposal methods for cigarette butts in many countries around the world. Nevertheless, they are not efficient and inadequate due to the elevated cost and the possible release of gaseous pollutants. To this end, there is a large attempt by the scientific community to develop economically and environmentally sustainable recycling solutions, and facing the blooming threat as well as the huge quantities of CBs, by incorporating its different parts in various applications, including recycling CBs as a corrosion inhibitor (Chakraborty et al., 2017; A. Singh et al., 2020), production of cellulose pulp (d’Henri Teixeira et al., 2017), utilization as a sound absorbing material (Escobar & Maderuelo-Sanz, 2017; Maderuelo-Sanz et al., 2018), preparation of activated and charred carbon (Hamzah & Umar, 2017), the synthesis of superhydrophobic sorbent (Ifelebuegu et al., 2018; Ou et al., 2016), porous carbon (Matos et al., 2017). Also, their incorporation into various construction materials has received considerable interest, several research works were conducted on the use of CBs such as lightweight fired brick, asphalt concrete, gypsum composites, and ceramics (Kurmus, 2021; Md & Abbas, 2021; Mohajerani et al., 2016, 2021; Romero-Gómez et al., 2022), as a viable solution that both conserves natural resources and avoids the harmful effects of cigarette butts. For example, interesting findings were observed by Gironi et al. (2020) who conducted an experimental study to evaluate the effectiveness of using cigarette butts at different replacement levels up to 10 % by weight as a fine powder in ceramic materials, in which they demonstrated that the use of 5% showed satisfactory values in terms of mechanical and physical characteristics. Likewise, Mohajerani et al. (2016) conducted an experimental investigation on the recycling of different incorporation rates of CBs (2.5%, 5%, 7.5%, and 10% content by weight) into fired clay bricks, the findings showed a lighter composite with satisfactory thermal insulation and energy performance and a compressive strength of 12.57 MPa by replacing clay with 2.5% of CBs in fired bricks.

As stated above, many studies have been carried out on the incorporation of CBs in construction materials. Although the use of cellulose acetate sourced from cigarette filters (CFs) is still limited, only a few research works were conducted on its incorporation in cementitious and gypsum materials. In concrete, a significant improvement in ductility was achieved with acceptable

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compressive strength which decreased by about 30% for 20 kg/m<sup>3</sup> (Luo et al., 2019). Likewise, recent studies conducted by Tannous et al. (2022) and Romero-Gómez et al. (2022) demonstrated the possibility of using cellulose acetate from cigarettes filters by up to 1.3% and 2.5% as a substitution of sand and gypsum respectively, could give satisfactory results in terms of workability, compressive strength, bulk density and total porosity in comparison with the conventional material.

A good number of previous studies have largely investigated the effects of fibers reinforced cementitious composites (FRC) with different lengths and content on the rheological behavior and mechanical properties of mortar-based composites, and very encouraging findings were concluded and approved the feasibility of using fibers for the enhancement of certain properties in comparison to synthetic fibers existing in the market. In particular, a significant improvement in various parameters such as toughness, tensile strength, elastic properties, acoustic and thermal insulation was achieved (Alyousef et al., 2020; Araya-Letelier et al., 2017; Candamano et al., 2021; Khelifa et al., 2021; Safiuddin et al., 2021). For example, Quiñones-Bolaños et al. (2021) investigated the potential use of coconut fibers with lengths of approximately 6.0 cm and diameters ranging from 0.1 to 1.5 mm for the enhancement of thermal comfort in low-income housing and observed an annual reduction of energy costs of cooling by 16%. As well, Naiiri et al. (2021) noticed an upgrading of mechanical and thermal properties, when exploring three different sizes of doum palm fibers (0.1, 0.2, and 0.3 mm) alkali-treated with NaOH solution for fiber content 0.5%.

In the same context, the current paper aims the investigation of the influence of incorporating various percentages (0, 0.5%, 1%, 1.5%, 2%, 2.5%, and 5%) of cellulose acetate fibers (CAFs) sourced from discarded cigarettes filters (CFs) as a partial replacement of fine aggregate on the physical, mechanical and thermal properties of cementitious mortars. For this purpose, the chemical composition, microstructure, water absorption, and density of cellulose acetate fibers (CAF) were tested in the first stage. Then, the workability, bulk density, porosity, water absorption, thermal conductivity, compressive and flexural strength of produced mortars were evaluated to conclude an overall about its potential use as a partial substitution of sand. Additionally, the environmental aspects and potential impacts associated with the incorporation of cellulose acetate fibers in terms of carbon dioxide emissions were compared with conventional mortars based on life cycle assessment (LCA) which has not been reported in previous research works.

## 4.2 Material and methods

### 4.2.1 Raw materials used in the investigation

Natural river sand, Portland composite cement, cellulose acetate fibers, and water were the principal materials used to prepare all investigated mortar mixes. Portland cement CPJ45 used in this study was manufactured by Holcim company following the requirements set by the Moroccan standard NM 10.1.004, **Table 4-1** presents its chemical composition, and its anhydrous contents calculated based on Bogue equations. According to the producer datasheet, the cement owes the following properties: average compressive strength at 28 days of 40 MPa and specific gravity of 3.15 g/cm<sup>3</sup>. River sand was employed as fine aggregate, with a specific gravity of 2.67 g/cm<sup>3</sup> and shows granular distribution suitable for mortar purposes compared to the required standards (**Appendix E**). The natural sand was extracted from a local aggregate supplier situated in Rabat. It was washed to clean it from deleterious materials (clay lumps and organic matter).

Table 4-1.chemical composition of cement

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	LOI at 1000 °C
17.76	3.82	2.93	52.03	2.33	0.29	0.79	14.43

Cigarette butts waste (CBs) incorporated in the tested mortar mixes, were collected manually with different characteristics without taking into account the brand of cigarette (**Fig 4-1-a and b**). After the collection of CBs, the acetate cellulose fibers were separated from the outer paper before being oven-treated at 60°C for 12 h to avoid material degradation, crushed into small particles, to obtain a homogeneous mixture, and stored in sealed bags until the composite samples were prepared (**Fig 4-1-c**).

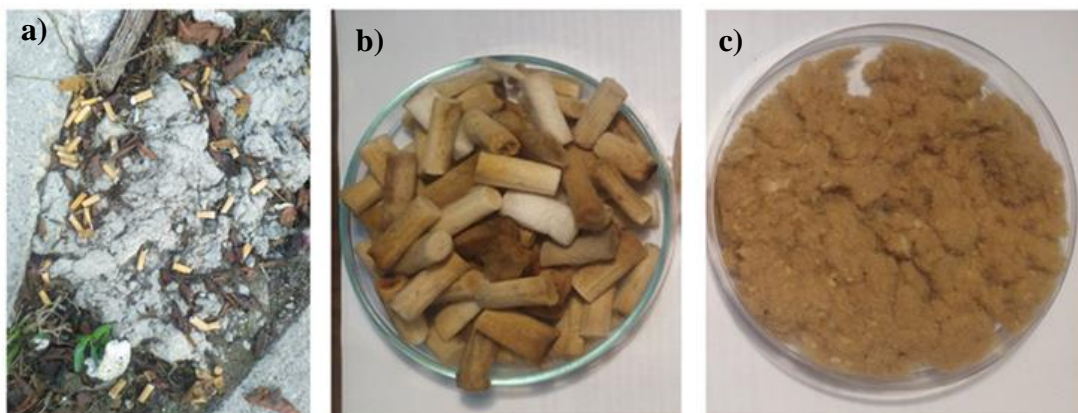


Figure 4-1.raw materials used for mortar production: (a) cigarette butts; (b) acetate cellulose fibers separated from the outer paper; (c) crushed cellulose acetate

The mortar was mixed with drinking water with a pH of about 7.5. Its chemical and physical characteristics comply with the requirements set by the NM 10.1.353.

#### **4.2.2 Characterization methods of raw materials**

Particles size distribution was carried out by wet sieving through a series of AFNOR sieves for the fraction  $> 500 \mu\text{m}$ , while the fraction  $< 500 \mu\text{m}$  analysis was performed using the Laser scattering particle size distribution analyzer Horiba LA-300, having a detection range of 0.1–600  $\mu\text{m}$ .

The chemical composition was carried out by X-ray fluorescence (XRF), using an AXIOS wavelength dispersion spectrometer (CNRST-UATRS), while the mineralogical characterizations of the raw material were performed by XRD analysis using X'PERT MPD PRO Configuration PW 3064/xx Spinner–PANALYTICAL. The scans covered a  $2\Theta$  range of  $5^\circ$  to  $80^\circ$ , with a nominal step size of  $0.0670^\circ$  and 121.0150 s/step.

#### **4.2.3 Mortars mix procedure**

The mortar samples were prepared with respect to cement to sand mass ratio of 1:3. Also, water to cement mass ratio was maintained constant at 0.6 to allow a reliable comparison between prepared specimens.

Totally six mortar specimens were prepared for performance evaluation by mixing cement, natural sand and adding cellulose acetate fibers (CAF) sourced from CBs with different substitution percentages to the mixture (0.5, 1, 1.5, 2, 2.5, and 5 wt%) per dry raw sand mass; these mixtures were denoted as CF0.5, CF1, CF1.5, CF2, CF2.5, and CF5 respectively.

For comparison purposes, samples without adding fibers were also prepared and characterized. Afterwards, the above-mentioned constituents were sufficiently mixed manually (Hand Mixing) in dry conditions to obtain a homogenous mix. Water is then added gradually and the mixing process continued for 5min. The required workability for the mortar composites was adjusted using a superplasticizer (SP) soluble in water to ensure the required workability of fresh mortar without compromising the strength properties.

The prepared blends were cast into prismatic molds with internal dimensions of  $40*40*160 \text{ mm}^3$  and  $50*50*50 \text{ mm}^3$  for the mechanical testing, and  $10*10*2 \text{ mm}^3$  for the thermo-physical properties. Once molded, they were vibrated to remove entrapped air bubbles. The hardened pastes were stripped from their molds after 24h and cured under laboratory conditions ( $T=25^\circ\text{C}$ ,  $\text{RH}=40$ ) until testing age (7 and 28 days). The different mix proportions for the mortar are shown in **Table 4-2**.

Table 4-2. Mix proportions for the mortar's mixtures

Constituant of mortar	RM	CF0.5	CF1	CF1.5	CF2	CF2.5	CF5
Cement (g)	450	450	450	450	450	450	450
Sand (g)	1350	1343.25	1336.5	1329.75	1323.00	1316.25	1282.50
W/C	0.6	0.6	0.6	0.6	0.6	0.6	0.6
CF (g)	0	6.75	13.5	20.25	27.00	33.75	67.50
SP (Wt. % of Binder)	1	1.5	2	2.5	3	3.5	5

#### 4.2.4 Testing methods

The following tests were performed with the purpose to study the properties of prepared mortars with and without CAF as a partial replacement of sand.

##### 4.2.4.1 Workability of mixtures

In order to study the influence of CAF additions on the early ages hydration behavior of tested mortars, a mini-slump cone with upper and lower diameters of 50 and 100 mm respectively, and a height of 150 mm was employed according to the ASTM C143 (Vardhan et al., 2015). It is worth noting, that gradually drier mixtures were achieved by increasing the rate of CAFs in the mixture, and a notable lack of cohesion was observed due to the hydrophilic character of the cellulose acetate. Therefore, the addition of a superplasticizer (SP) is mandatory to permit the incorporation of more fibers in the mortars.

##### 4.2.4.2 Flexural and compressive strength

The mechanical performance of the molded composites was performed via the measurement of both compressive and flexural tests.

The flexural and compressive strengths ( $R_c$ ) of the synthesized mortars were measured in prismatic samples  $40 \times 40 \times 160 \text{ mm}^3$  and  $50 \times 50 \times 50 \text{ mm}^3$  after 7 and 28 days of curing according to the ASTMs C109 and C190, respectively, using a hydraulic press with a load cell of 25 kN and loading rate of 1.6 kN/s until mortars failure occurred. For each formulation, at least three replicate samples were tested and the average values  $\pm$  standard was considered as the representative strength value at the selected age and reported in the current research and they were compared with the RILEM standard specifications. The compressive strength ( $R_c$ ) and flexural strength of the synthesized mortars were measured as follows:

$$\text{Compressive strength (MPa)} = \frac{\text{Load (Newton)}}{\text{Area of specimen (mm}^2\text{)}} \quad (4.1)$$

$$\text{Flexural strength (MPa)} = 1.5 \cdot \frac{F \cdot L}{b \cdot d^2} \quad (4.2)$$

Where; F is the flexural strength of prepared specimens (MPa), L is the distance between supports (mm), b is the width of the prism and d is the thickness of the prism (mm).

#### 4.2.4.3 Water absorption

The tightness of mortar is one of the most important properties to judge its quality and performance. It measures the amount of water that penetrates mortar when come into contact with water. Water absorption of the prepared mortar mixes was carried out according to the standard ASTM C140 after 28 days of the casting. Briefly, the difference between the weight of dry mortar samples and its weight after water immersion was used to determine the percentage of water absorption in the cementitious materials using the following formula:

$$\text{Water absorption} = \frac{m_a - m_0}{m_0} \times 100\% \quad (4.3)$$

Where  $m_a$  is the mass of the wet sample and  $m_0$  is the mass of the dry-oven mortar.

#### 4.2.4.4 Density measurement

The bulk density of produced composite samples was computed based on the dimensions and dry mass of different specimens according to the ASTM C642-13.

#### 4.2.4.5 Apparent Porosity

Apparent porosity ( $P_0$ ) of prepared mortars was performed using the Archimedes method as described by the ASTM C20-00

$$P_0 = \frac{m_{\text{sat}} - m_{\text{dry}}}{m_{\text{sat}} - m_{\text{hyd}}} \times 100 \quad (4.4)$$

#### 4.2.4.6 Thermal properties

Thermal properties are an essential criterion of masonry materials, as thermal conductivity influences the usage (Mohajerani et al., 2016). The transmission of heat from one side of the masonry materials to the other should be minimized as much as possible when making building bricks. Thermal conductivity was experimentally investigated using the asymmetric hot plate. Unlike the traditional method, a hot plate permits the measurement of thermal conductivity using only one sample. Readers are directed to our previous study to learn more details about this technique (Mounir et al., 2015). The conductivity of the samples is calculated by the following equation:

$$\phi_T = \phi_S + \phi_P = \frac{U^2}{R_{eS}}; \lambda_S = \frac{e_S}{T_0 - T_1} \times \left[ \frac{U^2}{R_{eS}} - \frac{\lambda_P}{e_P} \times (T_0 - T_2) \right] \quad (4.5)$$

#### 4.2.4.7 Microstructural characterization

The effect of cigarette fibers on the surface morphology of mortar composites was carried out by analyzing the microstructural morphology using scanning electron microscopy (QUATTRO S-FEG-Thermofisher scientific) coupled, with an energy dispersive X-ray spectrometer (EDX) for elemental analysis of prepared mortars. The purpose of the SEM micrographs is to analyze the apparent adhesion of the fibers with the matrix and to observe the presence of micro cracks that probably decrease the mechanical properties of the tested mortars.

#### 4.2.5 Environmental impact assessment

In the current study, the life cycle assessment (LCA) methodology based on the guidelines specified by ISO 14040 (2006) was conducted to examine all environmental effects related to the production of mortars throughout its life cycle, from raw material acquisition and extraction to manufacturing. The assessment is broken down into the following steps: a) Goal and scope definition; b) inventory analysis; c) impact assessment and d) its interpretation according to ISO 14044 (2006). The primary objective of this study is to assess and compare the environmental impact of blended mortars in terms of CO<sub>2</sub> emissions. As illustrated in **Fig. 4-2**, The system boundary includes the following steps: a) Collection and preparation of cellulose acetate fibers (sorting and grinding); b) extracting cement and sand; c) mixing process, and d) transportation.

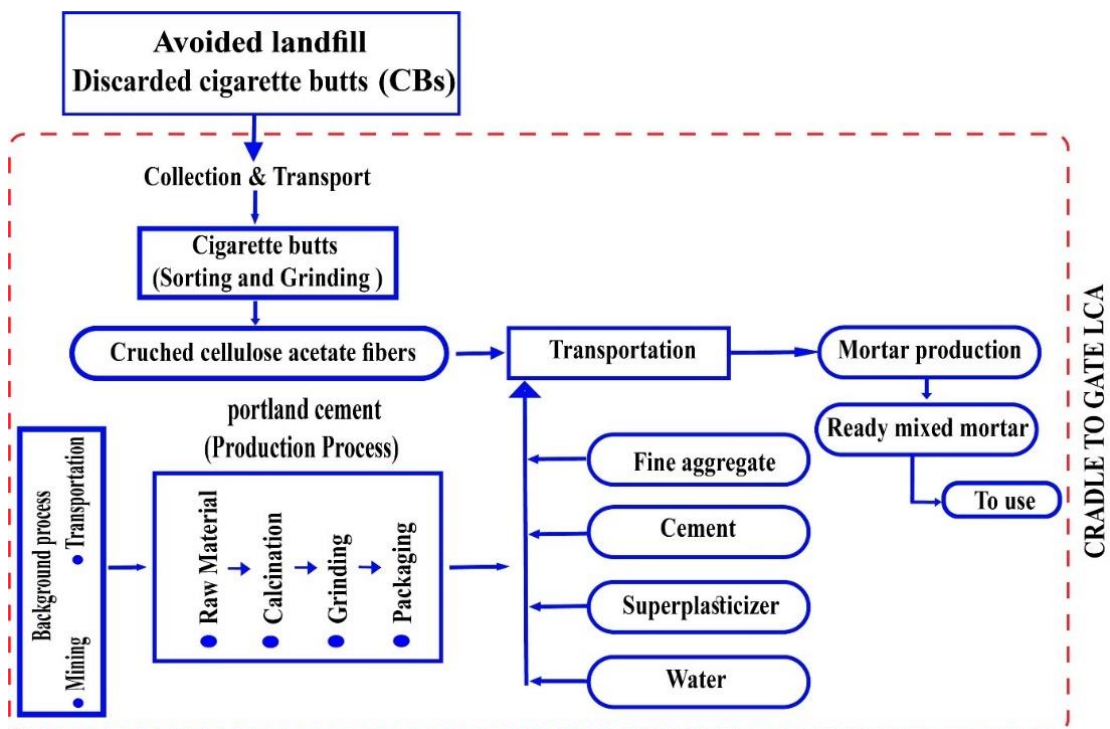


Figure 4-2. Schematic outlining of the system boundary for the prepared mortar considered in this study.

## 4.3 Results and discussions

The blended mortars were subjected to multiple tests to monitor the effects of incorporated cellulose acetate fibers on the properties of mortar during the fresh and hardening state.

### 4.3.1 Characterization of cellulose acetate fibers

#### 4.3.1.1 Mineralogical characteristics

XRD analysis was conducted on the used cigarettes filters, as shown in **Fig.4-3**, the X-ray diffractogram of cigarette filters is perfectly consistent with the spectrum of raw cellulose acetate described in the literature (Prakash et al., 2021), with two distinct peaks characterizing the presence of cellulose acetate in cigarette filters. The cellulose acetate is widely known as a bio-binder that may effectively bond the fibers to mortar.

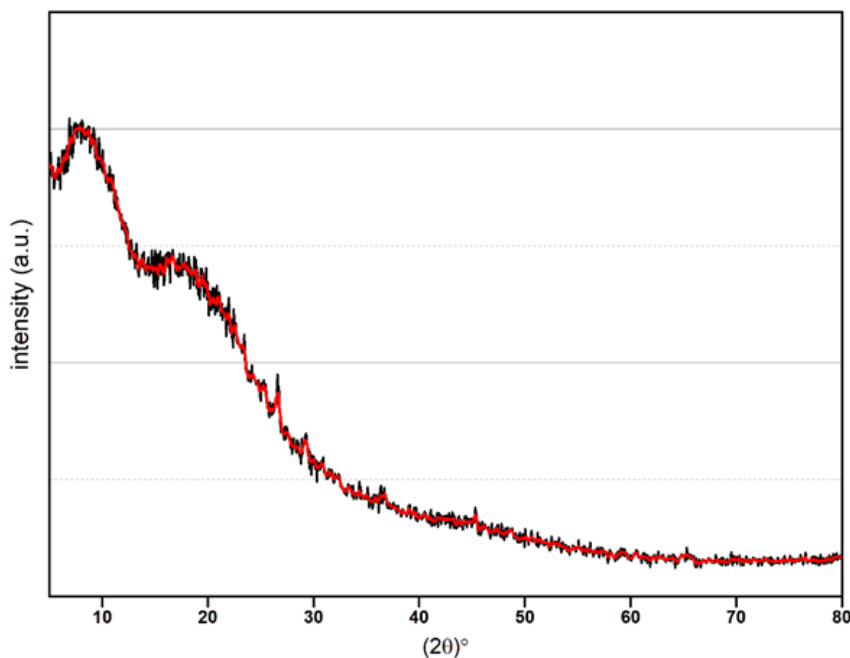


Figure 4-3. XRD pattern of cigarette filters used in the current study.

#### 4.3.1.2 Microstructural characterization

Microstructural analysis of cigarette filters before and after crushing is presented in **Fig.4-4**, it showed an agglomeration of fibers, and a clear damage of cellulose acetate was observed as a result of the smoking process and laboratory depollution techniques (**Fig.4-4-b**), which could lead to the formation of a highly porous mortar with limited mechanical performances.

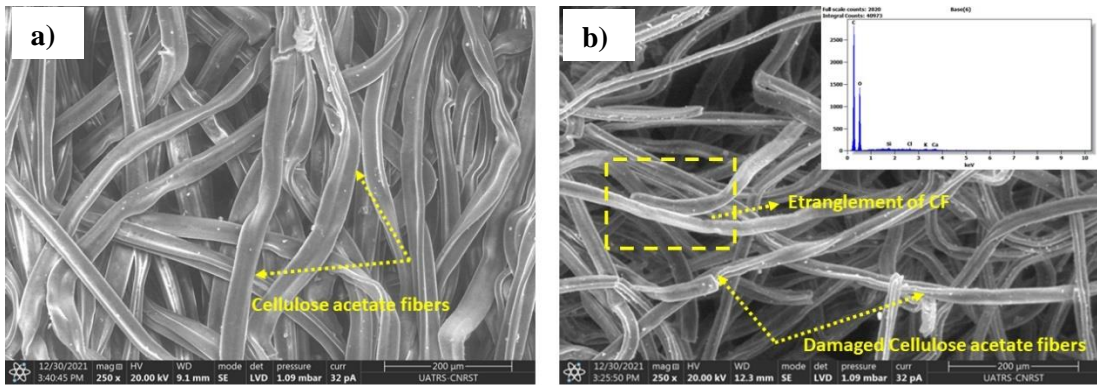


Figure 4-4. Scanning electron microscopy images: (a) cigarette filters before crushing, (b) crushed cellulose acetate sourced from cigarette filters

### 4.3.1.3 Physical characteristics

Concerning the water absorption, it was performed by immersing cellulose acetate fibers in water as a function of time (1 min, 5 min, 20min, 24h, and 48h), the test was triplicated to ascertain the obtained results and computed the standard deviation. The results presented in **Fig.4-5** showed an absorption rate of roughly 485% during the first minute of immersion which was well above that of corn cob, lavender straw and rape straw reported to be 48%, 100% and 218% respectively (Ratsimbazafy et al., 2021). Also, a dramatically increased to nearly 860% at 48h was observed, which reflected the hydrophilic character of cellulose acetate fibers compared to the cited-above plant aggregates studied previously by Ratsimbazafy et al., (2021). Therefore, cellulose acetate sourced from smoked cigarettes filters can be considered much more hydrophilic than some vegetal fibers used in previous studies and could interfere perfectly with the hydration of cement. The measured bulk density of cellulose acetate fibers was  $0.39 \pm 2 \text{ g/cm}^3$  and  $0.61 \pm 4 \text{ g/cm}^3$  without and with compactness, respectively.

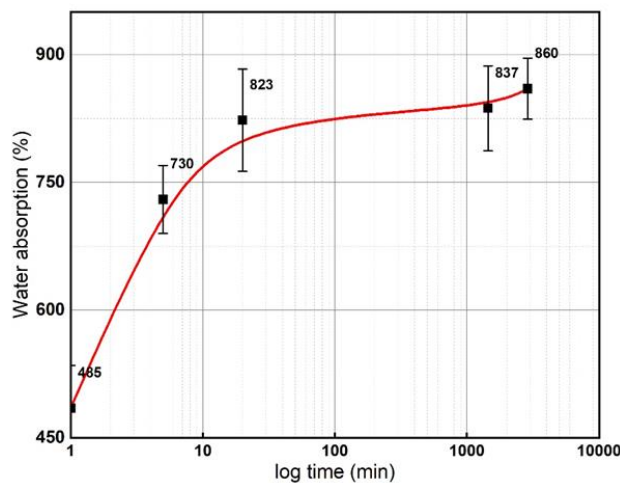


Figure 4-5. Water absorption of cellulose acetate fibers used in the current study.

### 4.3.2 Workability of prepared mortars

The workability is one of the important characteristics of a mixture. Any mixes must be sufficiently workable to be properly cast and consolidated with the actions accessible to fill the forms as well as to secure the reinforcement and other incorporated substances (Rashad & Gharieb, 2021). The workability of blended mortars was conducted as per ASTM C143 using the mini-Abrams cone (Vardhan et al., 2015), to estimate the relative fluidity of fresh mortar mixtures at various replacement levels of cellulose acetate fibers. By evaluating the findings presented in **table 4-3**, it is observed that the workability of mortars was significantly affected by the amount of cellulose acetate fibers incorporated in the mixture. The slump of the reference mixture showed the highest flowability (55 mm), with the inclusion of fibers in the mixture, the decrease in workability was not very pronounced (around 12%) until 1 %. However, workability was dramatically decreased in the mortar mix having 5% fibers content by about 74.5% as compared to the RM. This indicates clearly that adding cellulose acetate fibers in the mixes made it stiffer than the control mortar which enhance its cohesiveness thereby leading to low workability (Alyousef et al., 2020; Rashad & Gharieb, 2021). Such a reduction in the workability of mortar composite by including cellulose acetate fibers was expected due to its higher surface area and hydrophilic character as compared to river sand due to which an increase of water demand will be required to wet the surface of blended mixes (Safiuddin et al., 2018, 2021, 2022; Varadharajan, 2020). Another possible reason for this reduction with incorporating CAFs is its irregular particle size distribution in comparison to the river sand. The obtained results seem to be similar to what was reported previously by Alyousef et al. (2020) and Safiuddin et al. (2022) who found a significant decrease in workability by incorporating sheep wool and carbon waste fibers in cementitious mixtures, respectively. Therefore, based on this present finding, the replacement rate of sand by CAFs in mortar should keep below 1% to obtain the required flowability.

Table 4-3. Slump test for the mortar's mixes (mm).

Mortar Mix	RM	CF0.5	CF1	CF1.5	CF2	CF2.5	CF5
Slump (mm)	55 ± 1.5	52 ± 2.3	48 ± 1.7	42 ± 3.6	34 ± 2.5	25 ± 1.3	14 ± 1.8

### 4.3.3 Dry bulk density and apparent porosity

The main values of the hardened bulk density and apparent porosity at 28-days of curing of the developed mortar composites containing different replacement rates of fine aggregates by cellulose acetate fibers are reported in **Fig.4-6**. As expected, **Fig.4-6-a** showed that the dry bulk

density was significantly affected by the amount of CAF, the bulk density was decreased from  $1850 \pm 9$  to  $1503 \pm 0.012 \text{ kg/m}^3$  by depending on fibers content. As understood clearly here, the incorporation of fibers reduces the mass density up to about 51% for 5% of CAF mass content as compared to the reference mortar RM (i.e., mortar without fibers). Nevertheless, the density of all specimens is still higher than the limit of  $1300 \text{ kg/m}^3$  for normal-weight mortars (Awoyera et al., 2022). Furthermore, the total porosity of the mortars tested increased remarkably from 18% (RM) to 20%, 23%, 28%, 32%, 35%, and 41% for 0.5%, 1%, 1.5%, 2%, 2.5% and 5% CBs content, respectively. The main reason behind the remarkable decrease in bulk density and the notable increase of apparent porosity is the porous structure and the hydrophilic character of cellulose acetate fibers, resulting in more voids entrapped in the mortar as a result of their entanglement during mixing, capturing water-filled spaces that evaporate and turn into pores, another reason is owing to the relatively lighter density of cigarette filters ( $0.39 \pm 2 \text{ g/cm}^3$ ), as compared to fine aggregates (Kunchariyakun et al., 2022). The decrease of bulk density and increase of apparent porosity as a function of cigarettes filters in various construction materials has been already reported in several previous research works conducted by Mohajerani et al. (2017), Kurmus & Mohajerani, (2021) and Romero-Gómez et al. (2022) on asphalt concrete, fired clay bricks and gypsum matrix, respectively. Additionally, Tannous et al. (2022) observed a significant decrease in porosity by about 60% when adding 1.3 % of cigarette fibers in cementitious matrix. In the same context, the incorporation of other natural fibers such as, pre-treated hemp and carbon fibers in cementitious composites concluded similar results (Candamano et al., 2021; Safiuddin et al., 2021).

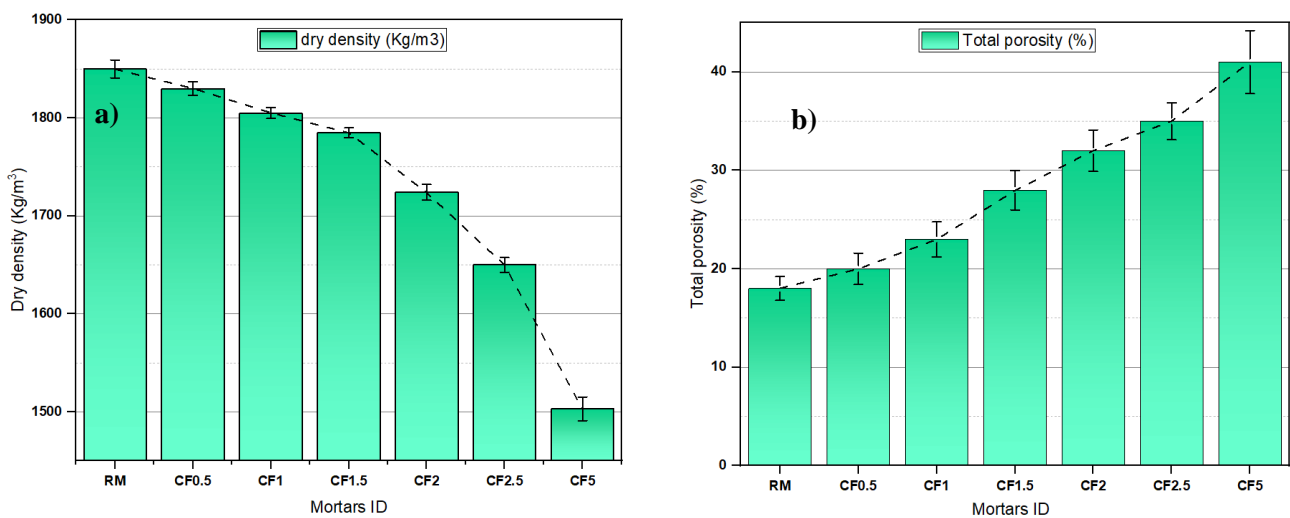


Figure 4-6. Hardened properties of prepared mortars after 28 days of curing; **a)** dry density, **b)** Total porosity.

### 4.3.4 Water absorption

To conclude an overview about the amount of water retention capacity of blended mortars at 28 days of curing. **Fig.4-7** presented the variation of water absorption of prepared composites as a function of the proportions of cellulose acetate fibers (CAF) in the mortars after 28 days of curing. As can be seen, the CF5 specimens exhibited the highest water absorption (25.10%) and apparent porosity (41%), in other words, a decrease by about 73% and 56% for water absorption and porosity were achieved as a result of the inclusion of 5% of cellulose acetate fibers (CAF). The addition of CAFs has an important effect on the water absorption rate of hardened mortars, the incorporation of only 1% increases the water absorption from  $14.5 \pm 0.25\%$  to  $16.5 \pm 0.2 \%$  and the apparent porosity from  $18 \pm 1.2 \%$  to  $23 \pm 1.78 \%$ . The increase of water absorption is mainly assigned to the hydrophilic character of CAF in comparison to fine aggregates as discussed in *section 3-1-3*, and the presence of open pores in the hardened mortar due to the creation of air bubbles trapping by studied fibers (Sakami et al., 2020). The same increase in water absorption and porosity has been already observed when adding cigarettes filters to various construction materials (Kurmus & Mohajerani, 2021a; Md & Abbas, 2021; Mohajerani et al., 2016) and similarly Awoyera et al. (2022) achieved the same conclusions by adding mineral wool and rice straw fibers in mortars.

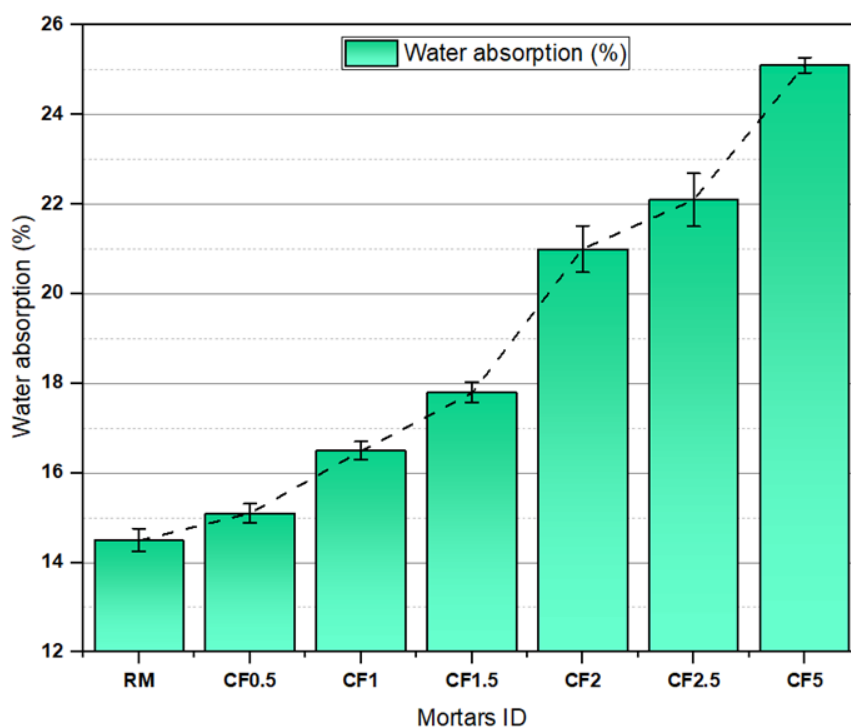


Figure 4-7. Water absorption of prepared mortars after 28 days of curing.

### 4.3.5 Mechanical properties

Compressive strength is without a doubt one of the most significant characteristics of building materials. The effect of curing age (7 and 28 days) of developed specimens containing various percentages of cellulose acetate fibers with a standard error bar is plotted in **Fig.4-8**. As it is seen, the experimental results revealed that the mortar containing cigarette fibers gains strength over long curing time as like reference mortar, indicating the hydration of the specimens for all the substitutions. Moreover, the compressive strength of the manufactured mortars decreased with an increase in the percentage of replacement of fine aggregate with CAF for both ages of curing. The reference mortar showed the highest compressive resistance at 28 days of curing (22.4 MPa). However, a gradually decreasing by about 37%, 44%, 50%, 54%, 61% and 70 % for CF0.5, CF1, CF1.5, CF2, CF2.5 and CF5 respectively, in comparison to the RM mix. The aforementioned significant reduction is mainly attributed to the heterogenic granulometric of CAF, which supported the development of pores and make the porous structure denser. Additionally, the low interfacial adhesion due to the agglomeration of fibers networks leads to several defects in the matrix, translated by the apparition of microcracks (Fiore et al., 2020). The decrease in strength with the addition of cigarette fibers implies that this waste acts only as filler and does not play a discernible effect in the hydration process. This is consistent with previous studies conducted on fibers reinforced cementitious materials (Boumhaout et al., 2017; Thanon Dawood & Hani Abdullah, 2020), in which authors observed a notable decrease of compressive resistance as a function of the addition of fibers reinforced cementitious composite materials.

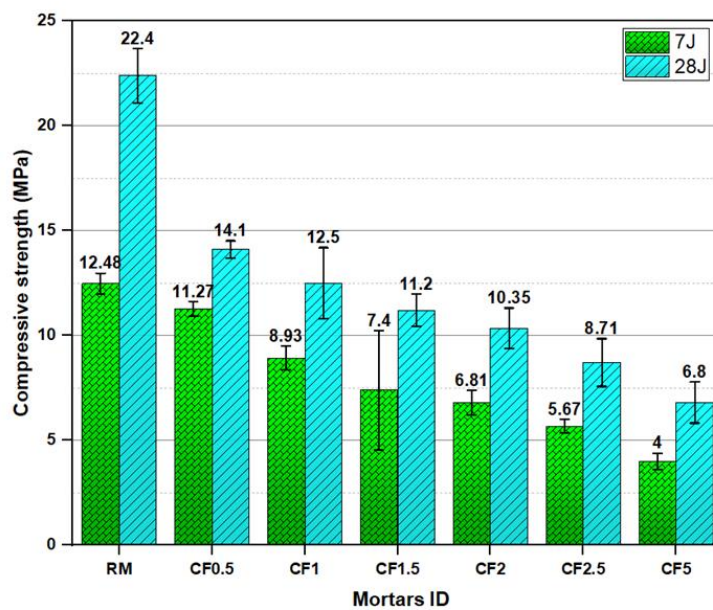


Figure 4-8. Effect of cellulose acetate fibers on compressive strength of mortars at the age of 7 and 28 days.

The flexural strength of different specimens with varying percentages of CAFs content at 28 days of curing age was examined using the three-point bending test. As highlighted in **Fig.4-9**, a notable enhancement of the flexural strength by about 8.92%, 11.38%, and 12% in comparison to the reference mix was achieved for the specimens CF0.5, CF1, and CF1.5, respectively. This is because the addition of cellulose acetate fibers leads to the bridging of cracks, which enhances the development of a cohesive matrix (Varadharajan, 2020). Similarly, Romero-Gómez et al. (2022) attained an increase of up to 9% with 2.5 % of cigarette fibers content by weight of the gypsum. Although, for addition of over 1.5 %, there was a linear decline of flexural strength from 3.64 to 2.1 MPa. The specimens CF5 exhibited the largest decrease in flexural strength by more than 42.30% in comparison to RM, these findings fit the conclusions made in sections 3.3 and 3.4, wherein further replacement over 1.5% rate leading to the development of porous structure and the weakening of bond strength between fibers and other constituents of mortars.

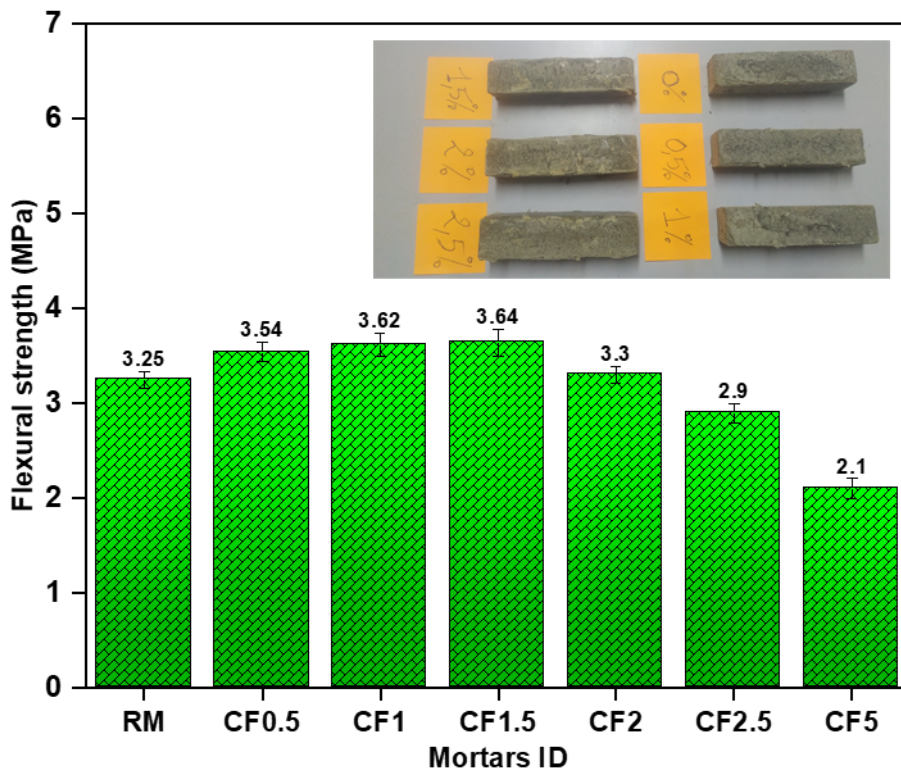


Figure 4-9. Effect of cellulose acetate fibers on flexural strength of mortars at the age of 28 days.

### 4.3.6 Thermal properties

Thermal insulation is one of the essential requirements for buildings located in areas with fluctuating temperatures (Awoyera et al., 2022). Linear fits between the thermal conductivity results of the prepared mortars and CAF content are shown in **Fig.4-10**. The thermal conductivity coefficient of the reference mortar was 0.8 W/m.k. The greater the rate of fibers within the

composite material, the lower the thermal conductivity was achieved. It is clearly observed a notable reduction in thermal conductivity depends on the amount of cellulose acetate fibers incorporated into the mortar matrix up to 0.42 W/m.k (CF5 specimens). Thus, with a progressive increase of cigarette fibers in mortar by 0.5%, 1%, 1.5%, 2%, 2.5%, and 5%, the thermal conductivity was decreased respectively by 5%, 8.75%, 15%, 26.25%, 36%, and 47.5% compared to the reference mortar (0.80 W/m.k ), corresponding to a substantial improvement in the thermal insulation capacity of the tested mortars with incorporated cigarette fibers. A recent research conducted by Romero-Gómez et al. (2022) revealed a steady downward linear trend of thermal conductivity by about 16% with incorporating 3.5% of CAFs content in gypsum matrix. The reduction can be explained, not only by the low thermal conductivity of the natural fibers in comparison to other constituents of mortars but also by the creation of voids inside the matrix due to the presence of fibers which increase the apparent porosity as discussed in the above sections. Similarly, the same trend has been observed by several authors when using natural fibers reinforced composite materials. For example, Boumhaout et al. (2017) and Sakami et al. (2020) observed a notable improvement in the thermal insulation performance of mortars by roughly 15% and 57% by incorporating 5% of doum palm and alpha fibers, respectively.

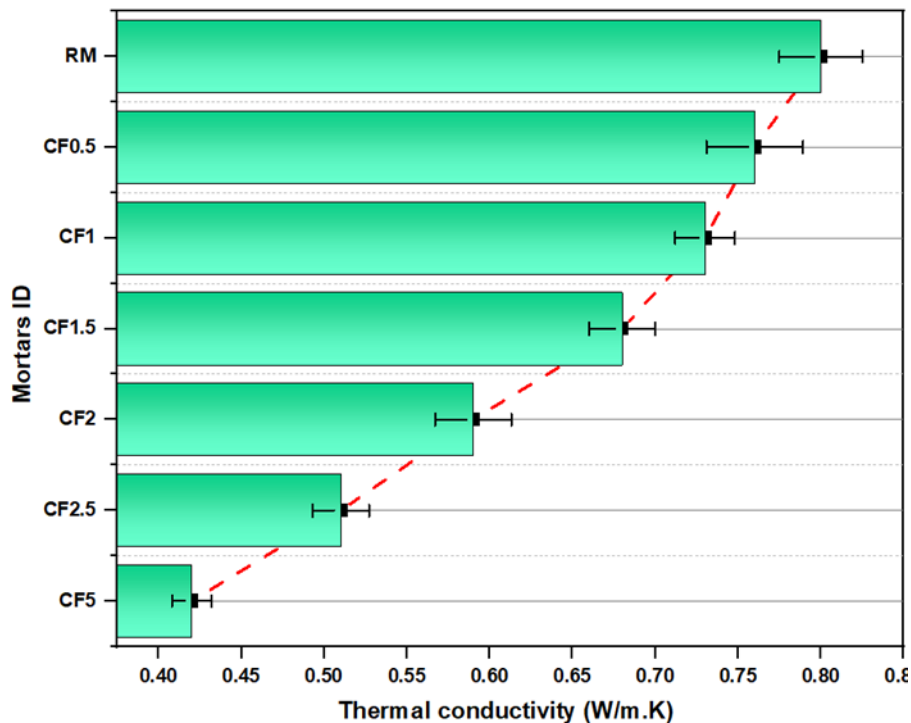


Figure 4-10. Thermal conductivity variation as a function of cellulose acetate fibers.

### 4.3.7 Effect of CAF on microstructural properties of mortar

Scanning electron microscope (SEM) with energy dispersive x-ray spectroscopy (EDS) was performed to evaluate the effect of cellulose acetate fibers sourced from cigarette filters (CFs) on the microstructure characteristics of mortars. SEM micrographs of fractured pieces taken from various mixtures at 28 days of curing are presented in **Fig.4-11**. The formation of C-S-H gel in all prepared specimens is a good indicator and proves the hydration of mortars processes with and without cigarettes fibers after 28 days of curing. Considering the SEM of selected mixes CF1 and CF5, the rougher surface, indicating the use of composite materials in mortar.

Firstly, a good adherence and homogeneous distribution were observed between the matrix and cigarette fibers until 1% of addition as shown in **Fig.4-11-b**, which indicates a good adhesion between cement matrix and cellulose acetate fibers. However, the SEM image of CF5 mortar shown in **Fig.4-11-c**, reflected that further addition of fibers has a tendency towards the creation of pores and an agglomeration of fibers in the matrix, a cluster of CAF can be identified in CF5 mortar which indicates an uneven distribution, porous structure and less inadequate contact between fibers and the matrix, which could be the primary reason for the remarkable weakening of mechanical performance compared to other prepared mortars and the micro-cracks observed surrounding the fibers. Therefore, based on these present experimental findings, the addition of CAFs in mortar should keep below 1% of the total sand content.

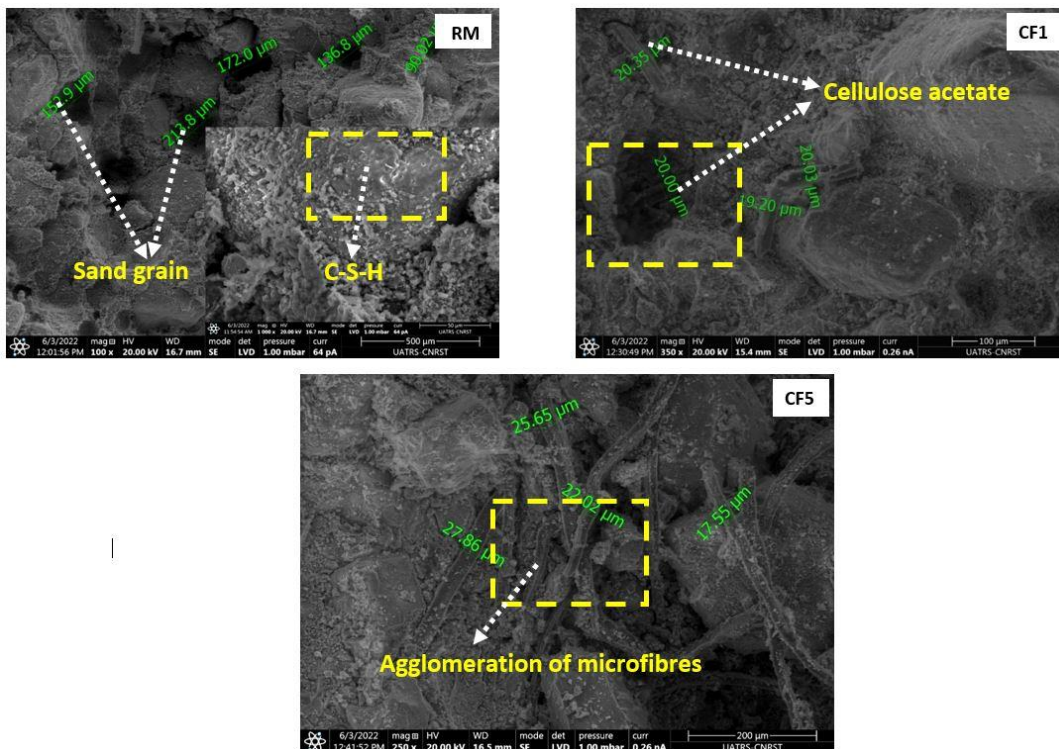


Figure 4-11. Scanning electron microscopy images of: *a*) RM; *b*) CF1 and *c*) CF5 samples at the age of 28 days.

### 4.3.8 Environmental impact analysis

The increase of the gases emission in the atmosphere contributes significantly to the greenhouse effect. Since the high consumption of cementitious materials, even a slight decrease in emissions during the whole process of production can have a notable impact on global warming through the reduction of gas emissions (Nikbin et al., 2022). In this paper, only the effect of carbon dioxide emissions due to the use of raw materials for mortar production is considered and has been assessed. **Table 4-4** presents the emission factors for raw materials used in mortar production. The factor influencing the difference in CO<sub>2</sub> emissions from each mixture is related to the content of cellulose acetate fibers and transportation distance. **Table 4-5** indicates the calculated amounts of carbon dioxide emissions from raw materials per 1000 cubic meters for different mortar mixtures.

Table 4-4. Emissions factors of raw materials.

Component	Emissions factors (kg CO <sub>2</sub> /kg)	References
Cement	0.885	(Guo et al., 2018)
Fine aggregate	0.0026	(K. H. Yang et al., 2015)
Water	0.00019	(S. W. Kim et al., 2015)
CAF	0.00071	(Nikbin et al., 2022)

Table 4-5. CO<sub>2</sub> emission evaluation of the mortar mixtures.

Mortars Id	Cement	Fine aggregate	CAF	Water	Total CO <sub>2</sub> emitted per 1000 m <sup>3</sup> of mortars
RM	398.25	3.51	0	0.0513	401811.30
CF0.5	398.25	3.49	0.0047	0.0513	401798.54
CF1	398.25	3.47	0.0096	0.0513	401785.78
CF1.5	398.25	3.45	0.0144	0.0513	401773.02
CF2	398.25	3.43	0.0192	0.0513	401760.27
CF2.5	398.25	3.42	0.0240	0.0513	401747.51
CF5	398.25	3.33	0.0479	0.0513	401683.72

As can be seen in **Table 4-5**, the comparative analysis between various mixes pointed to a remarkable reduction in the environmental impacts associated with the incorporation of cellulose acetate fibers (CAFs), when compared to conventional production (RM). By increasing cellulose acetate fibers amount by 1%, 1.5%, 2.5%, and 5%, a significant decrease of CO<sub>2</sub>-eq emissions from raw materials by roughly 25.52, 38.27, 63.78 and 127.58 (CO<sub>2</sub>-kg/ 1000 m<sup>3</sup>) was achieved, respectively. This reduction is mainly attributed to the partial replacement of sand by CAFs, and consequently the decrease of fossil fuels in the machinery to extract the sand, helping to reduce

the emission of atmospheric gases that cause global warming (GW). It is important to underline that the environmental feasibility associated with the use of CAFs could be improved by taking into account the reduction of emissions due to the decrease in the transportation of fine aggregate from the quarry to the construction sites, which is estimated to be 0.00017 CO<sub>2</sub>-kg per km (Habert et al., 2013).

### 4.3.9 Environmental/ sustainability issues

In 2015, The United Nations announced the 17 sustainable goals (SDGs) as a plan to promote social inclusion, economic growth, and environmental protection. The construction sector has a great potential to participate effectively in the achievement of these SDGs. In this light, the incorporation of CAFs in cementitious mortars has several economic and environmental benefits as shown in **Fig.4-12**, including the control, management, and minimization of the huge amounts of CBs discarded annually throughout the world and keeping those materials in use not in landfills by transforming them into alternative resources of sand in construction materials. The incorporation of 1 wt% of CAFs in the mortar formulations could permit the recycling of approximately 13.5 kg in each cubic meter of mortar. Undoubtedly, Upcycling cigarettes filters extracted from discarded cigarettes buttes (CBs) would have a significant environmental impact not only through the mitigation of hazardous effects of cigarette buttes if were not managed appropriately but is also an excellent alternative to reduce the consumed amount of fine aggregate and the associated depletion of natural resources, thus reducing the gaseous emissions associated with the extraction process of fine aggregates.

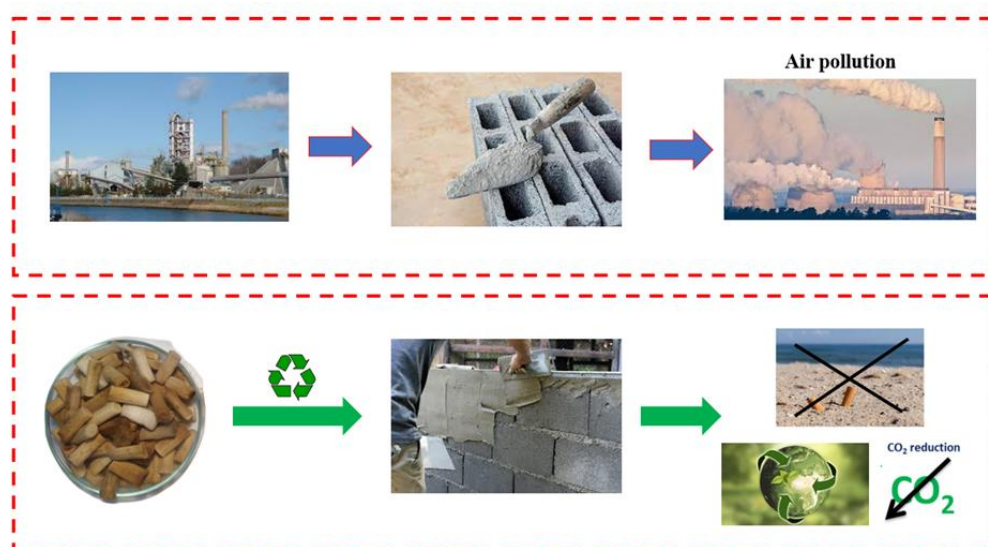


Figure 4-12. CAFs recycling as a solution to reducing emerging global crises.

In addition, the prepared mortars have a great potential to participate effectively in the achievements of the SDGs as shown in Figure 4-13. The flowchart illustrated the relationship between the elaborated mortars and the achievement of some sustainable development goals (SDGs) as follows:

- SDGs 6, 13, 14, and 15 (Clean water and sanitation, Climate action, life below water, and life on land): The CBs could participate in the release of dangerous pollutants in the adjacent environment e.g., seawater, freshwater, soils, etc. if disposed of unscientifically in open dumpsites and uncontrolled landfills as discussed by many authors in the literature (Green et al., 2020; Morales-Segura et al., 2020), therefore the recycling of these little waste permit to ensure their environmental friendly disposal and protecting aquatic resources by preventing cigarette butts from entering to oceans and freshwater and consequently its potential treatment cost, which reflects the direct contribution in the achievement of the above-cited SDGs.
- SDG 9: Industry, Innovation, and Infrastructure- elaborated mortars can be used as a sustainable alternative to traditional construction materials, promoting innovation and industrial development in the building and construction sector.
- SDG 11: Sustainable Cities and Communities – applying the prepared mortars in construction can help promote sustainable urban development by reducing the environmental impact of buildings and improving their durability and resilience.
- SDG 12: Responsible Consumption and Production – the use of elaborated mortars will participate in responsible consumption by reducing the use of natural resources and the amount of waste generated in the construction sector.
- SDG 13: Climate Action – the mortars containing CAFs have a lower carbon footprint than traditional cement-based mortars, and can help to mitigate climate change by reducing greenhouse gas emissions associated with the production of fine aggregates.

To sum up, the prepared mortars have a less environmental impact in addition to better impact performance and can be introduced as an environmentally friendly mix. Based on the recommendations established by RILEM (T. Salem et al., 2020), although using CAF wastes in mortars decreases the compressive strength, till 5 wt% the prepared materials have sufficient mechanical resistance for use in non-structural applications ( $R_c < 15$  MPa) with improved insulation properties ( $\phi_T < 0.75$  W/m.k) such as prefabricated blocks, surface coatings and insulating mortars (Tannous et al., 2022).

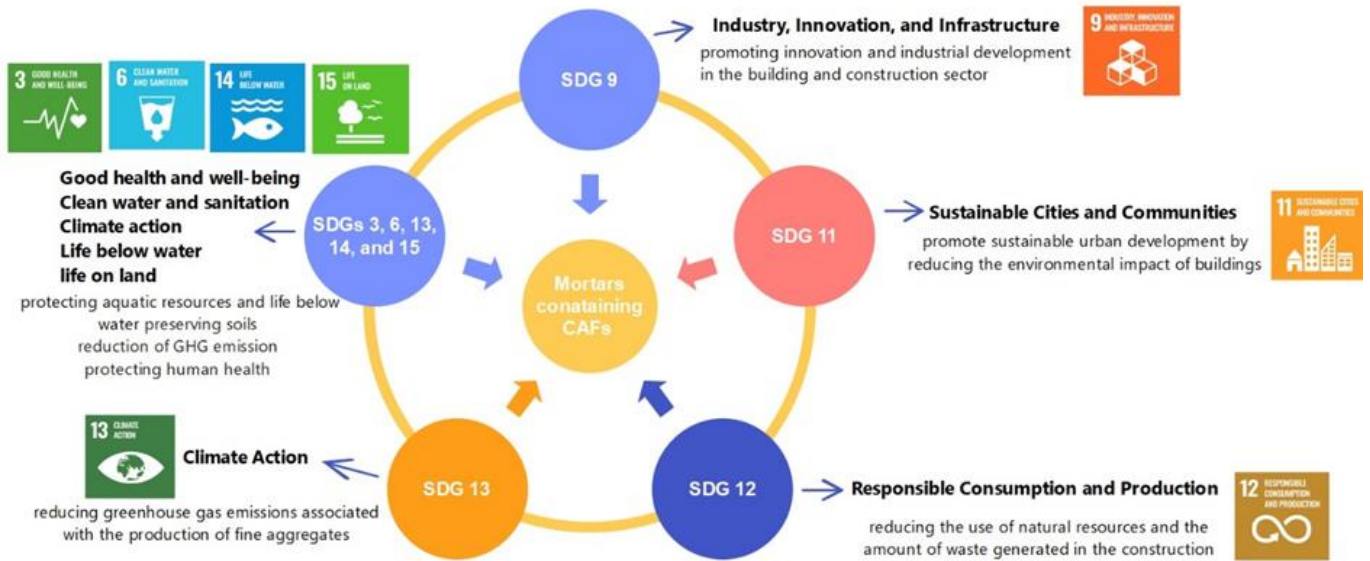


Figure 4-13. Flowchart showing the relationships between SDGs and recycling of CAFs.

## 4.4 Conclusion

In this research, the possible recycling of cigarette butts (CBs) by using cellulose acetate fibers (CAF) as a partial replacement of sand in cementitious mortars was investigated. To this end, fresh and hardened properties of prepared mortars incorporating different percentages of CAFs (0, 0.5%, 1%, 1.5%, 2%, 2.5% and 5%) at various curing ages were studied. The obtained findings permit us to draw the following conclusions and perspectives:

- Cellulose acetate fibers sourced from CBs were characterized by a high-water absorption compared to other bio-sourced fibers examined previously.
- The mortar workability was significantly decreased as a function of the rate of incorporated cigarette fibers, in spite of the addition of SP. Therefore, the replacement rate of sand by CAF in mortar should keep below 1% to obtain the required workability.
- A stepwise increase of cigarette fibers percentage in the mortar resulted in increasing its water absorption and apparent porosity, and a significant decrease in its dry bulk density.
- An increase of cigarette fibers addition leads to a decrease in compressive strength, which can be explained by the increase of porosity in the matrix and also by a weaker CAF/matrix adhesion.

- The thermal conductivity involves linearly with CAF percentage in mortar. Thus, the progressive increase of cigarette fibers additions leads to a substantial improvement in the thermal insulation performance of the tested mortars.
- Life cycle assessment (LCA) confirmed the environmental feasibility of using CAF in mortars in terms of CO<sub>2</sub> emissions.

## **4.5 Recommendations**

The results obtained from the current paper showed that CBs could be used as a source of cellulose acetate fibers for cementitious mortars. However, further experimental campaigns are highly recommended:

- To investigate the effect of the CAFs sizes on mechanical and thermal properties;
- Additional studies should be conducted to examine to effects of incorporating cellulose acetate fibers (CAF) in concrete;
- To assess the leaching of toxic elements from the prepared mortars, using TCLP tests;
- At last, the economical aspect should be investigated;

The current paper confirmed the potential of using cigarettes fibers wastes for the production of mortar. However, further experimental campaigns need to be performed to evaluate the possible leaching of pollutants from prepared mortars will be of interest in the future.

## Chapter V: Effects of encapsulating cellulose acetate microfibers on the mechanical, thermal and environmental properties of geopolymers: a new solution to mitigate the cigarettes pollution

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### Highlights:

- cellulose acetate microfibers (CAFs) used in the elaboration bio-geopolymers for the first time.
- It was observed that the elaborated geopolymers, exhibited satisfactory properties.
- Satisfying Mechanical and physical properties
- A notable improvement of thermal insulation was achieved when adding CAFs.
- The TCLP showed that the release of pollutants is within the USEPA guidelines.
- Elaborated geopolymers contribute to the solving of the environmental impacts associated with cigarette butts.
- The prepared materials could be used as an excellent for sealing in landfills (passive/ active barriers).

## **Chapter V: Effects of encapsulating cellulose acetate microfibers on the mechanical, thermal and environmental properties of geopolymers: a new solution to mitigate the cigarettes pollution**

### **General summary**

Cigarette butts (CBs) are one of the major sources of total solid waste that lead to several environmental issues. This study aims to evaluate the effects of cellulose acetate fibers (CAFs) sourced from discarded cigarette as fiber-reinforcement on the physico-mechanical properties and thermal conductivity of alkaline activation materials (AAMs). At first, an optimisation of the AAM mixture design was conducted based on various content of fly ash (FA) and metakaolin (MK). Afterwards, the optimal mixture was prepared with various percentages of CAFs (0, 0.2, 0.4, 0.6, 0.8, 1 and 1.5 wt%), and the properties of the developed samples were tested including the physico-mechanical, thermal conductivity, microstructural analysis, and concentration of the leached metal(oid)s. The characterizations showed that CBs are mainly composed of CAFs that displayed a high hydrophilic character. The encapsulation of extracted CAFs reduces the compressive strength, P-wave velocity, and density, whereas the flexural strength, porosity, and water absorption were slightly increased. Also, a slight enhancement in thermal insulation capacity was observed with increasing the incorporation rate (up to ~9.57%). The microstructural characterizations including XRD, FT-IR, and SEM/EDX analyses demonstrated the formation of geopolymeric gel N-A-S-H, C-A-S-H, and C-S-H in all the developed geopolymers, and the development of porous structure with ensuing incorporation of CAFs. The leaching test (TCLP) showed that the released contaminants were within the regulatory limits set by the USEPA. Encapsulating CAFs in geopolymers can improve their properties while also reducing the environmental impact of CAFs, making it a promising solution for mitigating cigarette pollution.

**Keywords:** Geopolymer, Cigarette butts, Cellulose acetate, AAMs, Waste management.

**Abbreviations:** **AAMs:** Alkali-activated materials; **CBs** (Cigarette butts): discarded part of the cigarette; **CFs:** Cigarette filters; **CAFs** (Cellulose acetate microfibers): the main constituent of CFs; **Metal(oid)s:** heavy metals and metalloids; **TCLP:** Toxicity Characteristic Leaching Procedure.

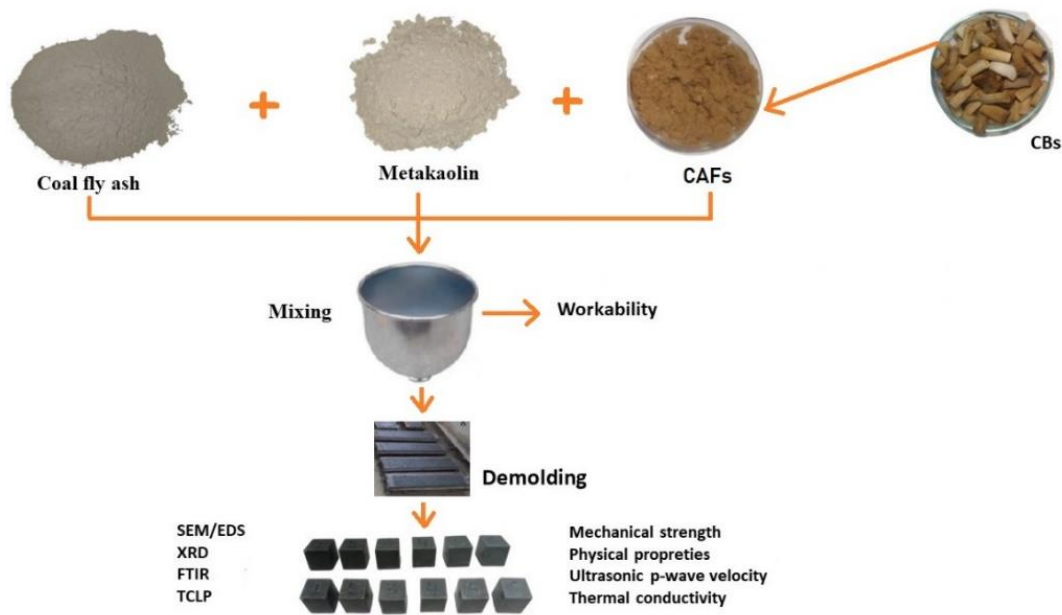


Figure 5-1. Graphical abstract of the chapter.

## 5.1 Introduction

The rapidly growing of urbanization and industrial sector is strongly associated with a massive increase in the generated quantity of MSW (J. Liu et al., 2022). According to a recent study conducted by Kaza et al (Kaza et al., 2018) the amount of waste will skyrocket increase by more than 50% by 2025, reaching roughly 3.4 billion tons. The international solid waste association (ISWA) stated that more than 40% of the generated quantity of waste worldwide is improperly disposed of and the most common disposal technique for MSW is landfilling and incineration (Law & Ross, 2019). Given its threats to human health and the environment (Bouzekri, El Fadili, et al., 2019; Fadili et al., 2022), the development of a sustainable approach for their valorization in different sectors is gaining greater interest.

The Building sector is responsible for more than 36% of the total energy consumption worldwide and 40% of the carbon dioxide (CO<sub>2</sub>) emissions (El Moustapha et al., 2022). Ordinary Portland cement contributes to roughly 6-7% of global greenhouse emissions according to the International Energy Agency (Barbhuiya & Pang, 2022), it is claimed that the production of 1 ton of ordinary portland cement (OPC) yields the release of nearly 1 ton of carbon dioxide into the atmosphere, in addition to significant pollution through the dust containing sulfur and nitrogen oxides, without forgetting the remarkable depletion and destruction of the quality of natural resources (Sabour et al., 2022).

Since it discovered by French scientist Joseph Davidovits in the 1970s, geopolymers or alkali-activated materials (AAMs) have attracted worldwide attention because of several advantages, including solving the issue of industrial waste disposal, reducing the gaseous emissions and achieving promising properties in terms of durability, fire resistance and mechanical performance as compared to conventional cement-based materials (Silva et al., 2020; B. Sun et al., 2022; Z. Zhang et al., 2014). El Moustapha et al. (2022) concluded that the CO<sub>2</sub> emissions caused by the synthesis of geopolymers were reduced by approximately 70-80% in regard to cement production. For the geopolymers synthesis, various aluminosilicate materials sources of aluminosilicate have been employed, they are mainly constituted of natural minerals and industrial byproducts, such as ground granulated blast furnace slag (GGBFS), limestone-calcined clay (J. Liu et al., 2022), metakaolin and fly ash (Wongsa et al., 2018; Z. Zhang et al., 2014).

Fly ash is a solid waste that is produced when coal-fired furnace flue gases are mechanically or electrostatically precipitated. While metakaolin is a non-renewable clay resource. Due to the toxic nature of FA owing to the presence of hazardous heavy metal(oid)s, direct landfilling of FA wastes not only poses serious environmental concerns but also a loss of valuable resources. Therefore, preparing an optimal matrix for the immobilization of toxic wastes, exhibiting satisfactory mechanical strength, and preserving natural resources is promising.

The synthesis of metakaolin-based geopolymers gives a positive impact in terms of compressive strength, durability, and encapsulation of pollutants. For example, Duan et al. (2016) and Zhang et al. (2014) studied the influence of partial substitution of fly ash by metakaolin on microstructure and mechanical properties and concluded a notable gain in strength and reduction of permeability with ensuing replacement level of FA by MK from 5% to 20%. Furthermore, Previous studies have shown that MK-based geopolymers have a better performance in sealing heavy metal(oid)s as compared to cementitious materials and FA-based geopolymers (P. Zhang et al., 2021). Therefore, the combination of MK and FA as geopolymer binders can permit the achievement of a good balance between the control of the carbon footprint and the ability to seal toxic metal(oid)s.

The tobacco industry is one of the most prevalent industries and contributes to the high income of many countries. Yearly, six trillion are manufactured and approximately 5.8 trillion are consumed by one billion smokers across the world (Zafeiridou et al., 2018), leading to the generation of more than 1.3 tons of toxic litter known as cigarette butts (CBs), which makes it one of the most abundant wastes on the planet (Rebischung et al., 2018). Considering the huge

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quantity of Cigarette butts (CBs) discarded in the environment, the use of waste this waste in lightweight geopolymer seems to be a very beneficial alternative not only for saving natural resources but also for eliminating its threats to the environment and public health.

Presently, the use of CBs in various construction materials including, gypsum composites, cementitious mortar, lightweight fired brick, asphalt concrete, ceramics, etc. (Kurmus, 2021; Md & Abbas, 2021; Mohajerani et al., 2016, 2021; Romero-Gómez et al., 2022) has attracted a notable interest, as a viable solution that both avoids the harmful effects of cigarette butts and conserves natural resources (Farzadkia et al., 2022; Marinello et al., 2020). For example, interesting findings were achieved by Mohajerani et al. (2016) who conducted an experimental investigation on the recycling of different incorporation rates of CBs (2.5 to 10 wt.%) into fired clay bricks, the outcomes showed a lighter composite with satisfying thermal insulation, energy performance and compressive strength of 12.57 MPa by replacing natural clay with 2.5% of CBs. Likewise, Girondi et al. (2020) demonstrated that the use of 5% of CBs in ceramics showed satisfying results in terms of physico-mechanical characteristics. Tannous et al. (2022) and Romero-Gómez et al. (2022) proved the feasibility of using cellulose acetate from cigarette filters by up to 1.3% and 3.5% as a substitution for natural sand and gypsum respectively, in terms of workability, compressive strength, bulk density and total porosity in comparison with the conventional material (Romero-Gómez et al., 2022; Tannous et al., 2022). As stated, many studies have been carried out on the incorporation of CBs in construction materials. Nonetheless, to the best of our knowledge cellulose acetate sourced from cigarette filters (CFs) has never been used in geopolymer synthesis.

Many previous studies have been carried out on the incorporation of natural fibers in various construction materials, and promising overall benefits were achieved compared to those obtained using synthetic microfibers existing in the market. In particular, a notable improvement in tensile strength, elastic properties, toughness, post-crack performance, acoustic and thermal insulation (Candamano et al., 2021; Korniejenko et al., 2016; Safiuddin et al., 2021). Zhou et al. (2020) investigated the influence of cotton fibers and powders on the properties of bio-geopolymer composites, with dosages up to 2 wt.% of FA, and satisfying physico-mechanical were obtained for specimens containing till 1%. Interesting findings were also achieved by Ye et al. (2018) when evaluating the effects of cellulose hemicellulose, and lignin on the morphology and mechanical characteristics of metakaolin-based geopolymers.

In the same context, the main objectives of the current work are; **(I)** optimizing the use of FA and MK for the synthesis of an AAMs cured at room temperature with satisfactory mechanical

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property, then (2) investigating the effects of different dosage percentages (0, 0.2%, 0.4%, 0.6%, 0.8%, 1%, and 1.5%) of cellulose acetate microfibers (CAF) sourced from discarded cigarette butts (CBs) on the physico-mechanical, thermal and microstructural properties of the optimum FA/MK geopolymer. The outcome of this study could have significant implications for reducing the negative environmental impact of cigarette waste.

## **5.2 Materials and Methods**

### **5.2.1 Raw materials**

In this study, Class F fly ash (FA) procured from the thermoelectric power plant located in Mohammedia, Morocco and metakaolin (MK) were used as the principal aluminosilicate-containing precursors to prepare the geopolymer pastes. The FA was firstly subjected to natural weathering in the laboratory condition for two months, which is beneficial for the immobilization of metal(oid)s, then grounded to finer particles and sieved through a 75  $\mu\text{m}$  sieve. MK powder was obtained after 3 h thermal activation at 750  $^{\circ}\text{C}$  of commercial kaolin (heating rate 5  $^{\circ}\text{C}/\text{min}$ ).

CBs waste were collected manually with different characteristics without taking into account the brand of cigarette. Further, the acetate cellulose fibers were separated from the outer paper before being oven-treated at 60  $^{\circ}\text{C}$  for 12 h to avoid material degradation, crushed into small particles, to obtain a homogeneous mixture, and stored in sealed bags until the composite samples were prepared.



Figure 5-2. Visual aspect of (from the left) the discarded cigarette butts, acetate cellulose fibers separated from the outer paper, and the crushed CAFs.

A combination of commercial sodium silicate ( $\text{Na}_2\text{SiO}_3$ ;  $\text{SiO}_2 = 30\%$ ,  $\text{Na}_2\text{O} = 15\%$ , and  $\text{H}_2\text{O} = 55\%$ ) and 10 M sodium hydroxide (NaOH) solution according to a weight ratio of 1 was used to prepare the activator solution. The sodium hydroxide (SH) used in this paper is hygroscopic flakes with the purity of 98%. The alkaline activator solution was premixed at an ambient temperature one day before casting to obtain a homogeneous solution (Kaur et al., 2018).

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## 5.2.2 Methodology and Mixture Proportions

The methodology followed in this study started with synthesizing geopolymer paste specimens based on FA and MK, denoted GMK<sub>X</sub> where X is the replaced FA content by dry mass of MK (Table 5-1). The mechanical strengths of developed mixtures were tested at 7 and 28 days of curing at room temperature to define the optimal geopolymer. Then, the reference that exhibited the highest compressive strength was used following the same procedure with CAFs sourced from CBs with different addition percentages per dry mass of precursors (0% up to 1.5 wt.%). These mixtures were denoted as GPC<sub>N</sub>, where N stands for the incorporation rates of CAFs as presented in Table 5-2. The content of CAFs was limited to 1.5% to keep the water-to-binder ratio (w/b) constant for all mixtures without using water-reducing admixtures.

Table 5-1. Mix proportion of geopolymer mixes containing FA and MK.

Ref	FA (wt.%)	MK (wt.%)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> O	L/S	NaOH (M)	SS/SH
GMK <sub>0</sub>	100	0	3.54	1.34	0.65	10	1
GMK <sub>10</sub>	90	10	3.42	1.40	0.65	10	1
GMK <sub>20</sub>	80	20	3.31	1.46	0.65	10	1
GMK <sub>30</sub>	70	30	3.21	1.52	0.65	10	1
GMK <sub>40</sub>	60	40	3.11	1.58	0.65	10	1
GMK <sub>50</sub>	50	50	3.02	1.65	0.65	10	1

For the mixture methodology, the minerals and the designated percentage of CAFs were sufficiently mixed manually, and then the alkaline activator solution was added while mixing gradually at a constant liquid/solid ratio. The homogeneous blends were poured into the molds, and once molded, samples were vibrated to remove entrapped air bubbles and attain good packing.

Table 5-2. Mix proportion of geopolymer mixes containing different CAFs content.

Ref	CAF (wt.%)	L/S*	NaOH (M)	SS/SH
GPC <sub>0.2</sub>	0.2	0.7	10	1
GPC <sub>0.4</sub>	0.4	0.7	10	1
GPC <sub>0.6</sub>	0.6	0.7	10	1
GPC <sub>0.8</sub>	0.8	0.7	10	1
GPC <sub>1.0</sub>	1	0.7	10	1
GPC <sub>1.5</sub>	1.5	0.7	10	1

\*The workability test was evaluated based on L/S = 0.65.

The prepared molds were sealed with polyethylene film to prevent moisture loss. The hardened pastes were de-molded after 48 h and cured under laboratory conditions ( $T=25\text{ }^{\circ}\text{C}$ ,  $\text{RH}=40$ ) until testing age.

### **5.2.3 Mixture proportions**

Fly ash, Metakaolin, and the designated percentage of cellulose acetate microfibers (CAFs) were sufficiently mixed manually, and then the alkaline activator solution was added gradually at a constant liquid/solid ratio of 0.70 in a mixer for 5 min. The homogeneous blends were poured into cubic and prismatic molds with internal dimensions of  $50\text{ mm}^3$  and  $20*20*80\text{ mm}$  for mechanical and physical testing, and  $10*10*2\text{ mm}^3$  for the thermal properties. Once molded, they were vibrated to remove entrapped air bubbles and attain good packing. The prepared molds were sealed with polyethylene film to prevent moisture loss. The hardened pastes were de-molded after 48h and cured under laboratory conditions ( $T=25\text{ }^{\circ}\text{C}$ ,  $\text{RH}=40$ ) until testing age (7 and 28 days).

### **5.2.4 Testing and analysis methods**

#### **5.2.4.1 Characterization methods**

The chemical composition was carried out by X-ray fluorescence (XRF), using Panalytical Axios wavelength Dispersive XRF Spectrometer (CNRST-UATRS). The mineralogical characterization was performed by XRD analysis using Panalytical X'PERT PRO MPD Configuration PW 3064/xx Spinner–PANALYTICAL. The scans covered a  $2\theta$  range of  $5^{\circ}$  to  $80^{\circ}$ , with a nominal step size of  $0.0670^{\circ}$  and  $121.0150\text{ s/step}$ . The granulometry was performed using the LA-300 laser scattering particle size distribution analyzer-Horiba Scientific, having a detection range of  $0.1\text{--}600\text{ }\mu\text{m}$ .

#### **5.2.4.2 Mechanical strength**

The mechanical strength of the synthesized geopolymers was measured in cubic and prismatic specimens of  $50\text{ mm}^3$  and  $20*20*80\text{ mm}$  after 7 and 28 days of curing following the standard specifications ASTM C109M-01 and ASTM C348-21 using a hydraulic press with a load cell of  $25\text{ kN}$  and loading rate of  $1.6\text{ kN/s}$  until geopolymers failure occurred. For each reference, at least three replications were tested, and the mean value  $\pm$  standard deviation was considered as the representative strength at the selected age and was reported in the current paper.

### 5.2.4.3 Workability

To assess the effect of the addition of CAFs on the flowability of prepared specimens, a mini-conical slump flow test method with upper and lower internal diameters of 50 and 100 mm respectively, and of a height of 150 mm was used according to the ASTM C143 (Vardhan et al., 2015). It is important to highlight that the slump test was conducted based on the same L/S ratio (0.65) used to prepare the optimum specimens (GMK30). Then, it was adjusted to 0.7 to attain the required workability for casting.

### 5.2.4.4 Bulk density, apparent porosity, and water absorption measurement

Bulk density, apparent porosity, and water absorption of the prepared binders were performed using the Archimedes method by boiling water as described by the ASTM C20-00, through the following equations:

$$\text{Bulk density } \left( \frac{\text{kg}}{\text{m}^3} \right) = \frac{\mathbf{m}_{\text{dry}}}{\mathbf{m}_{\text{sat}} - \mathbf{m}_{\text{hyd}}} \times 100 \quad (5.1)$$

$$\text{Apparent porosity } (\%) = \frac{\mathbf{m}_{\text{sat}} - \mathbf{m}_{\text{dry}}}{\mathbf{m}_{\text{sat}} - \mathbf{m}_{\text{hyd}}} \times 100 \quad (5.2)$$

$$\text{Water absorption } (\%) = \frac{\mathbf{m}_{\text{sat}} - \mathbf{m}_{\text{dry}}}{\mathbf{m}_{\text{dry}}} \times 100 \quad (5.3)$$

Where;  $m_{\text{dry}}$ : mass of the dry-oven geopolymer (24 h at 105 °C).

$m_{\text{sat}}$ : air-saturated mass of the specimen immersed in boiling water for 24 h.

$m_{\text{hyd}}$ : mass of impregnated specimen suspended in water.

### 5.2.4.5 The Ultrasonic pulse velocity (UPV)

Ultrasonic pulse velocity (UPV) is a non-destructive test widely used to assess the compactness and cohesiveness between particles in different construction materials, based on the measure of the velocity of ultrasonic wave pulses passing through the hardened materials within a specified time. In this paper, the UPV was performed after 28 days of curing following the requirements of ASTM C579-16 using 58-E4800 UPV tester.

### 5.2.4.6 Thermal properties

Thermal conductivity was experimentally investigated using the asymmetric hot plate. Unlike the traditional method, a hot plate permits the measurement of thermal conductivity using only

one sample. Readers are directed to our previous study to learn more details about this technique (Mounir et al., 2015). The conductivity of the samples is calculated by the following equation:

$$\phi_T = \phi_S + \phi_P = \frac{U^2}{ReS}; \lambda_S = \frac{e_S}{T_0 - T_1} \times \left[ \frac{U^2}{ReS} - \frac{\lambda_P}{e_P} \times (T_0 - T_2) \right] \quad (5.4)$$

#### **5.2.4.7 Microstructural characterization**

The effect of cellulose acetate microfibrils on the surface morphology of synthesized geopolymers was carried out by analyzing its microstructural morphology using scanning electron microscopy (QUATTRO S-FEG-Thermofisher scientific) coupled, with an energy dispersive X-ray spectrometer (EDX) for elemental analysis. The purpose of the SEM micrographs is to analyze the apparent adhesion of the fibers with the matrix and to observe the presence of micro cracks that probably decrease the mechanical properties of the tested geopolymers.

#### **5.2.4.8 TCLP**

To assess the potential environmental and health impacts, particularly those related to the release of pollutants throughout the decomposition of CAFs and FA, leaching tests following the European standard EN 12457-2 were performed (Zouch et al., 2022). Firstly, the specimens were grounded and sieved through a 4-mm sieve and mixed with distilled water following a solid: liquid ratio of 1:10 under continuous agitation for 24 h, then the digested solution was filtered through Whatman No.42 filter paper and diluted to the required volume using ultrapure water. metal contents were analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Brand Horiba Jobin Yvon, type Ultima Expert). Analyses were triplicated to guarantee the precision and maintain the quality of the extraction method, and only if the relative standard deviation (RSD) for three replicates of each sample was less than 5%, the measurement was retained and reported in the current paper.

## 5.3 Results and discussion

### 5.3.1 Raw material characterization

#### 5.3.1.1 Fly ash and metakaolin

The chemical composition of starting materials was listed in **Table 5-3** and their micrographs were shown in **Fig.5-3**, respectively. The main oxides in the FA and MK used as aluminosilicate sources are SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with a Si/Al ratio of about 1.46 and 1.01, respectively. Suggesting that can provide sufficient silicon and aluminum atoms required for the polymerization reaction. The FA has a low concentration of CaO, at 6.279 % (<10%), and it is classified as low calcium fly ash (Class F FA) according to the ASTM C618-12.

Table 5-3. Chemical composition of used precursors by XRF analysis (wt. %).

Ref	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	LOI at 1000 °C
FA	47.4	27.4	4.51	6.28	1.05	0.52	1.89	7.17
MK	51.4	39.0	1.24	0.11	0.64	0.08	0.245	4.33

The morphology of FA and MK is observed using scanning electron microscope (SEM) images, FA particles consist of pherospheres, spheres, and cenospheres in the range of 1.5-10 μm (Sun et al., 2022), this spherical shape helps to provide better workability and flowability, whilst the micrograph of MK showed a denser structure with irregular particles.

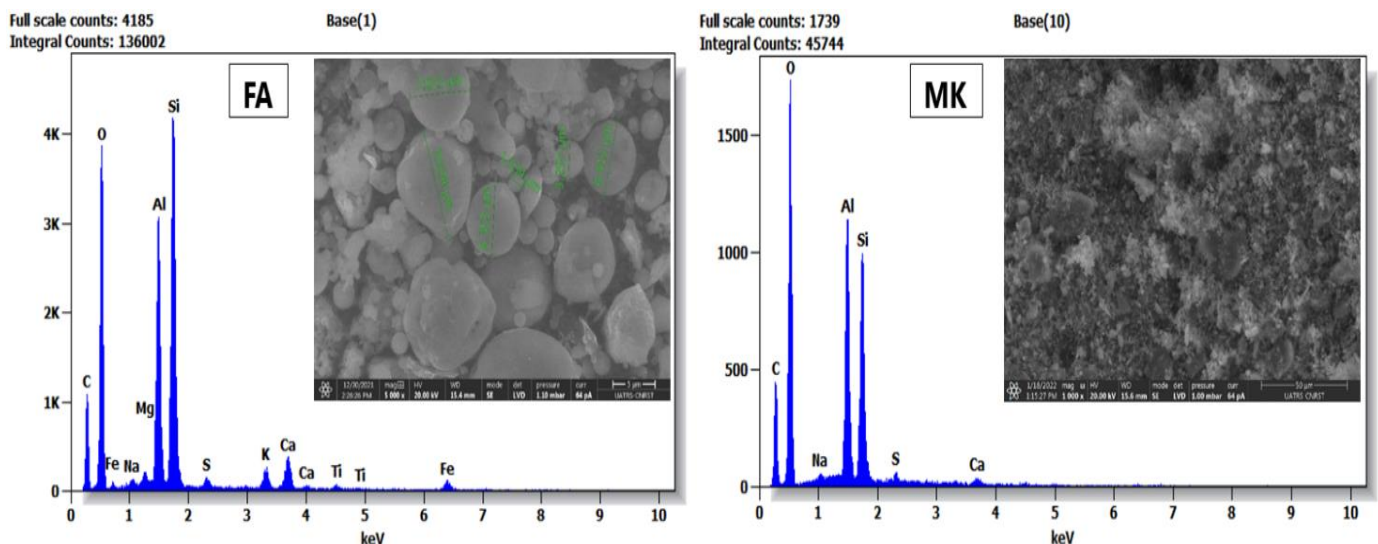


Figure 5-3. SEM-EDS micrographs showing the microstructure of (from the left) FA and MK

The mineralogical composition was evaluated using XRD analysis as shown in **Fig.5-4**, the diffractogram of fly ash showed the dominance of crystalline peaks, affiliated to quartz, hematite, and mullite, the large hump observed in the range (15-35°, 2θ) reflects the existence of a large amorphous fraction in the used precursors (L. Yuan et al., 2022).

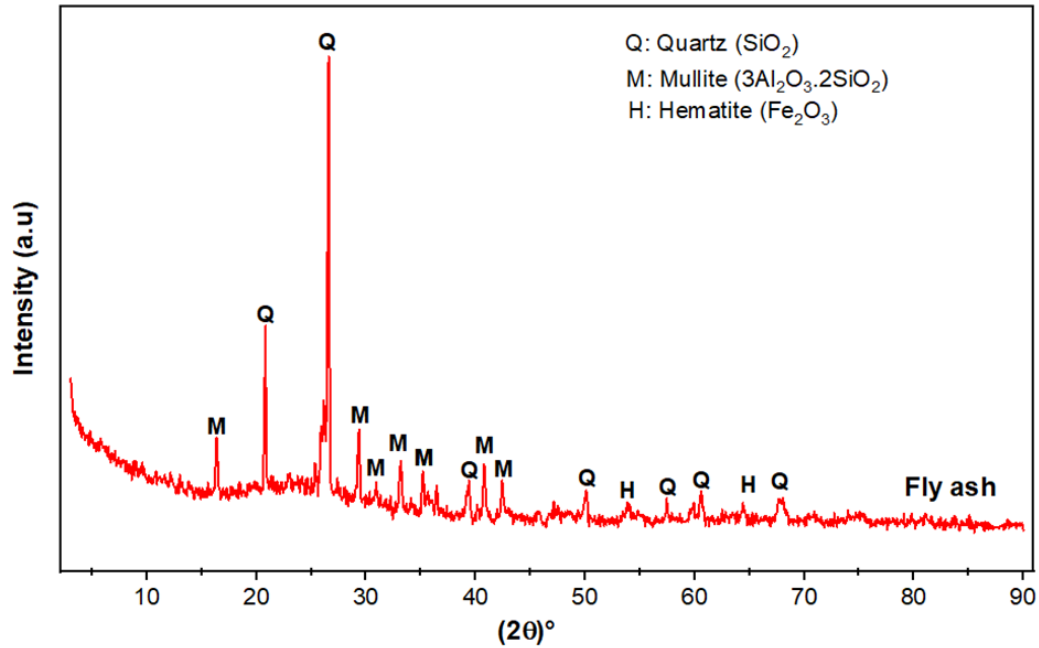


Figure 5-4. The XRD analysis results of fly ash.

The particle size analysis of the powders plotted in **Fig.5-5** indicates the dominance of the fine fraction which will help in better packing and improve the density of the elaborated geopolymer paste.

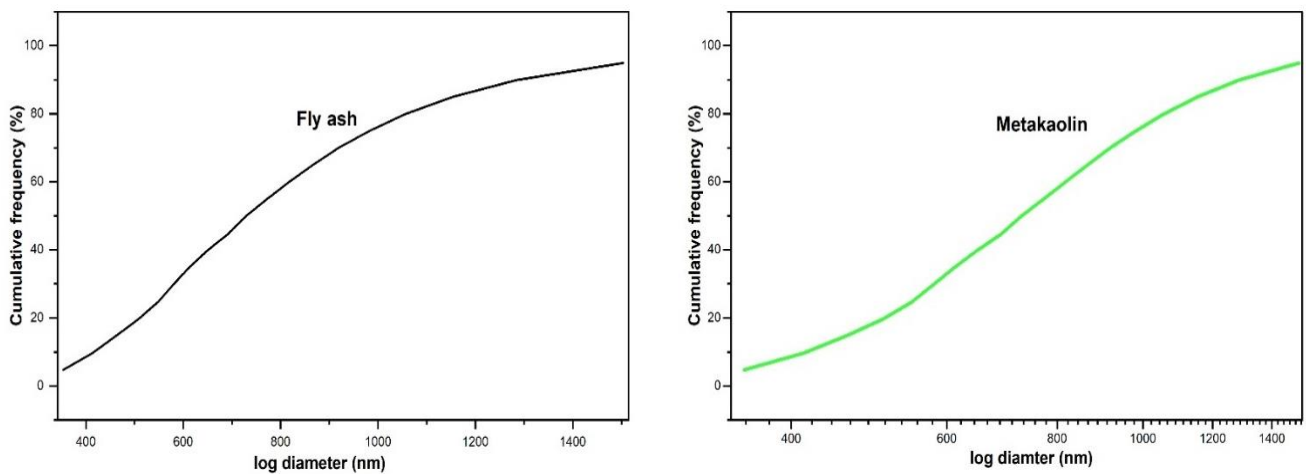


Figure 5-5. Granulometric curve of Fly ash and metakaolin.

### 5.3.1.2 Cellulose acetate fibers characteristics

FTIR analysis was conducted on the collected cigarette filters as-received without any preparation, as shown in **Fig.5-6**.

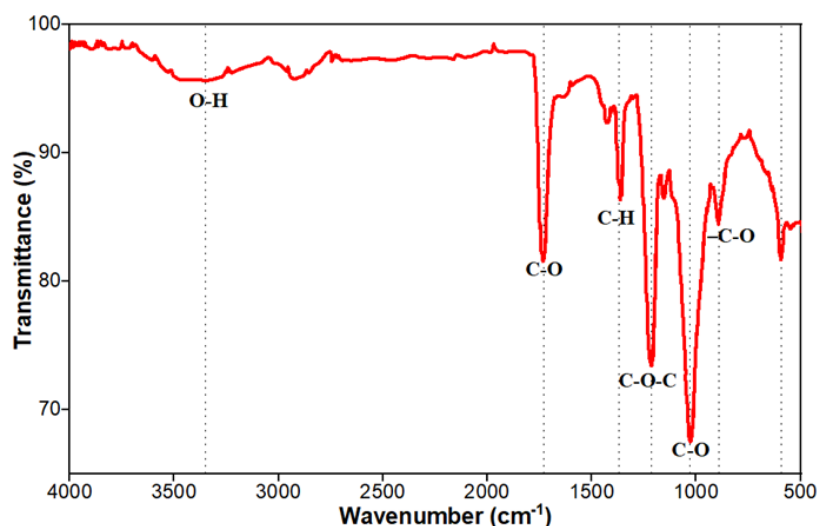


Figure 5-6. FTIR of CFs used in the current study.

The FTIR diffractogram of cigarette filters is perfectly consistent with the spectrum of raw cellulose acetate described in the literature (Prakash et al., 2021; Tannous et al., 2022). The band located at  $3350\text{ cm}^{-1}$  corresponds to O-H bending and stretching vibration. In addition, the band located at  $1738\text{ cm}^{-1}$  could be assigned to the bending vibration of C=O chemical bond in aliphatic esters, another two bands were observed at  $1370\text{ cm}^{-1}$  and  $1030\text{ cm}^{-1}$  mainly related to the C-H symmetric deformation in C-CH<sub>3</sub> and CH<sub>3</sub> bonds, and stretching mode of C-O bond in aliphatic secondary alcohol, finally a strong peak was noticed at  $1215\text{ cm}^{-1}$  owing to the C-O-C asymmetric stretching. The presence of the absorption peaks at  $894\text{ cm}^{-1}$  could be attributed to the combination of -C-O stretching and -CH<sub>2</sub>- rocking vibrations. Therefore, based on the FTIR analysis, we can conclude that the examined cigarette filters are composed mainly of cellulose acetate.

The hydrophilic character of CAFs was appraised based on the water absorption test, which was performed by immersing cellulose acetate fibers in water as a function of time (1 min, 5min, 20min, 24h, and 48h), the test was triplicated to ascertain the obtained results and computed the standard deviation. The results presented in **Fig.5-7** showed an absorption rate of roughly 485% during the first minute of immersion which was well above that of corn cob, lavender straw, and rape straw reported to be 48%, 100%, and 218% respectively (Ratsimbazafy et al., 2021). Also, a dramatically increased to nearly 860% at 48h was observed, which

reflected the hydrophilic character of cellulose acetate fibers compared to the cited-above plant aggregates studied previously by Ratsimbazafy et al., (2021). Therefore, cellulose acetate sourced from smoked cigarette filters can be considered much more hydrophile than some vegetal fibers used in previous studies and could interfere perfectly with the hydration of AAMs. In addition, the measured bulk density of cellulose acetate fibers was  $0.39 \pm 2 \text{ g/cm}^3$  and  $0.61 \pm 4 \text{ g/cm}^3$  without and with compactness, respectively.

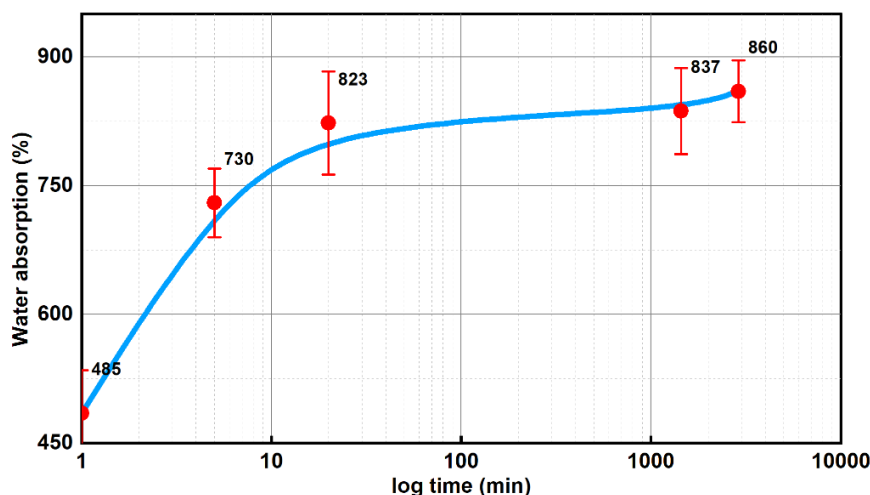


Figure 5-7. Water absorption of CFs used in the current study.

The morphology and EDX analysis of the CAFs is shown in **Fig. 5-8**. A remarkable agglomeration and damage of fibers were observed, this is mainly attributed to the presence of polarized hydroxyl groups at the surface of CAFs leading to electrostatic-based interactions between them, which originated from the smoking process and laboratory depollution techniques. This fact could increase significantly the porosity of prepared geopolymers and therefore limit their mechanical properties.

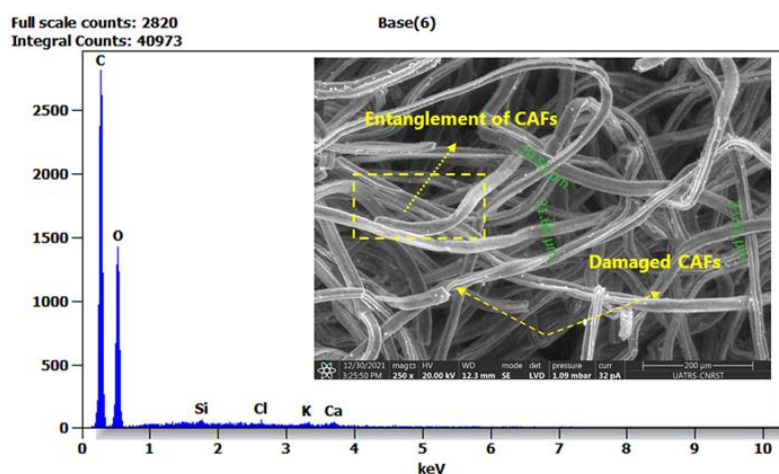


Figure 5-8. SEM-EDX of the crushed CAFs sourced from CFs.

The average diameter and length of used CAFs were 21.55  $\mu\text{m}$  and 2 mm, respectively. It is nothing that cellulose acetate is widely known as a bio-binder that may effectively bond the fibers to various construction materials. Although, their hydrophilic character makes them vulnerable to high moisture absorption, thus conferring poor wetting with the matrix and weakening fiber–matrix interface.

### 5.3.2 Optimization of FA-MK system

The compressive strength of the manufactured geopolymers with various replacement levels of metakaolin and fly ash at 7 and 28 days of curing time at ambient temperature were examined and the results have been summarized in **Fig.5-9**.

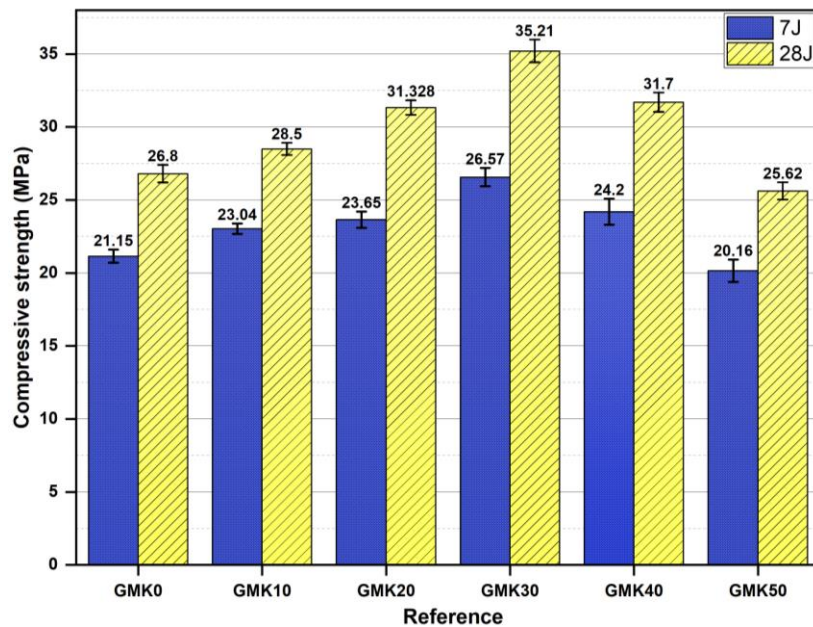


Figure 5-9. Effects of MK content on compressive strength of geopolymers at 7-d and 28-d, after curing at room temperature.

Firstly, it is evident that all samples gained considerable compressive strength at the early age, which is mainly owing to the calcium provided by fly ash. Then, with the increase in the content of metakaolin up to 30% in the mix, an increase of up to 31.4% was achieved in comparison to the reference sample for a curing period of 28 days, as a result of a notable increase of geopolymeric gel (Kakria et al., 2020). Above 30% of metakaolin content, a notable reduction in compressive strength in comparison to the control mix (GMK0) was noted at all curing ages. The addition of more than 30% of MK has decreased the compressive strength due to the generating of voids in the structure, another possible reason is attributed to the high alumina

content of MK which reduces the Si/Al ratio as shown in **Table 5-1**, which will significantly influence the mechanical properties of the geopolymer.

### 5.3.3 Workability

The properties of the prepared geopolymers containing different percentages of cellulose acetate microfibers at fresh state were appraised through the workability test using the mini-slump cone. By examining the obtained results plotted in **Table 5-4**. It can be observed that the reference mixture without cellulose acetate microfibers (CAFs) displayed the highest workability (135.2 mm). Then, the flowability was found to reduce proportionally and gradually drier mixtures were attained by increasing the content of cellulose acetate microfibers in the matrix. These findings indicated the significant influence of CAFs content on the workability of elaborated geopolymers, the addition of CAFs in the mixtures made it stiffer and enhance its cohesiveness thereby leading to low workability (Alyousef et al., 2020; Rashad & Gharieb, 2021), such results are expected and principally owing to the porosity texture, lower density, rough surface, irregular stripes and the hydrophilic character of the microfibers (Wongsa et al., 2020). Subsequently, an increase in water demand will be required to wet the surface of blended mixes (Safiuddin et al., 2018, 2021, 2022; Varadharajan, 2020). This is in agreement with the research conducted by Wongsa et al. (2020) on the properties of high calcium fly ash geopolymer mortar reinforced with natural fibers, namely coconut and sisal fibers with varying proportions (0, 0.5, 0.75, and 1.0 v %) who also reported a remarkable decrease of flowability when adding fibers in the matrix.

Table 5-4. Fresh and hardened properties of the developed mixtures ( $\bar{x} \pm SD$ )

Specimens	GPC <sub>0</sub> (GMK <sub>30</sub> )	GPC <sub>0.2</sub>	GPC <sub>0.4</sub>	GPC <sub>0.6</sub>	GPC <sub>0.8</sub>	GPC <sub>1.0</sub>	GPC <sub>1.5</sub>
<b>Slump (mm)</b>	135.2 ± 1.7	134.2 ± 1.3	133.2 ± 2.0	131.9 ± 1.7	130.3 ± 2.1	129.1 ± 1.5	127.5 ± 2.7

### 5.3.4 Hardened properties

#### 5.3.4.1 Mechanical characteristics

GMK30 exhibited the highest compressive strength among examined specimens and was subjected to various tests to monitor the effects of incorporating cellulose acetate microfibers on the properties of geopolymers during the fresh and hardening state. The effect of curing ages on the compressive strength of geopolymer binders containing various cellulose acetate microfibers (CAFs) content is presented in **Fig. 5-10-a**. As it is observed, the experimental findings

revealed that the specimens containing cigarette fibers gained strength over long curing time as like reference geopolymer, indicating the continuous hydration of the specimens for all the substitutions. Although the inclusion of cellulose acetate microfibers significantly decreased the mechanical resistance, the compressive strength for the reference geopolymer mix GMK30 at 28 days of curing is 35.21 MPa. Further, a gradually decreasing by about 4.57%, 14.46%, 21.90%, 23.90%, 33.40 % and 40.64 % for GPC<sub>0.2</sub>, GPC<sub>0.4</sub>, GPC<sub>0.6</sub>, GPC<sub>0.8</sub>, GPC<sub>1</sub>, and GPC<sub>1.5</sub> respectively. The aforementioned reduction is mainly attributed to the heterogenic granulometric and agglomeration of CAFs, which supports the development of pores and makes the porous structure denser (Alomayri & Low, 2013; Fiore et al., 2020). Another reason behind

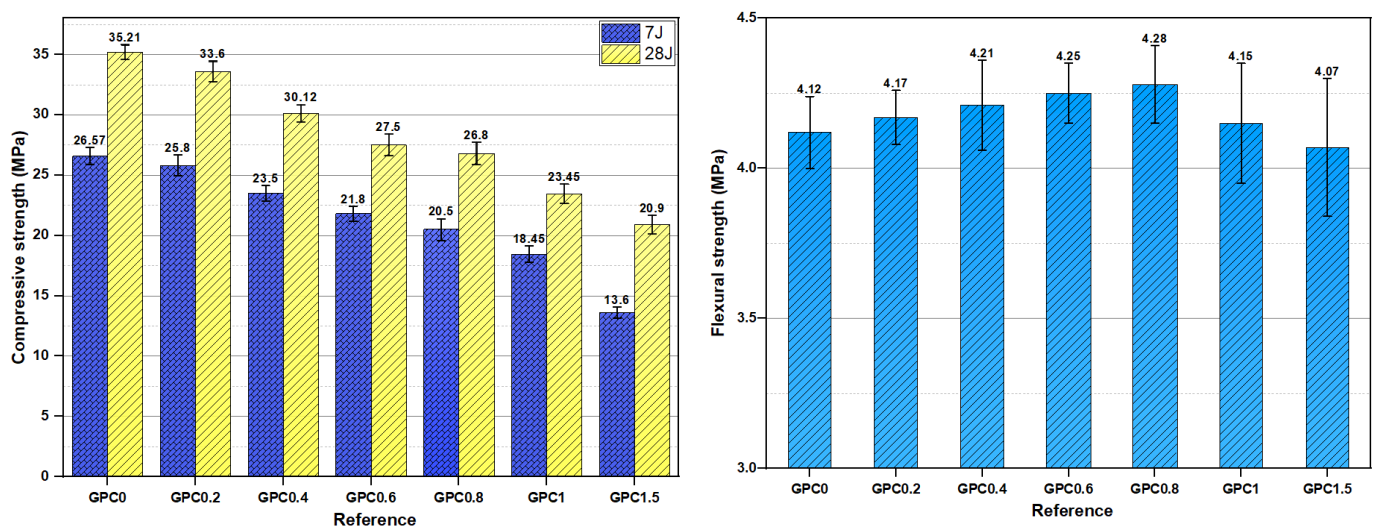


Figure 5-10. Evolution of geopolymers' mechanical strength incorporating different rates of CAFs. From the left : compressive strength, flexural strength at 28-d.

this decrease is the hydrophilic character and the lower density of cigarette filters which lead to the creation of pores within the matrix. This is in agreement with previous studies conducted on fibers reinforced AAMs, Zhou et al. (2020) reported a slight decrease of about 15% by incorporating 2% of cotton stalk fibers in class F fly ash-based geopolymers, and a similar trend has already been observed also by Ye et al. (2018) when investigating the influence of cellulose, hemicellulose, and lignin on the mechanical and morphology of metakaolin-based geopolymer.

Technically, the compressive strength of geopolymers also meets the strength specifications for low to middle-grade structural applications. All blended geopolymers show compressive strength values after 28 days of curing higher than the minimum value of 13.10 MPa established by the ASTM C90-16-a standard for load-bearing concrete masonry units.

An improvement in flexural strength up to ~ 4 % was achieved by embedding 0.8% of CAFs content (**Fig.5-10-b**). Although, for further addition, a linear decline was attained. This

indicates that the surplus of CAFs rather deteriorates the flexural strength development, these outcomes fit the observations made previously by Romero-Gómez et al. (2022) who found a notable decrease in flexural strength for content over 2.5% due to the apparition of CAF clusters and pores within the gypsum matrix. Zhou et al. (2020) (B. Zhou et al., 2020) also noticed an improvement in flexural strength till a 1% addition of cotton stalk fibers, further a notable reduction was observed. The decrease is mainly attributed to the low strength and porous structure of microfibers themselves (Alomayri & Low, 2013; P. Zhang et al., 2021).

It is worth noting that the specimens containing CAFs displayed non-linearity during fracture whereas a linear fracture behavior was observed for the reference geopolymer. This indicates the feasibility of using cellulose acetate fibers to overcome brittle failure in geopolymers (Alomayri & Low, 2013).

#### **5.3.4.2 Bulk density, apparent porosity, and water absorption**

The values of the hardened bulk density and apparent porosity at 28 days of curing of the geopolymer composites containing various percentages of cellulose acetate microfibers are plotted in **Fig.5-11**. It is observed that with the addition of cellulose acetate microfibers, a slight increase in the porosity of the matrix was achieved in comparison to the reference geopolymer paste. The porosities of GMK30, GPC<sub>0.2</sub>, GPC<sub>0.4</sub>, GPC<sub>0.6</sub>, GPC<sub>0.8</sub>, GPC<sub>1</sub>, and GPC<sub>1.5</sub> were 17.6%, 17.85%, 18.40%, 19.10%, 20.46%, 21.85% and 23.61%, respectively. The observed notable increase in porosity was previously reported by researchers dealing with cellulosic-fibers-reinforced geopolymers (Masi et al., 2015; Payakaniti et al., 2017; Poletanovic et al., 2020; B. Zhou et al., 2020). Thus, when increasing the CAFs content, the liquid evaporation was greater, leading to the highest porosity (Gómez-Casero et al., 2022). In other words, the increase in porosity is attributed to the excess water trapped by the hydrophilic fibers in the geopolymer matrix escaping during the curing process (Gómez-Casero et al., 2022; Zulkifly et al., 2021). Additionally, the measured bulk density of reinforced geopolymers ranged between 1.38–1.65 g/cm<sup>3</sup>, indicating a decrease of 1.21%, 3.64%, 6.67%, 9.1%, 13.94% and 17.58 % for 0.2, 0.4, 0.6, 0.8, 1 and 1.5 wt% of fibers loading, respectively. The observed decrease is attributed to the higher porosity as a consequence of entrapped air bubbles during the mixing process (Poletanovic et al., 2020). Furthermore, the density of cellulose acetate fibers itself is lower in comparison to the density of metakaolin and low-calcium fly ash and could be another reason behind the observed decrease. Similarly, Zhou et al. (2020) noticed a reduction in density in the range of 4-8% with the inclusion of 0.5-2% by weight of cotton stalk fibers.

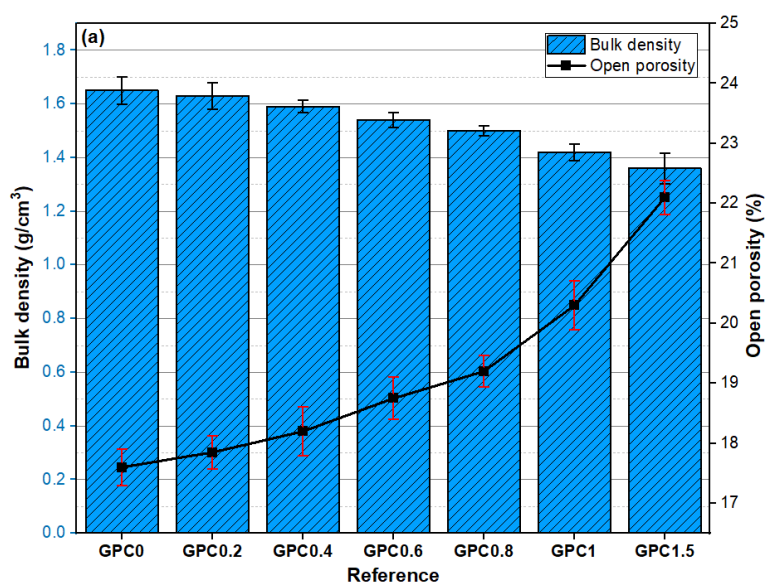


Figure 5-11. Physical characteristics of blended geopolymers at 28 days of curing: bulk density and apparent porosity.

The water retention capacity of elaborated geopolymers at 28 days of curing as a function of cellulose acetate fibers (CAFs) content is presented in **Fig.5-12**. As observed the reference specimen exhibited the lowest water absorption (10.50 %) as compared to other geopolymers. The embedding of CAFs has a significant effect on the water absorption rate of geopolymers, the addition of 0.2, 0.4, 0.6, 0.8, 1, and 1.5 wt% increased the water absorption by nearly 2.86%, 4.95%, 9.52%, 13.33%, 21.90%, and 39.05% respectively. This mainly owing to the hydrophilic character of cellulose acetate fibers discussed in section 3-1-2 and the presence of intrinsic pores in the cellulose acetate microfibers itself as observed through SEM images. A similar increase in water absorption and porosity has been already observed when adding cigarette filters to various construction materials, such as cementitious mortar (Tannous et al., 2022), gypsum composites (Morales-Segura et al., 2020; Romero-Gómez et al., 2022), lightweight fired clay bricks (Mohajerani et al., 2020), and ceramic materials (Gironi et al., 2020). Also, the same conclusions have been reported in previous papers dealing with cellulosic-fibers-reinforced geopolymers, such as hemp fibers reinforced alkali-activated fly ash and fly ash/slag mortars, carbon fibers reinforced fly ash geopolymeric composites (Payakaniti et al., 2017; Poletanovic et al., 2020). For example, Zhou et al. (2020) found a pronounced water absorption increase of roughly 28% with only 0.5% of cotton stalk fibers.

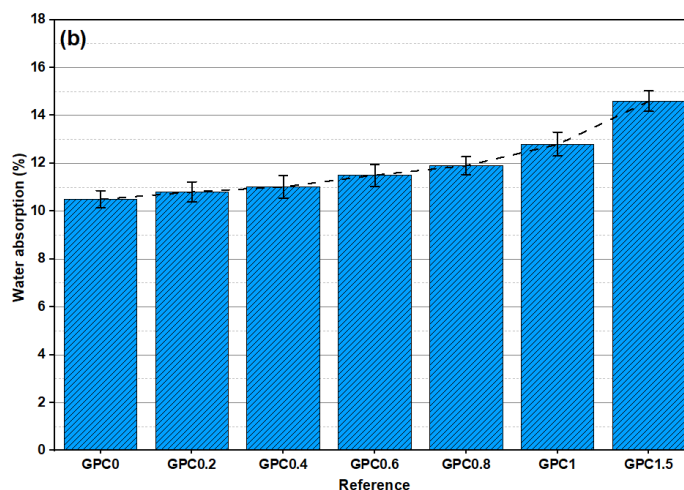


Figure 5-12. Physical characteristics of blended geopolymers at 28 days of curing: water absorption.

### 5.3.5 Ultrasonic pulse velocity

To evaluate the internal cohesiveness and compacity, the ultrasonic pulse velocity test was employed in the current paper as shown in **Fig.5-13**. The reference geopolymer showed the highest UPV (3590 m/s), indicating the small number of voids and the cohesiveness between particles into the matrix. Further, it is observed a linear trend between the incorporation rate of cellulose acetate microfibers and the decline in the velocity of geopolymers, with approximately 8.50 % decrease when 1.5 % CAFs content was embedded. This reflects that CAFs addition yields the formation of more pores, which has led to a notable increase in porosity and a decrease in their bulk density resulting in slower velocity waves in more time. In other words, the discontinuities created by air voids in the matrix can obstruct and slow down the ultrasonic velocity. The addition of 0.2, 0.4, 0.6, 0.8, 1, and 1.5 wt% of CAFs decreased the ultrasonic pulse velocity by roughly 0.50%, 1.23%, 2.65%, 4.46%, 6.52%, and 8.50%, compared to the reference specimen, respectively. The results obtained in this section are consistent with the previous findings, Wongsu et al. (2020) reported a moderate decrease in UPV by incorporating various proportions of coconut and sisal fibers (0, 0.5, 0.75, and 1.0 v %) in high calcium fly ash geopolymer mortar. Concerning the use of cellulose acetate fibers from CBs, only one study examined the UPV in which Romero-Gómez et al. (2022) noticed a decrease of ~8% when 3.5 % CAFs content was added to gypsum matrix. To sum up, although the observed decrease, the UPV of all geopolymers still ranged between 3500 and 3000 m/s, and they are classified in a good to a moderate category in terms of quality based on the classification given by the International atomic energy agency (Asil & Ranjbar, 2022).

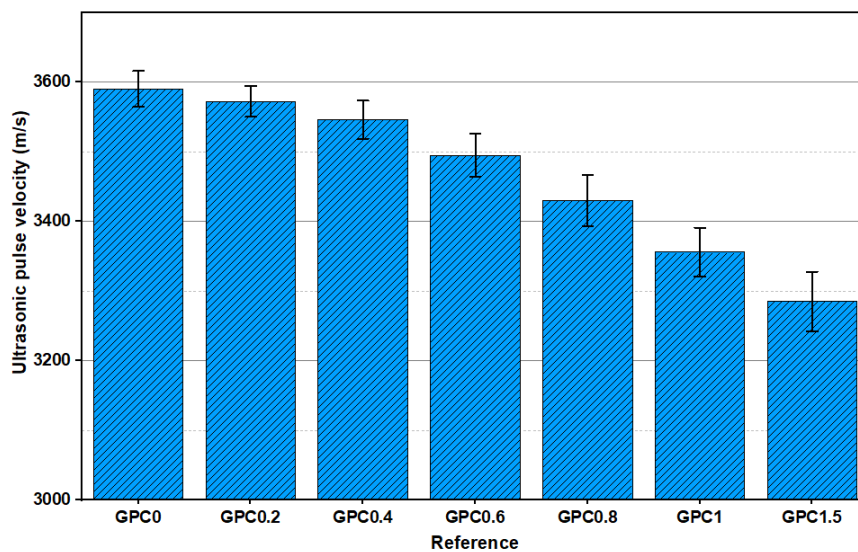


Figure 5-13. Ultrasonic pulse velocity of blended geopolymers after 28 days of curing.

### 5.3.6 Thermal conductivity

The thermal conductivity  $\pm$  standard deviation of the produced geopolymers with various CAFs percentages is presented in **Fig.5-14**. As observed the control specimen with no CAFs addition displayed the highest thermal conductivity coefficient ( $0.47 \pm 0.015$  W/m.k). The thermal conductivity followed the same trend of compressive strength and bulk density. The higher the dosage of the CAFs content stalk fiber is, the lower the compressive strength, bulk density, and thermal conductivity were attained. Thus, with the progressive increase in cellulose acetate microfibers in geopolymers by 0.2%, 0.4%, 0.6%, 0.8%, 1%, and 1.5%, the thermal conductivity was decreased respectively by 0.85%, 2.13%, 4.15%, 5.74%, 7.23%, and 9.57% compared to the reference specimen, corresponding to a promising improvement in the insulation capacity. Similarly, Romero-Gómez et al. (2022) reported a steady downward linear trend of thermal conductivity by about 16% with incorporating 3.5% of CAFs content in gypsum composites. The decrease could be justified, not only by the low thermal conductivity of cellulose acetate microfibers in comparison to FA and MK but also by the creation of voids inside the matrix due to the presence of microfibers which increase the porosity as discussed in **section 5.3.4.2**. Likewise, it was noticed a notable decrease in the thermal conductivity trend after the addition of the natural fibers to geopolymers mixture, as in the conducted present research. For example, Sakami et al. (2020) and Boumhaout et al. (2017) reported a notable decrease in thermal conductivity coefficient by approximately 57% and 15% by embedding 5% of doum palm and alpha fibers in cementitious mortars, respectively. Technically, based on the specifications set by RILEM (T. Salem et al., 2020), although using CAFs wastes in

geopolymers decreases the compressive strength, the prepared materials have sufficient mechanical resistance for use in non-structural applications with improved insulation properties ( $\phi_T < 0.75 \text{W/m.k}$ ) such as prefabricated blocks, surface coatings, and insulating mortars (Tannous et al., 2022).

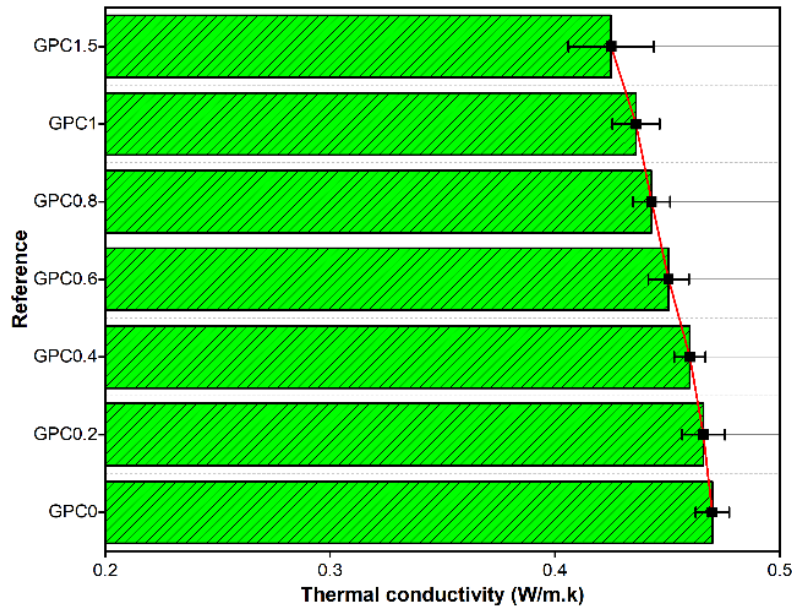


Figure 5-14. Thermal conductivity of blended geopolymers after 28 days of curing.

### 5.3.7 X-ray powder diffraction (XRD)

**Fig. 5-15** shows XRD diffractograms of the developed geopolymers after 28 days of curing at room temperature, to highlight the phase transformation after the geopolymerization process. It can be observed that the prepared composite showed a broad hump feature in the range ( $15-40^\circ, 2\theta$ ) indicating the formation of amorphous phase in the specimens composed mainly of C-S-H (calcium silicate hydrate), N-A-S-H geopolymeric gel (sodium aluminum silicate hydrate) and C-A-S-H gel (calcium aluminum silicate hydrate) due to the alkaline reaction of MK and FA (Tchakouté et al., 2016; L. Yuan et al., 2022). Also, several remaining peaks attributed to mullite, hematite, and quartz originating from the precursors were observed persistent for all geopolymers, reflecting that these crystalline phases are chemically inert in the alkaline environment. It is important to highlight that the addition of CAFs did not lead to the apparition of new crystalline phases, suggesting that cellulose acetate fibers did not react with the synthesized geopolymer gel to produce a new crystal substance (B. Zhou et al., 2020). Only a distinct hump peak in the range ( $7-10^\circ, 2\theta$ ) indicates the presence of cellulose acetate within the geopolymer matrix (see Fig. 4-3).

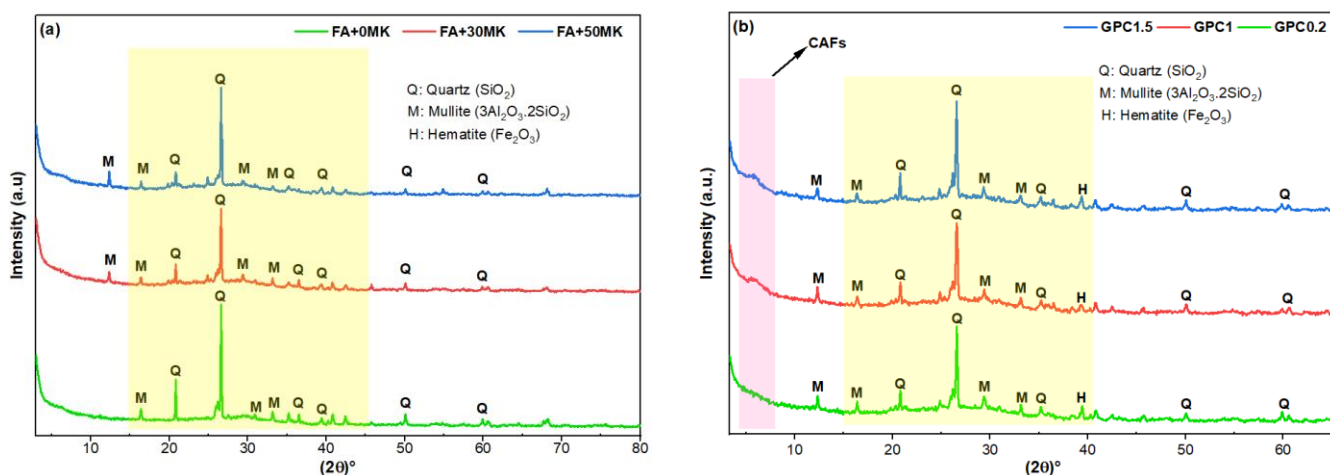


Figure 5-15. XRD diffractograms of blended geopolymers at 28-d of curing; a) MK-FA geopolymers, b) geopolymers containing CAFs.

### 5.3.8 Fourier Transform Infrared (FTIR) Spectroscopy

**Fig. 5-16** displays the FTIR spectra of elaborated CAFs/geopolymer composites after 28 days of curing at ambient temperature, to point out the change of chemical bonds after geopolymerization with and without cellulose acetate microfibers. By examining the data, all specimens showed a major intense band in the range between  $900$  and  $1100\text{ cm}^{-1}$  related to the asymmetric stretching vibrations of the Si/Al-O-Si bonds indicating the formation of aluminosilicate gel (Ca/Na-A-S-H) and confirming that the geopolymerization reaction has occurred. The bands located at  $3669\text{ cm}^{-1}$  and  $1652\text{ cm}^{-1}$  in all spectra correspond to O-H bending and stretching vibration and highlight the presence of water molecules in all geopolymers, it is owing to physically and free-bound water molecules trapped on the pores and/or the surface of the gel (Gómez-Casero et al., 2022; Ye et al., 2018). In addition, the band located at  $540\text{ cm}^{-1}$  could be assigned to the bending vibration of the cyclosilicate (Si-O-Al bond). The chemical composition of cellulose acetate microfibers in geopolymer composites was represented in the peaks located at  $1452\text{ cm}^{-1}$ ,  $1493\text{ cm}^{-1}$ , and  $2902\text{ cm}^{-1}$ , corresponding to the alkane CH stretching vibrations of the methylene groups (Ye et al., 2018) assigned to the presence of cellulose acetate in cigarette filters. By comparing the infrared spectroscopy of reference geopolymer with those containing 0.2 and 1.5% of CAFs by dry mass weight of FA-MK, it is observed the apparition of several peaks' characterize the presence of CAFs in the matrix. However, its addition did not alter any characteristic of the FTIR spectra, indicating that the incorporation of CAFs does not have any influential effect on the geopolymerization process.

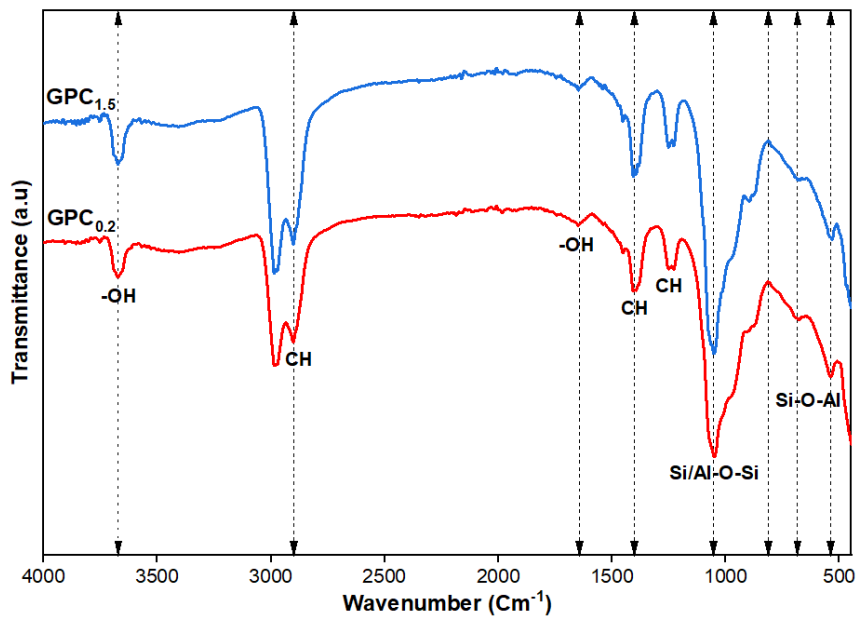


Figure 5-16. FT-IR spectra of the geopolymer-based composites.

### 5.3.9 Microstructure analysis

Scanning electron microscope (SEM), energy dispersive X-rays spectroscopy (EDS), and elemental mapping were employed to evaluate the effect of cellulose acetate microfibers on the physical and mechanical properties of prepared geopolymers. The analysis was performed on the fractured surfaces obtained after the compression testing of control mix GMK30 and two optimum mixes GPC<sub>0.4</sub>, and GPC<sub>1.5</sub> after 28 days of curing at ambient temperature, as presented in **Fig. 5-17**. The micrographs showed a homogenous and dense structure consisting mainly of

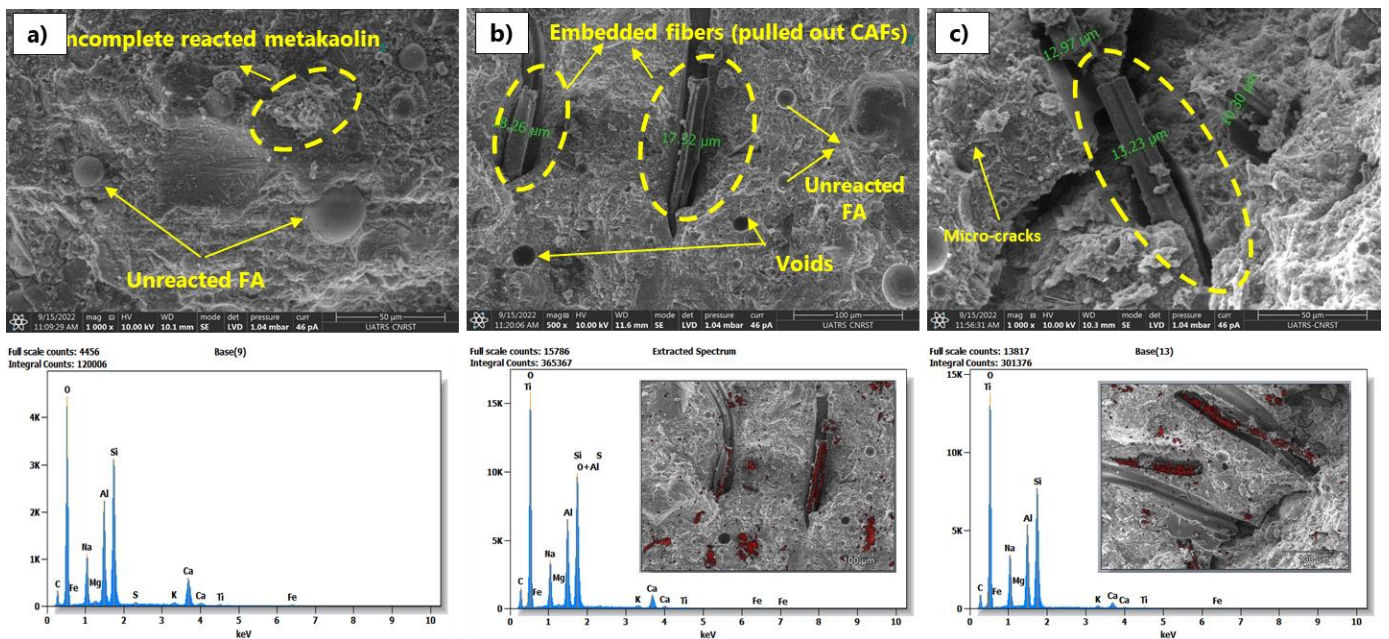


Figure 5-17. SEM images, EDS and mapping analysis of the geopolymer binders at 28-d of curing; a) GMK30, b) GPC<sub>0.2</sub>, c) GPC<sub>1.5</sub>

alumino-silicate gel (C, N)-A-S-H as reflected by the high amount of Al, Si and oxygen according to the elemental analysis (EDS) depicted in **Fig 5-17-a**.

A good adhesion between the matrix and the microfibers (Fig.14-b), confirmed by the presence of geopolymer layer on fibers ends pulled out from the matrix (Behera et al., 2018), only small spots were observed due to the degradation of fibers within the matrix under the action of alkali activating solution and the air bubbles trapped in the binders throughout the dissolution and poly-condensation process (Kallamalayil Nassar & Kathirvel, 2023), which could be the main reason behind the reduction in mechanical performance and the enhancement of thermal insulation as discussed in the above sections. Although, SEM micrographs of GPC<sub>1.5</sub> showed that micro-fibers were randomly distributed and not fully integrated with the matrix, also straight and curvilinear small cracks owing to crack deflections by cellulose acetate microfibers (**Fig.5-17-C**). This is consistent with previous findings in which it has been demonstrated that the further addition of microfibers in cementitious and AAMs materials yields to non-homogeneous structure due to the dispersion of agglomeration of fibers within the matrix (B. Zhou et al., 2020).

### 5.3.10 TCLP

Discarded cigarette butts contain a myriad of pollutants, including heavy metal(oid)s, PAH, etc. Therefore, when encapsulating them in construction materials like AAMs, their potential toxicity is one of the main concerns that must be addressed.

Table 5-5. The results of EN 12457-2 toxicity characteristic leaching procedures (TCLP), mg/L (ppm)

Element	CAFs	FA	GMK30	GPC <sub>0.2</sub>	GPC <sub>1</sub>	GPC <sub>1.5</sub>	Permissible limits*
Arsenic (As)	0.006	0.35	<0.001	<0.001	<0.001	<0.001	5.0
Cadmium (Cd)	0.004	0.10	<0.001	<0.001	<0.001	<0.001	1.0
Lead (Pb)	0.0035	0.65	<0.001	<0.001	<0.001	0.0015	5.0
Barium (Ba)	3.50	24.18	2.44	2.5	2.65	2.71	100
Cuivre (Cu)	0.05	0.84	0.01	0.016	0.019	0.035	25
Nickel (Ni)	0.4	2.50	< 0.001	< 0.001	< 0.001	< 0.001	20
Zinc (Zn)	0.1	1.03	0.086	0.091	0.12	0.17	2.0
Chromium (Cr)	0.015	2.17	0.09	0.002	0.0034	0.006	5.0

\*USEPA standard

Furthermore, the commercialization of the proposed recycling application requires an environmental assessment of the possible transfer of pollutants from the prepared geopolymers. In this view, **Table 5-5** shows the leaching test results of raw materials and the elaborated geopolymers containing different CAFs content. By examining the findings, it is seen that the leaching concentrations have been reduced for all metal(oid)s, the sample with the highest metal(oid)s concentration was GPC1.5 with a moderate concentration of Ba, Cu, and Zn. However, the leaching amounts of all metal(oid)s were lower than the threshold environmental regulatory limits established by the US Environmental Protection Agency (EPA). The sample with the highest metal(oid)s concentration was GPC<sub>1.5</sub>. However, it is observed that the leaching amounts of all selected metal(oid)s were lower than the threshold regulatory environmental limits established by the US environmental protection agency (EPA). Particularly, Cd, Ni, Pb, and As were not detected in all specimens. This fact reflects the efficiency of geopolymerization process in the immobilization of pollutants present in the raw materials during the solidification of the gel-geopolymer networks (Z. Gu et al., 2023). This study' findings are in line with previous research, it has been demonstrated that geopolymerization pathway enhances the solidification and stabilization of heavy metal(oid)s in comparison to the traditional cementation technique due to several factors including complexation and electrostatic interaction. In addition, the physico-chemical properties of water environments, including pH, salinity, ionic strength, etc. suggested being examined in future studies because they can influence the leaching rate and metal concentration leached. Also, polycyclic aromatic hydrocarbons (PAHs) should be evaluated as it is considered one of the most pollutants in cigarette buttes (Jin et al., 2018; B. Kim et al., 2021; Rafieizonooz et al., 2024; S. Sun et al., 2018). Although, the physicochemical properties of water environments, including pH, salinity, ionic strength, etc. suggested to be examined in future studies because they can influence the leaching rate and metal concentration leached. Also, polycyclic aromatic hydrocarbons should be evaluated as it is considered one of the most pollutants in cigarette buttes (Dobaradaran et al., 2020; Kurmus et al., 2021).

### **5.3.11 Environmental sustainability benefits**

Elaborated geopolymers containing cellulose acetate microfibers sourced from discarded cigarette butts (CBs) are an environmentally friendly material with promising mechanical, physical, and thermal properties. Transforming FA and MK into alternative resources used in construction permits to avoid the harmful effect of their disposal, which is discussed widely in

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the literature (Akhbarizadeh et al., 2021; Asensio-montesinos et al., 2021; Dobaradaran, Schmidt, & Kaziur-cegla, 2021; Slaughter et al., 2011). Akhbarizadeh et al. (2021) (Akhbarizadeh et al., 2021) and (Rafieizonooz et al., 2024) demonstrated experimentally that discarded CBs and FA could be an important source of heavy metal(oid)s in aquatic environments and ecosystems. Through the proposed solution, the incorporation of only 1 wt% of these microfibers in the geopolymers matrix could permit the recycling of approximately 10 kg of CAFs in each ton of geopolymer paste, particularly the leaching tests guaranteed that the elaborated materials are not hazardous. However, to confirm the environmental and economic feasibility of this recovery method life cycle assessment is required.

## **5.4 Conclusion**

In this chapter, the alkali-activation process was employed to ensure the safe disposal of FA and CBs and explore its potential utilization through the analysis of workability, mechanical performance, physical properties, and microstructure of the elaborated geopolymers. In summary, based on the findings discussed reported in this research work, the following conclusions can be drawn:

- Cellulose acetate microfibers (CAFs) sourced from CBs were composed mainly of cellulose acetate and characterized by a high hydrophilic character compared to other bio-sourced fibers evaluated previously.
- By increasing the CAFs contain a significant increase in water absorption and apparent porosity of prepared geopolymers, and a remarkable decrease in its dry bulk density was achieved.
- Geopolymeric pastes exhibit satisfactory mechanical properties in terms of compressive and flexural strength.
- The increase in CAFs content was accompanied by a significant decrease in mechanical resistance due to the increase in porosity and the weaker CAFs/matrix adhesion.
- The thermal conductivity and UPV declined linearly with CAFs percentage in mortar. Thus, the progressive increase of cigarette microfibers addition leads to a substantial improvement in the thermal insulation performance of the tested geopolymers.

## **5.5 Recommendations**

The results obtained from the current paper showed that CBs could be used as a source of CAFs for geopolymer materials. However, further in-depth experimental campaigns are highly recommended:

- The investigation of the effect of CAFs size on mechanical, physical, and thermal properties;
- Pretreatment of CAFs must be performed to assess the fiber-matrix bonding;
- Taking into account various parameters during TCLP, like pH, salinity, etc.;
- Life cycle assessment (LCA) is required or at least, the economical aspect should be investigated;

## **Chapter VI**

# **CONCLUSION AND RECOMMENDATIONS**

## **Conclusion and Recommendations**

This chapter presents conclusions of the conducted studies, implications and future recommendations. The current research investigated comprehensively the impact of landfilling and open dumpsites on soils, aquatic resources and its potential implications on human health and adjacent ecosystem. In alignment with the thesis objectives, a series of systematic and detailed studies were conducted to develop environmentally and economically sustainable and practical techniques to recycle Cigarette butts (CBs) and incineration ashes in the preparation of cementitious and geopolymer materials. All objectives relative to the study have been achieved, and a summary of each chapter has been concluded as follows:

**In chapter 1**, a detailed review was conducted on the impact of landfilling and open dumpsites on the environment and human health. The study also reviewed regulations related to waste management and the potential impact of heavy metal(oid)s on human health. Various studies related to the toxicity and recycling options of cigarette butts and incineration ashes were also discussed comprehensively to determine the feasibility and sustainability of the proposed valorization methods. This bibliographical analysis highlighted the urgent need for policymakers and the scientific community to enforce strategies enabling the reuse of waste and avoid the negative implications of landfilling.

**In chapter 2**, an investigation of soils contamination due to the accumulation of heavy metal(oid)s was carried out to bring out the impact of landfilling. To this end, soil samples were collected around Oum Azza landfill and Benguerir open dumpsite. The metal(oid)s content was measured using ICP-AES, and various pollution indices (Igeo, PIN, EF, PLI, PERI), chemometric expertise (HCA, PCA...) and Montecarlo simulation for human risk assessment were employed to highlight the impact of anthropogenic activities on its ecosystem. The obtained outcomes demonstrated clearly

**The Third chapter**, demonstrated clearly the negative impact of Oum Azza landfill on its surrounding water resources in terms of heavy metal(oid)s, organic pollution, and major ions based on the use of several indicators (PIN, WQI), multivariate statistical analysis and human risk assessment (HHRA). It was demonstrated that water around this area is not suitable for agricultural and drinking purposes.

**In chapter 4**, the effects of cellulose acetate microfibrils (CAFs) sourced from discarded cigarette filters (CFs) as fiber-reinforcement on the physico-mechanical properties thermal conductivity and microstructure of cementitious mortars were evaluated. To this end, 7 samples

containing different dosage percentages (0, 0.5, 1, 1.5, 2, 2.5, and 5 %wt of sand) of cellulose acetate microfibers (CAFs) and various tests were conducted. The results showed a lightweight mortar with satisfying properties till 1% of CAFs within the matrix. Applying mortar containing acetate cellulose fibers is recognized as a more environmentally friendly mixture in terms of reducing CO<sub>2</sub> emissions and could participate significantly in the achievement of SDGs.

**In chapter 5**, cellulose acetate from cigarette butts was used to produce geopolymer materials. Firstly, At first, an optimisation of the AAM mixture design was conducted based on various content of fly ash (FA) and metakaolin (MK). Then, the optimal specimen containing 30% MK-70%FA was mixed with different percentages of cellulose acetate microfibers (CAFs) and subjected to various analysis, including thermal conductivity, porosity, bulk density, water absorption, mechanical strength, P-wave velocity and microstructural analysis. The results indicate a decrease in compressive strength, density, and P-wave velocity, while the flexural strength, porosity, and water absorption were slightly increased. Likewise, a slight enhancement in thermal insulation capacity was achieved (up to ~9.57%). The microstructural analysis including FTIR, XRD and SEM/EDX demonstrated the formation of geopolymeric gel N-A-S-H, C-A-S-H, and C-S-H in all the developed geopolymers, and the development of porous structure with ensuing incorporation of CAFs. The leaching test (TCLP) following the European standard EN 12457-2 showed that the released contaminants from the elaborated geopolymers were within the regulatory limits set by the USEPA. Encapsulating CAFs in geopolymers can improve their properties while also reducing the environmental impact of CAFs, making it a promising solution for mitigating cigarette pollution.

This research work demonstrated clearly the negative impact of all kinds of landfills based on pollution indices and risk assessment methodology. Then, various ways of investigation to better understand the behavior of cigarette butts and incineration by-products were carried out in laboratory. The use of these by-products for the production of construction materials has several scientific, environmental, economic and social advantages. To this end, and for further investigation, further in-depth experimental campaigns are highly recommended as listed below:

- i. Conducting a systematic review Pollution threat to water and soil quality by dumpsites and non-sanitary landfills in Morocco and MENA region.
- ii. A life-cycle assessment (LCA) is recommended to analyse the environmental impacts of incorporating CBs in the production cementitious mortars and geopolymers.

- iii. It is recommended to investigate the leaching performance of toxic metal(oid)s at the various liquid to solid ratios, as described in EPA Methods 1314 and 1315 to consider the leaching of bricks subjected to various disposal or use scenarios.
- iv. Measuring the hydraulic conductivity of the prepared mortars and geopolymers in order to assess its effectiveness as a passive/active barrier in landfills.
- v. Developing innovative geopolymers such as phase change geopolymers, photo-catalytic geopolymers could be used for wastewater and leachate treatment

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# **APPENDIX**

## Appendix A: Geological structure and Hydrogeological conditions (Oum Azza)

The study area belongs to the plateau of Ain Aouda (Rabat, Morocco), which is attached to the field of the coastal Meseta. It consists of schists, sandstones and limestones that are strongly tectonized and are uncomfortably surmounted by the Miocene marls and the Plio-Quaternary formations in intercalations in shale Quartzite or sandstone benches meet (Bayoudi et al., 2019).

Concerning hydrogeological conditions, Under the plateau of Ain Aouda, a surface water table of limited productivity develops. The feeding of this water table is carried out exclusively by rainwater, its natural discharge is carried out from springs and seepages along oued Akrach in the north and oued Kourifla in the east and southeast.

The underground flow is carried out within a heterogeneous material of the Plio-Quaternary (silty sands, silty alluvium, calcarenites) and in the first altered fringe of the Viséen basement (shales).

Wells G1-G6 and the other wells on the south side of the site are dug in the first altered fringe of the Viséen basement and in the calcarenites characterized by high porosity. The limited productivity of these water points is conditioned by the low thickness of the saturated layer of the water table.



**Figure A-1.** synthetic stratigraphic column of the studied region (Bayoudi et al., 2019)

**Appendix B: Total and available heavy metal(oid)s around Benguerir’ open dumpsite (mg/kg dry weight)**

Table 1: Total and available fraction of heavy metal(oid)s around Benguerir’ open dumpsite (mg/kg dry weight)

Station	Pb		Cu		Cr		Zn		Ni		Cd		Fe	
	TF	AF	TF	AF	TF	AF	TF	AF	TF	AF	TF	AF	TF	AF
<b>S0</b>	115.52	21.37	21.55	3.52	44.65	5.9	90.78	12.36	21.7	2.06	6.8	1.35	325.9	40.71
<i><b>50 m from the landfill</b></i>														
<b>S1</b>	52.7	9.58	54.5	10.29	58.27	7.12	190.5	23.52	6.3	0.73	3.18	0.7	854.22	106.5
<b>S2</b>	80.2	10.02	39.532	7.45	14.38	1.53	30	3.78	9.8	1.56	1.68	0.52	852.83	83.45
<b>S3</b>	20.5	2.93	14.377	2.8	68.192	7.1	92.73	12.54	4.2	0.41	1.72	0.61	327.84	41.3
<b>S4</b>	6.7	0.6	12.931	1.62	10.2	2.33	45.29	6.2	3.1	0.15	1.64	0.37	222.18	26.47
<b>S5</b>	10.56	1.18	6.775	0.85	29.172	3.28	32.28	4.1	22.3	3.8	1.4	0.28	354.2	51.6
<b>S6</b>	7.46	1.24	8.539	0.93	24.69	1.56	22.43	2.93	12.9	1.25	1.36	0.14	528.65	60.2
<i><b>100 m from the landfill</b></i>														
<b>S7</b>	28.5	4.08	17.56	2.05	40.5	5.43	35.25	4.87	34.2	3.4	2.6	0.85	265.15	36.1
<b>S8</b>	25	4.52	18.15	2.24	28.95	3.6	21.8	3.66	9.4	0.86	2.26	0.74	317.64	38.14
<b>S9</b>	3.7	0.23	14.25	1.76	12.5	1.4	49.75	6.24	2	0.1	0.78	0.1	257.74	27.49
<b>S10</b>	2.2	0.1	2.9	0.12	10.3	0.9	7.92	0.98	2	0.1	0.8	0.25	259.64	28.53
<b>S11</b>	9.96	1.2	10.97	1.84	11.16	1.2	12.72	1.52	7	0.25	1	0.28	453.62	41.67
<b>S12</b>	13	2.5	3.76	0.62	6.86	0.76	19.62	2.16	4	0.17	1.34	0.335	456.65	39.45
<i><b>200 m from the landfill</b></i>														
<b>S13</b>	3.3	0.21	2.5	0.1	13.64	1.51	31.85	2.75	3	0.12	3.24	1.26	456.36	23.8
<b>S14</b>	8.2	0.77	8.64	1.23	6.5	0.24	33.35	2.6	1.25	0.1	1.44	0.36	507.98	28.22
<b>S15</b>	8.6	0.5	3.1	0.5	10.22	0.68	14.81	1.21	6	0.21	1.08	0.26	423.22	24.89
<b>S16</b>	4	0.12	4.26	0.75	4.05	0.11	27.16	1.83	4	0.14	0.36	0.09	298.28	15.7
<b>S17</b>	8.5	0.46	5.4	0.2	3.73	0.08	31.12	3.27	4	0.14	0.6	0.12	267.84	15.04
<b>S18</b>	9.6	0.78	3.45	0.18	4	0.1	18.25	1.52	4.3	0.13	0.38	0.09	289.22	17.31

*TF: Total Fraction AF: Available Fraction*

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**Appendix C: Total heavy metal(oid)s around Oum Azza' landfill (mg/kg dry weight)**

<b>Metal(oid)s</b>	<b>Cd</b>	<b>Pb</b>	<b>As</b>	<b>Cr</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>Fe</b>
<b>S1</b>	2.91	78.97	2.85	24.66	39.19	8.79	85.41	6281.00
<b>S2</b>	2.06	64.90	2.93	13.43	17.19	3.27	51.24	6139.00
<b>S3</b>	1.82	25.03	1.36	51.90	38.27	9.33	66.99	6339.50
<b>S4</b>	0.89	22.30	1.48	28.80	53.73	16.48	76.14	6014.50
<b>S5</b>	0.92	28.18	2.09	11.34	9.64	2.92	37.78	6118.50
<b>S6</b>	0.95	31.08	1.99	14.58	29.62	12.52	55.68	6583.00
<b>S7</b>	2.93	45.25	2.99	17.66	38.27	13.97	67.74	6289.00
<b>S8</b>	1.16	42.84	2.54	28.08	42.50	12.03	72.59	6420.00
<b>S9</b>	0.80	29.42	1.17	20.52	21.34	7.19	67.20	6160.50
<b>S10</b>	0.82	23.13	1.38	19.20	28.89	9.26	57.62	6079.50
<b>S11</b>	0.75	22.15	1.62	31.08	46.92	9.35	65.05	6317.50
<b>S12</b>	0.93	25.25	2.25	17.66	28.27	11.97	67.74	6000.00
<b>S13</b>	0.68	16.23	0.98	40.56	26.42	10.04	40.36	6025.00
<b>S14</b>	0.75	22.15	1.62	31.08	45.92	9.35	45.05	6271.50
<b>S15</b>	0.89	22.30	1.48	28.80	21.73	16.48	36.14	6010.00
<b>S16</b>	0.69	19.54	2.16	19.70	22.27	2.76	38.22	6060.00
<b>S17</b>	0.64	21.06	1.65	9.71	15.13	4.75	45.85	6072.50
<b>S18</b>	0.92	13.18	2.15	11.34	13.64	2.92	37.78	6172.50
<b>S19</b>	0.74	12.24	1.80	12.55	14.20	3.05	45.75	6316.00
<b>S20</b>	1.06	14.90	2.74	13.43	17.19	3.27	51.24	5819.00
<b>S21</b>	0.35	16.51	2.19	12.45	19.44	12.09	46.70	6151.00
<b>S22</b>	0.42	21.30	1.79	14.32	32.15	11.47	41.50	6072.50
<b>S23</b>	0.29	16.50	1.81	11.02	27.15	9.50	36.19	6160.50
<b>S24</b>	0.31	15.12	2.31	13.07	18.40	6.12	31.67	5671.50
<b>S25</b>	0.27	13.40	2.11	12.50	16.30	5.80	29.20	6236.50
<b>S26</b>	0.30	19.76	1.83	15.06	19.54	8.22	34.68	6121.00
<b>S27</b>	0.74	21.24	1.15	12.55	14.20	3.05	45.75	6431.00
<b>S28</b>	0.24	12.50	0.94	13.10	15.30	4.60	34.50	6268.50
<b>S29</b>	0.21	14.23	0.52	12.18	14.11	3.96	29.49	6486.50
<b>S30</b>	0.25	15.20	0.63	10.54	16.20	5.02	32.50	6412.00

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### Appendix D: Groundwater parameters around Oum Azza' landfill

Table D1. physicochemical parameters of samples collected in wet season

Samples	pH	EC	Turbidity	BOD <sub>5</sub>	COD	TDS	NO <sub>3</sub> -	OP	NH <sup>4+</sup>
G1	6.9	4712	7	10	67	3221	11.4	1.3	3.6
G2	7.45	3548	6	7	45	2386	10.21	1.05	2.11
G3	7.3	3125	7	9	50	2513	11.62	0.98	1.65
G4	7.56	3154	8	4	47	2103	11.32	1.1	2.7
G5	7.8	2029	5	3	34	1492	9.6	1.05	1.3
G6	7.45	2374	5	5	11	1939	12.3	1.21	1.22
G7	7.1	1513	4	2	7	1163	8.22	0.29	0.17
G8	6.95	943	2	1	7	697	6.5	0.64	0.13
G9	6.5	1021	3	1	6	954	6.1	0.5	0.1
G10	7.12	1289	4	1	9	936	7.4	1.12	0.35
G11	7.4	964	3	1	6	891	8.2	0.3	0.15
G12	7.42	1136	2	1	6	981	7.51	1.02	0.4
G13	7.8	1052	4	1	6	782	3	1.1	0.36
G14	6.9	897	1	1	17	723	6.1	0.94	BDL
G15	6.55	830	2	1	8	583	7.85	0.76	BDL
G16	7.3	651	3	1	9	510	3.92	BDL	BDL
G17	7.45	710	2	1	11	474	4.1	BDL	BDL
G18	7.3	638	1	1	14	467	5.45	BDL	BDL
G19	7.14	721	4	1	6	508	3.2	BDL	BDL
G20	6.85	592	3	1	6	386	2.8	BDL	BDL

All the values are in mg/l except, pH, EC ( $\mu\text{s}/\text{cm}$ ) and Turbidity (NTU)

Table D2. physicochemical parameters of samples collected in dry season

Samples	pH	EC	Turbidity	BOD <sub>5</sub>	COD	TDS	NO <sub>3</sub> -	OP	NH <sup>4+</sup>
G1	7.24	5032	7	8	84	3232	12.5	1.52	4.25
G2	7.45	3728	6	7	80	2389	10.83	1.5	3.56
G3	7.3	3457	7	8	75	2532	12.05	1.47	3.45
G4	7.56	3263	9	4	61	2125	12.11	1.66	4.1
G5	7.8	2200	5	3	69	1502	10.23	1.45	2.1
G6	6.95	2986	10	2	45	1949	14	1.78	3.6
G7	7.05	1817	7	2	12	1163	9.53	1.1	0.47
G8	6.9	1081	2	1	10	711	7.9	0.9	0.3
G9	6.85	1490	1	2	7	968	6.8	0.9	0.24
G10	7.1	1462	3	1	6	954	7.95	1.7	0.5
G11	6.85	1390	3	1	9	906	9	0.8	0.41
G12	7.3	1526	1	1	7	998	7.94	1.23	0.23
G13	7.49	1215	4	1	8	803	3.6	1.4	0.2
G14	6.92	1142	3	1	8	746	7.04	1.3	BDL
G15	7.36	908	5	1	6	592	8.21	1.05	0.2
G16	7.12	796	2	1	7	530	4.01	BDL	BDL
G17	7.5	736	2	1	9	480	4.6	BDL	0.15
G18	7.1	721	2	1	8	481	6.12	BDL	0.18
G19	7.36	793	3	1	6	514	3.4	BDL	BDL
G20	7.1	685	10	1	8	424	2.9	BDL	BDL

All the values are in mg/l except, pH, EC ( $\mu\text{s}/\text{cm}$ ) and Turbidity (NTU)

Table D3. Major ions content in studied wells (n=20)

Samples	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	So <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>
G1	360.17	210.4	356.5	32.46	492	381.5	1368.21
G2	326	186.01	127.29	11.68	365.02	392.47	977.36
G3	375.4	163.5	133.82	11.04	403.12	421.52	953.5
G4	287	92.33	233.05	10	122	381.04	954.01
G5	221.42	83.16	135	5.62	94.5	212.5	729.45
G6	341.33	124	189.4	7.3	65.3	246.91	961.23
G7	131.458	21.62	161	2.6	50.6	307.08	465.07
G8	108.1	13.18	72.98	2.86	67	204	218.5
G9	137.26	20.01	136.81	7.45	94.1	221.6	337
G10	72.23	15.33	207.45	7.05	83	335.5	212.43
G11	89.5	17.48	162.15	6.7	78	215.36	322
G12	92.5	32	159	4.32	66.5	285.49	341
G13	75.4	15.72	135.02	3.11	113	247.3	192.5
G14	103.6	32.76	79.4	5.75	128.02	195	178.4
G15	56.28	12.4	125.1	3.83	67.45	131.25	187.12
G16	92.03	18	50.89	2.42	96	107.61	143
G17	64.15	15.21	71.4	3.6	104.3	95.3	119.7
G18	82.9	11.03	56.07	1.29	93	106.84	115.62
G19	74.8	11.78	63.75	1.8	96.08	92.7	167.3
G20	57.3	17.09	51.4	2.4	81.35	108.05	124.8

All the values are in mg/l, the presented results are the average of values measured in both seasons

Table D4. heavy metal(oid)s content in studied wells (n=20)

Samples	Pb	Cd	Cu	Cr	Zn	Ni	As	Hg	Fe
G1	14.9	5.8	17	11.25	140	20.6	9.41	BDL	308.47
G2	15.7	4.25	15.4	9	78	21.3	8.94	BDL	307.45
G3	10.26	4.1	17	7	72.25	18.5	8.43	BDL	284.26
G4	9.15	3.86	8	8.4	52	14.7	6.1	BDL	194.5
G5	12.3	2.56	14	6.5	64	19.3	7.35	BDL	275.3
G6	9.1	2	6	9	60	17.56	4.16	BDL	162.4
G7	8.56	2.36	9	8.35	74	13.8	1.42	BDL	53.1
G8	7.44	1.56	12	4.5	50	15.9	8.5	BDL	4.5
G9	5	4.37	10	1.2	25.46	11.46	5.13	BDL	6.94
G10	4.9	3.2	18	0.45	19.25	8.1	3.58	BDL	4.16
G11	3.48	1.25	10	0.7	21.6	5.87	2.47	BDL	5.7
G12	4.56	2.89	3	0.7	7.45	3.12	4.24	BDL	3.45
G13	7.15	3.4	2	1	7.62	22.5	7.1	BDL	3.05
G14	4.6	2.56	3	0.23	0.56	18.4	4.36	BDL	3.26
G15	6.72	0.4	1	0.74	1.6	5.75	0.3	BDL	2.7
G16	3.25	1.25	0.2	0.3	3.5	3.25	0.75	BDL	3.6
G17	5.6	0.75	1.5	0.25	2.4	0.78	0.6	BDL	1.46
G18	2.3	0.92	0.8	0.4	1.45	1.64	0.45	BDL	2.8
G19	5	0.26	1.6	0.2	0.92	1.52	0.25	BDL	7.95
G20	2.26	0.3	1.37	0.2	1.78	1.3	0.78	BDL	1.2

All the values are in µg/l, the presented results are the average of values measured in both seasons

Table D5. Factor loading for groundwater samples around MSW landfill.

<b>Parameters</b>	<b>F1</b>	<b>F2</b>	<b>F3</b>
Ca <sup>2+</sup>	<b>0.941</b>	-0.184	-0.102
Mg <sup>2+</sup>	<b>0.948</b>	-0.225	0.100
Na <sup>+</sup>	<b>0.748</b>	0.241	-0.100
K <sup>+</sup>	<b>0.828</b>	-0.040	0.330
SO <sub>4</sub> <sup>2-</sup>	<b>0.795</b>	-0.212	0.529
HCO <sub>3</sub> <sup>-</sup>	<b>0.850</b>	0.340	-0.034
Cl <sup>-</sup>	<b>0.973</b>	-0.143	-0.115
EC	<b>0.988</b>	-0.088	0.018
pH	<b>0.733</b>	-0.312	-0.403
BOD <sub>5</sub>	<b>0.935</b>	-0.236	0.201
COD	<b>0.936</b>	-0.228	0.083
TDS	<b>0.991</b>	-0.072	0.009
NO <sub>3</sub> <sup>-</sup>	<b>0.842</b>	0.054	-0.359
OP	<b>0.733</b>	0.543	-0.250
NH <sub>4</sub> <sup>+</sup>	<b>0.953</b>	-0.177	-0.100
Pb	<b>0.899</b>	-0.022	-0.022
Cd	<b>0.809</b>	0.405	0.256
Cu	<b>0.751</b>	0.319	0.124
Cr	<b>0.903</b>	-0.118	-0.275
Zn	<b>0.919</b>	-0.036	-0.013
Ni	<b>0.752</b>	0.389	-0.071
As	<b>0.794</b>	0.388	0.194
Fe	<b>0.933</b>	-0.221	-0.018
<b>Eigenvalue</b>	17.48	1.50	1.05
<b>Variability (%)</b>	76.02	6.54	4.55
<b>Cumulative %</b>	76.02	82.56	87.11

*PCA loadings >0.7 are shown in bold*

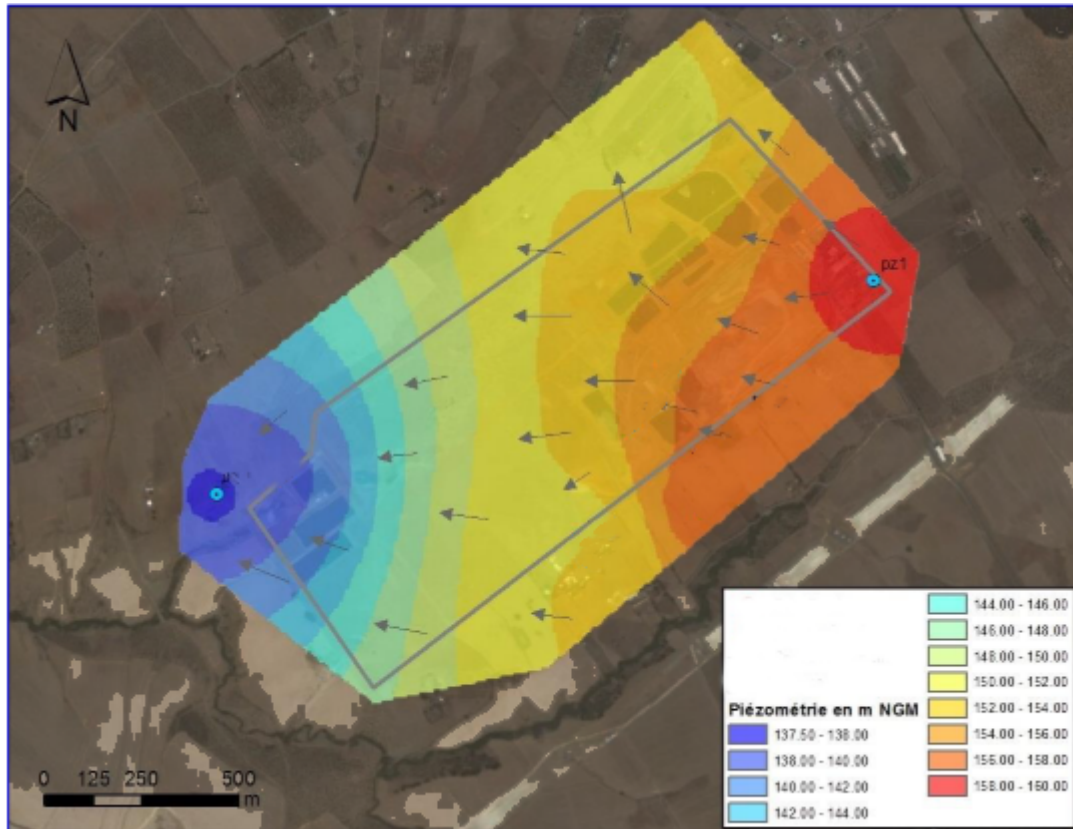


Figure D-1. Piezometric map of the study area

**Appendix E: Granulometric curve of used materials**

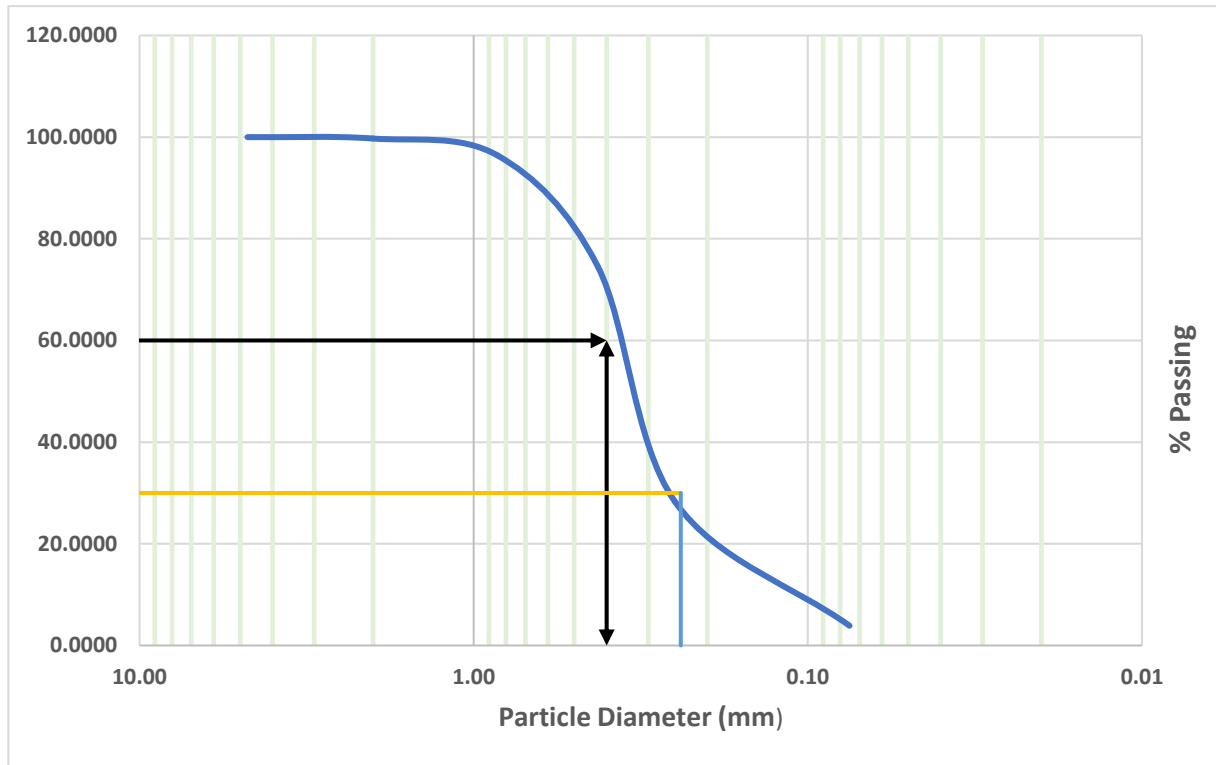


Figure E-1. Cuvre granulométrique of sand

## Appendix E: List of Publications and Communications

### JOURNAL PUBLICATIONS :

- Effects of encapsulating cellulose acetate microfibers on the mechanical, thermal and environmental properties of geopolymers: a new solution to mitigate the cigarettes pollution– **Journal of Building Engineering (Q1). Cite Score: 6.4, Impact Factor: 7.15**  
[Hamza El Fadili \\*](#), Mohammed Ben Ali, Amine El Mahdi Safhi, Mohammed El Mahi, Ayoub Aziz, El Mostapha Lotfi
- Determination of properties and environmental impact due to the inclusion of cigarettes fibers in mortar: a new solution to mitigate the CBs pollution - **Environmental Science and Pollution Research (Q1). Cite Score: 6.6, Impact Factor: 5.19**  
[Hamza El Fadili \\*](#), Mohammed Ben Ali, Mohammed El Mahi, Nabil Khatib, El Mostapha Lotfi, Najoua Labjar
- Ecotoxicological and pre-remedial risk assessment of heavy metals in municipal solid wastes dumpsite impacted soil in Morocco - **Environmental Nanotechnology, Monitoring & Management (Q1). Cite Score: 7.3**  
[Hamza El Fadili \\*](#), Mohammed Ben Ali, Nouredine Touach, Mohammed El Mahi, El Mostapha Lotfi
- A comprehensive health risk assessment and groundwater quality for irrigation and drinking purposes around municipal solid waste sanitary landfill: A case study in Morocco- **Environmental Nanotechnology, Monitoring & Management (Q1). Cite Score: 7.3**  
[Hamza El Fadili \\*](#), Mohammed Ben Ali, Mohammed El Mahi, Asitha T. Cooray, El Mostapha Lotfi
- Assessment of trace metals contamination in sediment and surface water of quarry lakes from the abandoned Pb- **Environment, Development and Sustainability Pollution (Q1). Cite Score: 4.4, Impact Factor: 4.08**  
Siham Bouzekri, [Hamza El Fadili](#), Moulay Laarbi El Hachimi, Mohammed El Mahi, El Mostapha Lotfi
- The study of metal (As, Cd, Pb, Zn and Cu) contamination in superficial stream sediments around of Zaida mine (High Moulouya-Morocco)- **Journal of African Earth Sciences journal (Q2). Cite Score: 3.9, Impact Factor: 2.47**  
Siham Bouzekri, Moulay Laarbi El Hachimi, Nouredine Touach, [Hamza El Fadili](#), Mohammed El Mahi, El Mostapha Lotfi
- Synergistic Effects of landfilling and intensive agriculture on the quality of soils and human health using DTPA, PMF receptor model, PCA and MCS – **Science of Total Environment (Q1). Cite Score: 14.1, Impact Factor: 10.75 (Under review)**  
[Hamza El Fadili \\*](#), Mohammed Ben Ali, Mohammed El Mahi, El Mostapha Lotfi

**List of communication :**

- Pollution indicators and chemometric expertise for the assessment of the impact of open dumps on soils located in their area (Benguerir, Morocco)- **Environment and Natural Resources: Challenges and Solutions (ENRSC2021).**
- Turning cigarette butts (CBs) into wealth: challenges et opportunities - **International Virtual congress on Water and Environment Studies (CI3E 2021).**
- Co-utilization of crushed waste glass and bottom ash as an eco-friendly replacement in mortars using Taguchi method - **International Congress on Materials & Structural Stability (CMSS 2021).**
- Enhancing the properties of lime mortar based eggshell waste and wood ash using sustainable biopolymer “Gum Arabic” - **International Congress on Materials & Structural Stability (CMSS 2021).**

**Certifications :**

- NEBOSH INTERNATIONAL GENERAL CERTIFICATE- **NEBOSH-UK.**
- IOSH Managing Safely- **IOSH-UK.**
- IOSH Train the trainer- **IOSH-UK.**
- OSHA, 30-hour Construction Safety and Health-OSH Academy (USA)- **OSH Academy-USA.**
- OSHA, 30-hour General Industry-OSH Academy (USA)- **OSH Academy-USA.**
- IRCA ISO 45001.



### Abstract

Recently, the proper management of solid waste for the reduction of its potential implications on the environment and human health is one of the most challenging issues faced worldwide due to the increase of public awareness and concern regarding protecting the environment. In the current thesis, comprehensive and detailed experimental studies were undertaken to evaluate the effects of landfilling activities on soils, water resources, and human health by taking the open dumpsite of Benguerir and the engineered landfill of Oum Azza, respectively as a case study. Then, some applications of dumped waste were deeply studied and several recycling methods were evaluated through the assessment of the effect of using discarded cigarette butts (CBs), Fly ash, and bottom ash in cementitious and geopolymer materials. The results highlighted through the use of several indicators (Geo-accumulation index, Pollution load index, Ecological risk indices, Nemerow pollution indice...), deterministic and probabilistic human risk assessment based on Montecarlo simulation, and statistical analysis (PCA, HCA) that landfilling can be seriously harmful to the soil, aquatic resources and human health. Especially, illegal landfilling in open dumpsites showed the highest potential for ecological and human health, nevertheless, they are not the only sources of pollution. It has been proven that regular landfills could have similar levels depending on the design, the collection systems for leachate and biogas, and the insulation systems. In addition, this research has discussed the Cigarette Butts (CBs) and incineration by-products pollution issues, potential recycling solutions, the results prove the possibility of their recycling in cementitious and geopolymer materials without compromising the physical, thermal and mechanical properties in comparison to conventional materials existing in the market. The prepared materials are recognized as a more environmentally friendly mixture in terms of reducing CO<sub>2</sub> emissions and could participate significantly in the achievement of sustainable development goals (SDGs) through keeping waste in use not in landfills.

**Keywords:** Leachate, Landfills, Open dumpsite, Cigarette butts, Fly ash, Mortar, Waste management.

### Résumé

La gestion appropriée des déchets solides pour la réduction de leurs implications potentielles sur l'environnement et la santé humaine est l'une des questions cruciales et perplexes auxquelles le monde contemporain est confronté. Dans le présent travail de thèse nous avons mené des études expérimentales spatiaux-temporaires, sur deux sites de décharges, un site à ciel ouvert situé dans la décharge sauvage de Benguerir et environs (8 ha), et l'autre site est un centre d'enfouissement technique d'une décharge contrôlée, de 13 communes de la région Rabat- Salé-Témarras- Bouznika et environs dénommée située dans la commune Oum Azza (Surface totale de 110 ha). Les études menées sont assez complètes et relativement bien détaillées et ayant pour objectifs principaux l'évaluation des procédés d'enfouissement et leurs impacts sur les sols, sur les ressources hydriques et sur la santé humaine grâce à l'utilisation de plusieurs indicateurs (indice de géo-accumulation, indice de charge polluante, indices de risque écologique, indice de pollution de Nemerow...), l'évaluation déterministe et probabiliste du risque humain basée sur la simulation de Montecarlo, et l'analyse statistique (corrélation, PCA, HCA). D'autre part, nous avons entrepris le volet du recyclage et de la valorisation, particulièrement pour certains types des déchets mis en décharge, ainsi nous avons entrepris des démarches de revalorisation des résidus des mégots de cigarettes, des cendres volantes et des mâchefers et nous avons réussi à les réutiliser et les intégrer dans les matériaux cimentaires et géopolymères sans qu'il y'ait des effets de nocivité ou toxicités ou de régénérations de déchets secondaires, aussi les qualités eco-environnementales de ces nouveaux matériaux innovés ont été prouvées, confirmées et mis en évidence, Lors de notre étude on a montré que des décharges ordinaires, et induiraient à des impacts environnementaux comparables voire très inquiétants, lors des procédés d'enfouissements et ce en fonction de leur conception, des systèmes de collecte des lixiviats et des biogaz, et des systèmes d'isolation. Les résultats obtenus lors des études et analyses physico-chimiques et les caractérisations thermiques et mécaniques des matériaux cimentaires et géopolymères élaborés ont montré que leurs comportements structuraux, et leurs propriétés physiques, thermiques et mécaniques n'ont été ni compromises ni altérées. Les matériaux préparés sont reconnus comme nouveaux matériaux composites respectueux de l'environnement en termes de réduction des émissions de CO<sub>2</sub> et pourraient participer de manière significative à la réalisation des objectifs de développement durable en gardant les déchets en usage et non dans les décharges.

**Mots clés :** Lixiviat, Décharges, Décharges sauvages, Mégots de cigarettes, Cendres volantes, Mortier, Gestion des déchets.

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