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Research Article

Marble sludges as environmentally friendly catalyst in olive pomace pyrolysis: Effect of sludge composition on pyrolysis product distribution and biochars

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Biochar; Catalytic pyrolysis; Marble sludge; Olive pomace

ABSTRACT

Waste management of olive pomace is difficult because of the high production amount and non-biodegradable organic substances. Catalytic pyrolysis process is one of the effective methods for olive pomace (OP) management and for obtaining valuable organic substances from it. Therefore, in this study, different types of marble sludge were used as catalyst in the olive pomace pyrolysis process at 500 °C temperature and 40% catalyst dose. While K1, K2, K3 are the sludges obtained from physicochemical treatment of travertine type marble processing wastewater with alum, $FeCl_3$ and PEL, respectively, K4,K5 and K6 are the corresponding physicochemical treatment sludges of natural stone type marble processing wastewater. Pyrolysis product yields and characteristics of pyrolysis biochars were investigated. The highest product yield for biochar liquid and gas fractions was obtained with the K1 catalyst. The biochar obtained for OP+K1 pyrolysis has the highest initial decomposition temperature. Biochar obtained by using K6 was more granular. Biochar having the highest calorific value (1193 cal/g) was obtained with the catalytic pyrolysis of OP with K4 catalyst. Biochars obtained with the K1 and K6 catalysts have similar calorific values. Besides calorific values, the characteristics of biochars indicated that these biochars can be used for diverse purposes either as additive or feedstock. Consequently, K1 catalyst can be recommended for olive pomace catalytic pyrolysis when biochars are evaluated in terms of product yield and biochar characteristics.

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INTRODUCTION

Türkiye is among the Mediterranean countries where olive and olive oil production is high. Approximately 225,000 tons of olive oil was produced in Türkiye in 2020 [1]. Olive pomace (OP), which is a solid waste consisting of olive seed, the pulp of the olive, water and oil, is generated during the olive oil production process. Waste management of OP is very difficult due to the high production amount of pomace, the difficulties in the treatment, and the presence of non-biodegradable organic substances in it. One of the effective methods for OP management and obtaining valuable organic substances from it is pyrolysis. Especially catalytic pyrolysis process has been studied commonly since it has important advantages over conventional pyrolysis process such as selectivity of valuable substances formed during the pyrolysis, enhancement of quality and quantity of pyrolysis products [2]. Although in OP pyrolysis various catalyst types were studied, carbonate-derived catalysts, such as dolomite ($CaMg(CO_3)_2$), potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3),

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iron carbonate ($FeCO_3$), calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), magnesium oxide (MgO) and lithium carbonate (Li_2CO_3), are mostly preferred among them since they are readily available and low cost [3, 4]. Thermal and mechanical strength of dolomite catalyst is high and therefore it can be used more than once with little performance degradation. In a study, it was emphasized that catalytic efficiency of dolomite in the pyrolysis process remain almost constant [5]. As for other catalyst types, performance on the product yields can be changed. For instance, in the study about catalytic effects of K_2CO_3 and Na_2CO_3 in OP pyrolysis process stated that catalytic effect of these on product yields are irregular but mostly K_2CO_3 had a better catalytic effect than the Na_2CO_3 [6]. Similarly, catalytic effect of $Ca(OH)_2$ and CaO vary with pyrolysis temperature and the material being pyrolyzed. In the pyrolysis process of OP and $Ca(OH)_2$, biochar quantity increased and liquid fraction decreased with catalyst [7]. Although various catalysts have been used to improve the process in OP pyrolysis, there are very few studies that partially place the waste material in the catalyst.

Marble processing plant wastewater is formed with the combination of marble dusts released during marble processing and the water used during marble cutting processing. These wastewaters are an important source of pollutants for the environment, agricultural lands, and water resources [8, 9]. For this reason, physicochemical treatment, such as coagulation-flocculation-sedimentation process, is applied commonly for the treatment of these wastewaters. It is important that the marble sludge produced as a result of this treatment process should not be released directly to the environment, as it will have adverse effects on the environment. It is important to apply economical and feasible alternatives that will provide recycling of these sludges to the system. Moreover, the properties of marble sludge varied based on the coagulant type used in the coagulation-flocculation-sedimentation process. Different coagulants and flocculants have been studied for andesite and travertine type marble processing wastewaters and it has been observed that the characteristics and structures of the physico-chemical treatment sludge obtained with each of them are different from each other [8, 9]. Therefore, in this study, first, different type of marble sludges were obtained as physico-chemical treatment sludge by applying alum and $FeCl_3$ as coagulant to travertine and natural stone type of marble processing effluents. Additionally, the sludges produced by using polyelectrolyte in the processing facility were collected. The prepared six types of marble sludges were studied as catalyst in the OP pyrolysis process. Thereby, marble sludges were utilized as environmentally friendly catalysts in OP pyrolysis by prevention of negative effects of marble sludges on environment and by providing conversion waste material to the useful products via pyrolysis. Pyrolysis biochars obtained from catalytic pyrolysis of OP-marble sludge mixtures were investigated in terms of surface morphology, surface acidity, thermal behavior, heating, and ash value. In this way, a symbiotic, sustainable, and environmentally friendly approach has been applied in the disposal of OP and marble sludge wastes.

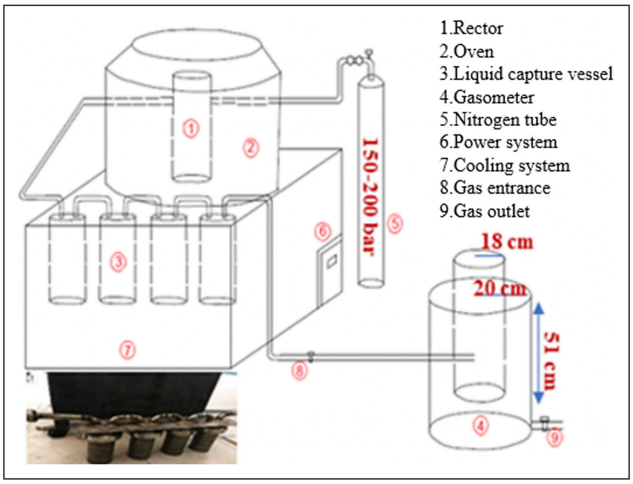


Figure 1. Fixed bed batch pyrolysis system.

Table 1. Types and given codes of the marble sludges

The type of marble whose processing wastewater was used	Chemical used in coagulation-flocculation treatment	Code of marble sludge in this study
Travertine	$Al_2(SO_4)_3$.18H2O	K1
Travertine	$FeCl_3$	K2
Travertine	PEL*	K3
Natural stone	$Al_2(SO_4)_3.18H_2O$	K4
Natural stone	$FeCl_3$	K5
Natural stone	PEL*	K6

*: Sludges produced by using polyelectrolyte in the processing facility.

MATERIALS AND METHODS

The studied OP samples were obtained from the Ernar Ind. Trade. Co. Ltd. olive oil production facility operating in Mersin/Erdemli-Türkiye. Travertine and natural stone type marble processing effluents were taken from the marble processing facility of REMAR Co.Ltd. (Konya-Türkiye). The coagulation-flocculation and sedimentation processes were carried out on the marble processing effluents with the help of alum ($Al_2(SO_4)_3.18H_2O$) and iron (III)chloride ($FeCl_3.6H_2O$) coagulants in a Jar test setup (VELP-FC6S model). Conditions determined in previous studies were used for the coagulation-flocculation and sedimentation process [8, 9]. After the coagulation-flocculation and sedimentation, the supernatant part of the samples was withdrawn, the remaining settled sludge was dried at 40–50°C and sieved through a 300-micron-sized sieve. The abbreviations of the marble sludge samples used in the study were indicated in Table 1.

Catalytic pyrolysis process of OP-marble sludge mixtures was conducted in fixed bed batch pyrolysis system (Fig. 1) with at least two replicates at 500°C temperature, 40% catalyst dose and with 100 g total weight of OP-marble sludge mixtures. The pyrolysis char and oil obtained after pyrolysis were collected separately, weighed on a precision balance, and recorded as a percentage. The pyrolysis gas was collected in the gasometer and the volume of the collected pyrolysis gas was calculated

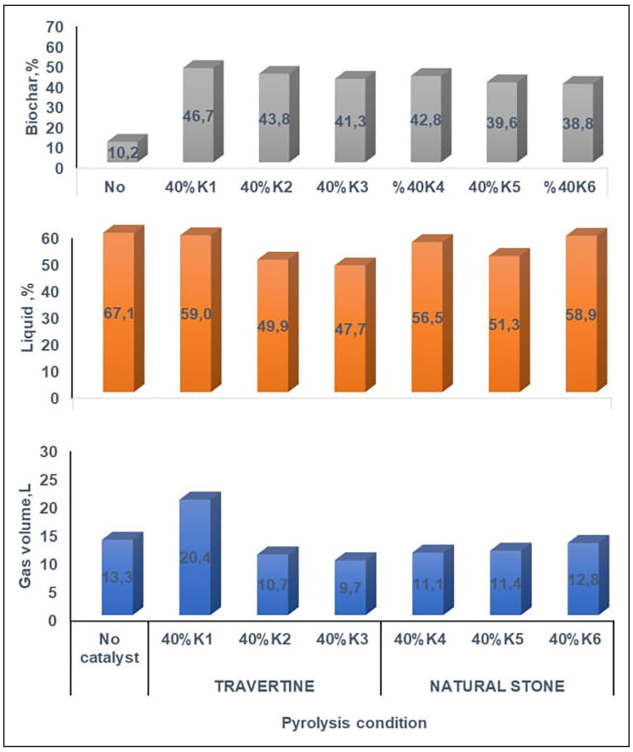


Figure 2. Pyrolysis product fractions obtained from the pyrolysis of OP with different catalysts at 40% dose and 500°C temperature.

by measuring the rise in the gasometer and gasometer surface area. SEM imaging, acidity analyzes, and thermogravimetric analysis (TGA) were performed for the characterization of the obtained pyrolysis biochars. Furthermore, ash content and calorific value of biochars were revealed. SEM analyses were conducted at JEOL-JSM-6610 model device, at 15 kV acceleration voltage. Surface acidity of the biochars were determined titrimetrically as follows: Isopropyl alcohol-toluene mixture (v/v; 1:1) and 1% phenolphthalein solution prepared with isopropyl alcohol was added to the sample as solvent and 0.1% N KOH solution was used for the titration of sample up to observing pink color. Equation 1 was used for acid value calculations.

$$\text{Acid value (mmol/g)}=(A-B)N/W \quad (1)$$

A: Standard alkali volume used in titration (mL)

B: Standard alkali volume used in titration of blank (mL)

N: Standard alkali normality

W: Sample weight (g)

As for TGA analyses, PerkinElmer TGA4000 Model device was used at a rate of 20 mL/min nitrogen gas flow, 20°C/min heating rate and 900°C target temperature. Leco AC-350 Model Calorimeter Device was used for the determination of heat values of biochars at 15–20 atm pressure.

RESULTS AND DISCUSSION

Pyrolysis Product Yields

The product amounts of OP obtained at 500°C, 40% catalyst dose with different catalysts were shown in Figure 2. Travertine marble sludges (K1, K2, K3) had higher pyrolysis biochar product amount compared to marble sludges obtained from natural stone (K4, K5, K6). Catalysts obtained by using alum chemical (K1 and K4) had higher biochar amount than catalysts obtained with $FeCl_3$ and PEL for both types of marbles. The highest amount of OP biochar belonged to K1 catalyst. Similar to biochar findings, pyrolysis liquid product quantities were very close to each other. The most obvious difference between the catalysts was observed for the pyrolysis product gases. The gas product volume of K1 catalyst was higher than other catalysts. The main components of all of the marble sludge samples are Ca, C, O, and Mg, and minor components were Al and Fe inorganics which come from the used coagulants in the physicochemical treatment process. Since the catalytic effects of each inorganic in the catalyst structures are different from each other, this also affected the amount of pyrolysis products. When all pyrolysis products were evaluated in general, the highest product yield in OP pyrolysis biochar liquid and gas was obtained with the K1 catalyst.

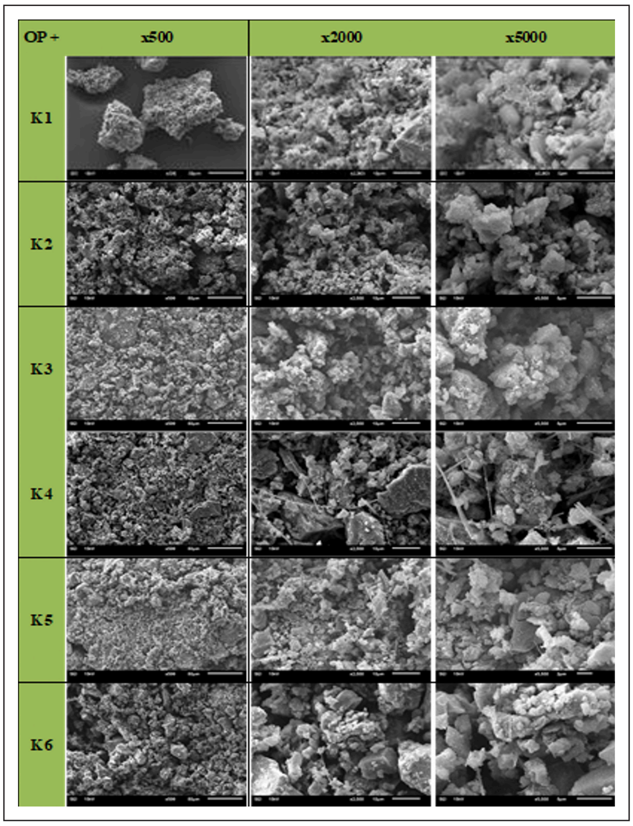


Figure 3. SEM images of pyrolysis biochars obtained from the pyrolysis of OP with different catalysts at 40% dose and 500°C temperature.

Characteristics of Pyrolysis Biochars

SEM images of biochars formed from catalyzed OP pyrolysis generally showed a rough and amorphous structure (Fig. 3). It has been reported that some amorphous carbon structures are formed during pyrolysis due to the degradation of cellulose and that these structures can form micropores [10]. It can be said that the biochar obtained from the OP

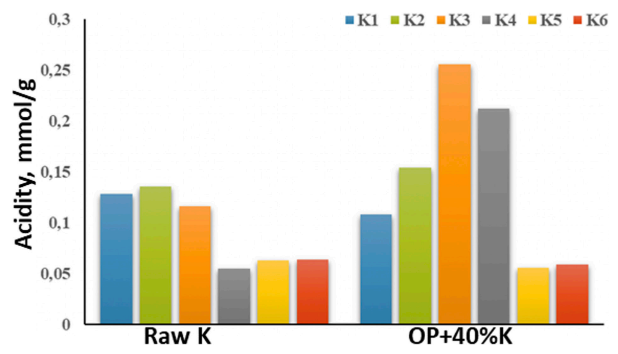


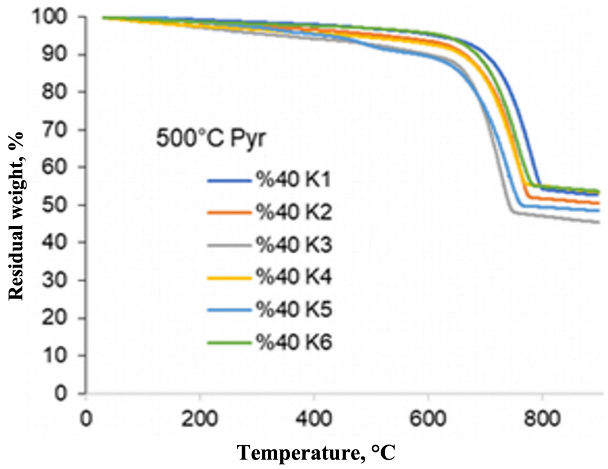
Figure 4. Surface acidity of biochars.

pyrolysis using K6 catalyst had a more granular distribution, and the lignocellulosic structures are more decomposed by the effect of this catalyst. A similar situation was observed in SEM images of biochars obtained with other catalysts.

The surface acidity values of the pyrolysis biochars obtained as a result of the pyrolysis of OP with different catalysts at 40% dose and 500°C were presented in Figure 4. According to the graph, acidity of raw catalysts generated from the travertine was higher than the raw catalysts of natural stone. However, this situation was not valid for the pyrolysis biochars. As for biochars, the highest surface acidity was observed at biochars obtained pyrolysis of OP with K3 and K4 catalysts. Therefore, it can be emphasized that used chemicals as coagulant during the physicochemical treatment of marble wastewater have effect on the biochar surface acidity.

The TGA thermograms and thermal resistance values of the pyrolysis biochars were presented in Figure 5. It can be stated that the thermal strengths up to about 420°C were close to each other and the residual masses of biochars obtained from pyrolysis with K1, K4 and K6 were similar to each other. Residual percentages ranged from 46 to 54.5%. DT1 (565°C) and T10 (701°C) values of OP+K1 pyrolysis biochars were higher than biochars obtained with other catalysts.

The heat values and ash percentages of raw catalysts, raw OP+K mixtures and pyrolysis biochars obtained at 40% dose, 500°C were presented in Table 2. The heating values of the raw catalysts were close to each other and vary in the range of 5.8–7.08 cal/g. Due to the high moisture content of the OP waste, the heating values of the raw OP+K mixtures



Sample		Thermal resistance values					Residual at 850°C (%)
Type	40% catalyst	DT1* (°C)	DT2** (°C)	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	
OP pyrolysis biochars, 5°C/min	K1	565	-	612	701	-	53.35
	K2	402	593	523	664	-	51.09
	K3	391	559	339	600	743	46.22
	K4	319	596	462	659	-	54.29
	K5	391	566	423	583	764	48.97
	K6	511	-	625	685	-	54.33

*DT1-first decomposition temperature; **DT2-second decomposition temperature; T5, 10, 50: Temperatures at which 5%, 10% and 50% decomposition occurs

Figure 5. Thermal characteristics of biochars.

were quite low and close to each other. While the biochar sample with the highest calorific value in OP+K pyrolysis was obtained with the K4 catalyst with a calorific value of 1193 cal/g, the biochar obtained with the K1 and K6 catalysts gave a similar calorific value. However, the calorific values of all biochars were mostly lower than the conventional fuel. This can be attributed to the high catalyst ratio found in the biochars. Therefore, usage of produced biochars as fuel is not recommended but they can be used as catalysts for another pyrolysis cycle thanks to high catalyst ratio.

Table 2. Heating value and ash percentages of raw catalysts, raw OP+K mixtures and pyrolysis biochars

Catalyst	K1	K2	K3	K4	K5	K6
Raw catalyst heat value (cal/g)	7.08	8.6	6	5.8	6.9	6.5
Raw catalyst ash content (%)	63.9	56.4	58.7	55.4	56.2	87.1
OP+40%K heating value (cal/g)						
Raw mixture	7.3	19.2	8.6	11.4	13.4	9.5
500°C Pyr	1041.1	800.2	781.1	1193.4	967.6	1087.6
OP+40%K ash content (%)						
Raw mixture	24.2	25.0	23.2	24.3	21.7	19.0
500°C Pyr	51.1	49.4	50.9	49.5	51.5	50.5

The ash contents of the raw catalysts vary between 55.38% and 87.06%, and the highest ash content belongs to the K6 catalyst. There was no direct reflection of the ash contents of the raw catalysts to the ash contents of the mixtures. In OP samples, no significant difference was observed in terms of ash contents for all catalysts and close values were obtained (Table 2). Pyrolysis biochar contained higher ash quantity than raw mixtures. This can be connected to the presence of the catalyst and increased concentration of inorganic components and organic matter pyrolytic reaction residues in the biochar content.

CONCLUSIONS

In this study, different marble sludge types were used in the OP pyrolysis process as catalyst and biochars obtained at catalytic pyrolysis process were examined in terms of surface morphology, surface acidity, thermal behavior, heating, and ash value. While the pyrolysis biochars and liquids quantity were close to each other for all catalyst type, obvious difference was observed in the gas volumes. The highest gas volume obtained at OP-K1 pyrolysis process. All biochar samples had rough and amorphous structure and OP pyrolysis using K6 catalyst had a more granular distribution, and the lignocellulosic structures are more decomposed by the effect of this catalyst. Although no systematic effect was obtained for the surface acidity of the biochars, an increment was observed in the surface acidity values of the biochars compared to the raw catalyst. As for thermal characteristics of biochars, it can be stated that OP-K1 biochars have higher DT1 (565°C) and T10 (701°C) values comparing to the others. The highest calorific values in OP+K pyrolysis biochars were obtained with K4 (1193 cal/g), K6 (1087 cal/g) and K1 (1041 cal/g), respectively. Usage of produced biochars as fuel is not recommended since their heat values are not high as much as conventional fuels, however; they can be used as catalysts for another pyrolysis cycle thanks to high catalyst ratio. All in all, K1 catalyst can be recommended for olive pomace catalytic pyrolysis when biochars are evaluated in terms of yield and characteristics.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Prioritization of upcycling and recycling applications for the management of waste printed circuit boards by using S-LCA and MCDM

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ABSTRACT

In this study, the upcycling and recycling applications for the management of waste printed circuit boards (PCBs) were compared through the sequential application of Streamlined Life Cycle Assessment (S-LCA) and Multi-Criteria Decision Making (MCDM) techniques. Upcycling applications were determined as gold, copper-tin alloy, lead, copper recovery and activated carbon production. And, portland cement, aggregate, sawdust, fiberglass and styrene butadiene rubber (SBR) productions were taken account as recycling applications. At the S-LCA stage, CML-IA baseline and ReCiPe 2016 methods were used for the characterization. For the MCDM study, environmental, technical and economic criteria were determined. Remarkable characterization results of S-LCA were used as the environmental criteria of MCDM. The Entropy method was used for the weighting of the criteria. TOPSIS method was used to compare the alternatives based on weighted criteria. S-LCA study shows that impact categories of Abiotic Depletion Potential (element basis), Total Ecotoxicity Potential and Human Toxicity Potential are the major impact categories. MCDM study shows that the gold recovery (0.9845) as an upcycling application and SBR production (0.7361) as a recycling application have been determined as the first applications to be applied to waste PCBs in terms of environmental, technical and economic aspects.

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INTRODUCTION

Rapid changes in technological devices and the decline in their lifespan has become a problem in the management of waste electrical and electronic equipment (WEEE). In 2019, the world generated a striking 53.6 million metric tons (Mt) of e-waste and is projected to expand to 74.7 Mt in 2030 [1]. WEEE is often referred to as urban mine, and the estimated value of all raw materials in global e-waste generated in 2019 was approximately USD 57 billion. This monetary value is largely concentrated in printed circuit boards (PCBs), which are the most valuable component of e-waste, comprising approximately 4–7% of the total mass of WEEE [2, 3]. The PCBs are composed of a mixture of metals (40%), plastics (30%) and ceramics (30%) (Van Yken et al. [2]). In addition to non-metal components, such as plastics, glass fibers and ceramics, there are a large number of valuable metals in waste PCBs, which have high economic value and industrial value [4]. Base metals such as copper, iron, aluminum, nickel, lead, chromium, and antimony are present in percentage levels, while other valuable elements such

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as gold, silver, and palladium appear at minute, but not negligible, ppm levels [5]. From that point of view, managing of the waste PCBs are a critical concern and should be realized based on circular economy principles because of their valuable metallic/non-metallic content. At that point, recycling and upcycling come to the fore.

Recycling is generally described as the reuse of waste materials and sometimes different process are required for waste recovery or converting into products, materials, or ingredients [6]. Recycling can reduce the use of raw materials and reduce waste through a closed loop system [7]. On the other hand, upcycling has been defined as "the enhancement of the value of waste material or discarded products through the recycling process. Upcycling converts waste streams into products of higher value than their starting forms [8, 9]. Upcycling of waste PCBs has more importance for the metallic parts of PCBs. WEEE, and also waste PCBs, can be candidate for sustainable resources since they contain precious and rare earth metals. For example, the concentration of Au in WEEE is higher than that in mined Au ores. The recovery of these valuable metals from solid wastes offers an alternative as critical resources become exhausted, and mitigates the negative environmental impact of traditional mining from ores and downstream solid waste disposal [8]. At that point, upcycling of waste PCBs supports urban mining which is also based on the value recovery of secondary raw materials from anthropogenic sources through biological, chemical, or physical procedures and technological input [10]. Traditional urban mining methods use extractive metallurgy, mainly pyrometallurgical and hydrometallurgical processes to liberate metals from encased platforms like waste PCBs [4, 8]. Pyrometallurgy is the traditional and most common approach for base metal and precious metal extraction from e-waste. However, pyrometallurgical facilities are complex and represent a significant economic investment [2]. Hydrometallurgical processes are more selective and leach metals from waste materials using specific strong acid mixtures known as lixiviants, but secondary aqueous waste streams of strong acid are generated [8, 11].

There are various upcycling and recycling applications to be applied to waste PCBs. On the other hand, it is difficult to determine in advance which of these applications would be more environmentally, technically, and economically viable. At that point, sequential application of Life Cycle Assessment (LCA) and Multi-Criteria Decision-Making (MCDM) techniques is very helpful to manage this problem. LCA is a useful tool to determine the environmental impacts resulted from products and services. An LCA allows for an evaluation of how impacts are distributed across processes and life cycle stages [12]. In the literature, there are various LCA studies for waste PCBs. Rezaee et al. [13] designed a study to investigate the environmental aspects of step-wise glycine leaching for precious metals recovery from waste PCBs. A comprehensive LCA focusing on metal recovery from low-grade PCBs was undertaken by Kouloumpis and Yang [14]. Pokhrel et al. [15] assessed the environmental and economic performance of recovering nine metal elements (aluminum (Al), copper (Cu), gold (Au), lead (Pb), nickel (Ni), silver (Ag), tin (Sn), zinc (Zn), and iron (Fe)) and two non-metal materials (resin and glass-fiber) from the waste PCBs. Another LCA study providing an environmental impact assessment of the black copper smelting route for the recovery of valuable metals from PCB was performed by Ghodrat et al. [16]. MCDM is a sub-branch of Decision Sciences and is based on the process of modeling and analyzing the decision process according to its criteria. MCDM techniques have been used in areas of energy-environment-sustainability, supply chain and quality management, materials, project management, security and risk management, manufacturing systems, production management, operational research and soft computing, technology management, strategic management, tourism management, knowledge management, and other areas. Among these, the application field of energy-environment-sustainability had a maximum share with 13% [17]. There are many MCDM studies regarding WEEE management [18–22]. Among them, the study of Grimes and Maguire (2021) [23] stands out regarding the subject of this study. They have used MCDM for critical metal recovery priorities from WEEE from the points of economic availability, political influences, ease of recycling, potential for substitution and likely development of new raw material sources. Their study did not consider environmental concerns and so on LCA. Le et al. [24] proposed a new model for evaluating metal recycling efficiency from PCBs. They used three criteria: mass, environmental impacts and natural resources conservation. They weighted the criteria by Entropy method and used LCA for environmental impacts (damage to ecosystems and damage to human health from Eco-Indicator 99 method) data. On the other hand, their study was limited with the metals and did not consider non-metallic end products. Different from the study of Le et al. (2013) [24], this study aims to prioritize the upcycling and recycling applications of based on metallic and non-metallic parts of waste PCBs by using LCA and MCDM techniques sequentially.

MATERIALS AND METHODS

For the purpose of the study, firstly five different materials replacements were determined for both upcycling and recycling. A Streamlined LCA (S-LCA) and MCDM studies were sequentially realized to evaluate these replacements.

Streamlined LCA (S-LCA) Study

A S-LCA was applied to less the data requirement for complex products that can be produced by upcycling and recycling methods. The S-LCA methodology used in this study follows the International Organization for Standardization (ISO) 14040 (2006) [25] and ISO 14044 (2006) [26] guidelines, which comprise four stages; Goal and Scope Definition, Life Cycle Inventory (LCI) Analysis, Life Cycle Impact Assessment (LCIA), and Interpretation.

Table 1. Material replacements by upcycling

Code	Parts of PCB to be processed	Material to be obtained by upcycling	Material to be replaced	Reference
U1	Metallic parts	Gold	Gold mine	[27]
U2	Metallic parts	Copper-tin alloy	Bronze production	[28]
U3	Metallic parts	Lead	Lead mine	[29]
U4	Non-metallic parts	Activated carbon	Activated carbon	[30]
U5	Metallic parts	Copper	Copper mine	[31]

Table 2. Material replacements by recycling

Code	Parts of PCB to be processed	Material to be obtained by recycling	Material to be replaced	Reference
R1	Non-metallic parts	Filling material to be used for self-compacting concrete	Portland cement (PC)	[32]
R2	Non-metallic parts	Filler to be used in the cement and construction industries	Aggregate	[33]
R3	Non-metallic parts	Performance enhancing agent for wood plastic composite	Sawdust	[34]
R4	Non-metallic parts	Soundproofing material	Fiberglass (FB)	[35]
R5	Non-metallic parts	Asphalt modifier product	Styrene butadiene rubber (SBR)	[36]

Table 3. Ecoinvent data for material replacement by upcycling

Material to replaced	Corresponding ecoinvent data	Reference
Gold mine	Gold production	[37]
Bronze	Bronze production	[38]
Lead mine	Primary lead production from concentrate	[39]
Activated carbon	Activated carbon production, granular from hard coal	[40]
Copper mine	Copper production, cathode, solvent extraction and electrowinning process	[41]

Table 4. Ecoinvent data for material replacement by recycling

Material to replaced	Corresponding ecoinvent data	Reference
Portland cement	Cement production, Portland	[42]
Aggregate	Sand quarry operation, open pit mine	[43]
Sawdust	Suction, sawdust	[44]
Fiberglass	Glass fibre production	[45]
Styrene butadiene rubber	Synthetic rubber production	[46]

Goal and Scope Definition

The purpose of this S-LCA study is to compare the material replacements obtained by upcycling and recycling applied/can be applied to waste PCBs from an environmental point of view. Functional unit was applied as a 1 ton of waste PCB. The system boundaries cover the direct replacement of the new material to be obtained by the upcycling and recycling, which will be applied to the waste PCB, with the existing material. The system boundaries are considered as cradle-to-gate, starting from the raw material acquisition for the existing material that the new product will replaced, and covering the production process of the material. The material replacements that can be obtained by upcycling and recycling applications are shown in Table 1 and 2, respectively.

Life Cycle Inventory

Ecoinvent data embodied in SimaPro 9.2 was used for the background data. The data sets corresponding to the materials to be replaced through upcycling and recycling were selected (Table 3 and Table 4).

Life Cycle Impact Assessment

Characterization calculations were performed by using CML-IA baseline (v3.06) and ReCiPe 2016 Midpoint (V1.04) characterization methods. Impact categories taking place in characterization methods were given in Table 5. Characterization results were normalized by using EU25+3, 2000 and World (2010) (which are included in CML and ReCiPe methods, respectively) normalization methods.

Table 5. Impact categories of the characterization methods

Impact categories	CML	ReCiPe
Abiotic depletion (element)	x	x
Abiotic depletion (fossil fuel)	x	x
Global warming potential	x	x
Ozon depletion potential	x	x
Human toxicity potential	x	x[a]
Freshwater aquatic ecotoxicity	x	x
Marine aquatic ecotoxicity	x	x
Terrestrial ecotoxicity potential	x	x[b]
Photochemical oxidation potential	x	x
Acidification potential	x	x[c]
Eutrophication potential	x	x[d]
Ionization radiation potential		x
Particulate matter formation potential		x
Land use		x
Water depletion		x

a: Carcinogenic and noncarcinogenic; b: Human health and terrestrial ecosystem; c: Terrestrial; d: Freshwater and marine.

MCDM Study

The flow chart followed for the MCDM study given in Figure 1. According to this flow chart, firstly criteria were determined (Table 6). The criteria of environmental criteria category will be the impact categories of the LCA study that have the higher results.

The importance weights of criteria were determined by using the entropy method. The entropy method evaluates the uncertainty in the information using probability theory. It shows that there is a wide distribution that presents more uncertainty than that of a sharply peaked one [47, 48]. Compared with various subjective weighting models, the biggest advantage of the EWM (….) is the avoidance of the interference of human factors on the weight of indicators, thus enhancing the objectivity of the comprehensive evaluation results [49]. This method includes first deciding objectives (decision matrix) and then calculations of the normalized decision matrix, probability of the attribute/response to take place, the entropy value of attribute/response, degrees of divergence (average information contained) by each response and after that entropy weight [50]. The smaller the entropy of the evaluated information criterion, the greater the weight of the information criterion [51].

The comparison of the upcycling and recycling applications was realized with TOPSIS method. The method is a technique to order preference by similarity to ideal solutions. This method determined the alternative closest to the positive ideal solution (PIS) and the farthest to the negative ideal solution (NIS) [52]. The method calculates the distances by using the n–dimensional Euclidean distance according to the number of the criteria of the problem [53]. Firstly, the normalized decision matrix by vector normalization is computed. The weighted normalized decision matrix is calculated. Positive and negative ideal solution sets are detected. For positive ideal solution, maximum and minimum criteria values are used for ascending order and descending order, respectively. For the negative ideal solution, the opposite approach is used. After then, the distance to the PIS and NIS from each alternative as separation values (Si^+ and Si^-) is computed by applying the Euclidean distance theory and the closeness coefficient for each alternative by using separation values is calculated. Finally, alternatives are ranked based on higher closeness coefficient [54, 55].

Table 6. The criteria for MCDM study

Criteria category	CN	Criteria	Ascending/descending order
Environmental	c1	LCA impact categories	Descending
	c2		
	c3		
Technical	c4	Ease of operation	Ascending
	c5	Operation time	Descending
	c6	Quality of material	Ascending
Economical	c7	Cost of energy	Descending
	c8	Operational cost	Descending
	c9	The value of product	Ascending

CN: Criteria number.

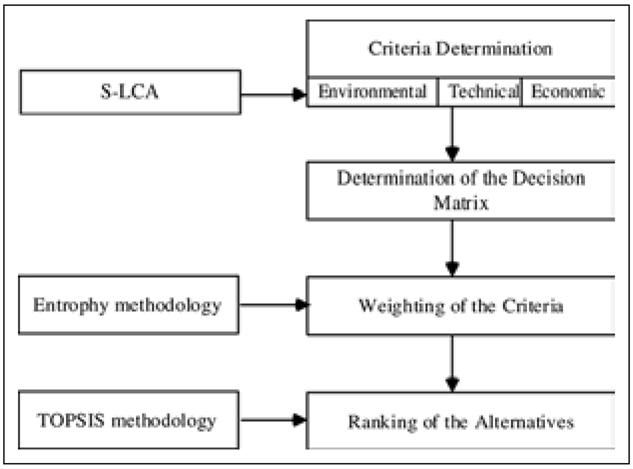

Figure 1. Flowchart of the MCDM study.

RESULTS

The characterization tables of material replacements that can be obtained by upcycling and recycling applications for CML according to impact category (IC) were given in Table 7 and 8. All the values in these tables are negative values which means these impacts will be avoided in the case of upcycling and recycling realized. The magnitude of negative values for upcycling applications are higher those of recycling applications. This situation depicts that, upcycling applications would be more environmentally effective than recycling applications.

Table 7. CML characterization results of upcycling applications

IC	Unit	Gold	Copper-tin alloy	Lead	Activated carbon	Copper
ADPe	kg Sb eq.	-5.81E+01	-2.05E-03	-6.81E-03	-9.97E-07	-2.02E-03
ADPff	MJ	-2.27E+05	-2.97E+01	-1.75E+01	-9.33E+01	-3.22E+01
GWP	kg CO_2 eq.	-1.80E+04	-2.57E+00	-1.99E+00	-8.29E+00	-2.79E+00
ODP	kg CFC-11 eq.	-1.69E-03	-1.91E-07	-7.02E-08	-1.14E-07	-2.21E-07
HTP	kg 1.4-DB eq.	-1.01E+04	-2.62E+01	-1.69E+00	-1.35E+00	-1.34E+02
FAEP	kg 1.4-DB eq.	-4.85E+03	-4.65E-01	-1.32E-01	-2.88E-02	-2.19E+00
MAEP	kg 1.4-DB eq.	-1.30E+07	-3.41E+03	-8.26E+02	-4.48E+03	-1.35E+04
TEP	kg 1.4-DB eq.	-5.96E+02	-7.30E-02	-9.78E-03	-7.27E-03	-3.62E-01
POP	kg C_2H_4 eq.	-4.53E+00	-5.80E-03	-1.99E-03	-2.41E-03	-2.08E-02
AP	kg SO_2 eq.	-1.63E+02	-1.57E-01	-5.28E-02	-5.24E-02	-5.47E-01
EP	kg PO_4 eq.	-4.36E+02	-6.46E-02	-5.38E-03	-3.74E-03	-2.19E-01

ADPe: Abiotic depletion (element); ADPff: Abiotic depletion (fossil fuel); GWP100: Global warming potential; ODP: Ozon depletion potential; HTP: Human toxicity potential; FAEP: Freshwater aquatic ecotoxicity potential; MAEP: Marine aquatic ecotoxicity potential; TEP: Terrestrial ecotoxicity potential; PbOP: Photochemical oxidation potential; AP: Acidification potential; EP: Eutrophication potential.

Table 8. CML characterization results of recycling applications

IC	Unit	PC	Aggregate	Sawdust	FB	SBR
ADPe	kg Sb eq.	-1.19E-08	-4.54E-10	-7.28E-08	-1.87E-06	-6.88E-05
ADPff	MJ	-2.35E+00	-2.54E-02	-2.69E+01	-3.22E+01	-7.42E+01
GWP	kg CO_2 eq.	-7.14E-01	-1.90E-03	-2.00E+00	-2.57E+00	-2.52E+00
ODP	kg CFC-11 eq.	-2.02E-08	-2.50E-10	-2.44E-07	-2.22E-07	-6.31E-07
HTP	kg 1.4-DB eq.	-1.82E-02	-1.86E-04	-2.26E-01	-1.49E+00	-2.34E-01
FAEP	kg 1.4-DB eq.	-6.30E-04	-8.69E-06	-1.33E-02	-1.31E-02	-1.54E-02
MAEP	kg 1.4-DB eq.	-1.03E+01	-2.27E-01	-3.24E+02	-1.97E+03	-4.70E+02
TEP	kg 1.4-DB eq.	-7.84E-04	-9.34E-07	-1.21E-03	-1.72E-03	-1.07E-03
POP	kg C_2H_4 eq.	-3.61E-05	-3.50E-07	-5.76E-04	-5.66E-04	-5.32E-04
AP	kg SO_2 eq.	-9.92E-04	-1.23E-05	-1.29E-02	-1.52E-02	-9.81E-03
EP	kg PO_4 eq.	-1.53E-04	-2.44E-06	-3.37E-03	-1.45E-03	-1.01E-03

ADPe: Abiotic depletion (element) (kg Sb eq.); ADPff: Abiotic depletion (fossil fuel); GWP100: Global warming potential; ODP: Ozon depletion potential; HTP: Human toxicity potential; FAEP: Freshwater aquatic ecotoxicity potential; MAEP: Marine aquatic ecotoxicity potential; TEP: Terrestrial ecotoxicity potential; POP: Photochemical oxidation potential; AP: Acidification potential; EP: Eutrophication potential.

Characterization tables of materials replacements by upcycling and recycling applications for ReCiPe were given in Table 9 and 10. These values are differing from CML results since the units are different except GWP. Total GWP values for upcycling and recycling applications calculated by CML and ReCiPe are the almost same (-1.8 E+04 kg CO_2 eq. and -7.81 E+00 kg CO_2 eq. for CML; -1.83 E+04 kg CO_2 eq. and 6.60 E+00 kg CO_2 eq. for ReCiPe, respectively). As same for the CML results, according to the ReCiPe results, gold recovery is the major replacement that can be the most effective from the environmental point of view.

Normalization results of upcycling and recycling applications were presented in Figures 2–5. Percentile distribution of the normalization values were used to determine which impact category and characterization result (between CML and ReCiPe) are going to be used for MCDM.

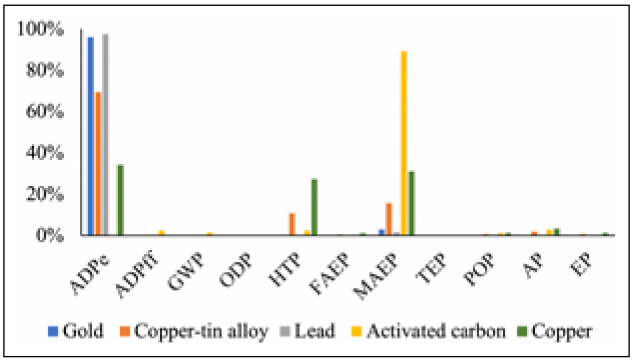

Figure 2. CML normalization results of upcycling applications.

Table 11 shows the impact category determination for MCDM. This determination was made based on the percentile distribution of upcycling and recycling applications calculated by CML and ReCiPe normalization methods. For upcycling,

Table 9. ReCiPe characterization results of upcycling applications

IC	Unit	Gold	Copper-tin alloy	Lead	Activated	Copper
GWP	kg CO_2 eq.	-1.83E+04	-2.61E+00	-2.02E+00	-8.54E+00	-2.84E+00
ODP	kg CFC-11 eq.	-1.32E-02	-3.19E-06	-9.96E-07	-1.59E-06	-6.70E-06
IRP	kBq Co-60 eq.	-1.57E+02	-5.76E-02	-1.76E-02	-1.29E-02	-5.36E-02
OFPhh	kg NO_x eq.	-1.65E+02	-2.74E-02	-1.07E-02	-1.82E-02	-5.20E-02
PMFP	kg PM 2.5 eq.	-4.83E+01	-4.85E-02	-1.34E-02	-1.67E-02	-1.59E-01
OFPte	kg NO_x eq.	-1.67E+02	-2.79E-02	-1.09E-02	-1.83E-02	-5.30E-02
TAP	kg SO_2 eq.	-1.34E+02	-1.31E-01	-4.40E-02	-4.28E-02	-4.58E-01
FEP	kg P eq.	-1.35E+02	-1.97E-02	-1.19E-03	-4.23E-04	-6.90E-02
MEP	kg N eq.	-6.84E-01	-3.31E-04	-9.39E-05	-1.10E-05	-1.09E-03
TEP	kg 1.4-DCB	-9.60E+04	-1.16E+03	-3.49E+01	-3.81E+00	-5.37E+03
FAEP	kg 1.4-DCB	-2.83E+03	-2.27E-02	-2.42E-02	-1.56E-03	-8.06E-02
MAEP	kg 1.4-DCB	-6.56E+03	-5.38E-01	-4.53E-02	-3.95E-03	-2.44E+00
HTPcar	kg 1.4-DCB	-1.36E+02	-3.29E-01	-1.89E-01	-2.29E-02	-1.60E+00
HTPncar	kg 1.4-DCB	-1.11E+05	-4.72E+01	-4.78E+01	-1.13E+00	-2.31E+02
LU	m^2a crop eq.	-6.67E+02	-1.43E-01	-2.05E-02	-5.44E-01	-3.28E-01
ADPe	kg Cu eq.	-4.26E+03	-1.31E+00	-5.31E-01	-5.32E-04	-1.89E+00
ADPff	kg oil ed	-5.41E+03	-7.00E-01	-4.07E-01	-2.14E+00	-7.61E-01
WD	m^3	-8.21E+04	-5.12E+01	-3.58E+00	-1.58E-02	-1.17E+02

GWP: Global warming potential; ODP: Ozon depletion potential; IRP: Ionization radiation potential; OFPhh: Ozone formation potential, human health; PMFP: Particulate matter formation potential; OFPte: Ozone formation potential, terrestrial ecosystem; TAP: Terrestrial acidification potential; FEP: Freshwater eutrophication potential; MEP: Marine eutrophication potential; TEP: Terrestrial ecotoxicity; FAEP: Freshwater ecotoxicity potential; MAEP: Marine ecotoxicity potential; HTPcar: Human toxicity potential (carcinogenic); HTPncar: Human toxicity potential, noncarcinogenic; LU: Land use; ADPe: Mineral depletion potential; ADPff: Fossil depletion potential; WD: Water depletion.

Table 10. ReCiPe characterization results of recycling applications

IC	Unit	PC	Aggregate	Sawdust	FB	SBR
GWP	kg CO_2 eq.	-7.01E-01	-1.85E-03	-1.88E+00	-2.39E+00	-2.33E+00
ODP	kg CFC-11 eq.	-4.89E-08	-1.48E-09	-3.27E-06	-4.99E-06	-2.76E-06
IRP	kBq Co-60 eq.	-2.94E-02	-9.14E-04	-3.73E-01	-3.40E-01	-2.56E-01
OFPhh	kg NO_x eq.	-1.05E-03	-1.71E-05	-1.88E-02	-7.79E-03	-4.95E-03
PMFP	kg PM 2.5 eq.	-2.65E-04	-4.33E-06	-5.52E-03	-3.98E-03	-3.03E-03
OFPte	kg NO_x eq.	-1.07E-03	-1.74E-05	-1.93E-02	-7.90E-03	-5.38E-03
TAP	kg SO_2 eq.	-7.83E-04	-9.30E-06	-9.78E-03	-1.23E-02	-7.97E-03
FEP	kg P eq.	-2.49E-06	-3.61E-08	-2.32E-05	-1.03E-04	-9.72E-05
MEP	kg N eq.	-3.31E-07	-7.48E-09	-5.29E-04	-3.43E-05	-9.34E-06
TEP	kg 1.4-DCB	-1.73E-01	-1.58E-03	-6.31E+00	-1.24E+01	-1.76E+00
FAEP	kg 1.4-DCB eq.	-7.11E-05	-7.41E-07	-3.07E-03	-3.71E-03	-1.66E-03
MAEP	kg 1.4-DCB	-1.04E+00	-1.19E-02	-5.69E+01	-2.47E+01	-2.11E+01
HTPcar	kg 1.4-DCB eq.	-8.06E-03	-3.34E-04	-1.40E-01	-1.64E+00	-4.61E-01
HTPncar	kg 1.4-DCB eq.	-9.95E-01	-1.10E-02	-4.86E+01	-1.25E+02	-1.86E+01
LU	m^2a crop eq.	-3.92E-04	-2.12E-04	-9.26E+01	-4.91E-03	-3.18E-02
ADPe	kg Cu eq.	-1.28E-04	-3.69E-06	-1.49E-03	-2.58E-03	-3.33E-03
ADPff	kg oil eq.	-5.40E-02	-5.93E-04	-6.38E-01	-7.77E-01	-1.74E+00
WD	m^3	-1.21E+00	-2.30E-02	-1.61E+01	-7.31E+00	-5.44E+00

GWP: Global warming potential; ODP: Ozon depletion potential; IRP: Ionization radiation potential; OFPhh: Ozone formation potential, human health; PMFP: Particulate matter formation potential; OFPte: Ozone formation potential, terrestrial ecosystem; TAP: Terrestrial acidification potential; FEP: Freshwater eutrophication potential; MEP: Marine eutrophication potential; TEP: Terrestrial ecotoxicity; FAEP: Freshwater ecotoxicity potential; MAEP: Marine ecotoxicity potential; HTPcar: Human toxicity potential (carcinogenic); HTPncar: Human toxicity potential, noncarcinogenic; LU: Land use; ADPe: Mineral depletion potential; ADPff: Fossil depletion potential; WD: Water depletion.

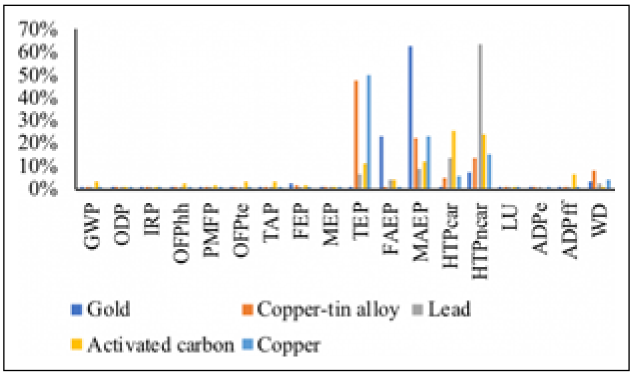

Figure 3. ReCiPe normalization results of upcycling applications.

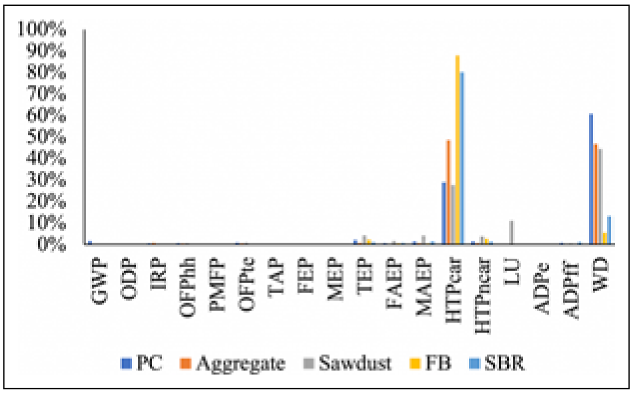

Figure 5. ReCiPe normalization results of recycling applications.

ADPe was found as the major impact category whereas FAEP and MAEP were determined as important categories for ReCiPe (Table 11, Level I). Then all three were selected for Level II. For recycling, ADPe and MAEP are the important impact categories for CML, those for ReCiPe were HTPcar and WD. Since MAEP has already been in Level II, only HTPcar was selected for Level II. So, ADPe, total ecotoxicity, and HTP (sum of HTPcar and HTPncar) were determined for Level III. The impact categories at the Level III were selected for the environmental criteria of the MCDM study and their characterization values were used in decision matrixes with the values/scores of technical and economic criteria for upcycling and recycling applications (Table 12 and 13, respectively).

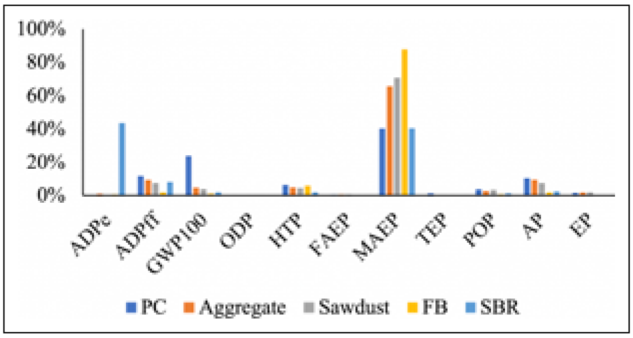

Figure 4. CML normalization results of recycling applications.

The weighting values of criteria obtained from Entropy method are given in Table 14. For both cases the c1 (ADPe) criterion was found to be the most important criterion. This situation resulted from the wide range of distribution in ADP values of upcycling and recycling applications.

TOPSIS results and general ranking of the alternatives are presented in Table 15 and Table 16. In these tables, Si^+, Si^- and Ci shows the distances from the ideal solution, nadir ideal solutions and relative closeness to the ideal solution, respectively. Table 15 shows that the gold recovery is the most important upcycling application with the highest Ci value (0.9845). Although the second upcycling application was the production of copper-tin alloy, it was observed that the Ci value (Ci: 0.1154) was quite low compared to the gold recovery. The Ci values of other upcycling applications are not remarkable (<0.1) compared to the values of gold recovery and copper-tin alloy recovery.

According to Table 16, recycling applications were prioritized as SBR>FB>PC>aggregate>sawdust. The highest Ci value is SBR (Ci: 0.7361), while other Ci values are closer to each other. There is no remarkable difference between PC and aggregate.

CONCLUSION

In this study, upcycling and recycling applications of waste PCBs were examined by using S-LCA and MCDM. S-LCA was applied by using material replacement data to have

Table 11. Impact category determination table for MCDM

Applications	Level I		Level II	Level III
	Major impact categories			
	CML	ReCiPe		
Upcycling	ADPe (96%)	FAEP (23%)	ADPe	ADPe
		MAEP (63%)	FAEP	[1]Total
			MAEP	
Recycling	ADPe (13%)	HTPcar (76%)	HTPncar	Ecotoxicity
	MAEP (71%)	WD (14%)		[2]HTP

1: The sum of terrestrial ecotoxicity, freshwater ecotoxicity and marine ecotoxicity; 2: The sum of human toxicity (carcinogenic) and human toxicity (non-carcinogenic).

Table 12. The decision matrix for upcycling applications

CN	Unit/Score	Upcycling applications[a]				
		U1	U2	U3	U4	U5
c1	kg Sb ed.	-5.81E+01	-2.05E-03	-6.81E-03	-9.97E-07	-2.02E-03
c2	kg 1,4-DCB	-1.05E+05	-1.16E+03	-3.50E+01	-3.82E+00	-5.37E+03
c3	kg 1,4-DCB	-1.11E+05	-4.75E+01	-4.80E+01	-1.15E+00	-2.33E+02
c4[b]	score	3	6	7	2	4
c5[c]	score	7	3	4	7	4
c6[d]	score	6	3	8	8	7
c7	$/ton	0.35	0.58	0.39	1.29	0.59
c8[e]	score	7	3	4	5	6
c9	$/ton	58,500	50,000	2,400	1,600	11,200

a: U1: Gold U2: Copper-tin alloy U3: Lead U4: Activated carbon U5: Copper; b: U1: Chemical + leaching=3, U2: Physical process +Thermal process =6, U3: Physical process =7, U4: Physical process + pyrolysis =2, U5: Chemical=4; c: Score value is defined to average operation times U1: 13h, U2: 1.5h, U3: 4h, U4: 12h, U5: 4.5h; d: U1: Higher than 95% gold dissolution. U2: Higher than %8 bronze dissolution. U3: Higher than 98% lead recovery. U4: Activated carbon recovery that has %98 adsorption capacity. U5: 98% copper recovery; e: U1: Chemical consumption. U2: No chemical consumption. U3: Nitrogen consumption. U4: CO_2 consumption. U5: Mineral acid consumption.

Table 13. The decision matrix for recycling applications

CN	Unit/Score	Recycling applications[a]				
		R1	R2	R3	R4	R5
c1	kg Sb eq.	-1.19E-08	-4.54E-10	-7.28E-08	-1.87E-06	-6.88E-05
c2	kg 1.4-DCB	-1.21E+00	-1.35E-02	-6.32E+01	-3.71E+01	-2.29E+01
c3	kg 1.4-DCB	-1.00E+00	-1.13E-02	-4.87E+01	-1.27E+02	-1.91E+01
c4b	score	7	7	6	6	5
c5c	score	9	8	7	3	8
c6d	score	5	6	6	7	5
c7	$/ton	0.06	0.32	4.36	0.13	0.44
c8e	score	4	3	5	4	6
c9	$/ton	85	0.080	210	1000	1900

a: R1: Portland cement. R2: Aggregate. R3: Sawdust. R4: Fiber glass. R5: Styrene Butadiene Rubber; b: R1: Physical process=7. R2: Physical process =7. R3: Physical process +Thermal process =6. R4: Physical process +Thermal process =6. R5: Physical process + pyrolysis=5; c: Score value is defined to average operation times R1: Average operation time 180 days. R2: 28 days. R3: 14 hours. R4: 1h; R5: 2 days; d: R1: 5% waste PCB addition R2: 10–25% waste PCB addition. R3: 10–20% waste PCB addition. R4: Virgin fiber glass production. R5: 4% waste PCB addition; e: R1: Chemical consumption. R2: No chemical consumption. R3: KH550 consumption. R4: Carbon powder consumption. R5 SBR consumption.

Table 14. Weighting values (w_i) of criteria for upcycling and recycling applications

CN	Upcycling applications	Recycling applications
c1	**0.295**	**0.333**
c2	0.249	0.123
c3	0.292	0.164
c4	0.017	0.002
c5	0.010	0.012
c6	0.009	0.002
c7	0.023	0.209
c8	0.008	0.006
c9	0.099	0.149

a rapid answer for environmental aspects. By using the MCDM, upcycling, and recycling applications were prioritized from an environmental, technical, and economic point of view. As a result, it is concluded that gold recovery and SBR production would be the primary focus applications for PCBs management in the circular economy concept.

This work has taken into account environmental, technical and economic aspects but can be extended to include other aspects such as social and applicability. Thus, more effective waste management will be ensured in terms of the circular economy. Additionally, this study was realized for only waste PCB, but it can be easily applied to other waste types as well. In conclusion, it is thought that the sequential application of S-LCA and MCDM provides a preliminary study that is useful in establishing a policy for waste management.

Table 15. TOPSIS results for upcycling applications

Applications	Si^+	Si^-	Ci	Ranking
U1	0.00770	0.4888	0.9845	1
U2	0.4819	0.0628	0.1154	2
U3	0.4883	0.0157	0.0311	4
U4	0.4888	0.0032	0.0066	5
U5	0.4802	0.0208	0.0415	3

U1: Gold; U2: Copper-tin alloy; U3: Lead; U4: Activated carbon; U5: Copper.

Table 16. TOPSIS results for recycling applications

Applications	Si^+	Si^-	Ci	Ranking
R1	0.3989	0.2041	0.3384	3
R2	0.4020	0.1916	0.3227	4
R3	0.4179	0.1178	0.2200	5
R4	0.3326	0.2679	0.4462	2
R5	0.1455	0.4057	0.7361	1

R1: Portland cement; R2: Aggregate; R3: Sawdust; R4: Fiberglass; R5: Styrene butadiene rubber.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Investigation of conversion of sunflower oil production wastes to high value compounds by supercritical CO_2

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ABSTRACT

The evaluation of wastes from edible oil production industry has increasing importance because of resources deficiency and growing population day by day. It was aimed to investigate the recovery potential of oil and valuable components from sunflower oil production wastes by using supercritical CO_2 (SC-CO_2) extraction as a green extraction method. In this context oil amounts, total phenolic content (TPC), total flavonoid content and antioxidant activities were analyzed. The waste samples obtained from filtration processes of the oil which were composed of oily bentonite (OB) and waxy perlite (WP). Soxhlet extraction was also applied on the waste samples to calculate extraction efficiencies of the SC-CO_2. It was observed that SC- CO_2 extraction was more effective for OB (27%, v/v) than WP (11%, v/v). In addition, the efficiency increased to 37% by mixing expanded perlite and OB sample to absorb moisture content of the waste and to increase the diffusion of carbon dioxide more easily. The statistical evaluation of the experiments was also conducted to determine the effect of independent variables on the recovery efficiencys. Pressure was detected more effective variables on the recovery values than temperature. The maximum recovery efficiencies of the oil and TPC were obtained at the 50 °C, 22.1 MPa and 60 °C, 20 MPa, respectively.

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INTRODUCTION

Recovery and reuse options for food processing industry wastes have increased importance to decrease food scarcity. Sunflower oil is the most consumed oil product in the World [1]. By-products of sunflower oil contain valuable components that can be used in the food industry [2]. Bio-oil production from sunflower seed husks by hydrothermal pre-treated pyrolysis has been reported as a recovery method [3]. Another study focused on the antioxidant activities of polysaccharides from the pulp of sunflower oil production [4]. Jadhav et al. [5] investigated the use of sunflower acid oil, which is a waste from vegetable oil refinery, as glucose-containing feedstock for sophorolipid production. In recent years, supercritical CO_2 (SC-CO_2) has been used as an innovative and environmentally friendly extraction method to produce high quality product [6]. Daraee et al. [6] studied the SC-CO_2 extraction of chlorogenic acid from sunflower (Helianthus annuus) seed kernels.

In all these studies, it is aimed to contribute to the food industry. However, as far as we know, the residual oil and valuable component potential in different fillers used in sunflower oil production stages has not been studied. At the same time, while many studies focus on a single waste

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material, our study aimed to evaluate several production wastes. In addition, these wastes can not be evaluated because they are flammable and are disposed of in municipal dumps. Therefore, the recovery potential of oil and valuable components from sunflower oil production waste was investigated with SC-CO_2 extraction.

MATERIALS AND METHODS

Materials

Samples were obtained from Guzeloglu food - Zevk sunflower oil company (Konya, Türkiye). Two main wastes were obtained from the production of sunflower oil after bleaching and winterization processes and were named as oily bentonite (OB) soil and waxy perlite (WP) soil, respectively. The production process of the company consisted of 4 stages: degumming and neutralization, bleaching, winterization (dewaxing) and finally deodorization. Deacidified neutral oil is firstly heated to certain temperatures and mixed with the bleaching adsorbent (bentonite soil) under vacuum. Bentonite/oil mixture is filtered through steel plate filters to separate oil from soil and to remove coloring matters, trace metals and hydroperoxide from oil. In winterization process, waxy substances which cause turbidity in the oil and spoil the appearance of the oil at low temperatures are removed from the oil by using an auxiliary substance (perlite) in a cold environment.

Experimental Design

The effect of pressure and temperature on the SC-CO_2 extraction was studied according to the experimental design (central composite design) created by using Minitab Software statistical program for the WP and OB sample (Table 1). The results were statistically evaluated by ANOVA test. Also, the effect of mixing expanded granular perlite with the wastes on SC-CO_2 extraction was investigated.

Table 1. Ranges of independent variables in the experiments

Independent variables	Min value	-1	Midpoint	+1	Max value
Temperature (°C)	36	40	50	60	64.1
Pressure (MPa)	7.93	10	15	20	22.1

SC-CO_2 Extraction

SC-CO_2 extraction was conducted with the Superex F-500 device (Biosan, Superex, Türkiye). The extractor has 500 mL column. Pressure and temperature of device can be increased up to 34.5 MPa and 70 °C, respectively.

For extraction experiments, 10 g sample was placed into device and falcon tube, in which the extract would accumulate, was placed in separator chamber. The CO_2 pump was started after temperature reached the desired value. The extraction process was carried out for 2 hours, the first 30 minutes being static and 90 minutes of dynamic flow mode. The extracts obtained from WP and OB were abbreviated as WPE and OBE, respectively.

Analysis Methods

Total oil content of the waste sample was analyzed by Soxhlet method [7] to determine extraction efficiency of the SC-CO_2 extraction method. Soxhlet extraction was applied to two raw samples. Extraction efficiency was calculated by dividing the amount of extract obtained by SC-CO_2 extraction by the oil content determined by the Soxhlet method.

The changes in the components of the extracts were monitored by total phenolic contents (TPC), total flavonoid contents (TFC) and antioxidant activity assays (ABTS and DPPH).

TPC of the samples were analyzed according to Singleton et al. [8] (with Folin–Ciocalteu reagent). Briefly, 20 µL of the extract was mixed with 1580 µL of methanol/water mixture and 100 µL of folin solution and then waited for 5 minutes. Then, 300 µL of sodium carbonate was added in the solution and vigorously mixed. The mixture was waited in the oven for 30 minutes at 45 °C for color development. At the end of the period, it was poured into numbered tubes and centrifuged at 4000 rpm for 5 minutes. The same procedures were performed for the witness sample. Finally, its absorbance at 765 nm was measured using a spectrophotometer (Hach-Lange, Dr 5000). A calibration chart was prepared using gallic acid as a standard. Total phenolic substance concentration (TFC) was expressed as mg gallic acid equivalents per 1 L of extract (mgGAE/L). Recovery efficiency (%RE, w/w) of TPC was calculated as the ratio of the TPC concentration in the extract to the TPC concentration obtained with the aid of n-hexane as soxhlet solvent.

TFC of the samples were analyzed according to Zhishen et al. [9]. The sample extracts were reacted with $NaNO_2$ and then with $AlCl_3$ to form a flavonoid-aluminum complex. The absorbance of these prepared solutions was read at 510 nm. Calibration chart prepared with quercetin standard was used in the calculation. The total amount of flavonoids was expressed in quercetin equivalents (mg QE/mL). TFC was calculated as mgQE/g by multiplying the TFC concentration by the volume of the extract in the mass of the extract.

Trolox equivalent antioxidant capacity were spectrophotometrically measured in respect of DPPH and ABTS radical scavenging activities (Hach-Lange, Dr 5000).

DPPH radical scavenging capacity were determined using 0.1 mM DPPH (2,2-diphenyl-1-picryhydrazyl radical) according to the Yu et al. [10]. 100 µL of sample was reacted with 1900 µL of methanolic DPPH• solution. The absorbance values of the mixture at 517 nm were read at 30 minutes after by zero with distilled water. Results were calculated with the aid of the trolox standard curve and expressed in trolox equivalents (µM TE).

ABTS radical cation scavenging capacity was determined as follows [11]; a 7 mM ABTS solution containing 2.45 mM potassium persulfate was prepared and the stock $ABTS^{\bullet+}$ solution was formed by keeping this solution in a dark environment at room temperature for 12–16 hours. $ABTS^{\bullet+}$ working solution was prepared by diluting the stock $ABTS^{\bullet+}$ solution with a water:etha-

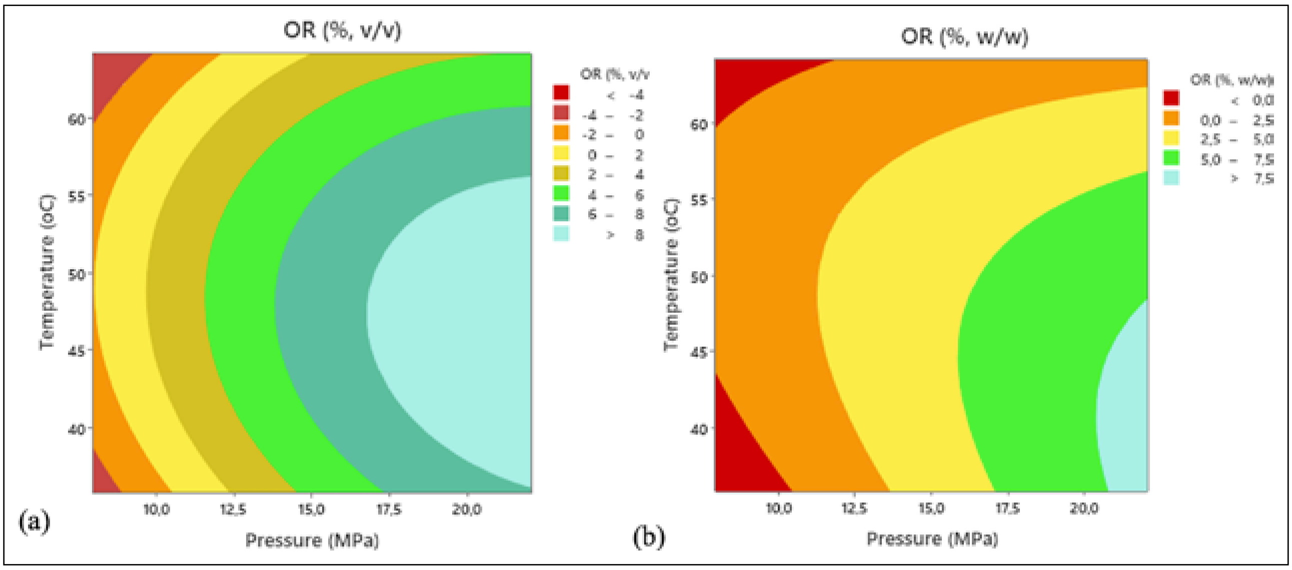

Figure 1. Binary effects of temperature and pressure on the oil recovery (OR) efficiency calculated by using **(a)** extract volume of WP and **(b)** extract mass of WP.

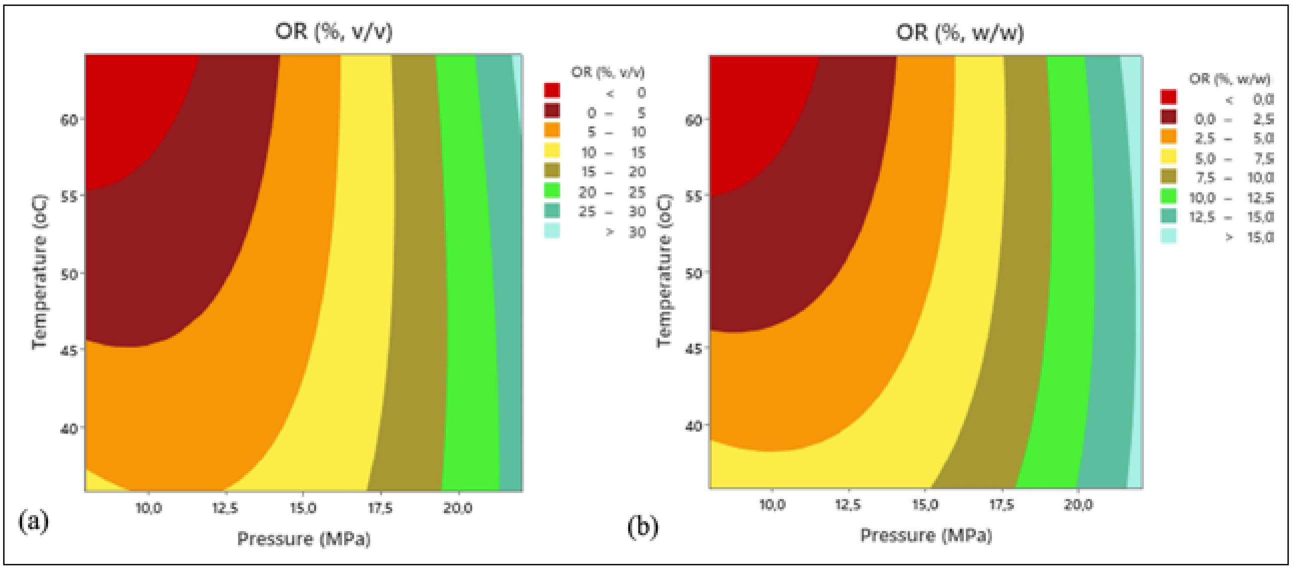

Figure 2. Binary effects of temperature and pressure on the oil recovery (OR) efficiency calculated by using **(a)** extract volume of OB and **(b)** extract mass of OB.

nol (1:1, v/v) mixture such that the total mixture had an absorbance of 0.70 at 734 nm. In the creation of the calibration chart and sample analysis; 1980 µL ABTS•+ working solution was added to 20 µL sample and mixed rapidly with the help of vortex, and its absorbance at 734 nm was determined after waiting for 6 minutes. Calibration chart was prepared using trolox as standard. The radical cation scavenging capacity was expressed in trolox equivalents (µM TE).

RESULTS AND DISCUSSION

Oil Recovery from the Waste Materials

Volumetric (v/v) and gravimetric (w/w) oil recovery (OR) efficiencies for SC-CO_2 extraction of the WP ranged from 1.5% to 11% and from 0.3% to 8%, respectively (Fig. 1). It was observed that amount of the extracts increased with the increase of pressure and decrease of temperature, and it was maximizing above 20 MPa. Similar to our results, it was reported that increased pressure (28–34 MPa) of SC-CO_2 and milling time of chia seeds increased oil yield, but higher temperature (60–80 °C) could decrease the yield [12].

Higher extraction efficiencys were obtained for SC-CO_2 extraction of the OB waste samples than WP. Volumetric and gravimetric oil recovery (OR) efficiencies for SC-CO_2 extraction of the OB wastes ranged from 0.2% to 27% (v/v) and from 0.5% to 16% (w/w), respectively (Fig. 2). The effect of expanded granular perlite (10 g) addition on the OB sample (20 g) was also investigated to increase the amount of extract at 40 °C and 20 MPa. Oil recovery efficiency in-

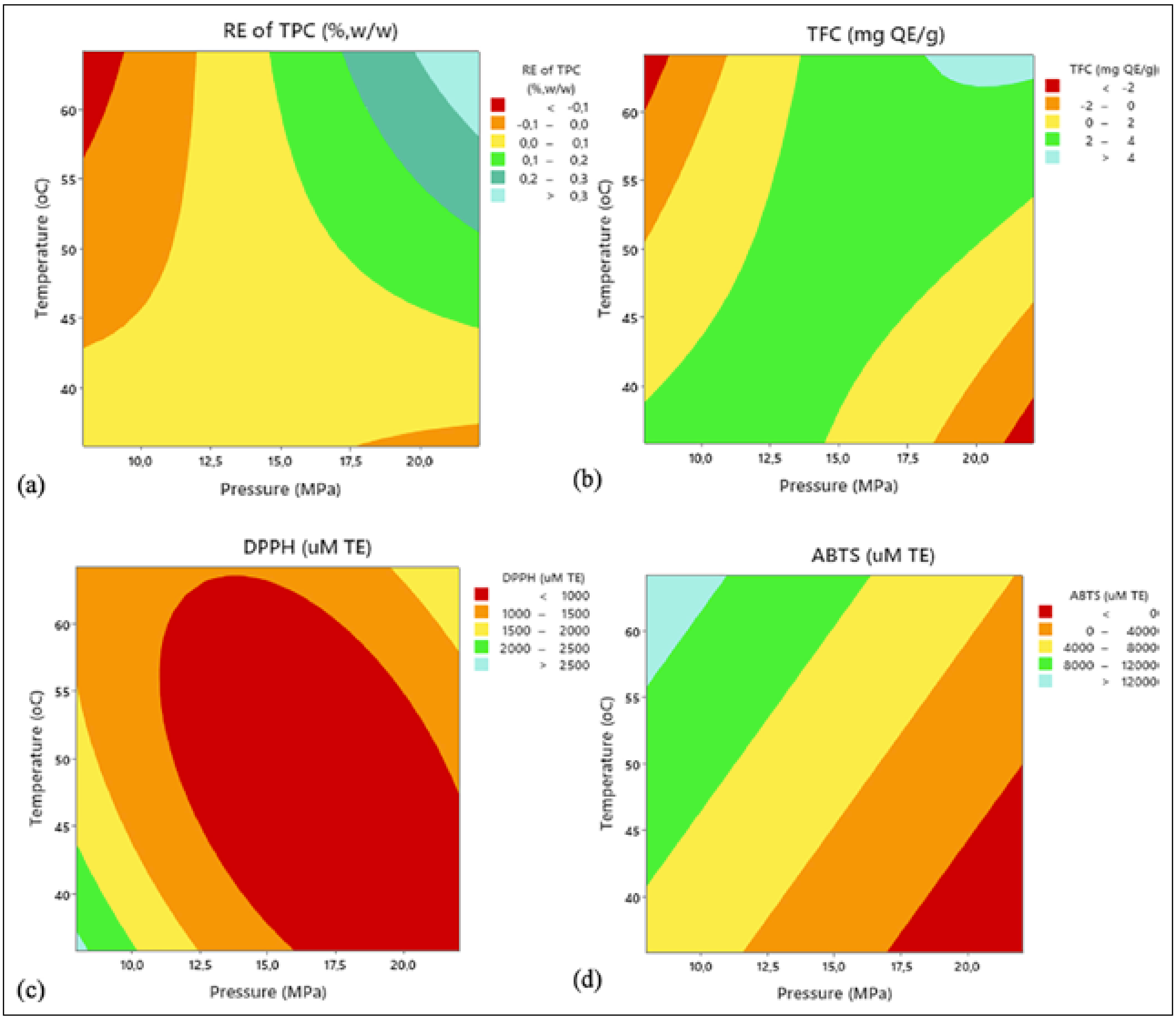

Figure 3. Binary effects of the experimental variables on the valuable components of WPE; **(a)** TPC value, **(b)** TFC value, **(c)** DPPH and **(d)** ABTS radical scavenging activity.

creased from 27% to 37% (v/v) and 16% to 19% (w/w) by using the expanded perlite. Expanded perlite might be absorb more easily the moisture content of the waste and also increase carbon dioxide diffusion with its porous structure.

Although higher extract amount usually can be obtained by using conventional chemicals such as hexane [12], it should be stated that SC-CO_2 extraction provides more stable, healthy extracts and lower toxic residue. However, it was reported in the literature that oil recovery efficiency of SC-CO2 could be comparable with Soxhlet extraction which used hexane [13]. This situation was caused by factors such as experimental variables or solvent selection. Similar to our study, the highest extract efficiency was obtained only at 40 °C and 25 MPa operating condition with SC-CO_2, and the extract efficiency obtained in Soxhlet extraction with hexane was achieved [13]. In the same study, it was stated that the sample obtained by SC-CO_2 extraction exhibited a higher oxidative induction time than that extracted with hexane.

The Change of Valuable Content

TPC recovery efficiencies of WPE were ranged between 0.001–0.3% (Fig. 3). The highest TPC recovery efficiency of WPE was above of 20 MPa and 60 °C. TFC/TPC ratio of the extracts were generally high and near to 1 showing high flavonoids content. TFC in the extract increased at the high pressure and temperature for WP extracts, while similar results were also obtained at lowest conditions (Fig. 3). Similarly, maximum TFC concentration for OBE was obtained as 3.94 mg QE /g at the condition of 60 °C and 20 MPa. It can be said that the increase in polarity and density of CO_2 at high pressure increases the solubility of some phenolic compounds [14]. Flavonoids are expected to be more soluble in SC-CO_2 than other phenolics because of their high molecular weight and relatively low polarity [15–17].

Antioxidant activities of WPE in respect of DPPH and ABTS radicals increased significantly by SC-CO_2 extraction compared to conventional extraction method

Table 2. Comparison of TPC, TFC and antioxidant activity values in literatures

Studies	Raw material	Extraction method	TPC (mg GAE/g)	TFC (mg QE /g)	Antioxidant activity (μMTE/g)	
In this study	WPE OBE	SC-CO_2	0–0.77 0–6.55	0–3.9 0.0–21	ABTS: 89–1878 72–9975	DPPH: 57–220 13–668
Neves et al. [18]	Sunflower cake (Shell and raw material mix)	Conventional extraction + Microwave-assisted extraction	12–14	–	ORAC: 180–260	
Ye et al. [19]	Sunflower florets	Pure solvents with increasing polarity (ethyl acetate, ethanol, methanol and water)	1.3–25	–	ABTS: 8.36–265.77	DPPH: 3.85–137
Weisz et al. [20]	-Dehulled sunflower kernels -Dehulled sunflower shells	Extracted twice by stirring aqueous methanol (60%) after n-hexane in a soxhlet extractor	29.38–41.8 0.4–0.86	–	–	–
Pajak et al. [21]	Sunflower seeds - sprouts	Shaking with methanol	4–9	25–45	ABTS: 32–72	DPPH: 24–48
Abdalla et al. [22]	Sunflower seeds	Shaking with methanol after n-hexane	22.2–33.1	1.02–3.34 mg RE/g	ABTS: 78–128.5	DPPH: 90.3–161.4

Table 3. ANOVA results for oil recovery (OR) efficiency and extract quality parameters of the WPE

ANOVA terms	OR (%, v/v)		OR (%, w/w)		TPC (%RE, w/w)		$DPPH^{\cdot}$ μM TE		$ABTS^{\cdot+}$ μM TE		TFC mg QE/g	
	F	p	F	p	F	p	F	p	F	p	F	p
Source	**Quadratic**		**Quadratic**		**Linear+ Interactions**		**Quadratic**		**Linear**		**Quadratic**	
Model	6.83	0.043	41.9	0.002	5.8	0.033	0.88	0.565	4.31	0.060	38.67	0.002
Temperature	1.66	0.267	28.5	0.006	2.03	0.204	0.01	0.927	2.93	0.131	10.94	0.030
Pressure	27.8	0.006	147	0.0002	10.72	0.017	1.23	0.329	5.68	0.049	9.63	0.036
Lack of fit	3.58	0.366	–	–	5.54	0.311	56.75	0.097	70.83	0.091	0.59	0.715
Std. dev.	1.83		0.53		0.072		524.6		4407.5		0.30	
R-squared	0.90		0.98		0.74		0.52		0.55		0.98	

(Soxhlet). The highest antioxidant activity of WPE was achieved at 50 °C and 7.93 MPa. Pressure was determined as the most effective experimental variable like for TFC results.

Antioxidant activity of the WPE was between 890 and 18780 μM TE in respect of ABTS radical, while it was found between 570–2200 μM TE for DPPH radical. Less antioxidant activity was found for WPE compared to the OBE sample. It was reported that antioxidant activity in the extracts of sunflower by-product obtained by using microwave-assisted extraction was in the range of 180 to 266 μM TE/g [18]. Although we obtained higher than the literature, the antioxidant activity showed a wide range of variation (Table 2). This may be a result of variation of the extracted compounds, which may be responsible for the antioxidant activity, under different experimental conditions. Valuable component measurement results obtained for various sunflower extraction methods show that TPC and TFC results of this study are comparable to the other studies, even though they have used conventional, more polar and hazardous solvents (Table 2).

The highest recovery of TPC (0.6%) and TFC (21.3 mg QE/g) for OBE was obtained at the operating conditions higher than 60 °C and 20 MPa (Fig. 4). TPC and TFC recovery of OBE was quite high compared to WPE. Although we obtained a lower total phenolic content compared to many studies, it was also seen that similar results were obtained (Table 2). It could be said that the reason for the TPC values similar to our results were the choice of raw material and solvent used. Abdalla et al. [22] achieved similar results with WPE in terms of TFC, but Pajak et al. [21] obtained much higher results than OBE. This may be due to the fact that methanolic extraction was performed without recovering the oil.

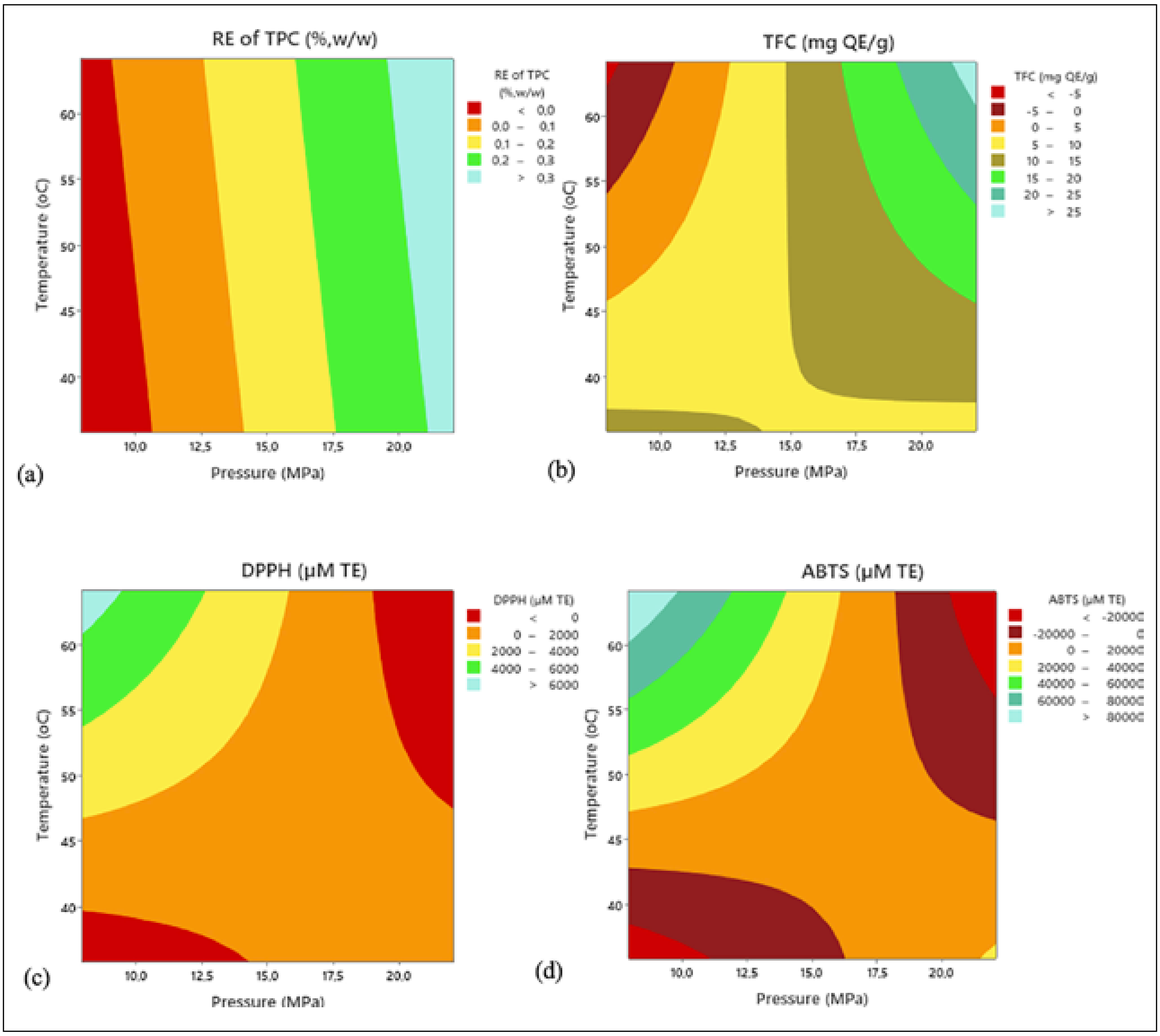

Figure 4. Binary effects of the experimental variables on the valuable components of OBE; **(a)** TPC value, **(b)** TFC value, **(c)** DPPH and **(d)** ABTS radical scavenging activity.

Table 4. ANOVA results for oil recovery (OR) efficiency and extract quality parameters of the OBE

ANOVA terms	OR (%, v/v)		OR (%, w/w)		TPC (%RE, w/w)		DPPH$^{\cdot}$ µM TE		ABTS$^{\cdot+}$ µM TE		TFC mg QE/g	
	F	p	F	p	F	p	F	p	F	p	F	p
Source	**Quadratic**		**Quadratic**		**Linear**		**Linear+ Interactions**		**Linear+ Interactions**		**Linear+ Interactions**	
Model	15.6	0.010	13.1	0.014	4.16	0.064	4.68	0.052	3.05	0.114	7.76	0.017
Temperature	2.74	0.173	3.81	0.123	0.10	0.764	3.29	0.12	2.21	0.188	0.04	0.851
Pressure	66.8	0.001	55.6	0.002	8.23	0.024	6.05	0.049	2.91	0.139	17.39	0.006
Lack of Fit	0.16	0.913	0.23	0.872	1.04	0.635	3.77	0.372	99.85	0.076	0.29	0.875
Std. dev.	3.18		1.90		0.142		1314.26		23663		3.70	
R-squared	0.95		0.94		0.54		0.70		0.60		0.80	

The highest antioxidant activity of OBE was achieved at 60 °C and 10 MPa for DPPH (6683 µM TE) and ABTS (99748 µM TE) radical. In addition, the extract of the expanded perlite-OB mixture had lower antioxidant capacity than OBE, while it had average TFC value. But RE of TPC (2.2%, w/w) is considerably higher than OBE.

Statistical Analysis

OR efficiencies for WPE were statistically significant in respect of the volumetric recovery (p value: 0.043) and mass recovery (p value: 0.002) (Table 3). The most significant variable on OR efficiency was pressure (p: 0.006 for volumetric recovery; p: 0.0002 for mass recovery). However, the temperature variable was significant only in mass recovery efficiency (p: 0.006). Similar results have reported in literature regarding the significance of experimental variables for extraction of sunflower seed kernels by SC-CO_2 extraction method [6].

It was also concluded that recovery efficiencies of TPC and TFC were found statistically significant (p: 0.033 and p: 0.002, respectively). Temperature and pressure provided the same level of significance for TFC while pressure was significant only for TPC.

Statistical importance of the experimental variables on the antioxidant activities was not significant (p: 0.565 for DPPH and p: 0.06 for ABTS). However, it was observed that pressure has significant effect on the ABTS antioxidant activity values of the extracts (p: 0.049).

The OR efficiencies for OBE were found to be statistically significant in terms of volumetric recovery (p: 0.010) and mass recovery (p: 0.014). Similar to WPE, the most significant variable was found to be pressure (p: 0.001 for volumetric recovery and p: 0.002 for mass recovery). The recovery efficiency of TPC for OBE was found as statistically insignificant (p: 0.064) while TFC (mg QE/g) was significant (p: 0.017). Contrary to WPE, DPPH antioxidant activity was found close to statistical significance (p: 0.052) while ABTS antioxidant activity was insignificant (p: 0.114) in OBE (Table 4).

CONCLUSION

It has been observed that SC-CO_2 extraction was more effective on the oily bentonite (OB) wastes to recover oil and valuable components than waxy perlite (WP) waste. The ANOVA tests of the developed models resulted in high coefficient of determination for oil recovery of WPE and OBE values for extract volume (R^2=90% and 95%) and mass (R^2=98% and 94%). It was detected that pressure variable was the most important variable affecting the significance for all results. A significant correlation was found between the TFC value of both samples and the independent variables of SC-CO_2 extraction. Oil recovery significantly increased up to 37% with the addition of expanded perlite into the waste sample before SC-CO_2 extraction. Although sunflower oil production industry waste samples were used in this study, results similar to the literature were obtained for TPC and TFC. Due to the high antioxidant content, TPC and TFC in the extracts, it may be possible to use these products in different sectors (cosmetics, pharmaceuticals, food, etc.).

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Utilization potential of poultry litter ash as phosphorus-based fertilizer

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ABSTRACT

A large quantity of poultry litter is globally generated as a result of expanding poultry industry. From several alternative technologies, one of the most feasible management for this waste is combustion, which exhausts poultry litter ash (PLA) as the main by-product. In this study, a PLA sample was examined for its utilization potential as a raw material for phosphorus-based fertilizer. According to the experimental results, Ca, P and K were determined as the major elements in the PLA sample with 29.54, 6.13 and 4.96%, respectively. Although the sample contains 2472 ppm Zn and 922 ppm Cu, their solubility determined by the leaching test is below the toxicity limit for hazardous waste. In terms of the major elements, about 290 mg/l Ca was detected in the leachate, resulting in a pH value higher than 13, whereas P concentration was found only 0.0092 mg/l. These two crucial results constitute the major difficulties for direct use of the PLA as a fertilizer. On the other hand, a usable P-rich product with low heavy metal contents and neutral pH can be obtained through acidification, heavy metal removal and neutralization processes. However, in this case, the feasibility of processes to be used should be carefully considered in economic point of view. In conclusion, direct application of the PLA sample examined as P-based fertilizer is not possible without any pre-treatments mainly due to its very high alkalinity and the low water solubility of P.

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INTRODUCTION

The substantial increases in global human population and the resultant incessant demand for food have resulted in an increased need for fertilizers. Therefore, sustainable fertilizer production, especially phosphorus-based (P) mainly met by non-renewable mineral sources has a vital importance. Although the worldwide phosphate rock is far from exhaustion with the estimated reserve more than 300 billion tons, its non-renewable characteristic, decrease in the amount of high-quality phosphate rock, the continuously increasing prices of P-based fertilizers and the need to keep the sustainability of agricultural systems have motivated researchers to look for lower-cost and renewable alternative phosphorus sources [1–3]. One promising solution can be the use of animal processing wastes for this purpose [1–4].

Poultry litter (PL) consists of a mixture of bedding material, waste feed, dead birds, broken eggs and chicken feathers. Expanding poultry industry generates high amount of poultry litter varying in the range of 1.5–5.7 kg of litter/bird [5–7]. Around 12 billion pounds of dry chicken manure is annually generated in the USA alone while this value is estimated more than 2 billion tons in Europe [8, 9]. Direct land spreading is accepted as the traditional method for the disposal of PL due to its high nutrient inclusion (N, K and P) for agricultural crops. However, intensive poultry farming causes some deleterious environmental impacts such as eutrophication of water bodies, spread of pathogens, production of phytotoxic substances, air pollution and greenhouse gases [5, 10–12].

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From various alternative technologies, thermal processes such as pyrolysis, gasification and especially combustion are considered as one of the most suitable management approaches of poultry litter mainly because of their technical, economic and environmental feasibilities. These feasible properties are suitability of poultry litter for thermal processes attributed to its relatively low moisture content as well as recovery of energy and nutrients attained as a result of the processes [5, 10]. In particular, combustion is accepted as the most widely used thermal process with commercial scale applications primarily due to its economic outcomes. In the USA, UK and Netherlands, combustion is currently and conventionally used for the production of heat and electricity. The main by-product or waste generated as a result of the process is poultry litter ash (PLA) including high nutrient contents [5, 13].

Chemically, as expected from a combustion by-product, PLA mainly consists of oxide forms of Ca, P and K in high amounts. In elemental basis, it generally contains 12–32% Ca, 6–15% K and 2–10% P, which is mainly determined by the poultry type, feeding properties, bedding materials and combustion conditions used. Relatively high K and P contents make PLA a potential raw material for fertilizers. Nevertheless, heavy metal contents of PLA especially Cu and Zn resulted from the respective poultry diet and bedding materials limit significantly its direct use depending on local legislation [5, 11, 14–16]. Since the reuse of waste is the main principle of economic and environmental sustainability, utilization potential of PLA as a phosphorus source should be studied in detail [14, 15].

In this study, a PLA sample resulted from the combustion of chicken litter was examined as a raw material for phosphorus-based fertilizer. Within this scope, several characterization analyses such as ICP-MS, SEM and EDX and a leaching test were conducted to determine its chemical composition, microstructural properties and leachability characteristics.

EXPERIMENTAL

Materials

The poultry litter ash (PLA) sample used is underflow product of cyclone in a biomass power plant. Prior to its utilization in the experimental stage, the PLA sample was first dried for 24 h at 105 °C. Analytical grade hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acids were used for the sample digestion. Distilled water was used throughout the experiments.

Methods

Inductively coupled plasma (ICP)-mass spectroscopy (MS) analysis, conducted by an Agilent 7800 instrument, was used to determine the elemental composition of the PLA sample as well as its heavy metal contents after the microwave assisted-acid digestion (MW-AD) based on the European standard EN 13656:2002 [16]. Leachability characteristics of major elements and heavy metals were investigated using distilled water to PLA ratio of 10 by mass in accordance with TS EN 12457-4 leaching test [17]. Similarly, the filtrate was analyzed by ICP-MS after the leaching test. Toxicity limits of heavy metals were determined through the regulation of hazardous waste in Turkish standard (Appendix 11-A) [17]. pH of the leachate was measured by a calibrated Mettler Toledo pH-meter. A high-resolution Zeiss Sigma 300 scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer was used to examine the microstructural properties and to determine the point elemental contents.

Table 1. Elemental inclusion of the sample

Element	Content (Wt. %)
Ca	29.54
P	6.13
K	4.96
Mg	2.83
Na	1.15
Si	0.92
Fe	0.37
Al	0.18

Table 2. Heavy metal contents in the PLA sample

Heavy metal	Concentration (ppm)
Zn	2472
Cu	922
Ni	35.36
Cr	30.17
Pb	27.82
Cd	13.04
Co	3.93

RESULTS AND DISCUSSION

Chemical Composition of the Sample

Elemental composition of the PLA sample is exhibited in Table 1. In accordance with the literature studies, since dicalcium phosphate is the main supplement in the poultry diet, Ca was detected as the highest-content element with 29.54% by weight as expected [13]. The other major elements were P and K with the respective contents of 6.13 and 4.96% resulted from the nutrients of Na, K and Mg typically added as chlorides. On the other hand, Si, Fe and Al were determined as minor elements with the concentrations less than 1%. All of these results are in line with the literature investigations conducted by Pandey et al., and Rivera et al., [5, 18].

Table 2 shows heavy metal contents in the sample. According to Table 2, concentrations of Zn and Cu are a way higher compared to the other elements examined with the respective 2472 and 922 ppm. All of the others, Ni, Cr, Pb, Cd and Co have a concentration less than 50 ppm. Similar results were also reported in the literature studies [15, 18].

Table 3. Solubility of the heavy metals and their toxicity limits

Element	Solubility (mg/l)	Toxicity limits (mg/l) (Appendix 11-A)		
		IW[a]	NHW[b]	HW[c]
Cd	0.0009	≤0.004	0.004–0.1	<0.1–0.5
Co	0.0001	NI[d]	NI[d]	NI[d]
Cr	0.4338	≤0.05	0.05–1	<1–7
Cu	0.0033	≤0.2	0.2–5	<5–10
Ni	0.0002	≤0.04	0.04–1	<1–4
Pb	0.0014	≤0.05	0.05–1	<1–5
Zn	1.1950	≤0.4	0.4–5	<5–20

a: Inert waste; b: Non-hazardous waste; c: Hazardous waste; d: Not included.

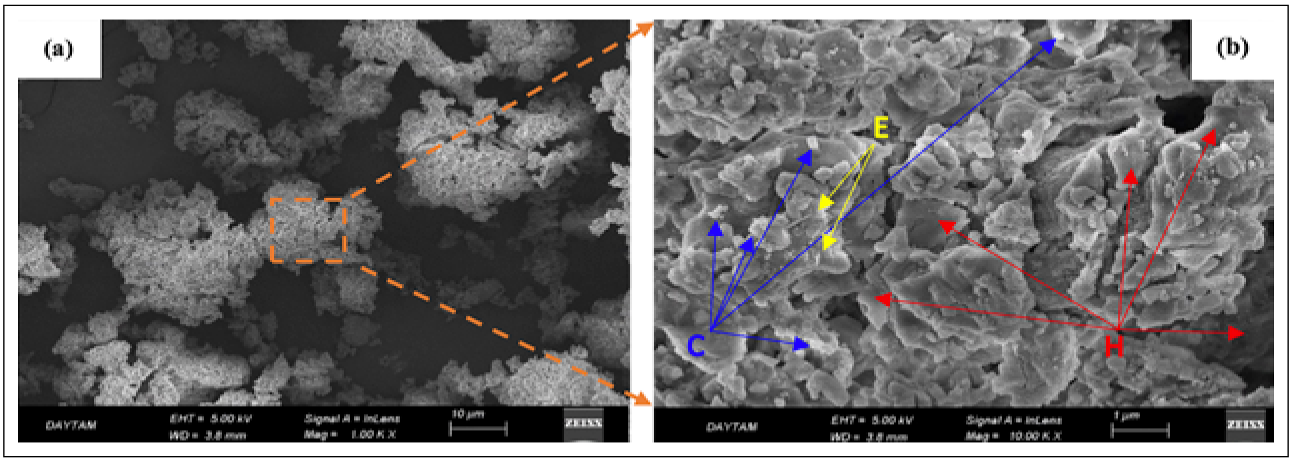

Figure 1. SEM images of the PLA sample. (H: Hydroxyapatite, C: Calcite and E: Ettringite).

Leaching Test Results of the PLA sample

Table 3 shows the leachability characteristics of the heavy metals from the PLA sample. As seen in Table 3, the PLA sample is clearly far from being considered as hazardous waste in terms of the solubility of all the metals examined except Cr and Zn, which were placed in non-hazardous waste region. Furthermore, leaching capacities of Cd, Co, Cu, Ni and Pb are even a way below the toxicity limits for non-hazardous waste. In other words, the sample can be labeled as an inert waste in terms of the solubility of these metals based on Appendix 11-A. Specifically, the solubility of Cr and Zn were determined to be 0.4338 and 1.1950 mg/l, respectively. Although the sample contains much higher copper (922 ppm) than chromium (30.17 ppm) which is indicated in Table 2, the higher solubility of chromium, 0.4338 mg/l, with respect to that of copper, 0.0033 mg/l, can be mainly attributed to its extremely high mobility, particularly its hexavalent state [19].

The leachability characteristics of Ca and P were also determined based on the leaching test conducted. The experimental results indicated that Ca and P concentrations in the leachate were determined as 289.8102 and 0.0092 mg/l, respectively. Low water solubility of phosphorus was also reported in the related literature which also indicates that phosphorus in waste materials has a low bioavailability, i.e., poorly available form to plants [3, 20, 21]. Therefore, prior to its use as a fertilizer, mainly acid treatment with chemical and biological methods must be used to form dissolved phosphates [3, 22]. In addition, pH of the leachate was measured as 13.12, which is certainly attributed to high water solubility of calcium. The general leaching test results show that direct use of the PLA as a fertilizer seems to be not possible mainly due to its low water-soluble phosphorus content and highly alkaline properties. All of these results are also well correlated with the literature studies [15, 18].

Microstructural Characterization

Figure 1 illustrates the SEM images of PLA sample. General view seen in Figure 1a indicates that PLA is generally composed of irregularly-shaped particles with an average size in the range of 60–70 µm. In addition, as seen in Figure 1b, particles tend to be more rounded as particle size decreases. Figure 1b also demonstrates that PLA sample mainly consists of two crystalline phases, hydroxyapatite ($Ca_5(PO_4)_3(OH)$) and calcite ($CaCO_3$), and also includes low amount of needle-shaped ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$) crystals. Moreover, according to the related literature, it may also contain other Ca-bearing compounds such as lime (CaO) and portlandite ($Ca(OH)_2$), and amorphous Ca-phosphate phase. Furthermore, potassium sulfate compounds can also be found as aphthitalite ($K_{2.25}Na_{1.75}(SO_4)_2$) and arcanite ($K_2SO_4$) [11, 15, 18].

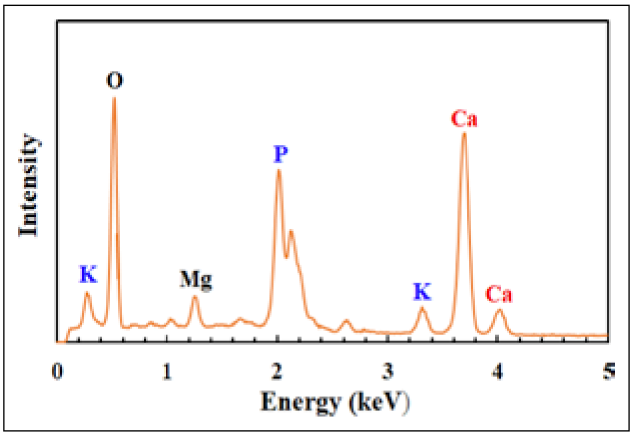

Figure 2. EDX spectra of the PLA sample.

Point elemental contents of PLA were examined using EDX analysis conducted during the SEM investigations. According to the EDX spectra shown in Figure 2, in line with the ICP-MS analysis, O, Ca, P and K constitute the main structure of the sample. Table 4 exhibits the point elemental contents based on the EDX measurements. As seen in Table 4, Ca, P and K contents were sequentially found as 36.40, 14.54 and 2.78% by weight. Compared to the ICP-MS results, lower K and higher Ca values were detected with EDX while much higher P content were obtained. This can be attributed to the nature of EDX, representing only the point where the measurement is taken not the whole sample. Similar differences were also reported in the related literature [15].

FINAL DISCUSSION

The ICP-MS analysis and TS EN 12457-4 leaching test conducted through the experimental stage have indicated that though its high P inclusion, 6.13%, the PLA sample examined has a very low water soluble-P content, which is determined to be only 0.0092 mg/l. This is the primary obstacle for its direct use as a P-based fertilizer. In order to increase the content of bioavailable phosphorus, various processes such as chemical and biological treatment methods must be used [3, 22]. In addition, high heavy metal contents of the sample constitute another limitation for its direct use due to strict local legislation. According to the Poultry Litter Protocol in the UK and Ireland, the upper acceptable concentrations of heavy metals for the use of poultry litter ash as agriculture fertilizer are given in Table 5.

As seen in Table 5, the PLA sample exceeds the upper acceptable limits in terms of Zn, Cu, Ni and Cd inclusions. This means that although the PLA is not labeled as a hazardous waste based on the TS EN 12457-4 leaching test exhibited in Table 3, its direct utilization as a fertilizer is not recommended due to potential threat to human health or the environment. A heavy metal removal process like ion exchange can be used to meet the limits [22, 23]. Furthermore, high alkalinity resulted from high water solubility of Ca also limits the direct use of the sample. For this reason, the leachate should be neutralized prior to its utilization [22].

Table 4. EDX point elemental contents

Element	Content (Wt. %)
O	44.74
Ca	36.40
P	14.54
K	2.78
Mg	1.54

Table 5. Upper acceptable limits of heavy metals within poultry litter ash used as a fertilizer

Heavy metal	Concentration within PLA sample the (ppm)	Upper limit in the UK and Ireland (mg/kg) [23]
Zn	2472	2063
Cu	922	596
Ni	35.36	24
Cr	30.17	31
Pb	27.82	244
Cd	13.04	3
Co	3.93	11
As	ND[a]	17
Hg	ND[a]	0.5
Mn	ND[a]	3500
Mo	ND[a]	45
Se	ND[a]	11
V	ND[a]	20

a: Not determined.

CONCLUSION

Overall results have suggested that although the poultry litter ash sample examined contains high amount of P (6.13%), its direct application as phosphorus-based fertilizer seems to be not possible mainly due to its very high alkalinity (pH 13.12) and the low water solubility of P (0.0092 mg/l). However, a soluble-P-rich product with a utilization potential as direct or partial replacement material can be obtained through few treatment steps, which are acidification, heavy metal removal and neutralization processes. Since P extraction by acid leaching is much more important than the other two processes, acid requirement is vital in this case for the economic feasibility of final product to be used as P-based fertilizer. Although the ash sample is not labeled as a hazardous waste in terms of the leachability characteristics of the heavy metals examined, its direct application on land is not considered as an environmentally friendly approach because of its highly-alkaline nature.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Composition and characteristics of excavated materials from a legacy waste dumpsite: Potential of landfill biomining

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ABSTRACT

Landfill biomining (LFBM) has been proposed as a viable method for the reclamation of legacy waste dumpsites as well as the subsequent recovery of valuable resources and land value spaces. Despite these advantages, the potential of LFBM faces a significant challenge due to the composition, characteristics and end-use of the excavated materials. This paper assesses the composition of the excavated waste obtained during the LFBM operation of the four legacy waste heaps at the Boragaon dumpsite in North-East India and determines the physicochemical characteristics crucial for the material and energy recovery from the key reclaimed fractions. The compositional analysis revealed that the proportion of combustible and non-combustible fractions decreases from the youngest heap HP4 to the oldest heap HP1 due to variations in the consumption habits of the local community and the inadequate recycling of recyclable materials. However, the proportion of fine fraction (FF) shows an increasing trend from HP4 to HP1, suggesting enhanced biodegradation of easily degradable waste over the years. The proximate and energy content analysis suggest that refuse-derived fuel (RDF) preparation is the most suitable valorization option for the combustible fractions since surface defilements are too high for good quality material recovery. The elevated amount of organic matter and leachable heavy metals indicate that unrestricted reuse of FF as earth-fill material can cause long-term settlements and groundwater contamination, respectively. Even though every dumpsite is different in characteristics, the findings of this case study can assist in developing new strategies for recycling excavated waste.

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INTRODUCTION

Open dumping of municipal solid waste (MSW) has been practised as a prevalent waste disposal method in most developing countries. It thrives because of the lack of appropriate technology, financial and human resources, coupled with the insufficient political will to improve the existing waste disposal practices. More than 90% of the MSW is disposed at non-engineered landfills or open dumpsites in India and other developing countries [1]. As a result, the existing dumpsites in urban India are overloaded with the heap of an extensive amount of legacy waste. These legacy waste dumpsites often lack of the necessary facilities and control measures to safely manage the gaseous and liquid by-products of waste decomposition [2]. It not only leads to human exposure to toxic chemicals via all three medium matrixes (i.e., air, water, and soil) but also causes significant pollution of these medium matrixes [3]. Moreover, natural anaerobic

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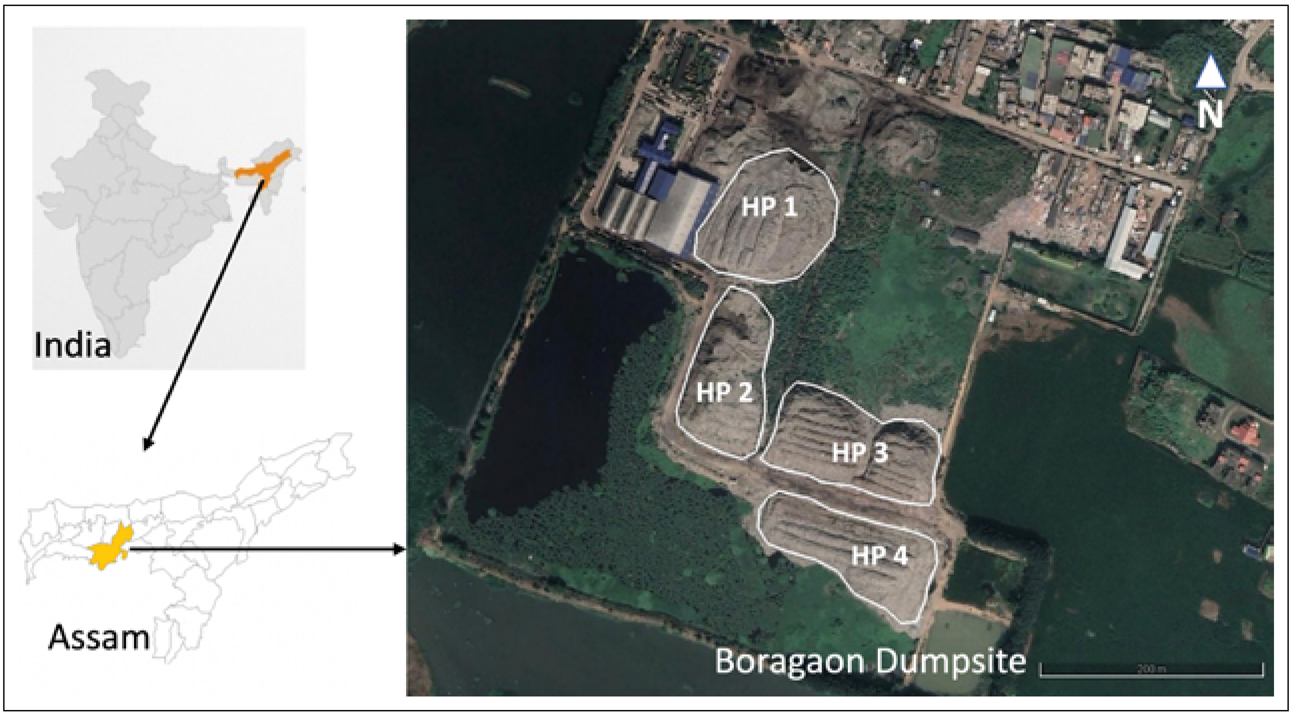

Figure 1. Map of the study area with marked heap locations (Source: Satellite image from Google Earth Pro, 2022).

decomposition of the MSW in the dumpsites releases greenhouse gases such as methane (CH_4) and carbon dioxide (CO_2), contributing nearly 80%–90% of the total landfill gas [4]. In terms of environmental risk, CH_4 is more dangerous since it has a global warming potential that is 28–36 times higher than CO_2 [5]. As a combustible gas, CH_4 also plays a significant role in fire incidents at dumpsites [6].

Indian cities are expanding to accommodate the increased population in such a way that waste disposal sites previously located in the suburbs have now become part of the city. Such disposal sites have emerged as one of the major concerns not only for environmental impacts and public health but also for the aesthetic beauty of the city [6]. Moreover, the landfill space requirement for the disposal of the MSW has increased and owing to this factor, the carrying capacity of the urban land leads to sustainability issues [7]. It has been reported that more than 10,000 ha of urban land is blocked by legacy waste dumpsites in India [8]. As a result, urban local bodies and municipal corporations are under pressure for the safe disposal of MSW. Considering the matter of sanitation seriously, the Government of India has launched Swachh Bharat Mission (SBM) to improve the health and safety of the population [9]. An integral part of this mission is cleaning up abandoned dumpsites to prevent further environmental degradation, reclamation of urban land and recovery of resources from the deposited waste. Landfill mining (LFM) is a viable method for accomplishing such goals in a sustainable manner [10]. In India, LFM is also referred to as landfill biomining, which involves excavation, stabilization and screening of dumped waste into different recoverable fractions [11]. With the help of LFBM potential, legacy waste dumpsites can also be retrofitted with sanitary infrastructure to mitigate environmental hazards.

Research on landfill reclamation and mining is being conducted worldwide to better understand the technical, financial, and societal limitations of this field. Waste composition and characterization are the most often discussed aspect of LFM research, as their potential depends on the energy and material recovery from the landfill's buried resources [12, 13]. The characteristics of waste rely on the composition of the dumped waste, which is influenced by a variety of factors, including the lifestyle of the local population, regional government regulations, the geographical location of the landfill, and climatic circumstances [14, 15]. Since the composition and characteristics of the waste vary from landfill to landfill and even within the landfill, one successful experience on an LFM project at one particular site need not be reproduced wholesale at another [16]. Therefore, it is necessary to conduct site-specific compositional and characterization analysis of the excavated waste in order to evaluate its potential for energy and resource recovery [17, 18]. A thorough understanding of the composition of the excavated waste and its treatability is also essential for planning appropriate treatment techniques for recoverable waste fractions in an LFM project. Previous literature shows that waste characterization studies yield crucial data for evaluating the potential of LFBM in India [11, 12]. Screening the waste based on distinct particle size categories and then physically or mechanically sorting at least the coarse particle into separate waste categories has been the primary method adopted in previous waste characterization studies [19]. During the characterization process, the physical and chemical properties of the segregated waste were also evaluated to identify the possible valorization routes of the waste component [12].

Figure 2. Onsite screening and segregation of the excavated waste.

Table 1. Parameters considered, methodologies adopted and instruments utilized for physicochemical characterization

Sample	Parameter/analysis	Method	Instruments used
Combustible fraction	Proximate analysis	USEPA 1684 and Dean 1974	Hot air oven and muffle furnace
	Gross calorific value	ASTM E711–87	Bomb calorimeter
FF	Moisture content	IS:2720 (Part 2)	Hot air oven
	Organic content	USEPA 1684	Muffle furnace
	Leaching potential	EN 12457-2, 2002	Rotary shaker and AAS

The present study aims to apprehend the composition of excavated waste from the recent LFBM project at Boragaon dumpsite in North-East India and to determine the physicochemical characteristics of key reclaimed fractions. The parameters crucial for the material and energy recovery from the excavated waste were the primary focus of the waste characterization. Recyclability and reuse feasibility were assessed by comparing the quality standards of waste fractions to the required quality criteria set by different regulatory agencies.

MATERIALS AND METHODS

Study Area

The dumpsite selected for the present case study is located at Boragaon (26°7'48" N, 91°39'36" E), near Guwahati city, in the Assam state of India. It has a land area of approximately (1×10^5) m^2 and consists of different waste fill heaps with filling heights varying from 3-3.5 m above the ground level, as shown in Figure 1 [20]. The non-segregated MSW collected by the city municipal corporation was dumped at the site since 2004. According to the information provided by the municipal authorities, approximately 1.7 million tonne of legacy waste is currently present at the site and distributed among those waste fill heaps. Waste disposal years for the selected heaps were as follows: Heap 1–2004 to 2008 (HP 1), Heap 2–2009 to 2012 (HP 2), Heap 3–2013 to 2015 (HP 3), Heap 4–2016 to 2019 (HP 4).

Compositional Analysis

During the LFBM operation, waste fill heaps were excavated and loosened up using hydraulic excavator, followed by spraying it with composting bio-cultures to hasten the decomposition of waste that hasn't been totally decomposed by microorganisms. Thus, the final product was not only become sterilized, stabilized and partially dry but also significantly reduced in volume. Stabilized waste was then fed into trommel screen, where it was segregated into three major fractions, i.e., combustible, non-combustible and FF as depicted in Figure 2. For compositional analysis, the mass of the excavated material feed into the trommel screen and the mass of the screened and segregated waste were measured. Subsequently, the composition of the screened fractions was further manually sorted into different subfractions, and the weight was determined. Since the FF was predominantly composed of degraded organic matter and could not be sorted manually, it was not separated into different streams. After hand sorting, representative samples of different subfractions and FF were collected in airtight polyethene bags and transferred to the laboratory to determine the physicochemical characteristics. Prior to analysis, the samples were kept in the laboratory at 4°C to prevent any alterations in the physicochemical properties.

Physicochemical Characterization

As combustible fraction and FF make up the majority of the total excavated waste, physicochemical characterization was mainly focused on these fractions to understand the possible energy recovery and waste-to-material valorization

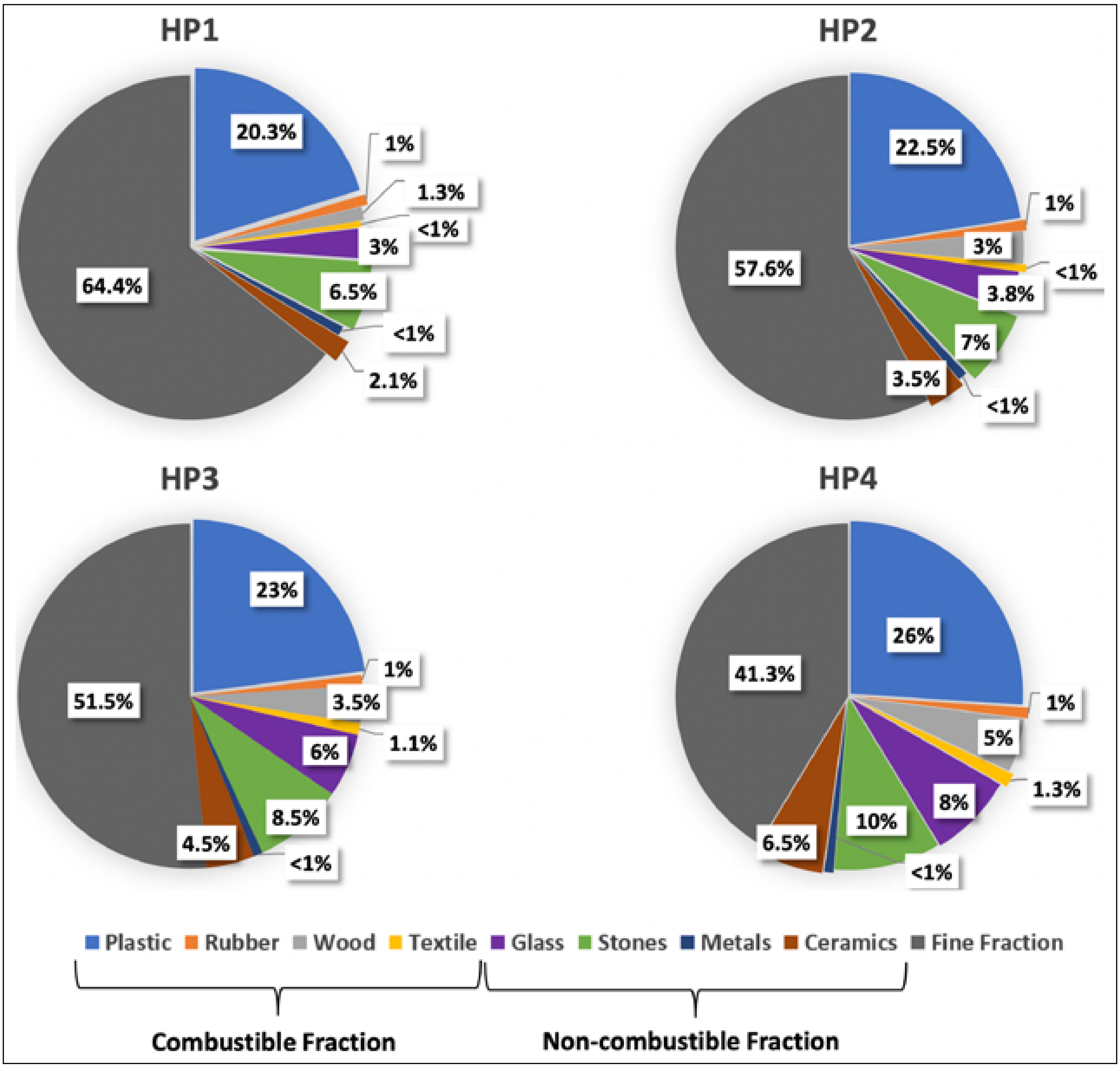

Figure 3. Composition of excavated waste from different heaps.

options. A brief overview of the parameters investigated, methodologies adopted and instruments utilized for the characterization study are shown in Table 1. For combustible fraction, proximate analysis and gross calorific value have been determined. On the other hand, moisture, organic matter, and leachable heavy metals concentration have been analyzed for FF. Proximate analysis was carried out in accordance with USEPA Method 1684 and Dean 1974 to measure the percentage of moisture, volatile solids, ash content and fixed carbon in combustible fractions [21, 22]. An automated bomb calorimeter was used to determine the gross calorific values according to ASTM E711–87 standard, and the results were expressed in MJ/kg [23]. The moisture content of the FF was assessed gravimetrically by heating about 500 g of sample to a constant mass in a thermostatically controlled hot air oven at 110±5°C, as per the IS:2720 (Part 2) (1973) [24]. The percentage of moisture content was then determined by calculating the difference between the pre-and post-drying weights. The organic content of the FF was determined by heating about 100g of dried sample in a muffle furnace at 550 (±50 °C) for 2 hours as per USEPA Method 1684 [21]. The percentage of organic material was then calculated by comparing the weight of the original dried sample to that after heating. To evaluate the preliminary environmental properties and possible utilization options for the FF, a batch leaching test was conducted according to EN 12457-2, 2002 [25]. As per the test procedure, the FF sample is mixed with deionized water at a liquid-to-solid (L/S) ratio of 10 L/kg dry matter for 24 hours. The eluates of the leaching test were then filtered through whatman 42 filter paper using a vacuum filtration unit. After that, extracts from the filtered eluates were analyzed for the concentrations of Cr, As, Mn, Zn, Cu and Al by atomic absorbance spectroscopy (AAS). All experiments were performed in triplicate, and the data are presented as mean with standard deviation values to ensure the reliability of the test results.

Table 2. Proximate analysis of the combustible fraction

Parameters	Sample locations				CPCB criteria for incineration
	HP1	HP2	HP3	HP4	
Moisture content (%)	22.1±0.3	24.6±0.7	27.8±0.4	36.5±0.6	<45%
Volatile matter (%)	41.2±0.4	42.4±0.2	46.5±0.3	50.1±0.4	>40%
Ash content (%)	30.8±0.5	25.9±0.4	18.1±0.5	5.8±0.2	<35%
Fixed carbon (%)	5.6±0.2	6.9±0.3	7.2±0.1	7.4±0.2	<15%

Mean±standard deviations, n=3.

RESULTS AND DISCUSSION

Composition of Excavated Waste

A heap-wise compositional analysis was conducted in the present study, and pie charts depicting the relative percentage (wt%) of various waste components were then created, as shown in Figure 3. Each pie chart was given a name that corresponded to the physical composition of the excavated waste of varying ages. HP4 represents the waste composition of the youngest heap, and HP1 represents the waste composition of the oldest heap at the dumpsite. It was found that the composition of waste significantly varied between the heaps depending on their ages. Since the composition of the inflow materials is crucial for the evaluation of resource potential and possible recovery routes, the excavated waste was shorted into different streams and categorized into three major fractions: 1) Combustible fraction, 2) Non-combustible fraction, and 3) FF.

Plastic, wood, rubber and textiles were considered as the combustible fraction found in the excavated waste. The result showed that the total amount of combustible materials gradually increased from 23% for HP1 to 33% for HP4. Plastic was the dominant component in the combustible fraction, contributing to 20.3%, 22.5%, 23% and 26% of the total waste for HP1, HP2, HP3 and HP4, respectively. The increment of plastic content from HP1 to HP4 demonstrates a rise in plastic usage over time. Because of the significant contamination, recycling plastic from excavated waste is a complicated process and may not be a cost-effective option. Therefore, the most efficient means of valorization of plastic is waste-to-energy conversion. The quantity of wood also increased from 1.3% for HP1 to 5% for HP4. The lesser mass fraction of wood in HP1 indicates its degradation over the years at the dumpsite, and the results are consistent with the findings of previous studies [16, 26]. No significant shift in the proportion of rubber and textiles was observed from HP1 to HP4. Unlike other studies, the paper fraction in the present study was almost absent for all the heaps.

An increase in the percentage of non-combustible fraction (12.5% for HP1 to 25.4% for HP4) was observed in the younger heaps. The most dominant component in the non-combustible fraction was stones, followed by glass, ceramics and metals. The stone content accounts for 6.5%, 7%, 8.5% and 10% of the total waste for HP1, HP2, HP3 and HP4, respectively. After appropriate pre-treatment, this fraction can be put to use in the construction sector [12]. Comparing the excavated waste from HP1 and HP4, a much higher percentage of glass and ceramics was found in the HP4. This may be due to the inadequate recycling of these materials by informal sectors, which results in the disposition of recyclables at the dumpsite. The negligible percentage (<1%) of metals in all the heaps could be attributed to a very efficient traditional (informal) collection system of scrap metal from households by waste collectors, often locally called 'Kabadiwalas' [27].

The proportions of FF were 64.4%, 57.6%, 51.5% and 41.3% of the total excavated waste for HP1, HP2, HP3 and HP4, respectively. This result indicates that the proportion of FF increases with age and contributes as a major fraction of total waste composition for all the heaps. Composting, aerobic, anaerobic degradation and other related processes break down the biodegradable fraction of the dumped waste into soil-like material or FF [28]. With more time passing, additional biodegradable components disintegrate, leading to a higher amount of FF in the more aged heaps of waste. In the Indian context, the higher mass of FF was also reported at the legacy waste dumpsites in Delhi, Mumbai and Chennai [12, 29, 30].

Physical and Chemical Characteristics

The previous LFM study revealed that an extensive range of laboratory analyses was used to assess the acceptability of recovered fractions [19]. However, time and resource constraints necessitate reducing the number of physicochemical parameters measured. Principal characteristics analyzed for the combustible fraction include moisture content, volatile solids, ash content and calorific value. The most critical parameters investigated for FF are moisture content, organic content and heavy metals concentration.

Proximate Analysis of Combustible Fraction

The most common approach to fuel characterization is the proximate analysis which involves the measurement of parameters like moisture content, volatile matter, fixed carbon, and ash content. The combustible components (plastic, wood, rubber and textiles) of the old waste were generally contaminated with fine particles of organic and inorganic matter that were attached to their surface (known as surface defilements or impurities) [31]. In the present research, combustible fractions were subjected to proximate analysis without any pre-treatment to more accurately reflect the current field practices. Table 2 shows the proximate analysis results of as-received combustible fractions from four different waste-filling heaps on dry basis.

Table 3. Calorific value of the combustible fraction

Sample locations	Gross calorific value (MJ/kg)
HP1	18.4±0.2
HP2	16.9±0.5
HP3	13.8±0.7
HP4	12.1±0.4

Mean±standard deviations, n=3.

Table 4. Moisture and organic content in FF

Samples location	Moisture content (%)	Organic content (%)
HP1	29.36±1.89	18.81±1.26
HP2	30.62±1.42	19.14±1.85
HP3	32.68±1.31	20.48±1.58
HP4	34.39±1.55	22.76±1.15

Mean±standard deviations, n=3.

In general, the presence of moisture is always an undesirable component of any combustible material. Heating capacity, combustion efficiency, and combustion temperature are all affected by moisture content [32]. As per the Central Pollution Control Board (CPCB) of India, feedstock for incineration must have a moisture content of less than 45% [33]. The moisture content of the combustible fraction for the four different heaps ranged between 22 to 37%. Hence, all samples meet the CPCB criteria of moisture content for incineration. Furthermore, it was observed that the moisture content of the combustible fraction exhibits a decreasing trend with increasing age. The youngest heap HP4 contained the highest moisture (36.5±0.6%), while the oldest heap HP1 contained the least moisture (22.1±0.3%).

For incineration treatment, the amount of volatile matter in waste samples is a strong indicator of the presence or absence of combustible components. As per the CPCB guidelines on criteria for selecting waste processing techniques, the volatile matter content in the waste sample must be higher than 40% for effective utilization of incineration technology [33]. The mean volatile contents in the combustible fraction from HP1, HP2, HP3 and HP4 were 41.2%, 42.4%, 46.5%, and 50.1%, respectively. The decline in volatile matter from HP4 to HP1 indicates that the amount of organic matter in the waste decreases over time as it decomposes into soil-like substances.

The ash percentages of the combustible fraction for the four different heaps varied from 6 to 31%. CPCB suggests below 35% ash content for mass-burning incinerators to maintain better efficiency [33]. The ash content of the combustible fraction significantly increased from the youngest heap HP4 (5.8±0.2%), to the oldest heap HP1 (30.8±0.5%). The higher amount of FF in the aged waste can be the main reason behind the elevated ash content in the combustible fraction from older heaps. Over time, the decomposition of organic matter results in the subsequent increase of FF, which gets attached to the surface of combustible materials and increases ash content [34]. The fixed carbon content varied from around 6 to 7.5%. Fixed carbon refers to carbon in its uncombine state which burns as solid mass in the combustion process [32]. The high proportion of fixed carbon implies that the incinerator needs more time for complete combustion. As per the CPCB guidelines, the fixed carbon content should be less than 15% for incineration.

Calorific Value of Combustible Fraction

Waste-to-energy conversion is the most favoured application for combustible fractions. The average gross calorific values on the dry basis of the mixed combustible fractions from the four heaps are shown in Table 3. Based on the results, HP1 has the highest calorific value (18.4±0.2 MJ/kg), followed by HP2 (16.9±0.5 MJ/kg), HP3 (13.8±0.7 MJ/kg) and lastly, HP4 (12.1±0.4 MJ/kg). The variations in the calorific values of the samples were mainly caused by their physical composition and inherent moisture content. The higher amount of moisture (36.5±0.6%) in the combustible fractions of HP4 relatively lowered its calorific value. For solid waste to be used as an energy resource or RDF in an incinerator facility, the CPCB suggests that it should have a calorific value of more than 6.3MJ/kg [33]. Therefore, combustible fractions from the four heaps can be used as RDF in a mass burn incineration facility. An increase in the calorific value of RDF samples can also be achieved through proper sorting, pre-cleaning and pre-drying of the recovered waste [35]. However, pre-treatment system development is resource intensive and requires specialized equipment and personnel for waste segregation.

Moisture Content and Organic Content in FF

Moisture and organic content are the two highly interconnected parameters influencing the processing routes and possible end-uses of the FF. Higher organic matter can increase the sorption of the water molecules, which in turn raises the moisture content for the FF. As smaller pores are more effective at holding water than larger ones, moisture is usually found in the FF due to capillary action [28]. For this reason, the moisture content is a pivotal factor in the management of the FF. The results of moisture content and organic content in FF from various heaps are shown in Table 4 on dry basis. The moisture content in FF was found to vary between 29.36% to 34.39%, with the least value at HP 1 and the highest value at HP 4, whereas the organic content was found to vary between 18.81% to 22.76%, with the least value at HP1 and highest value at HP 4. The relatively high level of moisture in the FF affects the processing efficiency of the other material (combustible and non-combustible fraction) recovered from the dumpsite. FFs were easily impregnated on the surface of the other course fractions primarily because of their high moisture levels. It must be emphasized that when the FFs were in their raw state, the presence of moisture promoted the creation of agglomerates and increased the proportion of surface defilements in the larger particles [28]. Along with the amount of mois-

Table 5. Leaching of heavy metals from FF in comparison with the regulatory levels

Heavy metals	Samples location				Regulatory levels						
	HP1	HP2	HP3	HP4	2003/33/EC			LAGA M20			
					Inert	Non-hazardous	Hazardous	Z0	Z1.1	Z1.2	Z2
Cr (µg/L)	143±2.83	169±3.61	179±7.09	242±2.83	50	1000	7000	15	30	75	100
As (µg/L)	BDL	BDL	BDL	BDL	50	200	2500	10	10	40	50
Mn (µg/L)	130±4.95	157±1.41	195±6.36	252±4.14	NSE	NSE	NSE	NSE	NSE	NSE	NSE
Zn (µg/L)	228±1.56	257±1.84	311±2.62	392±6.17	400	5000	20000	100	100	300	400
Cu (µg/L)	118±1.35	129±7.15	138±1.55	144±6.39	200	5000	10000	50	50	150	200
Al (mg/L)	16.6±0.65	23.3±0.63	25.5±0.6	27.4±0.84	NSE	NSE	NSE	NSE	NSE	NSE	NSE

Mean±standard deviations, n=3; NSE: No standard established; BDL: Below detection limit.

ture, the amount of organic matter in FF affects its density, compressibility and decomposition rate [36]. As the organic matter decomposes due to the presence of moisture, the amount of organic content in the FF decreases. This results in a continuous shift in the fundamental engineering and biochemical characteristics of FF until the organic matter is unavailable to microorganisms and cannot be degraded any more. For example, if the organic matter in FF is high, it can cause long-term creep settlement in earthworks, as reported in previous studies [37]. As per the Indian standard code (IRC-37-1984) for road construction, the upper limit of organic content for soil to be used as subgrade material should not be more than 1–3% [38]. This means that if the FF is utilized as an earth-fill material, it will likely cause long-term settlements owing to its gradual decomposition over time.

Leaching Potential of Heavy Metals From FF

An assessment of the leaching potential of heavy metals from the FF is essential for evaluating its suitability before off-sites applications [39]. The leaching test results can provide important information about whether or not the standards set up for various purposes are being met. Many leaching experiments are available to characterize materials or to perform regularity controls to ensure that the materials in question are suitable for use. The European Standard EN 12457-2 batch leaching test was conducted in the present study to evaluate the leaching potential of heavy metals from the FF in normal water under experimental conditions. According to the European Union (EU) regulations, the analysis of leachate composition is crucial for determining the landfill acceptability as well as contamination potential of waste materials like the FF. The results of leachable heavy metals from the EN 12457–2 batch leaching test are shown in Table 5. The leached concentration of Cr, Mn, Zn, Cu and Al from FF were found to vary between 140-245, 125-255, 226-398, 116-150 and 1600-2800 µg/L, respectively. The comparison of the concentration of metals in leachate shows that aluminium is the most abundant heavy metal, followed by zinc, chromium, manganese and copper. Arsenic concentrations were found below the detection limit for all leachate samples. In India, there are no regulatory threshold limits (RTLs) of heavy metals concentration for the reuse of mining waste. Therefore, the leached concentrations of heavy metals from the FF were compared with the RTLs of the EU council decision (2003/33/EC) and the German technical bulletin (LAGA M20) [40, 41]. The EU legislation classifies waste materials based on the concentrations of different heavy metals into three categories, i.e., inert, non-hazardous and hazardous. As per the leaching test results, all FFs are classified as non-hazardous but not inert due to elevated leaching of Cr than the RTLs imposed by the EU council decision. The German technical bulletin, LAGA M20, distinguishes the reuse potential of waste materials in four distinct ways. The class Z0 allows reuse without any restrictions, Z1.1 allows reuse without any sealing to avoid groundwater contamination, Z1.2 allows reuse if the waste material is separated from the groundwater table by a layer of cohesive soil, and Z2 allows reuse if the top layer is sealed. On comparing the results with LAGA M20, it was observed that the FF could not be used directly under any class mentioned in the standard due to significantly higher levels of chromium. The concentration of copper and zinc was also found to exceed the Z1.1 class for all FF samples. This indicates that the unrestricted reuse of FF as earth-fill material can increase heavy metal concentrations in the underneath soil and groundwater.

LFBM Potential for India

The Ministry of Housing and Urban Affairs (MoHUA) estimates that there are 142 million tonnes of legacy waste lying at different dumpsites across 472 cities in India [8]. Most of these dumpsites were constructed before municipal solid waste regulations were enacted, so they lacked essential environmental sanitation facilities. Implementing LFBM operation can provide environmental benefits by rehabilitating the existing dumpsites and offers many possibilities to recover secondary resources and land value spaces. But several obstacles need to be overcome before LFBM project can be executed efficiently. The primary obstacle is encouraging stakeholders to pursue LFBM initiatives, and the secondary obstacle emerges during the valorization of recovered waste. Most international research has indicated that the profits of LFM are related to the recycling of metallic portions [16, 18, 42]. However, the excavated waste from the Indian dumpsites mainly consists of FF and combustible fractions, while the amount of metal is very low [12, 29, 30]. Finding sustainable ways to utilize FF and combustible fractions is very important for the success of the LFBM project. As a sustainable option, FF can be used as earth-fill material in infrastructure development projects such as road and rail embankments, filling low-lying areas and old quarry sites for land reclamation. This practice of reusing FF could reduce the overexploitation of virgin and non-renewable materials like native soil and river sand. However, the prospect of their reuse remains unresolved due to the vast amount of leachable heavy metal availability and high organic content, which causes groundwater contamination and settlement failures, respectively. It is still a challenge for engineers and scientists who are trying to find a way to solve this problem. Although the waste-to-energy conversion shows great promise for the combustible fraction, it may be difficult to sell as fuel due to variations in feedstock quality caused by contaminants. For example, the cement manufacturing sectors are sometimes unwilling to purchase RDF prepared by the combustible fractions as fuel for co-firing because of quality concerns. This fraction could be put to efficient use by the application of pre-cleaning procedures such as sorting, cleaning, and drying. LFBM operation has the potential to create local environmental impact and public health risk due to the release of high strength leachate, landfill gas, odour and dust during excavation and material handling [43]. The severity of these impact depends on various factors related to nature of the excavated waste, the extent of the exposed working face, local weather condition, duration of the LFBM operation, and proximity to surface or groundwater resources and neighbouring residential populations. Appropriate mitigation measures are needed to be taken before implementation of the LFBM project.

The Indian government has taken several initiatives to improve its waste management systems. The government can play a significant role in encouraging entrepreneurs to undertake LFBM projects by providing subsidies. From the Indian context, the potential of LFBM would be the valuable space recovery, rehabilitation of the existing dumpsites and utilization of combustible fraction as fuel.

CONCLUSION

The present study provides an overview of the compositional analysis and physicochemical characteristics of excavated waste obtained during LFBM at a legacy waste dumpsite. The results demonstrate that the composition and characteristics of the excavated waste vary based on the disposal year of the fresh MSW at different heaps within the dumpsite. The proportion of combustible and non-combustible fraction of the excavated waste shows a declining trend from the youngest heap HP4 to the oldest heap HP1due to the variations in purchasing power and consumption habits of the local community and the inadequate recycling of recyclable materials by informal sectors. In contrast, the proportion of FF shows an increment from HP4 to HP1, suggesting increased biodegradation of the easily degradable MSW over the years. The potential for valorization of the combustible and FF was evaluated based on their physicochemical properties. For the combustible fractions, RDF preparation was found to be the most viable option since the amount of surface defilements was too high for good-quality material recovery. The proximate and energy content analysis suggests that the use of pre-cleaning methods can decrease the ash content and enhance the heating value of RDF. Moisture and organic content are interconnected parameters of crucial importance, as processing routes and potential end applications for FF depend to some extent upon their quantities. The elevated amount of organic matter in FF will likely cause long-term settlements during its utilization as earth-fill material. Leaching tests of the FF reveal a significant release of Al, Zn, Cr, Mn and Zn in all leachate samples. Comparison of the heavy metal concentration in leachate with the RTLs of EU and German technical bulletin emphasized that the unrestricted reuse of FF as earth-fill material can cause heavy metal contamination in the underneath soil and groundwater. To stop the spread of contaminants, it is important to look into the pre-treatment methods for FF before they are reused or to explore novel valorization strategies for this resource.

From this study, it is clear that compositional analysis and characterization of the excavated waste are essential steps in developing plans and formulating new proposals for recycling and recovery technologies that can be implemented during the mining of a legacy waste dumpsite. Even though every dumpsite is different, the results from this case study can contribute to the development of approaches for the characterization of legacy waste and the identification of critical issues that need more research. Apart from resource recovery from the dumped waste, if the purpose is also to remediate the legacy waste dump sites and reclaim the land, then LFBM is not far from cleaning a potentially contaminated area, freeing up the contaminated masses and creating new space with high value and new possibilities, which often is considered as a very expensive operation.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Interpretation of odor complaint records with BTEX pollutants and meteorological factors: Çorlu case study

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ABSTRACT

Air pollution in urban areas increases as a result of emitted air from different sources within the mixing layer of troposphere. Odor pollution is amongst the primary reasons behind environmental nuisance and occurrence of citizen complaints. Frequent exposure to odorous compounds and/or odor nuisance are increasingly associated with air pollution problems. Besides, there is no universally accepted environmental odor management method reported so far. Level of air pollutants emission, distance of emission sources to residential areas, topography, geographical and meteorological conditions have influence on imposed level of air pollution and odor pollution in cities.

This study is built on the citizen odor complaint data (based on frequency, intensity, duration, odor tone and location (namely the FIDOL factors) collected in Çorlu/Tekirdağ through the GIS integrated public participated platform, namely the Çorlu KODER mobile application. The annual odor complaint data was briefly introduced and given an evaluation with the mobile app users demographic information. The obtained data between August 28-November 2 of 2021, was subjected to interpretative evaluation and statistical analysis with BTEX (benzene, toluene, ethylene benzene and xylen) concentrations, inorganic air pollution concentrations and meteorological factors. In light of the obtained results, temperature, wind speed, relative humidity and toluene concentration were found to play a significant role on the number of citizen odor complaints. The EU reported limit value, lower rating threshold and upper rating threshold for BTEX pollutants have been exceeded several times.

The average Toluene/benzene ratios obtained during the study show that; non-traffic sources contribute significantly to VOC emissions. Air pollutants transportation mechanism from neighbouring OIZ settlements become a prominent justification and support the hypothesis that residential areas of Corlu are under the effect of industrial air pollution and odor pollution constituents. There is low level of negative correlation between the benzene measured in Çorlu and WS (r=-0.63). Below 2.4 m/s, the average number of odor complaints (ANOC) tend to increase, while above this level odor complaints are diminished). The ANOC remained around 4 for $[C]_{BTEX\ total} < 4$ ug/m^3 and reached to 18 for $[C]_{BTEXtotal} > 8$ ug/m^3. Above $[C]_{Toluen}=3$ ug/m^3 conditions, Daily ANOC increase from 7 to 19. Over $[C]_{Toluen}= 4$ ug/m^3 conditions, it reached up to 23. Increses in the number of daily ANOC by temperature is distinct over 21 C^0 and reaches to 35.

The GIS integrated citizen complaint collection platforms are critical for real-time data collection of environmental complaints with high spatiotemporal accuracy. Citizen odor complaint surveys are useful monitoring tools and obtained data sets can be used to identify sensitive areas where and when specific actions should be taken and air pollutants measuement studies be performed.

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INTRODUCTION

Air pollution and odor pollution are serious environmental issues with regard to air quality and handled as public health problems. It constitute of inorganic and organic components originating from industrial processes, energy production, housing and traffic [1–4]. It is an indicator of environmental change that affects health, human well-being and is subject to the most frequent public complaints [5, 6]. Environmental information is necessary for governments to follow environmental policies and management goals. The collected information also may serve in identification of environmental problems, regional and temporal citizen complaints and disorders. Data related to pollution, ecosystem and landscape, also epidemiological and psychological data have a determining role on a healthy environment, health and life style [7].

All European countries are required to comply with the framework and for air quality management as described in the Air Quality Directive (AQD) 2008/50/EC (EU, 2008) which opens the door for the use of other supplementary techniques, such as air quality models and indicative measurements [8]. Because of their physical, operational, maintenance and economical aspects, stable air quality monitoring stations (AQMS) are preferred to be built only at the most representative location. Mobile AQMS are mainly used with intent to increase spatial sampling density. Passive samplers are inexpensive to deploy and operate [8–10], they only allow the quantification of cumulative air pollutant levels, and cannot identify short-term pollutant episodes [8, 10].

Due to widespread economic development models, the level of interaction between the residential area and the surrounding industrial activity and tend to rise day by day [11]. Air pollutant emission levels, the distance of emission sources to residential areas, topography, geographical conditions, seasonal and daily variation of meteorological factors have influence on the imposed level of air pollution, odor pollution, odor annoyance and nuisance levels [12–15]. Around metropolitan and industrial settlements, emitted air pollutants can be accumulated under influence of the wind speed/direction (called dry deposition) and may result in wet deposition on the ground as a result of relative humidity and precipitation [16–18]. High RH favors the partition of semi-volatile species into the aerosol phase [19–22].

Volatile organic compounds (VOCs) constitute the major component of the atmospheric composition and compose of large group of organic chemicals and characterized by their volalitity [23]. Odorous VOCs may originate from natural and anthropogenic sources [24]. The most common VOCs are called BTEX (Benzen, toluen, ethylbenzen and xylen) which contitute more than 60% of the non-methane VOCs within the urban atmosphere [25]. The odorous VOCs can be subcategorized into five main groups; alkanes, alkenes, halogenated hydrocarbons, aromatic hydrocarbons (where the BTEX pollutants belong) and helogenated aromatics. Aromatic hydrocarbons accounts for about the 97% of paint solvents composition where toluene is dominating [26, 27]. According to literature, based on cumulative measurement carried out on a number of VOCs in industrial areas and around the neighboring residental areas; the ratio of odorous VOCs to the total VOCs were reported to be distinctly high [5]. According to another literature finding, toluene concentration may reach 15-20 times of the remaining BTEX pollutants in an industrial area under dominance of spraying, painting and petrochemical processes and manufacturing [5, 20, 27, 28]. Inorganic compounds have low molecular weights and play a determining role on the odor sensing mechanism by binding to olfactory receptors and affecting odor levels [2]. An odor may be characterized by its hedonic tone and by intensity. While the acceptability of an odor is defined hedonic tone parameter, it may also be descriptive of some characteristic properties of odor (sweat, spicy, lime etc.) On the other hand, the odor intensity assessment ranges from the detection threshold to the level of disturbance [3]. Mostly, toluene is found related with sour and burnt descriptions. While, benzene is associated with aromatic, sweet definitions. Odor issues caused by those two air pollutants are analogously described by most of the citizen as "solvent like" smell. Majority of exposed odors are described as; oily, burnt oil, gas, garlic, varnish like, petrochemical, burned match and many others inline with the study area and odor emitting sources at its surroundings.

Research is limited on the evaluation between odor pollution and industrial emissions. Sole use of odorous VOC concentrations would be inadequate for the assessment of odorants strength and perceived nuisance; therefore odor indexes, odor units, odor activity values etc. and similar approaches are used with intent to determine certain thresholds [29, 30]. Odor pollution and/or odor episodes are tracked by using traditional sensorial techniques such as dynamic olfactometry (EN Standard 12725:2003) and impact models, scheduled field observations according to European standard EN 16841:2016 and recording from residents by citizen surveys. The "odor hours" definiton ise used for the hours which have recognizable odor for at least 10% of the time period), while "odor nuisance" occurs due to series of odor episodes experience, and "odor episodes" are composed of several odor hours within a limited period of time. The ability to smell a certain odor in the populations follows a log normal distribution and >96% of the population theoretically have a normal sense [31]. The collected sensorial data have potential to be used in environmental odor characterization of the study area from a nuisance perspective [12, 32–34].

A pioneering study have integrated olfactometric field survey data with the CALPUFF emission dispersion model outputs with intent to determine the major contributing source of odor issue in a residental area [10, 32, 35]. Use of electronic noses may actualize classification of the analyzed air, and assign the air sample to a certain olfactory class. An e-nose is composed of a sensor matrix, data processing system and a system for pattern recognition in order to represent human odor sensing mechanism [3]. Citizen surveys are eligible for collecting real time data and can be descriptive of the full odour episode. [34, 36, 37]. The intermittent and variable natures of environmental odors require continuous monitoring to capture short-term episodes [38, 39]. Social participation can be used for identifying odor episodes, keeping records of odor issues, and allow building sensory databases [3]. Specific guidelines [40] emphasizes the importance of annoyance assessment. [36, 41, 42]. Continent wide projects like the D-noses and Prolor have developed useful models that are able to determine the time-dependent effect levels of the odor source on living spaces [12, 32].

This study was carried out at Çorlu/Tekirdağ and built on collected annual citizen odor complaint data, meteorological factors, inorganic and BTEX air pollutants values between the August 28 2021 –November 2 2021 period. Citizen odor complaints were collected by use of a mobile application in residental area of Corlu around which number of OIZs are positioned. The annual odor complaint data was briefly introduced considering the user demographic profile. This study aims to reveal out the relation between the number of citizen odor complaints and their spatiotemporal distribution with constituents of air pollution (that arise from neighboring industrial activity), meteorological factors and their interactions. Accordingly, the number of odor complaints between August 28 – November 2 of 2021 was subjected to correlation and multi-variance statistical analysis with the measured BTEX concentration, inorganic air pollutant concentration and the meteorological parametes; Windspeed, temperature and relative humidity. The incidence of odor complaints occurence in certain ranges of relative humidity, temperature, wind speed and total and specific BTEX parameters were given an evaluative discussion.

MATERIALS AND METHODS

This study is structed on a descriptive cross-sectional measurement and field study including; the statistical examination of the relationship between meteorological factors, odor complaint records and inorganic-organic (BTEX) air pollutants.

Odor complaints were collected through the mobile application named Çorlu KODER, that is served as a complaint collection mechanism offered by the Municipality of Çorlu and developed by Corlu KODER project group from Çorlu Engineering Faculty (as described at http://corlukoder.com website and under Corlu KODER mobile app privacy policy document https://corlukoder.com/privacy-policy.pdf).

Location of Interest

Tekirdağ city host over 1100 factories (with the frequency of occurrence; textile, paper, packaging, chemical and metal industries respectively). In Tekirdağ, there are total of 14 organized industrial zones, while 5 of them established around Çorlu district and its immediate surroundings. 4 of the organized industrial zones (OIZ) are lined up in the west-east direction along Çorlu, where the Velimeşe OIZ (where more than 500 facilities operate) is one of the closest one to residental areas of Çorlu and located between Çerkezköy and Çorlu (alongside the North south direction).

Corlu is the area where the new settlement is located and the traffic is concentrated while Çerkezkoy (at the north) host one of the Turkey's largest OIZ under which more than 270 facilities operate [43]. The topographical properties (as indicated in Figure 1) can be described as land appearance in the form of way plains and is uneven, with low to mid slope values. Çorlu is under the influence of a transition type climate where Black Sea, Mediterranean and continental climate characteristics are encountered together. Cold air masses descending from the north and humid-warm air currents coming from the south, the Mediterranean and the Aegean affect the climate structure of the region. Typical directions of the wind are NNE-NE and rarely from the directions of SW-SSW around Corlu [44].

Collection of Odor complaint Data

The GIS integrated public participated (PPGIS) odor complaint collection and management platform Corlu KODER was developed under project collaboration between Tekirdag Namık Kemal University, Faculty of Engineering and Municipality of Corlu. The developed odor complaint collection mobile app Corlu KODER was introduced and publicized as a free service of Municipality through the IOS and Android app merket platforms. The odor complaint collection started by 2020 October and been carried out in Corlu city that has over 200k population. The number of verified mobile app users are >1600.

The proposed methodology is built on collecting citizen odor complaints based on FIDOL factors (frequency, intensity, duration, tone and location of the odor complaint) through a mobile application [45].

Mobile app users, are able to define the percieved level of odor strength and describe the odor tone (by level of annoyane or satisfaction). Çorlu KODER mobile app users may interprete percieved odor with its potential source by making selection from a list of odor type/sources. On the other hand, citizen odor complaint locations are recorded according to geographical coordinate system. Citizen odor compliant records are monitored and managed thorugh a web based compliant management panel by Municipality and the University.

Air Pollution and Meteorological Data Collection

The air pollutant data source is the official Air Quality Monitoring Network website of the Ministry of

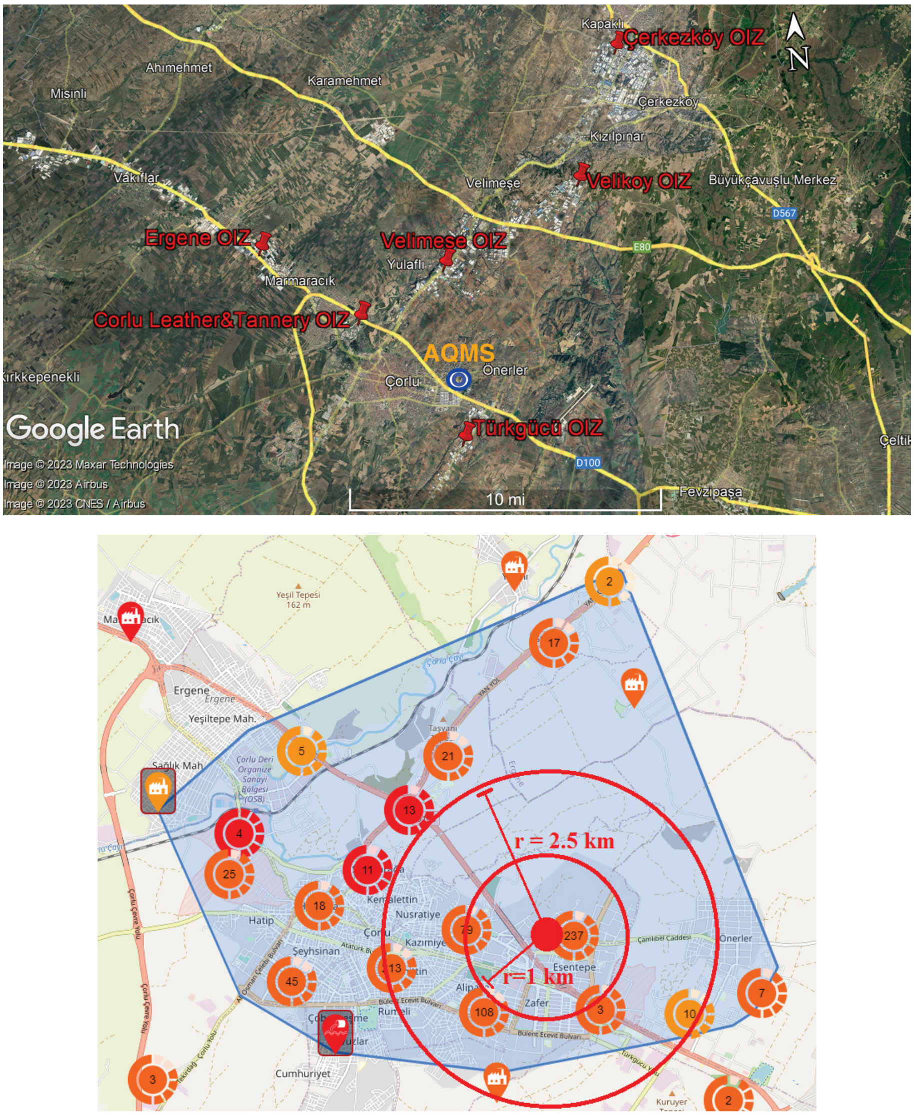

Figure 1. Organized Industrial Zones locations around Corlu and distribution of total number of odor complaints around the BTEX measurement station; Cerkezkoy, Velimese, Kapakli, Ergene, Corlu 1-2. OIZs.

Environment, Urbanization and Climate Change. Daily average values were used and taken as references all along the study. PM_{10}, SO_2, NO_x, O_3 data, and meteorological parameters; air temperature (T), wind direction (WD), wind speed (WS), relative humidity (RH) and Atmospheric pressure (AP) were used as as received from General Directorate of Meteorology (MGM) Tekirdag.

BTEX (benzene, toluen, ethylbenzene, o-xylene and m,p-xylene) concentrations were measured as Daily averages by the mobile air qulity monitoring station of Ministry of Environment, Urban Planning and Climate Change, temporarly located at Esentepe avenue of Corlu between August 28 to November 2 2021 period. Measured BTEX concentration data were used as received from the Marmara Clean Air Central Directorate of the Ministry of Labor and Social Security. BTEX measurement was carried out according to EN-14662-2 standard method based on active carbon sampling and GC-MS analysis. The sampling was performed at the mobile sampling device positioned at the Hürriyet district of Corlu, as shown in Figure 1.

Statistical Analysis

Correlation analysis were performed between the daily variation in meteorological factors, BTEX concentrations,-inorganic air pollutant concentrations, and the total number of odor complaints. Multiple regression analysis can be built on a dependent variable between two or more independent variables were considered [46] Outputs of the analysis, was used to explain the relationship with a linear model and determines the effect levels of the independent variables [46, 47].

Regarding data acquisition, data obtained from the air pollutant measurement stations, the number of reported odor complaints and the meteorological parameters were calculated and used as daily average values.

All analysis and evaluation were performed on the complaints records (reporting unpleasant odor issues (hedonic tonebetween -4 and -1) within August 28 – November 2 2021 period. Sturges classification method was applied to determine the ideal class range and number for wind speed, temperature, relative humidity parameters. Average number odor complaint reports distribution within those class intervals was given an evaluation and discussion [15]. Annual odor complaint data was solely introduced and used for interpretation with the mobile app users demographic information.

RESULTS AND DISCUSSION

Odor Complaint Records

The total number of annual odor complaints (NAOC) (reported by over 550 individual users) is 2389 between the November 2 2020 to November 2 2021 period. While between August 28 – November 2 of 2021, number of odor complaints is 868 (reported by over 400 individual). Regarding the total NAOC; the average number of daily odor complaints (calculated based on the days with at least one complaint: 277 days of 365) was calculated as 10 with a standard deviation (±) of 7. Referringly, an odor episode day is defined as the day with NOC > 17 [data not shown] [34]. In this context, there are 20 odor episode days between the 28 August - 2 November 2021 period, annually the total number is 40.

Interpretation of the Citizen Demographic Information with Annual Odor Complaint Data

Comparing the evaluation findings carried out on annual odor complaint data and August 28-November 2 2021 period specific data, difference was not significant in the distribution of the number and type of complaints according to the age and gender of the users. For this reason, only the evaluation made on the annual data is provided under this section.

Percentage distribution of total number of Corlu KODER mobile app users according to their gender and age is presented in Figure 2. Male and female users constitute %57-%43 of the total users respectively. Users between 31-40 ages constitute the %40 of the total number users. Annually, 63% of the total number of odor complaint records belong to male users and 37% to female users. While, 22% of odor complaints were reported by users aged between 31-35, and 24% from 36-40. 35% of odor complaints reported by users aged between 41-55.

According to randomly selected 10 odor episode; 12% of total odor complaints reported by users between the ages of 31-35. 15%, 18% and 9% of total odor complaints were reported by users aged between 41-45, 46-50 and 51-55 (Figure 3). Distribution of odor complaints according to user gender did not possess a significant difference between the annual and odor episode specific data,

Effect of user age and gender on odor complaint characteristics

Users aged between 35-40, 45-50 and 55-60 have reported odor issues with higher intensities (Figure S1). The hedonic tone scores of the users in the 50-55 age range are more homogeneously distributed on the scale of the parameter.While users between 40-45 reported odor issues with low hedonic tones (-4).

58% of the total number of odor complaints reported by male users are between 4-6 intensity (referring to strong – extremely strong), while it is 77% for female users (data not shown). 63% of the total NOC reported by male users are between -4 and -3 hedonic tone (representative of very

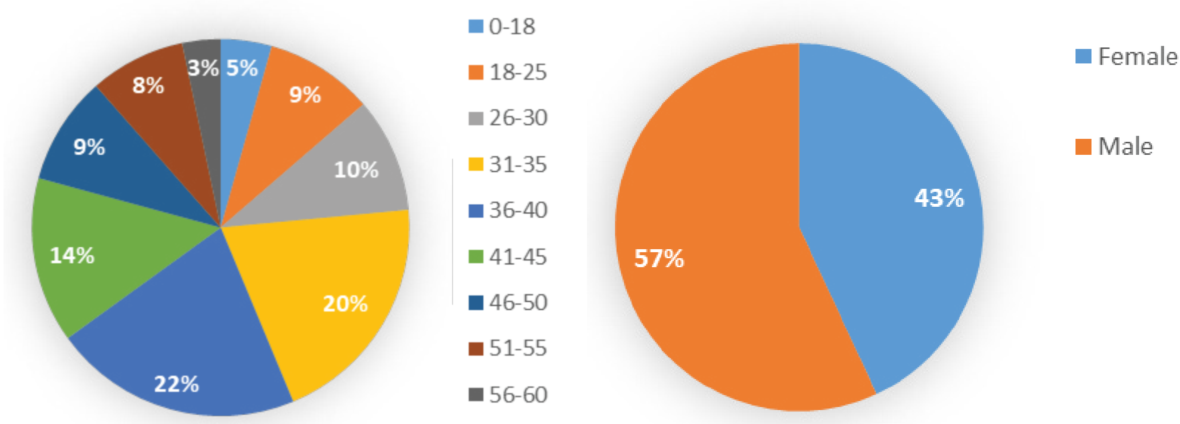

Figure 2. Percentage distribution of the total number of users by age range and gender.

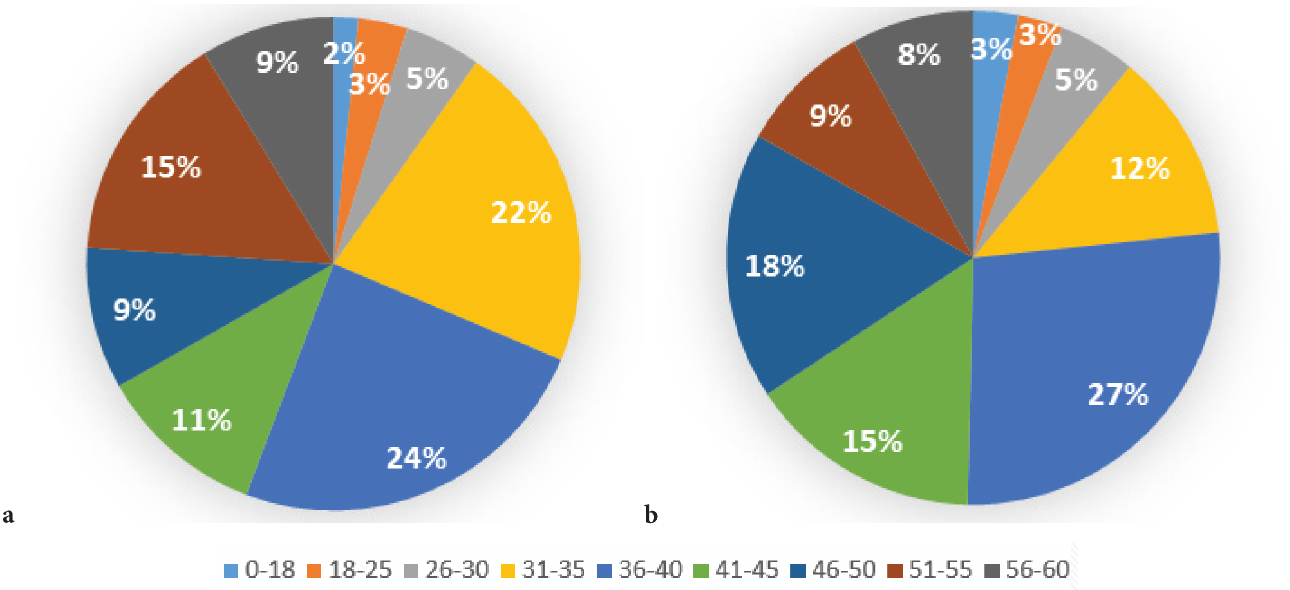

Figure 3. a) Annual and b) odor episode specific percentage distribution odor complaints within user age intervals.

unpleasant and extremely unpleasant odors), while it is is 73% for female users (Figure S2).

Regarding the distribution of odor complaints according to sources, 11% of total odor complaints reported by male users belong to urban sources, while it is 18% for female users. 64% of total odor complaints reported by male users were associated with industrial sources, while it is 57% for female users (Figure S3). It is seen that majority of urban odors were reported by users at 36-40 age interval. Also the majority of industrial odor complaint were reported by users between 41-55, which is distinctly higher than 26-40 interval. Besides, most of the food industry based odor complaints were reported by users between 56-60 ages (Figure S3).

Source Distribution of Odor Complaints within the Study Period

According to distribution of citizen odor complaint characteristics among the odor sources, 80% of the odor complaints were found interrelated with industrial sources between August 28 – November 2, 2021 (Figure 4).

On the other hand, according to analogic evaluation by users; odor complaints are interpreted with various types of odors and possible sources; examples like"Chemical" or "Plastic" are most widely encountered. Besides, chimney, gas, leather, sulphurous compounds, ammonia, asphalt and rubber stand out as other types of related odors/odor sources (Figure 5). Also, the distribution of annual odor complaint data among odor sources exhibited a similar trend with the study period in Corlu (not shown). The distribution profile is analogous with recent research carried out in different industrial areas [20].

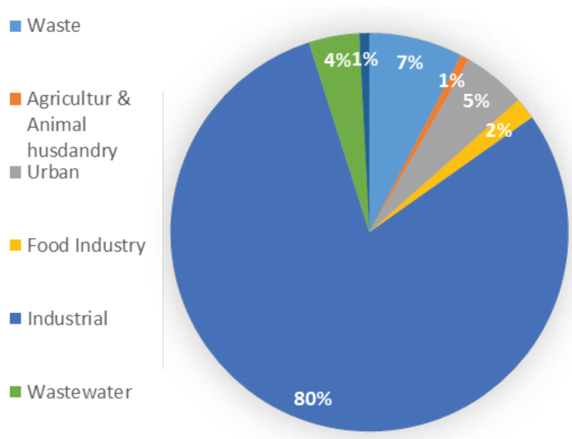

Figure 4. Odor complaints by source.

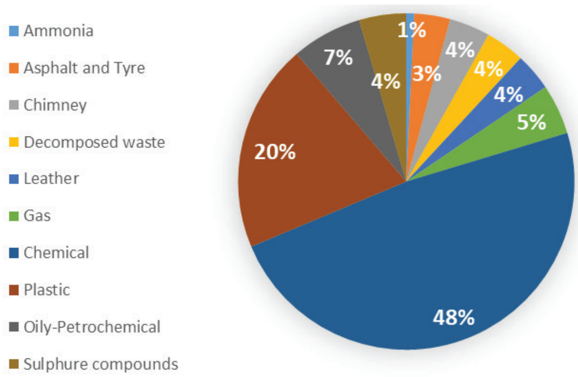

Figure 5. Odor complaints by type.

Spatial Distribution of Odor Complaints within the Study Period

The average percentage of odor complaints with in 1 km diameter (taken the mobile AQMS location as center) is >12% while for the 3rd week (between the September 12-18) the value is >20%. The percentage of odor complaints within 5 km diameter is >58%, that can be interpreted with the population density distribution in different parts of Corlu [48]. Spatial distribution and exact location of OIZs and odor emission source characteristics (point-line-clustered), have a determining role on citizen reported odor issues occurence, spatial distribution and characteristics [16]. Windspeed and wind direction play a determining role on the pollutants spead mechanism by diffusion and advection [36 conti,40,49,50]. Within the studied period; winds from NW-N and NW directions are dominating (f4-j). Also, the percentage of days with wind speed values higher than the average is 50%, and for the rest of the period it is around 30%. The level of correlation between the number of odor complaints, BTEX pollutants and wind-speed, also the number of odor complaints occurence within certain wind-speed intervals are revealed out and given discussion under the statistical analysis section.

Inorganic Air Pollutant Concentration Levels

During the study period, the PM_{10} parameter has exceeded the national limit/threshold (50 μg/m^3) values for 27 days. For the $PM_{2.5}$ parameter, the limit/threshold values have never been exceeded. O_3 has been reported to increase between 6-8 September to 83-89 ug/m^3 that are close to national daily limit values of 120 μg/m^3 (data not shown).

BTEX Concentration Levels

The BTEX concentrations measured in Çorlu Esentepe neighborhood are given in Table 1. Toluene and (m,p)-xylene constitute the highest concentration among BTEX compounds (3.09 and 3.49 ug/m^3 respectively). Between the days 44 and 49 (week 7), there is an increase in the level of m-p Xylene contrubiton to the total BTEX value. During the study period, the EU reported limit value of 5 μg/m^3 for BTEX pollutants in residental areas have been exceeded 5 times for toluen, 8 times for p-m xylen and 4 times for o-xylen. While the EU reported, lower rating threshold (LRT) (2 μg/m^3) and upper rating thresholds (URT) (3.5 μg/m^3) for toluen have been exceeded 55 and 17 times respectively. The LRT (2 μg/m^3) and URT (3.5 μg/m^3) for ethylbenzene have been exceeded 5 and 2 times respectively. The LRT (2 μg/m^3) and URT (3.5 μg/m^3) for p-m xylen have been exceeded 43 and 9 times respectively. The LRT (2 μg/m^3) and URT (3.5 μg/m^3) for o-xylen have been exceeded 9 and 4 times respectively [53]. These values are at comparable level with the measured BTEX concentrations according to the passive sampling study performed in Corlu at 2017; Toluen, Ethylbenzen, m-p xylen and o-xylen concentrations have been reported as: 2.7-6 μg/m^3, 1-1.7 μg/m^3, 3.5 – 6.3 μg/m^3 and 1 – 1.5 μg/m^3 [28].

According to literature, the concentrations measured in urban areas are lower compared to industrial areas. The traffic composition, the type, number and distribution of the industries established in the region, the fixed emission sources and the differences in the meteorological conditions may bring along the measurement differences between studies. According to literature, for the case that the Toluen/benzene (T/B) ratio in urban atmosphere is between 1-4, traffic emissions are considered to be the main source of toluene and benzene [25]. In this study, the average T/B ratio was calculated as 5 and is an indicator that toluene is emitted from sources other than traffic emissions (Table 1) [26, 52].

Despite the fact that they are released into the atmosphere from the same sources, the variation in the rates of OH oxidation in the atmosphere bring along the difference. in (m,p)xylene/Ethylbenzene occurence levels. Xylen to Ethylbenzene (K/E) ratio is used as a parameter to express the intensity and duration of photochemical reactivity in the atmosphere (the photochemical age of the atmosphere) [53]. The K/E values above 3.0 are considered high and low between 1.0-1.5. The range of 2-4 in K/E ratios represents fresh emissions [53, 54].

In this study, the K/E ratio was calculated as 3.30 on average. Accordingly, it can be said that the environment in which the study is carried out is under the influence of fresh emission sources throughout the study period. The fact that the K/E ratio is in the range between 2-4, is closely related to the distance of the measurement station to the air pollutant source. There are six OIZs located within 1.5 km (Turkgucu, Corlu), 5 km (Ergene), 10 km (Velimese) and 15 km. (Cerkezkoy) km of the air quality monitoring stations. It is an expected result that air masses will age until they reach the measurement stations.

Major industrial activites carried out in the Turkgucu, Corlu 2, Ergene and Velimese OIZs can be listed as textile manufacturing, dyeing, paper and products, chemical manufacturing, leather and tannery, rubber and plastic [55,56].

Benzene are mainly released into the atmosphere from dyes, pesticied, lubricants, detergent and pharmeceuticals industry. Ethylbenzene are derived from adhesive and paint using processes,pesticides and fragrance agents. While, m-xylene, o-xylene and p-xylene mainly result from solvent using industries such as; paint and plastics, herbicides. While toluene, result from solvent use in paints and inks, foams [29]. On the other hand, (m,p)-xylene and o-xylene compounds and ethylbenzene are emitted from vehicle exhausts, evaporation of solvents and industrial activities to the atmosphere. According to literature, the total number of textile industry/facilities operating in Ergene basin exceeds 600 by 2017, most of which is located in Tekirdağ. These facilities are distributed as 67 in Çorlu, 72 in Velimeşe, 20 in Türkgücü, 37 in Vakıflar and 26 in Ulaş [55]. The most common volatile organic air pollutant compounds (including the toluene, xylene, n-hexane, n-heptane) are emitted into the atmosphere from the stenter chimneys connected

Table 1. Daily average BTEX pollutant concentrations and # of odor complaints between the 28th August – 2 November 2021 period

	µg/m³						Toluen/ Benzen	(m+p) Ksilen/ Etilbenzen	# of odor complaints
Day	**Benzen**	**Toluen**	**Etilbenzen**	**p,m-Xylen**	**o-Xylen**	**Total BTEX**			
1	0.65	4.13	0.84	2.71	1.49	9.82	6.34	3.22	23
2	0.66	3.38	0.83	2.61	1.45	8.93	5.13	3.14	42
3	0.64	3.36	0.91	2.91	1.52	9.34	5.28	3.20	50
4	0.55	3.21	0.64	2.01	1.08	7.49	5.87	3.13	20
5	1.06	5.08	0.87	2.91	1.38	11.30	4.79	3.34	87
6	0.62	2.62	0.65	2.08	1.10	7.08	4.20	3.23	28
7	0.48	5.61	2.59	9.64	8.40	26.73	11.60	3.72	20
8	0.50	4.07	0.72	3.59	2.53	11.41	8.19	4.96	28
9	0.45	3.31	0.53	2.68	1.38	8.35	7.40	5.04	20
10	0.39	4.25	0.61	2.26	1.31	8.83	10.79	3.69	3
11	0.46	2.59	0.60	1.93	1.12	6.70	5.60	3.22	2
12	0.37	2.19	0.62	2.15	1.20	6.54	5.89	3.47	2
13	0.61	2.71	0.57	2.10	1.13	7.12	4.42	3.67	6
14	0.76	3.45	0.67	2.13	1.10	8.11	4.56	3.17	19
15	0.88	3.56	0.71	2.40	1.20	8.75	4.06	3.38	13
16	0.71	2.73	0.54	1.90	0.98	6.87	3.84	3.50	30
17	0.77	6.06	1.11	3.38	1.55	12.88	7.85	3.06	16
18	0.83	6.06	1.07	3.51	1.68	13.15	7.28	3.27	38
19	0.68	3.68	0.69	2.36	1.22	8.62	5.45	3.44	39
20	0.59	5.10	0.80	2.79	1.45	10.74	8.58	3.48	21
21	0.62	4.11	0.81	2.75	1.48	9.77	6.59	3.39	14
22	0.67	2.92	0.71	2.51	1.40	8.22	4.36	3.53	10
23	0.67	3.94	0.90	3.04	1.65	10.19	5.92	3.39	24
24	0.57	3.07	0.84	3.05	1.46	8.98	5.35	3.63	16
25	0.55	2.13	0.49	1.50	0.76	5.43	3.89	3.08	9
26	0.78	3.89	0.76	2.58	1.19	9.20	4.97	3.39	10
27	0.58	2.66	0.55	1.78	0.94	6.51	4.61	3.26	12
28	0.67	3.38	0.70	2.15	1.08	7.98	5.06	3.07	23
29	0.56	2.30	0.61	1.97	0.99	6.43	4.13	3.24	7
30	0.67	3.43	0.57	1.96	0.94	7.57	5.15	3.41	7
31	0.56	4.66	0.51	1.73	0.87	8.33	8.29	3.38	5
32	0.61	2.55	0.48	1.59	0.79	6.02	4.18	3.32	27
33	0.42	1.92	0.41	1.34	0.67	4.75	4.61	3.30	8
34	0.45	2.45	0.50	1.58	0.80	5.78	5.45	3.16	2
35	0.51	1.98	0.48	1.50	0.78	5.24	3.92	3.15	5
36	0.59	2.29	0.44	1.44	0.75	5.51	3.91	3.25	6
37	0.70	3.24	0.64	2.16	1.00	7.73	4.65	3.40	12
38	0.50	2.37	0.52	1.78	0.82	5.99	4.78	3.45	21
39	0.42	1.71	0.43	1.51	0.76	4.83	4.12	3.55	8
40	0.50	2.32	0.52	1.85	0.96	6.14	4.65	3.57	5
41	0.42	1.66	0.44	1.53	0.82	4.87	3.90	3.43	4
42	0.58	2.23	0.50	1.70	0.93	5.95	3.84	3.41	3
43	0.65	5.55	0.74	2.54	1.23	10.71	8.54	3.42	0
44	0.63	3.28	9.09	28.73	14.12	55.85	5.23	3.16	2
45	0.76	2.36	4.51	13.76	7.26	28.65	3.11	3.05	3
46	0.77	2.34	3.45	10.10	5.28	21.94	3.03	2.93	3
47	1.02	2.77	2.86	8.57	4.42	19.65	2.71	2.99	3
48	1.05	3.94	2.20	6.54	3.42	17.15	3.76	2.98	3
49	0.74	2.48	1.84	5.46	3.16	13.67	3.34	2.97	4
50	0.77	2.62	1.79	5.34	3.19	13.72	3.38	2.98	4
51	0.73	2.04	1.23	3.62	1.89	9.51	2.78	2.95	12
52	0.48	1.39	1.03	2.90	1.48	7.27	2.92	2.82	33
53	0.54	2.17	1.09	3.20	1.63	8.62	4.02	2.94	4
54	0.62	2.05	1.02	2.89	1.75	8.33	3.31	2.83	8
55	0.50	2.20	0.84	2.46	1.23	7.23	4.42	2.94	7
55	0.60	2.25	0.86	2.59	1.30	7.61	3.75	3.00	1
56	0.49	1.29	0.79	2.28	1.22	6.07	2.61	2.90	1
57	0.72	1.82	0.81	2.38	1.27	6.99	2.55	2.95	10
58	0.79	2.54	0.73	2.22	1.14	7.43	3.21	3.04	2
59	1.03	3.80	0.86	2.65	1.36	9.69	3.70	3.07	2
Average	**0.64**	**3.09**	**1.09**	**3.49**	**1.87**	**10.17**			

Extreme BTEX values between 13th – 15th October are intentionally removed and not listed to the stenter machines of the the textile finishing process. The average number of stenter chimneys around the study area is over 700; mainly located in the Velimeşe OIZ and Ergene OIZ. As a result, the high BTEX concentrations can be interpreted with the number and location of OIZs around Corlu [55, 56].

Accordingly, an interpretative evaluation was made in the next section, considering the relation between total number of odor complaints, BTEX measurement results and meteorological parameters [5, 20].

Statistical Analysis and Interpratative Evaluation of BTEX concentrations, Odor complaints and Meteorological Factors

The daily BTEX concentrations, inorganic air pollutant concentrations, meteorological factors and temporal distribution of total number of odor complaints within the August 28 -November 2 2021 periods were evaluated by using statistical analysis. The correlation findings are presented in Table 2.

The level of correlation is moderate between the total number of odor complaints and toluene concentration, with correlation coefficient (r) of 0.52. Since the data collection methodology have some limitations such as; uniformity of sensing and judgement differences between citizens, the correlation coefficient can be assumed quite significant.

Also, the level of correlation is moderate between the total number of odor complaints and temperature (r=0.64), and between the total numer of odor complaints and NO_2 (r=0.50). High correlation was found between temperature and toluene concentration (r=0.71). Also the level of correlation was high between Benzene and NO_x (r=0.72). Very high correlation was found between the p-m Xylen, o-Xylen and Ethylbenzene (r=0.96 and 0.95)

It can be concluded that the average wind speed in Çorlu is negatively correlated with NO_X and NO_2 parameters. Negative and low level of correlation is reported between the relative humidity (RH) and total number of odor complaints (-0.33) Theoretically RH may enhance the citizens' sense of small by trapping odor molecules and is listed among the parameters that have a deteriorating effect on the atmospheric diffusion mechanism. Therefore, significance of RH values below and above certain thresholds have been examined by ANOVA analysis (Table S1)

Also, there is strong negative correlation between the average wind speed in Çerkezköy and NO_2 values in Çorlu (-0.75) and also with Benzene (-0.65). Those findings are also supportive of the negative correlation coefficient (r= -0.48) between total number of odor complaints and wind speed in Çerkezköy. Odorous compoounds can be transported considerable distances in just a matter of minutes depending on the strength of the source, weather patterns, wind speed and direction [57]. Mostly, it is reported that slight air pollution scenarios are under the effect of windspeed and horizontal diffusion capability. The dispersion of odors is partly determined by the presence of wind. And Below certain limits, odor stagnation may be favoured [60]. Discussion was supported with the NOC distribution within certain windspeed intervals according to the Sturges classification (Table 3) [16, 57, 59]. There is low level of negative correlation between the benzene measured in Çorlu and wind speed (r=-0.63). While correlation is obtained with the rest of BTEX (r values < 0.38).

In the light of the obtained correlation findings; two independent variables were selected. By 2 way ANOVA analysis, it was examined whether those two variables have significant effect on the total number of daily odor complaints. For this purpose, two evaluations were made as stated below;

a- The analysis were performed with an assumption of certain conditions; i) above and below the daily average BTEX value ii) below and above the relative humidity average value.

b- Similarly, the 2-way ANOVA analysis were performed, based on the number of odor complaint records collected in conditions below or above the daily average Toluene concentration and relative humidity.

For the case that the relative humidity values are below the average, the BTEX values make a significant contribution on the total number of odor complaints variation. Similarly, under the conditions where the BTEX value is above the average, the RH values make a significant contribution on the total number of odor complaints (Table S1: Sig value=1 demonstrate significant effect on number of odor complaints).

The mean and standard deviation of odor complaint numbers significantly differed based on toluene concentration range above or below the mean value. The results did suggest that the contribution of toluene to number of odor complaints in the residental area of Corlu become prominent in comparison with the other BTEX air pollutant concentration levels (Table S2).

Frequency of Odor Complaints Occurence within Certain Intervals of Meteorological Parameters and BTEX Concentrations

The number of odor complaints encountered in specific daily average wind speed, temperature, relative humidity and BTEX concentration intervals (specifically Toluene and total BTEX) are demonstrated in (Table 3 and 4). The parameters were sub-classified, class width and class numbers were set by using the Sturges classification method [15,58].

For common weather situations with mean temperature, winds-speed and relative humidity that are nearly horizontally uniform, turbulent transport in any horizontal direction nearly cancels transport in the opposite direction, and thus can be neglected. But vertical transport is significant [17, 18, 60].

The total NOC within each WS interval is expressed in Table 3. The daily average number of odor complaints makes a decent increase and keep increasing between 0.8

Table 2. Correlation analysis of daily average BTEX and inorganic air pollutants concentrations with meteorological factors and number of odor complaints

	# of odor comp.	*Benzen*	*Toluen*	*Etilbenzen*	*p,m-Xylen*	*o-Xylen*	*T [°C]*	*P*	*PM10 (µg/m³)*	*SO_2 (µg/m³)*	*NO_2 (µg/m³)*	*NOX (µg/m³)*	*O_3 (µg/m³)*	*Sum of BTEX*	*Avg WS Corlu*	*Avg RH Corlu*	*Avg WS Cerkezkoy*
# of odor comp.	1.00	0.24	0.52	0.01	0.04	0.03	0.64	-0.38	0.34	-0.06	0.50	0.18	0.22	0.16	-0.42	-0.33	-0.48
Benzen	0.24	1.00	0.33	0.57	0.50	0.44	0.10	-0.24	0.36	0.27	0.72	0.72	-0.30	0.59	-0.63	0.28	-0.65
Toluen	**0.52**	0.33	1.00	0.31	0.38	0.34	0.71	-0.52	0.47	0.02	0.56	0.18	0.19	0.63	-0.33	-0.40	-0.42
Etilbenzen	0.01	0.57	0.31	1.00	0.96	0.95	0.02	-0.10	0.11	0.03	0.18	0.48	-0.41	0.88	-0.37	0.22	-0.34
p,m-Xylen	0.04	0.50	0.38	0.96	1.00	0.98	0.07	-0.16	0.09	0.06	0.19	0.41	-0.37	0.93	-0.28	0.19	-0.28
o-Xylen	0.03	0.44	0.34	0.95	0.98	1.00	0.09	-0.18	0.05	0.00	0.10	0.32	-0.32	0.91	-0.28	0.19	-0.26
T [°C]	0.64	0.10	0.71	0.02	0.07	0.09	1.00	-0.70	0.31	-0.33	0.41	-0.16	0.63	0.26	-0.27	-0.52	-0.33
P [hPa]	-0.38	-0.24	-0.52	-0.10	-0.16	-0.18	-0.70	1.00	0.06	0.32	-0.42	0.04	-0.30	-0.33	0.28	0.06	0.32
PM10 (µg/m³)	0.34	0.36	0.47	0.11	0.09	0.05	0.31	0.06	1.00	0.31	0.27	0.22	0.11	0.15	-0.15	-0.17	-0.20
SO_2 (µg/m³)	-0.06	0.27	0.02	0.03	0.06	0.00	-0.33	0.32	0.31	1.00	0.19	0.47	-0.36	0.01	0.00	0.23	-0.04
NO_2 (µg/m³)	0.50	0.72	0.56	0.18	0.19	0.10	0.41	-0.42	0.27	0.19	1.00	0.71	-0.14	0.40	-0.66	0.07	-0.75
NOX (µg/m³)	0.18	0.72	0.18	0.48	0.41	0.32	-0.16	0.04	0.22	0.47	0.71	1.00	-0.62	0.36	-0.55	0.45	-0.56
O_3 (µg/m³)	0.22	-0.30	0.19	-0.41	-0.37	-0.32	0.63	-0.30	0.11	-0.36	-0.14	-0.62	1.00	-0.23	0.12	-0.69	0.09
Sum of BTEX	0.16	0.59	0.63	0.88	0.93	0.91	0.26	-0.33	0.15	0.01	0.40	0.36	-0.23	1.00	-0.29	0.06	-0.32
Avg WS Corlu	-0.42	-0.63	-0.33	-0.37	-0.28	-0.28	-0.27	0.28	-0.15	0.00	-0.66	-0.55	0.12	-0.29	1.00	0.00	0.96
Avg RH Corlu	-0.33	0.28	-0.40	0.22	0.19	0.19	-0.52	0.06	-0.17	0.23	0.07	0.45	-0.69	0.06	0.00	1.00	0.01
Avg WS Cerkez	-0.48	-0.65	-0.42	-0.34	-0.28	-0.26	-0.33	0.32	-0.20	-0.04	-0.75	-0.56	0.09	-0.32	0.96	0.01	1.00

Table 3. Average Number of odor complaints and average BTEX concentrations within certain wind speed intervals

Wind speed (Corlu)	# of odor complaints	Average Total BTEX
0 - 0.8 m/s	0	0
0.8 - 1.6 m/s	13	9.2
1.6 - 2.4 m/s	20.7	10.1
2.4 - 3.2	11.7	13.2
3.2 - 4	9	9.6
4 - 4.8	6	7.2
4.8 - 5.6	3.3	5.8
>5.6	2.8	6.8

Table 4. Average Number of Odor Complaints within Daily Average BTEX concentration, Toluen concentration, temperature and relative humidity intervals

Total BTEX (μg/m³)	Average # of odor complaints
1 - 4	4
4-6	7.6
6-8	9.8
>8	18
Toluen (μg/m³)	**Average # of odor complaints**
0-2	5.3
2—3	7.3
3—4	19.4
4—5	14.4
>5	33
Temperature (0C)	**Average # of odor complaints**
12--15	3.4
15--18	6.4
18-21	10
21-24	17.7
>24	35.4
Relative humidity	**Average # of odor complaints**
<66	7.9
66-72	13.4
72-78	24.6
78-84	4.3
>84	2.8

– 2.4 m/s interval. While the daily average NOC tend to decrease for WS > 2.4 m/s conditions. The total BTEX concentrations reflected to the average number of daily citizen odor complaints where; the average number of odor complaints remained around 4 for $BTEX_{total} < 4$ μg/m³. The average number of odor complaints demonstrated a lineer increase for the $BTEX_{total}$ conditions between 4-8 μg/m³ and > 8 μg/m³ [5,29,61].

The daily average Toluen concentration remained around 3 μg/m³ during the study period. As demonstrated in Table 4, above the 3 μg/m³ toluen concentration, average NOC have increased from 7.3 to 19.4. Over the $[C]_{toluen}= 4$ μg/m³ conditions, average NOC increased up to 23. In line with the obtained results, it was concluded that the toluene concentration was associated with the increase in the NOC.

The increases in the average number of daily odor complaints by temperature is distinct. Over 21 ^{0}C, the average number of daily odor complaints increases from 10 to 17.7 and reaches over 35 [15,57]. In this study, increased number of odor complaints between the 55-78 RH conditions can be ascribed to trapping of odorous compounds close to the surface by RH [62]. The average number of daily citizen odor complaints have reached to its maximum, between RH conditions 72-78 (average RH was 70 during the study period).

CONCLUSION

In this study, the relationship between the citizen odor complaints, BTEX concentrations and meteorological factors were investigated in Çorlu residental area. The nearby OIZs and industrial activity were found to have a determining role on the occurence of citizen odor complaints. Number of odor complaints generally increased during high atmospheric BTEX concentration conditions. Also the level of BTEX concentrations and number of odor compliants were found to be related with meteorological factors such as temperature, relative humidity and wind speed.

Regarding the demographic profile of mobile app users; %46 of total odor complaints were reported by users between 30-40 ages. Within the odor episode days, the total number of odor complaints were distributed more homogenously within age intervals. User gender was not find effective on odor complaint source distribution. Users between 35-40 ages have reported more urban odors as compared to remaining users. On the other hand users between 40-50 ages have reported more industrial odors as compared to users between 25-40. Regarding odor tone and intensity, female users have reported odor issues with higher level of intensity and annoyance.

Average Toluen/Benzene ratio was calculated as 5 and is indicative of non-traffic source of toluen emission. The type and level of total BTEX pollutant concentrations were found related with the nearby industrial activities around Corlu. There is a significant correlation between the total number of odor complaints and toluene concentrations. Also high correlation was found between temperature and toluene concentrations. Regarding the days above average BTEX concentrations (> 8 μg/m^3), the RH value have significant effect on the total number of odor complaints. Below average RH conditions, the toluene concentration has a significant effect on the total number of complaints.

The average number of odor complaints increases between 0.8-1.6 and 1.6-2.4 m/s windspeed levels, and exhibits a lineer decrease within 2.4-5.6 m/s windspeed interval. Also, the average number of odor compliants increases, when the BTEX concentrations are between 4-8 μ/m^3 and increase over >8 μg/m^3. The average number of odor complaints exhibits an almost lineer increase from 5.3 to 33, when the Toluen concentrations increase from 0-2 μg/m^3 interval to >5 μg/m^3.

Besides the air pollutant measurement and air quality indexes, there is a lack of clear indicators regarding the level of odor discomfort in the field. Citizen odor complaint surveys are useful monitoring tools and can be used to identify sensitive areas where volatile organic compounds should be measured and monitored. Besides, measurement/monitoring studies such as field olfactometry, odorous VOC measurement can be planned, also building odor sensor networks can be realized accordingly.

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Occurrence of bromide and bromate in chlorinated indoor swimming pools, and associated health risks

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ABSTRACT

Swimming is a physical activity that is accessible to people of all ages in all seasons. However, continuous organic and inorganic precursor load and disinfectant dosing make pool water chemistry much more complex than other disinfected waters. Carcinogenic bromate compound is one of the hundreds of disinfection by-products in pool water. The occurrence of bromate in pool waters depends on the precursor content of filling water, the disinfection process, operating parameters, and the purity of disinfectants. While the average filling water bromide concentrations of University Campus indoor swimming pool in Gülbahçe –Urla (SP1) and Buca public indoor swimming pool (SP2) were determined to be 182 µg/L and 11.0 µg/L, respectively, the average bromate concentrations of SP1 and SP2 were 59.4 µg/L and 68.3 µg/L. Estimated chronic-toxic health risks of accidental ingestion of pool water during swimming (between 10^{-3} and 10^{-1}) were lower than the threshold level ('1'). Although the carcinogenic risks in central tendency scenario ($<10^{-6}$) indicate negligible risks for swimmers, worst case scenario indicates carcinogenic risks (medians were ranged from 1.61×10^{-6} to 9.42×10^{-6}) for highly exposed specific swimmer groups. Bromate accumulation in swimming pools needs attention for mitigating the health risks for swimmers.

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INTRODUCTION

Swimming is one of the most common sports activities that people of all age groups can do. With the '*Yüzme Bilmeyen Kalmasın*' project initiated by the Ministry of Youth and Sports in Türkiye; people are encouraged to increase their interest in swimming [1]. Within the scope of this project, the total number of pools (Olympic, semi-Olympic and non-Olympic) in Türkiye which was 46 in 2002 increased to 610 in 2022. Although the number of indoor and outdoor swimming pools in Türkiye is not known, the increase in the number of swimming pools opened in recent years can be considered as an indicator of people's interest in swimming. Swimming pool disinfection is vital to maintaining a safe and healthy swimming environment. Swimming pools must be disinfected continuously to prevent microbial activities that cause waterborne outbreaks and infections caused by swimmer-borne pathogens (viruses, bacteria and fungi) [2, 3]. Chlorine is the

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most widely used disinfectant for swimming pools, as it is effective at killing a wide range of microorganisms and due to its low cost [4, 5]. Besides chlorine; sodium hypochlorite, chloramine, ozone, chlorine dioxide, ultraviolet radiation (UV) etc. are also used effectively [6, 7].

Disinfection of swimming pools may generate potentially hazardous byproducts known as disinfection byproducts (DBPs). Organic or inorganic disinfection by-products are formed due to the reaction in the pool water during disinfection. Organic DBPs occur when disinfectant reacts with organic matter in the pool water, such as sweat and urine [8, 9]. These byproducts can cause irritation of the eyes and lungs, as well as other health problems [10, 11].

Pool operators should carefully adjust the amount of chlorine required for disinfection to reduce the risk of DBPs, monitor the amount of residual chlorine in the pool to ensure continuity of disinfection, and regularly test pool water for DBPs. To ensure that sufficient disinfection efficiency is maintained in the pool water, residual chlorine concentration in swimming pool is regulated. In Türkiye, the concentration of free chlorine in the chlorinated pool water is regulated to be between 1-1.5 mg/L in indoor swimming pools, and 1-3 mg/L in outdoor swimming pools, while free chlorine concentrations in pools where other disinfection methods (UV, ozone, chlorine dioxide, and others) are used are limited to 0.3-0.6 mg/L [12].

Inorganic disinfection byproducts (bromate, chlorite and chlorate) are also detected in the water [13]. Bromate is classified as a possibly 2B carcinogen (possibly carcinogenic) to human [14]. There are several reasons for the formation of bromate detected in disinfected water. Bromate is formed when ozone is udes as the disinfectant in bromide-containing waters [15, 16]. It also forms with the use of disinfectants containing chlorine. Chlorine is an oxidizing substance. When the water is disinfected with chemicals containing chlorine, if the water containing residual chlorine contains a certain amount of bromide ion, this ion is converted to bromate by chlorine oxidation. In Türkiye, the most commonly used chlorination methods in swimming pools are sodium hypochlorite dosing and hydrolysis to separate free chlorine molecules from the saline solution. When disinfected with chemicals containing chlorine, the chlorine mixes with the water and forms hypochlorous acid, which dissociates into hydrogen atoms and hypochlorite ions. It is the sum of the chlorine residue (free chlorine), hypochlorous acid, hypochlorite ion and aqueous chlorine concentrations in the pool as a result of disinfection [17]. Bromate formation on chlorination of bromide ingredient waters is very slow process due to the low disproportionation rate constant of hypobromous acid (HOBr). Bromate formation in chlorinated water starts with the formation of HOBr with reaction between hypochlorous acid (HOCl) and bromide ion results bromide oxidation by HOCl to form HOBr and Chloride (Cl^-). HOBr is in equilibrium with hypobromite ion (OBr^-) (acid dissociation constant, pKa=8.8). Further, disproportionation of HOBr forms the reduced species (-1 and +1 valance) of Br and oxidized species (Bromate, BrO_2^-, Br^{+3} and Br^{+5}) [18]. Bromide ion to bromate conversion rate was less than 1.3% at the overdosing chlorine condition (5 mg/L) [19].

Electrolysis could be used for production of sodium hypochloride (NaOCl) from saline solution. During the electrolysis process, bromate could be formed as an unintentionally produced by-product due to the chemical conversion of bromide to bromate [20-23]. Bromate formation rate in electrolysis process depends to impurities in chlorine precursor salt [24, 13].

Bromate formation is not a primary concern in water chlorination as the formation process is slow in disinfection. However, it might be a significant concern in chlorinated waters due to the continuous disinfectant dosing and the non-volatile structure of bromate [25] that may result in bromate accumulation in swimming pools. Considering that swimming pools are closed systems, bromate levels tend to increase continuously since bromate is not volatile and water-soluble compound, and bromate entry into the pool due to continuous disinfectant dosing. For those reasons, neglected bromate levels in chlorinated water could be a significant risk factor for swimmers. Swimmers may be exposed by aerosol inhalation, dermal absorption (depending on skin permeability) or accidental ingestion pathways [26, 27]. In the article presented at the EUROTOX 2021 symposium, Röhl reported that 73-98% of the bromate exposure of swimmers occurred through the oral pathway [28].

After the NaOCl solution is produced, it is stored for sale or application after sale. During storage, the chlorine concentration in the disinfectant decreases under high temperature conditions. No significant change is observed in cold seasons. Bromate in solution exhibits a stable state unaffected by temperature [21]. The decrease in the chlorine concentration in the disinfectant during storage causes more disinfectant to be fed into the water to arrange regulatory levels and results co-dosing of bromate to the pool waters.

Reports of potential hazards and environmental levels of bromate in pool water are scarce in the literature. The aim of this study is to investigate the presence of bromate in two different indoor swimming pools and their filling waters, accidental oral exposure, and associated health risks. To the best of our knowledge this is the first study that investigate the occurrence of bromate in Turkish public pools and estimates associated health risks.

MATERIALS AND METHODS

Sampling and Analyses

Sampling campaign was conducted simultaneously in two Semi-Olympic indoor swimming pools that those were in Gülbahçe-Urla (University Campus-SP1) and Buca (Public Pool-SP2) from April-2019 to May-2019 (Figure 1).

While the pool water volume of SP1 was 900 m^3, pool water volume of SP2 was 579 m^3. They were filled with municipal water, and continuously circulated. Coarse particles, human body residues (hair, skin, etc.), and textile fibers in pool water were filtered in sequential coarse and fine sand filters and returned to pool from bottom nozzles after disinfectant (sodium hypochlorite) dosing. Temperature, pH, and free chlorine levels were continuously controlled to ensure regulatory limits.

Both pool water and filling water were sampled. While the physico-chemical parameters (water temperature, pH, bromide and bromate) were analyzed in pool waters, only bromide and bromate were the targeted parameters in filling water. Pool water samples were taken at 3 different points at a depth of 20 cm and 40 cm from the edge of the pool and combined. Water samples for bromate analysis were collected in Teflon-faced amber bottles (40 mL). Sodium sulfite was spiked in all samples for quenching the chlorine. Samples were kept at +4°C and analyzed within 48 hours.

pH, electrical conductivity (EC), and temperature parameters were measured with the Hach Lange HQ40D device. Bromide (Br^-) and bromate (BrO_3^-) ions were analyzed based on SM 4110 [29] using Ion chromatography coupled with CD20 conductivity detector (Dionex ICS-5000) in Environmental Research Center of Izmir Institute of Technology.

Exposure and Risk Assessment

Chronic-toxic health risks and carcinogenic risks associated with accidental ingestion of bromate pool water were estimated deterministically using Equations (1), (2) and (3). Exposure scenarios were constructed for four age groups, 6 to <11 years, 11 to <16 years, 16 to <21 years, and adults, in central tendency and worst cases (Table 1). In central tendency scenarios, median levels of pool water ingestion rate, body weight, and swimming duration were used for estimation of health risks, while those were upper-bound values of ingestion rate and swimming time and lower-bound for

Figure 1. Sampling points.

Table 1. Variables of exposure and risk assessment

Parameter	Central Tendency	Worst Case	Reference
C	**Individual**	**Individual**	**This study**
IR	6 to < 11 year: 0.025 L/h	6 to < 11 year: 0.096 L/h	[30]
	11 to < 16 year: 0.029 L/h	11 to < 16 year: 0.152 L/h	
	16 to < 21 year: 0.019 L/h	16 to < 21 year: 0.105 L/h	
	Adults: 0.013 L/h	Adults: 0.092 L/h	
A x EF	6 to < 11 year: 30.2 h/year	6 to < 11 year: 96 h/year*	[30, *34]
	11 to < 16 year: 27.8 h/year	11 to < 16 year: 96 h/year*	
	16 to < 21 year: 29 h/year	16 to < 21 year: 96 h/year*	
	Adults: 9 h/year	Adults: 96 h/year*	
ED	30 years for adults and 5 for other age groups		Assumed
CF	0.001		This study
BW	6 to < 11 year: 26.5 kg	6 to < 11 year: 21.3 kg	[31, 32]
	11 to < 16 year: 49.2 kg	11 to < 16 year: 39.4 kg	
	16 to < 21 year: 58.3 kg	16 to < 21 year: 53.53 kg	
	Adults: 65 kg	Adults: 48 kg	
AT	27375 days		[35]
SF	7×10^{-1} per mg/kg-day		[33]
RfD	4×10^{-3} mg/kg-day		[33]

body weight in worst case scenario. While the pool water ingestion rates and activity times of swimmers were taken from Exposure Factors Handbook [30], body weights of combined female and male Turkish Citizens [31, 32] were used for assessment of bromate exposure. Product of exposure duration, and exposure frequency was assumed to be equal to averaging time in CTR estimation. Reference dose (RfD) and slope factor (SF) of bromate were taken from the Integrated Risk Information System [33].

$$CDI = \frac{C \times IR \times A \times EF \times ED \times CF}{BW \times AT} \quad (1)$$

$$CR = CDI \times SF \quad (2)$$

$$CTR = \frac{CDI}{RfD} \quad (3)$$

where, CDI: chronic daily intake (mg/kg-day), C: bromate concentration in pool water (μg/L), IR: accidental ingestion rate of pool water (L/hr), A: activity time (hr/day), EF: exposure frequency (day/year), ED: exposure duration, CF: conversion factor (μg/L to mg/L), BW: body weight (kg), AT: average time (day), CR: carcinogenic risk (unitless), SF: slope factor (per mg/kg-day), CTR: chronic toxic risk (unitless), RfD: reference dose (mg/kg-day).

RESULTS

Physico-chemical parameters of filling water and pool water

Both of the studied swimming pools were filled with municipal water. Pool water temperature and pH was in agreement with the Türkiye guidelines setting physical parameters for swimming pools [12] (Table 2). The average bromide ion concentrations of filling water of SP1 and SP2 were determined to be 182 and 11.0 μg/L, respectively, with ranges of 162-203 μg/L and 8.58-12.9 μg/L. Filling water bromide concentrations of SP1 were determined to be around two order of magnitude higher than SP2. Relatively higher bromide levels of filling water of SP1, located in coastal zone of Karaburun Penninsula, might be due to the effects of seawater intrusion to the groundwater and/or difference of geogenic factors [36]. Coastal freshwater bromide ion could reach as high as 4 000 μg/L [37]. Bromide ions of swimming pool samples could not be analyzed due to overlapping of the peaks of inorganic chlorinated compounds and bromide.

The average bromate concentrations of SP1 and SP2 were determined to be 59.4 and 68.3 μg/L, respectively. Bromate concentrations in swimming pools were determined to be higher than the regulatory levels for Türkiye

Table 2. Physico-chemical characteristics of filling waters and pool waters

Parameters	Sample	Average	Minimum	Maximum
pH	FW1	6.98	6.95	7.01
	SP1	7.46	7.02	7.76
	FW2	*N.D.	*N.D.	*N.D.
	SP2	7.45	7.40	7.50
Bromide (µg/L)	FW1	182	162	203
	SP1	*N.D.	*N.D.	*N.D.
	FW2	11.0	8.58	12.9
	SP2	*N.D.	*N.D.	*N.D.
Bromate (µg/L)	FW1	*N.D.	*N.D.	*N.D.
	SP1	59.4	53.8	62.2
	FW2	2.13	0.55	2.96
	SP2	68.3	59.4	62.2

*N.D.: not determined

or European drinking water (10 µg/L) [38, 39]. Although there was a two order of magnitude difference of bromide concentrations between both sample pools, no significant difference was observed between the two pools, the difference in the bromate concentrations was not significant. While the bromate was not detected in the filling water in Italy, pool water concentrations were determined to be in the range of 10-48 µg/L [40]. Righi reported that the bromate could be formed in chlorinated bromide ingredient waters [40]. However, our findings support the bromate occurrence in chlorinated pools might be significantly affected by the co-dosing of pre-occurrence bromate with sodium hypochlorite for arranging the regulatory free chlorine levels in pool water. Also, bromate was detected in commercial sodium hypochlorite solutions that were used in disinfection of potable waters and pool waters [41]. Due to the continuous dosing of sodium hypochlorite disinfectant to ensure the regulatory disinfectant levels in pool water, co-dosing of bromate within sodium hypochlorite solution might be the most important bromate accumulation factor in chlorinated swimming pools. Non-volatile structure and chemical resistance to degradation results accumulation of bromate in swimming pools. Accidental ingestion of bromate-contaminated pool water during swimming activity, especially high levels for low age swimmers, might be pose a significant health risk for swimmers. Carcinogenic risk associated with bromate exposure of swimmers should be considered on public health mitigation efforts.

Bromate Health Risks in Swimming Pools

CTR levels of bromate exposure through accidental ingestion of pool water are shown in Figure 2. Exposure scenarios were constructed as described in the section on Material and Methods. In the central tendency scenario, CTR levels of bromate exposure were estimated to be lower than 3.00×10^{-2}, even in the maximum level with the medians of 1.60×10^{-2}, 9.84×10^{-3}, 5.46×10^{-3}, and 3.31×10^{-3} for the age groups of 6 to <11, 11 to <16, 16 to < 21, and adults, respectively. Those median CTR levels of bromate exposure in the worst-case scenario were 6.31×10^{-2}, 6.43×10^{-2}, 3.72×10^{-2}, and 3.20×10^{-2}, respectively. The maximum CTR levels in the worst-case scenario were estimated to be ranged from 5.61×10^{-2} to 1.13×10^{-1} for the considered age groups. While the maximum CTR levels were estimated to be lower than the threshold level of '1', synergistic effects of multi-compound exposure might be occurring with significant CTR for especially younger swimmers.

Central tendency scenario CR levels of bromate exposure due to the swimming activity are shown in Figure 3.

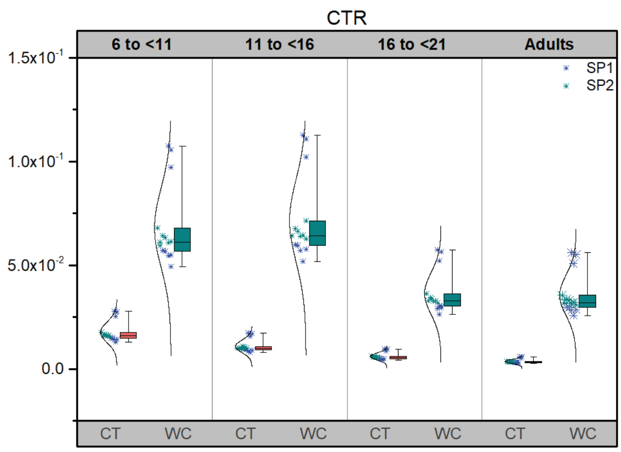

Figure 2. Bromate-associated CTR levels of accidental ingestion of pool water (CT: central tendency scenario, WC: worst case scenario).

CR levels are divided into four categories [32, 42]: safe zone was $CR \leq 10^{-6}$, acceptable risk zone was $10^{-6} < CR < 10^{-5}$, low priority risk zone was $10^{-5} < CR < 10^{-4}$, and high priority risk zone is $CR \geq 10^{-4}$. The CR of the bromate in the central tendency exposure scenario ranged in the safe zone for all age groups with the median levels of 2.46×10^{-7} for 6 to <11 age group, 1.40×10^{-7} for 11 to <16 age group, 8.09×10^{-8} for 16 to <21 age group, and 9.15×10^{-9} for adults (Figure 4). CR levels of bromate ingestion during swimming in the worst-case scenario were estimated to be higher than the safe zone level. The median CR levels of 6 to <11, 11 to <16, 16 to <21, and adult groups in the worst-case scenario were estimated to be 3.01×10^{-6}, 3.16×10^{-6}, 1.61×10^{-6}, and 9.42×10^{-6}, respectively. While the maximum CR was estimated for adults with the level of 1.65×10^{-5}, the lowest level was estimated for the 16 to <21 age group. 16 to <21 age group had a lower CR than adults, which might be due to the shorter exposure duration despite swallowing more pool water than adults. While the CR levels of < 21 age swimmers were estimated to be in the acceptable risk zone, upper quartile CR levels of adults were in the low priority zone. CR and CTR levels in SP2 tended to be close to the median levels due to the concentration variation being lower than the SP1. Disinfectant dosing system stability, treatment system efficiency, and partial refilling strategies might affect pool water bromate levels, which directly affects the health risk levels. While the bromate formation potential of chlorinated bromide content waters is near the negligible levels, pool waters (SP1) affected by seawater intrusion needs to be studied in detail on toxic bromate and brominated organic by-product formation due to the high bromide ions in the filling water. Variation of bromate concentrations in SP1 might be the result of the seawater intrusion of source water. Detailed long-term studies are needed to cover the gap in bromate levels in chlorinated swimming pools.

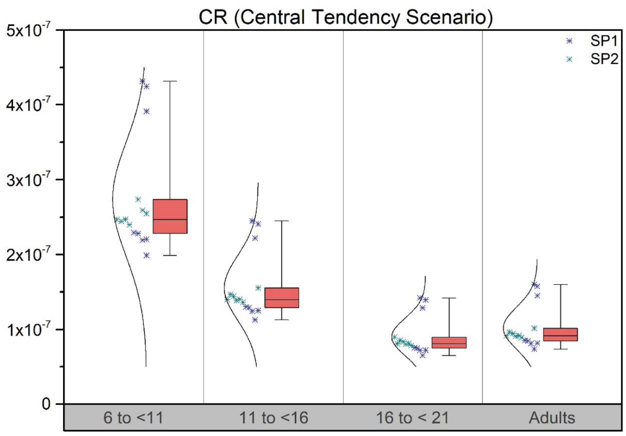

Figure 3. Bromate-associated CR levels of accidental ingestion of pool water (Central Tendency Scenario).

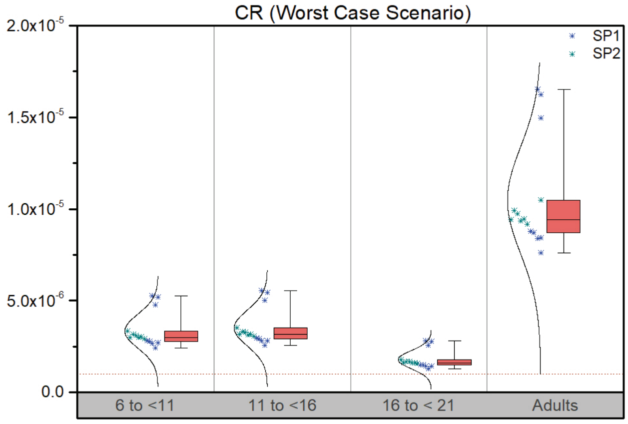

Figure 4. Bromate-associated CR levels of accidental ingestion of pool water (Worst Case Scenario).

CONCLUSION

Bromate ion is not taken into account in the TS EN 901 standard [43] for the chemical substances (sodium hypochlorite) used in the treatment of water. Depending on the manufacturing process and purity of chlorine salt, bromate contents of commercial sodium hypochlorite solutions may vary in broad range. The results of this monitoring study indicate that the bromate concentrations in pool waters are not dependent to bromide concentrations of filling waters, whereas co-dosing with commercial sodium hypochlorite solution might be the possible significant bromate contamination pathway in chlorinated pool waters.

Chronic-toxic risk (CTR) and carcinogenic risk (CR) levels associated with accidental ingestion of pool water were estimated for four age groups in central tendency and upper-bound (worst case) scenarios. Estimated CTR levels were lower than the threshold level even in maximum exposure case. However, synergistic effects of co-exposure to toxic compounds in swimming pools may result in increased chronic-toxic effects of bromate. While the CR levels in central tendency scenario were estimated to be in the safe zone ($<10^{-6}$), worst case scenario shows the bromate exposure pose a significant CR for specific (highly exposed) groups. The CR levels of lower age groups being higher than those of elders was due to their higher accidental ingestion rate and lower body weight. However, the highest CR levels were estimated for the adults due to the higher exposure frequency and exposure duration. Although lower CR were estimated in central tendency scenario, co-exposure to toxic compounds in pool waters might be pose a significant health risks due to the synergistic effects of co-exposure.

Bromate occurrence and associated health risk assessments shows that bromate should be considered in regulation of pool waters considering chemistry. Bromate contents of commercial sodium hypochlorite solutions should be regulated to avoid in-situ exposures from disinfected waters. Pool water replacement strategies and treatment systems should be optimized to reduce accumulation of non-volatile toxic compounds. Also, swimming pools in coastal zones, that are effected by seawater intrusion, should be specifically designed, and managed due to the highly toxic brominated by-product formation potentials of bromide ions.

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Improved portable generator performance with bio-ethanol fuel and its impact on bio-sustainability

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ABSTRACT

Clean air, renewable energy, climate change, safe environments, and the opportunity to live in a healthy community are just a few of the many issues that fall under the umbrella of environmental sustainability. The creation of bioenergy and biomaterials has the potential to retain the energy-environment relationship while simultaneously fostering cleaner, lower-carbon settings. Scientists are investigating renewable energy sources like ethanol to enhance sustainability and the planet›s health. Fuel ethanol is a feasible alternative to gasoline since it has a lower carbon footprint and a higher energy density. This research summarizes ethanol›s potential as a bio-sustainable fuel option for portable generators in India. Bio-ethanol testing was done on a portable generator with an ethanol-gasoline blend, and the findings are presented in this study. Compared to using standard gasoline, the results show 9% to 25% increased thermal efficiency and 6% to 28% decreased fuel usage. The results showed a decrease of 6%–23% in carbon monoxide and 3%–11% in unburned hydrocarbon emissions.

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INTRODUCTION

In current flex-fuel engines, a fuel composition sensor may automatically adjust fuel injection and spark timing to maximise combustion of any percentage of the resulting blend. Ethanol is the most widely available commercial biofuel, and there have been about 60 million ethanol-capable vehicles, motorcycles, and light-duty trucks sold around the world. The internal combustion engine of a flexible-fuel car, also known as a dual-fuel vehicle, can run on either ordinary gasoline or an alcohol or ethanol-based fuel. The gasoline or a gasoline/ethanol blend up to eighty five percentage content can be used to power a vehicle with a flexible fuel engine [1, 2].

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"Bio-sustainability" describes a regenerative and restorative economic approach. Differentiating between technical and biological cycles, its major goal is to ensure that all products, components, and materials always have the highest possible level of utility and value. Focusing on making the most of scarce resources, bio-sustainability seeks to maximise the reuse and recycling of those items for as long as it's financially possible to do so. Bio-refining is one of the most crucial essential enabling technologies of bio-sustainability, as it helps to complete cycles of raw biomass materials, minerals, water, and carbon. Hence, bio-refining is the best method for the large-scale, ecologically sound utilisation of biomass in the bio-economy. Optimal social, economic, and environmental outcomes will arise from the cost-competitive co-production of food and feed components, bio-based products, and bioenergy [3–5].

Bioenergy is gaining popularity as a renewable energy source that can help manage increasing energy costs. It also has the potential to generate revenue for disadvantaged farmers and rural populations globally. Bioethanol derived from agricultural residual-biomass offers significant environmental, socioeconomic, and strategic advantages and is a viable, cleaner substitute for conventional fossil fuels [6, 7]. The study looked into how a bio-ethanol engine burnt the ethanol. Improved performance and thermal efficiency were the goals of an inquiry into the use of high-compression hydrous ethanol reforming and supercharging in lean-burn circumstances. When ethanol was mixed with gasoline, nitrogen oxide emissions went up [8]. Hydrocarbon and carbon monoxide emissions are reduced to their minimum levels. It was shown that varying the ethanol-to-gasoline ratio in fuel mixes led to noticeably varied energy efficiency and pollutant levels under a wide variety of loading circumstances. Emissions levels were found to be higher when the engine was under more strain, but lower when the percentage of ethanol was raised [9].

The research looked at the effects of combining ethanol and gasoline on power, torque, fuel consumption, and emissions using analytically studied steady-state engines. Research on the usefulness of gasoline-ethanol blends in engines has primarily concentrated on ethanol mix rates up to 20% [10]. Several studies showed minimal to no reactivity at 10% volume ethanol, indicating that engine operating conditions have a greater influence on the characteristics of the engine and the contaminants it produces at low ethanol blend levels. More focus recently has been placed on the efficiency of spark-ignition (SI) engines using ethanol-gasoline blends while keeping the fuel-air ratio constant [1].

The volumetric efficiency typically decreases with increasing engine speed and decreasing ethanol concentration in the fuel mixture. This is a measurable phenomenon. When the percentage of ethanol in the fuel mix exceeds that of gasoline, the amount of harmful emissions is significantly cut down [11]. More saturated hydrocarbon emissions were produced when the percentage of ethanol in the fuel mix was raised above 25%. Higher ethanol concentrations in the fuel mixture led to the release of more aromatic chemicals and unburned ethanol than lower ethanol concentrations did. When the vehicle picked up speed, it also reduced its emissions across the board. This is because there are more oxygen atoms in an ethanol molecule than in those of other types of alcohol, which is why it has a higher boiling point. The fuel will require more air to burn, so make preparations accordingly [12].

There is a strong correlation between the widespread adoption of fuels with 10–15% ethanol and the possibility to drastically reduce emissions. Increased ethanol content in fuels reduced emissions significantly compared to conventional fuels. Through the use of a dual fuel system, emissions of carbon monoxide, hydrocarbons, and smoke were all noticeably cut down. The amount of carbon dioxide and nitrogen oxides released into the environment, however, rose with both the oxidation of the combustion process and the temperatures at which the combustion occurred [13, 14].

The amount of water used in the production process has a direct effect on the amount of energy needed to produce ethanol. Hydrous ethanol increased the flame's growth and decreased the time it took to spread, but had no influence on the flame's stability. The mixture of gasoline, methanol, and ethanol was tested for its consistency and homogeneity after being combined [15]. Methanol increases power output over gasoline in any mixture, regardless of operating conditions. Adaptations to the combustion system have been made to allow for the use of novel fuels such methanol/gasoline, ethanol/gasoline, and their respective combinations. As a result of these and other variables, it is difficult to establish generalisations about the effect of ethanol or methanol on emissions. As a result of the interconnected nature of these elements, drawing conclusions is difficult. In tests, using fuel blends with less than 20% ethanol had no discernible effect on either engine performance or torque. As the percentage of blending was increased, however, the engine's performance dropped [16–18]. In order to achieve bio-sustainable aims, this study provides an overview of ethanol as a potential alternative fuel for flex-powered portable generators. In this study, we provide the findings of Bio-ethanol tests performed on a light-duty portable generator operating on an ethanol-gasoline with incremental blend.

MATERIAL AND METHODS

Ethanol has a higher octane rating than gasoline, which means that it can help to increase the performance of high-compression engines. In fact, many high-performance engines are designed to run on fuels that contain ethanol. However, lower-compression engines may not see the same benefits and could even experience a decrease in performance. Ethanol is a renewable fuel that can be produced domestically and has a higher octane rating than gasoline, thus it may be used in place of gasoline without compromising on performance. Several rural areas have high unemployment rates and can benefit greatly from

Table 1. Properties of Bio-ethanol

Sl.No	Property	Unit	Ethanol	Gasoline	ASTM Testing
1	Lower Heating Value	(MJ/kg)	26.9	44.0	ASTM D240
2	Kinematic Viscosity, at 20 °C	(cSt)	1.5	0.5	ASTM D445
3	Density, at 15 °C	(kg/m^3)	785	737	ASTM D4052
4	Flash Point	(°C)	14	-40	ASTM D93
5	Research Octane Number	RON	115	90	ASTM D2699
6	Motor Octane Number	MON	100	82	ASTM D2700
7	Oxygen (%)	-	35	0	ASTM E385
8	Stoichiometric air/fuel ratio	-	8.9	14.5	ASTM D5291

the manufacturing of ethanol. To some extent, ethanol, a bio-organic fuel, could replace fossil fuels in cars. It could greatly help in decarbonizing transportation and enhancing environmental performance [13]. The effects of blending ethanol with gasoline on fuel quality are examined. In this case study, we use empirical evidence to show that blending ethanol with gasoline dramatically boosts both knock resistance and full-throttle performance. Basic effects of ethanol combustion are examined, as well as the reduced enrichment need under high speed/high load circumstances, which could lead to smaller, slower designs [1].

Ethanol can be used as a standalone fuel or combined with gasoline for spark-ignition engines. The BIS Standard 2796: 2013 in India allowed for an ethanol blend of 10% in gasoline in 2013, and this percentage may increase in the future. It would be very helpful to understand how ethanol-blended fuel performs in a modern gasoline engine. The Indian government formerly required 10% ethanol in gasoline as part of an effort to lessen the country›s reliance on foreign oil [13].

Portable generators are still often utilised for power generators in India, despite their high pollution rates. However, several adjustments will be needed to increase the engines' combustion rate and thermal efficiency. Since renewable energy sources are not always available throughout India or during all seasons. Ethanol is an alternative fuel produced primarily from corn and sugarcane. To reduce the reliance on fossil fuels and carbon footprint, ethanol is an attractive alternative to gasoline. With the inclusion of OH components, gasoline not only improved full combustion but also had less harmful emissions. The gasoline engine's flaw was that it could only run for brief periods of time due to the decrease of harmful emissions, which had an influence on the combustion potentiality or capacity to burn for a shorter time [19]. The properties of gasoline and ethanol was tabulated in Table 1 [19].

EXPERIMENTAL DATA

A low-duty power generating engine that uses flexible fuel was tested. A spark ignition engine with a compression ratio of 5:1 and a peak output of 4hp at 3300 rpm was chosen for this experiment. Single-cylinder, four-stroke air-cooled engine with 175 cc work capacity as tabulated in Table 2. Both with and without an bio-ethanol blend, the essential test runs were performed under four load conditions, spanning from 25% to 100% capacity, to ensure the optimum performance and lowest emissions. A light duty power producing engine is shown in Figure 1 [14]. It was essential to initially start the engine with gasoline, and after that, it was put through a series of tests that continued until the conditions of its steady-state operation were determined. The hydrocarbon, carbon monoxide, and oxygen emissions, in addition to the brake thermal efficiency and specific fuel consumption, were all put to the test. Each and every one of the test runs was carried out with weights that were in direct proportion to the total load weight.

Table 2. Experimental engine specification

Parameter	Description
Engine type	Four-stroke, single-cylinder
Cooling system	Air-cooled engine
Compression ratio	5:1
Rate Power	4 hp @ 3300 rpm
Displacement	175 cc

Emission measurements were analysed using the Crypton CGP-680 Analyzer (Table 3)[20]. This exhaust gas analyzer is totally microprocessor-controlled and uses Non-Dispersive InfraRed techniques. The device is capable of measuring carbon monoxide, carbon dioxide, and hydrocarbons. Electrochemical oxygen measurement and a chemical sensor for detecting nitrogen oxide are utilised in a second channel provided. When working at pressures between 750 and 1100 bar, the reaction time to 95% of the final measurement is just ten seconds. To function properly, a minimum flow rate of five lpm must be maintained.

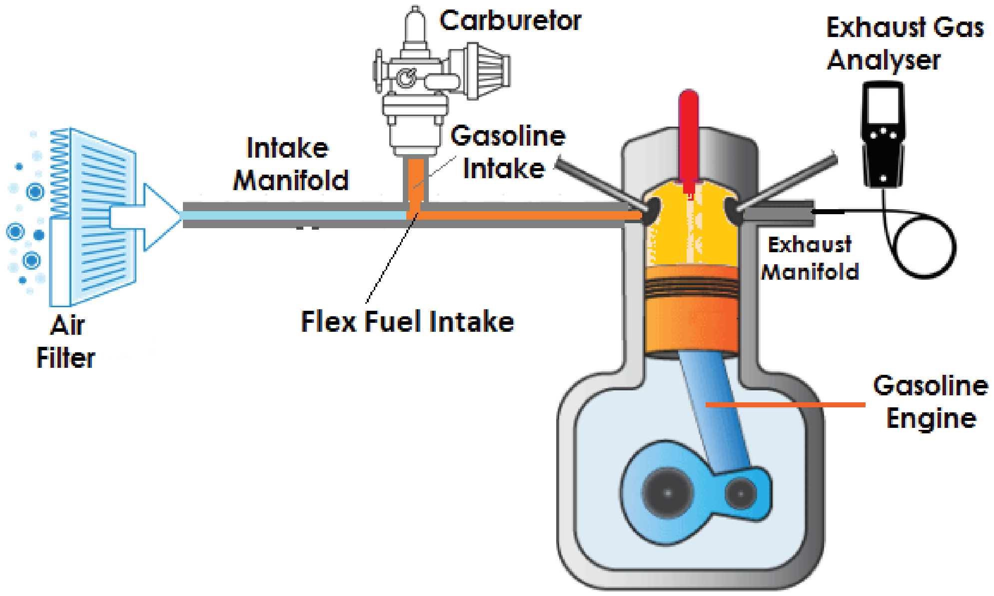

Figure 1. Schematic diagram of the Bio-ethanol Setup [14].

Table 3. Instrumental parameters of Emission analyser

Measurement	Range	Accuracy	Resolution	Instrument
CO	0 to 10%	± 0.03%	0.01% vol.	Crypton 680 series Analyser NDIR technique
HC	0 to 10000 ppm	± 10 ppm	1 ppm vol.	Crypton 680 series Analyser NDIR technique

The exhaust system was hooked up to a Crypton CGP-680 Analyzer so that emission levels could be determined for different fuel combinations and operating loads. By comparing the findings to those obtained from base fuel measurements, the percentage of deviation for each parameter can be determined [20].

The exhaust system was connected to an emission analyser from the Crypton 680 series during the experiment so that emission levels could be determined for different fuel mixtures under different loads. To calculate the percentage of variation for each parameter, one needs to compare the measured value with the value for the base fuel. The engine was started with gasoline and put through a battery of tests to ensure it was operating at a constant rate. Emissions of carbon monoxide, hydrocarbons, and fuel consumptions were analysed, along with thermal efficiency. In order to simulate the actual load, the test runs were performed using weights of varying sizes. The same procedures are used when enriching gasoline with a blend of bio-ethanol. In this study, an air-cooled, spark-ignition, single-cylinder, four-stroke engine with an incremental load was used to explore the effects of Bio-ethanol on engine performance and emissions. Tests were conducted using bio-ethanol at 10%, 15%, 20%, and 100% concentrations. In this paper, BE refer to bioethanol and BE10 referred to 10% of bioethanol and 90% of gasoline. BE15 referred to 15% of bioethanol and 85% of gasoline and similarly, BE20 referred to 20% of bioethanol and 80% of gasoline. BE100 is 100% bioethanol.

RESULT AND DISCUSSION

Study on Brake Thermal efficiency

When ethanol was added to the mixture, combustion efficiency increased (as seen in Figure 2). Maximum ethanol thermal efficiency increases to 9.4%, 16.2%, and 25.2%, showcasing a substantial performance enhancement at full load. When combined with oxygen, ethanol accelerates combustion and increases energy efficiency. Because of its improved efficiency and other distinguishing features, this cycle becomes closer to its intended state of constant volume combustion. The Bio-ethanol engine benefits from this development since higher hydrogen flame velocities and a more diverse set of flames result in greater efficiency. The combustion process is slowed down during testing with varied loads when ethanol is not present. However,

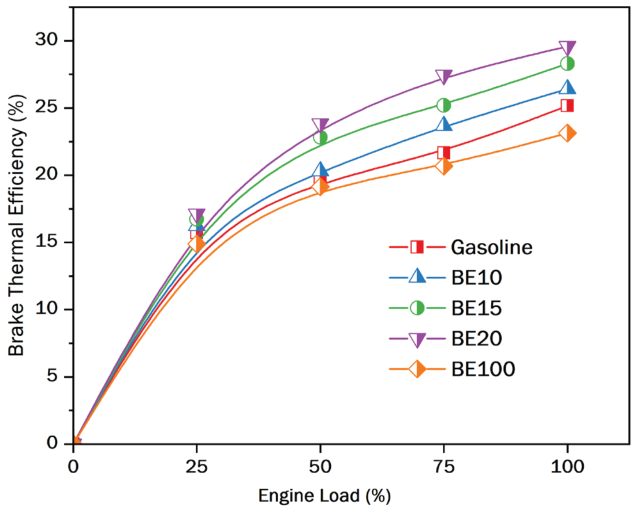

Figure 2. Study of Bio-ethanol on brake thermal efficiency.

ethanol dramatically sped up the combustion process, which improved the efficiency of the heat produced. Ethanol and gasoline have a lower stoichiometric ratio. It's possible that the same amount of air can be used to burn the larger quantity of fuel. Because the lean mixture entirely occupies the remaining space, more fuel is used [17].

Study on Specific fuel consumption

Figure 3 depicts the ethanol and conventional gasoline brake fuel consumption under four different loads. It was demonstrated that gasoline consumption will grow regardless of the mix condition, even if the starting engine load was reduced. It's also important to note that ethanol's smaller heating valve compared to gasoline means that temperature fluctuations will be load-dependent.

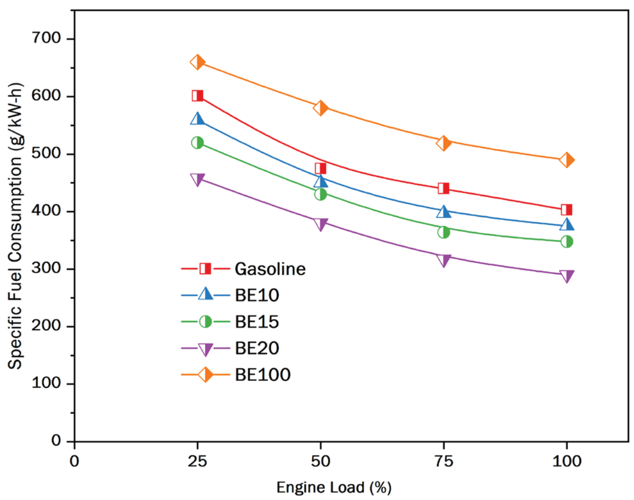

Figure 3. Study of Bio-ethanol on specific fuel consumption.

The specific fuel consumption of the engine is reduced by 6% to 28% depending on the blend when ethanol is included. Results showed that when compared to utilising gasoline, fuel consumption was reduced by 28% when using 20% ethanol. With the addition of hydrogen and oxygen, gasoline was able to burn more efficiently, producing a bigger flame thrust and higher calorific values than was previously possible with gasoline alone [12].

Study on Carbon Monoxide Emission

The rate of CO emissions versus engine load is shown in Figure 4. The amount of carbon monoxide (CO) released depends on several elements, the most important of which are the efficiency of the combustion and the air-to-fuel ratio. The engine was maintained at its most fuel-efficient cruising speed in order to minimise CO2 emissions. The combustion process was enhanced and CO emissions were decreased by using ethanol in tandem with oxygen. Emissions reductions may have resulted from the use of oxygenated chemicals, which improve CO combustion in the cylinder or in post-combustion activities. The diluting the gas may not be the only option for reducing CO emissions. There is a 6%-23% range for CO reduction when using ethanol blends that promote better combustion and enhance the efficiency of lean-running engines. Chemically speaking, ethanol is preferable because it burns more quickly and has a broader range of combustibility. When a mixture of ethanol and gasoline is ignited, it burns quickly and fully, destroying the pure gasoline altogether [8, 21].

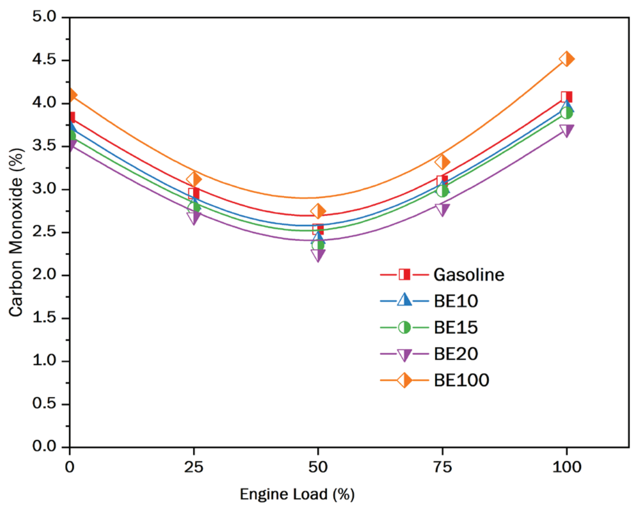

Figure 4. Study of Bio-ethanol on carbon monoxide.

Study on Unburned Hydrocarbon Emission

Adding ethanol reduced the amount of unburned hydrocarbons released into the exhaust for all loads, as seen in Figure 5. Results showed that when ethanol and HC were used together, the HC concentration was significantly reduced in all loads tested. Better engine performance and more complete combustion were both results of using ethanol. As a result of variations in ethanol flow rates, the percentage decreases in unburned hydrocarbon volume varied from 3% to 11%. Hydrogen's quicker quenching time than gasoline's lowers hydrocarbon emissions. Due to the poor flammability of ethanol and the comparatively high in-cylinder pressure and temperature produced by the rapid flame velocity, fuel mixes containing ethanol reduced hydrocarbon emissions. Because of the increased oxygen provided by the ethanol mixture, combustion is more complete and produces less HCs [22].

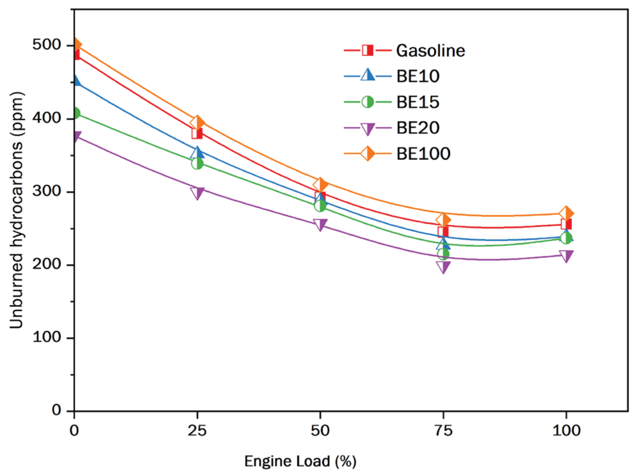

Figure 5. Study of Bio-ethanol on unburned hydrocarbon.

Influential study of Bio-ethanol on portable generator performance

Contour plots are made through Minitab software with full factorial design, which comes under the design of experiments. In this paper, bioethanol ratio and engine load were selected as the parameters, and fuel consumption, efficiency, and emission formation were studied as the response parameters. A contour plot can show the relationship between a fitted response and two continuous variables when a model is stored. A contour plot shows data in two dimensions. Connecting spots with the same response value forms contour lines.

According to the contour plots in figure 6 and 7, the amount of fuel consumption, the greater load condition, and the percentage of bio-ethanol utilised in the fuel had the greatest impact on the total amount of energy that was consumed by the engine. In addition, the amount of gasoline that is consumed is significantly affected by the amount of bio-ethanol that is present in the fuel mixture. The lowest values are attained when the engine is working at maximum load circumstances with a concentration of 20% bio-ethanol. It is hypothesised that the origin of this occurrence is an increase in the quantity of oxygen that is present in the air, which causes a quicker rate of burning [16]. Ethanol burns faster with oxygen. This cycle approaches constant volume combustion due to its increased efficiency and other properties. This improves bio-ethanol engine efficiency by increasing hydrogen flame velocities and flame diversity. Without ethanol, variable load testing slows combustion. Ethanol accelerated combustion, increasing heat efficiency. Ethanol and gasoline have lower stoichiometry. The same air might burn more fuel. The lean mixture fills the leftover area, using more fuel [23].

As a direct result of this contour plots Figure 8 and 9, the amount of fuel that can be burnt effectively was lowered. It is possible that the quantity of carbon monoxide and hydrocarbons that are emitted into the environment can be decreased by using biofuel blends that include at least 20% bio-ethanol. In addition, ethanol has a lower carbon-to-hydrogen ratio than gasoline, which means that it has a higher

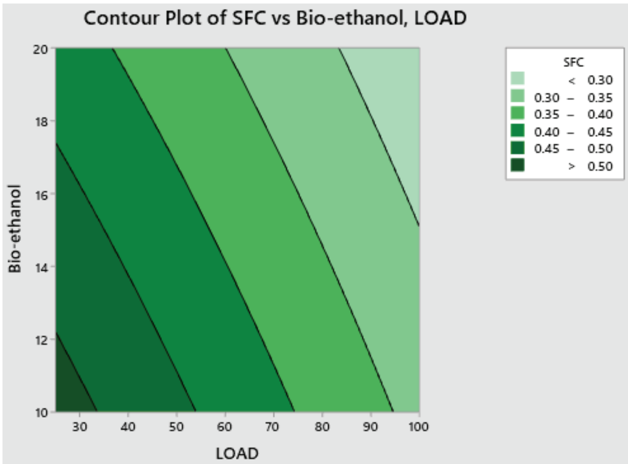

Figure 6. Influential study on Fuel Consumption.

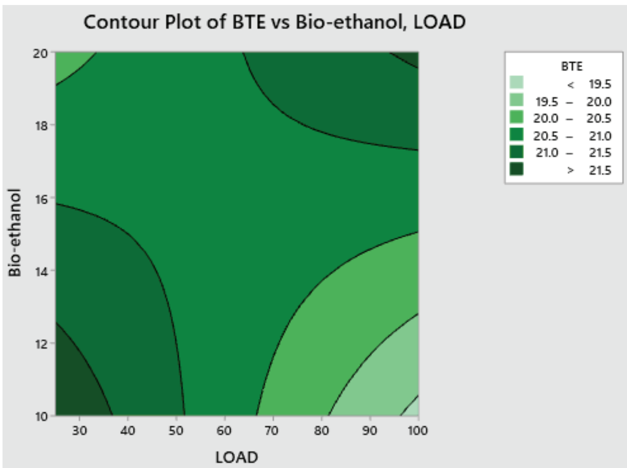

Figure 7. Influential study on Brake thermal efficiency.

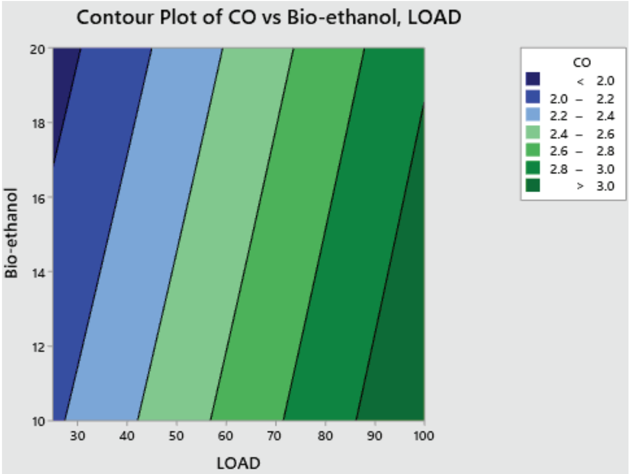

Figure 8. Influential study on Carbon Monoxide emissions.

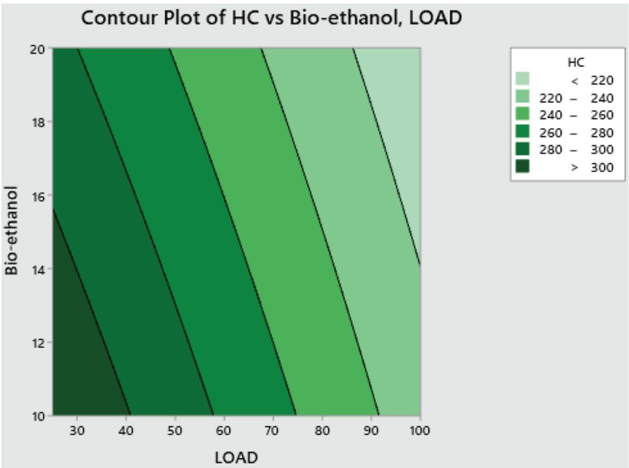

Figure 9. Influential study on Hydrocarbon emissions.

oxygen content. This can lead to more complete combustion and lower emissions of pollutants like carbon monoxide and hydrocarbons. There is a proportional reduction in the amount of carbon monoxide and hydrocarbons released whenever there is a larger proportion of bio-ethanol present. When applied at a concentration of 20%, bio-ethanol produces the fewest amounts of carbon monoxide and hydrocarbon emissions possible. This can be explained in part by the rapid acceleration of the combustion process that takes place at such a height, which is a significant contributor to the phenomenon [10, 16].

IMPLICATIONS FOR ENVIRONMENTAL AND BIO-SUSTAINABILITY

Biodiversity is a crucial component in promoting sustainable development and enhancing the economic prosperity of societies by providing a continuous supply of natural resources and ecological services. Integration of recycling and bioconversion for enhanced process performance is also assessed. The goal of this work is to make it easier to recycle bio-waste for applications in bio-sustainability. In order to commercialise and promote the use of alternative commodities, more research, market analysis, and funding are required. Use a comprehensive, methodical approach that incorporates several fields and makes extensive use of data to enhance existing practises and develop innovative new ones in order to get the most out of bio-waste [24]. Issues on a global scale can be helped by bio-sustainable practises. By using biomass as an alternative to petroleum, the environmental effect of producing bioenergy and biomaterials could be reduced. Carbon management and GHG emission reductions could benefit from the bio-refinery associated with sustainable waste management. By cutting down on emissions of greenhouse gases, a low-carbon economy is exemplified by a waste bio-sustainable refinery's approach to processing its raw materials [25].

In comparison to fossil fuels, bio-ethanol may be safer due to its ability to be diluted in water, broken down by bacteria, and dissipated quickly. Since ethanol can be produced in nearly any country, it is the most economical energy option. Ethanol can be made from a variety of plants, including corn. Many types of ethanol exist, but the most common variety is simply called "E10," and the percentage of E10 in blends varies from country to country, typically falling within the range of 10 to 15%. The United States and Brazil are only two of the many places where a high-ethanol gasoline blend (anything from 50% to 85% ethanol) is legal [9, 26]. The simplicity of producing ethanol results in lower production costs than those of fossil fuels. Only carbon dioxide and water are released as by-products when ethanol is burned as fuel. Carbon dioxide emissions are a little contributor to the pollution problem. "Atmospheric carbon neutrality" is thought to result from the combustion of ethanol made from biomass sources like corn and sugarcane. This is because carbon dioxide is taken in by the biomass during its growth, and this may offset the quantity of carbon dioxide released during ethanol combustion. The three main foci of bio-sustainability are the feedstock, the production process, and the distribution of the final product. The firm never gave the afterlife of the product the respect it deserved. How the product will be maintained after its useful life has ended is not something that has been thought through [3, 24, 25].

Bio-ethanol produces significantly fewer greenhouse gas emissions than gasoline or diesel. When bio-ethanol is burned, it releases carbon dioxide, but this is offset by the carbon dioxide absorbed by the crops used to produce it. In contrast, gasoline and diesel are produced from fossil fuels, which release carbon dioxide that has been trapped underground for millions of years and contribute to the accumulation of greenhouse gases in the atmosphere. The production of bio-ethanol can promote sustainable agriculture practices. It can encourage farmers to grow crops specifically for energy production, which can help to diversify their income streams and reduce their reliance on traditional crops [2].

Emissions reduction from a portable gasoline generator is the primary focus of this investigation. Damage to the blood's ability to carry oxygen to and from tissues makes carbon monoxide a serious health risk. When blood comes in contact with carbon monoxide, haemoglobin is quickly converted to carboxy-hemoglobin. Because of the presence of carbon monoxide in the lungs, haemoglobin is not able to reach a fully oxygenated state. It has also been shown that exposure to this hydrocarbon lowers the production of white blood cells, suppresses the immune system, and makes the body more vulnerable to infection. There's also the fact that different stages of a plant's life cycle are susceptible to different levels of pollutant photo toxicity [14, 19].

CONCLUSION

The utilization of bioenergy is gaining popularity as a renewable energy source that has the potential to address the issue of rising energy costs. Additionally, it may provide a source of income for the farmers and rural communities across the globe. Bioethanol derived from residual biomass of agriculture offers significant environmental, socioeconomic, and strategic advantages. It is a viable and cleaner substitute for conventional fossil fuels, and can be regarded as a secure liquid fuel alternative. Using an ethanol-gasoline blend, an experimental investigation was conducted on a light-duty portable generator to improve engine performance, reduce hazardous emissions, and meet bio-sustainable norms.

- The particular fuel consumption of an engine can be reduced by as much as 28% depending on the blend, and ethanol is mostly responsible for this effect. Ethanol has a maximum thermal efficiency of 26% at full load.
- The unburned hydrocarbon volume was reduced by between 3% to 11%. Increased combustion and better lean-running engine performance from ethanol blends can lead to a 6-23% decrease in carbon monoxide emissions.

In order to achieve bio-sustainable aims, this research summarises ethanol's potential as an alternative fuel for portable generators. Overall, the use of bio-ethanol can provide a number of environmental benefits compared to traditional fossil fuels. The diversification of the energy mix can potentially decrease reliance on fossil fuels, particularly for nations that import oil. The creation of new markets and job opportunities for farmers, rural communities, and biofuel industries can be facilitated by them. In addition, they have the potential to decrease energy expenditures and enhance energy availability in geographically isolated or economically disadvantaged regions.

CONFLICT OF INTEREST

The authors declare no potential conflicts of interest regarding the research, authorship and/or publication of this article.

DATA AVAILABILITY

The data used to support the findings of this study are included within the article.

AUTHOR'S CONTRIBUTIONS

All authors are contributed equally to bring out this article.

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Research Article

From rubbles to digital material bank. A digital methodology for construction and demolition waste management in post-disaster areas

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ABSTRACT

In 2020, European countries generated 807 mln tons of construction and demolition waste (CDW), accounting for 37.5% of total waste production. The UE Waste Framework Directive of 2008 established as a priority goal to increase the percentage of reuse, recycling and recovery of nonhazardous construction waste to a minimum of 70% by 2020. Pending the report that will define compliance with this goal, the average percentage currently stands at around 50%, of which only 3% involves upcycling operations. This doctoral research defines an operational methodology aimed at implementing digital processes for circularity in the AEC sector, with a focus on post-earthquake emergency Italian contexts. The treatment of CDW in earthquake-affected areas for the purpose of recovery/reuse, in a perspective of circularity, represents an underexplored field and limited, as in the rest of UE, to downcycling operations. By defining planning strategies and digital tools and procedures, the research aims to facilitate the reuse of building elements from post-earthquake demolition and reconstruction operations. The final output of the research consists of a cloud database, a Digital Material Bank (DMB), of informed building elements from post-earthquake selective demolition operations that can be reused in the construction market as a secondary raw material. The CDW management of the 2016 Central Italy earthquake is identified as the scope of application, with a focus on the situation in the Marche region. Finally, the main limitations and possible future scenarios of the research are reported.

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INTRODUCTION

The term Industry 4.0 identifies the digitalization process affecting the economic sectors of contemporary society since the beginning of the 21st century. The objective of this model is to operate a complete integration of *IoT* (*Internet of things*) in these sectors. As reported by Chapman and Butry, the construction industry, or *AEC* (*Architecture, Engineering and Construction*), lags considerably behind others today [1], despite the environmental, economic and social impact this sector exerts globally.

According to the *Global Status Report for Buildings and Construction 2022,* the greenhouse gas emissions of the AEC industry reached the peak of 13.2 Gt in 2019. The global COVID-19-pandemic, and the subsequent decline in economic activity, reduced the AEC's emissions in 2020 (11.7 Gt). In 2021 we witnessed pre-pandemic levels being reached and exceeded, with a new peak of 13.6 Gt, 37% of

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global emissions[1] (Figure 1) [2]. The situation will presumably get worse for both the massive increase in investments (+51.9% in 2021 compared to 2015) and the growth in global population[2].

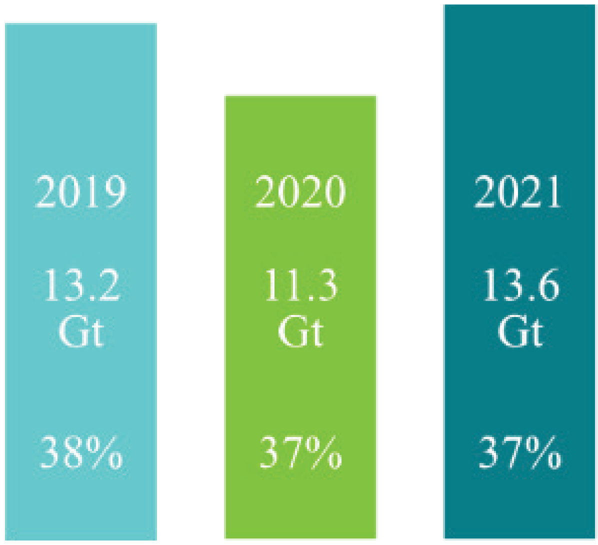

Figure 1. Greenhouse gas emissions from the AEC Industry (2019-2021).

The trend of waste production of the AEC industry, or *CDW* (*Construction and Demolition Waste*) is aligned with emissions. In 2020, Europe generated 807 mln tons of CDW, accounting for 37.5% of total waste production[3] [4]. In this regard, the *Waste Framework Directive* of 2008 established as a priority goal to increase the percentage of reuse, recycling and recovery of nonhazardous construction waste to a minimum of 70% by 2020[4] [5]. Pending the 2022 report, the average percentage currently stands at around 50%, mostly coming from downcycling applications, while only 3% for upcycling operations (Figure 2) [6].

While the overall construction waste average is in line with UE, the geomorphological features of the Italian territory aggravate the situation, behind one of the highest seismicity countries in Europe. To date, the production of demolition waste in earthquake-affected areas represents one of the main issues and challenges for Italy. Waste produced in such contexts generally belongs to two categories: waste from the demolition of unsafe and/or collapsed buildings, and provisional works dismantled at the end of safety operations. An estimated 497,486 tons of debris were removed in the province of Ascoli Piceno, following the earthquake of central Italy in 2016[5]. The treatment of this waste for the purpose of recovery/reuse, in a perspective of circularity, represents an underexplored field and limited, as in the rest of UE, to downcycling operations. On one

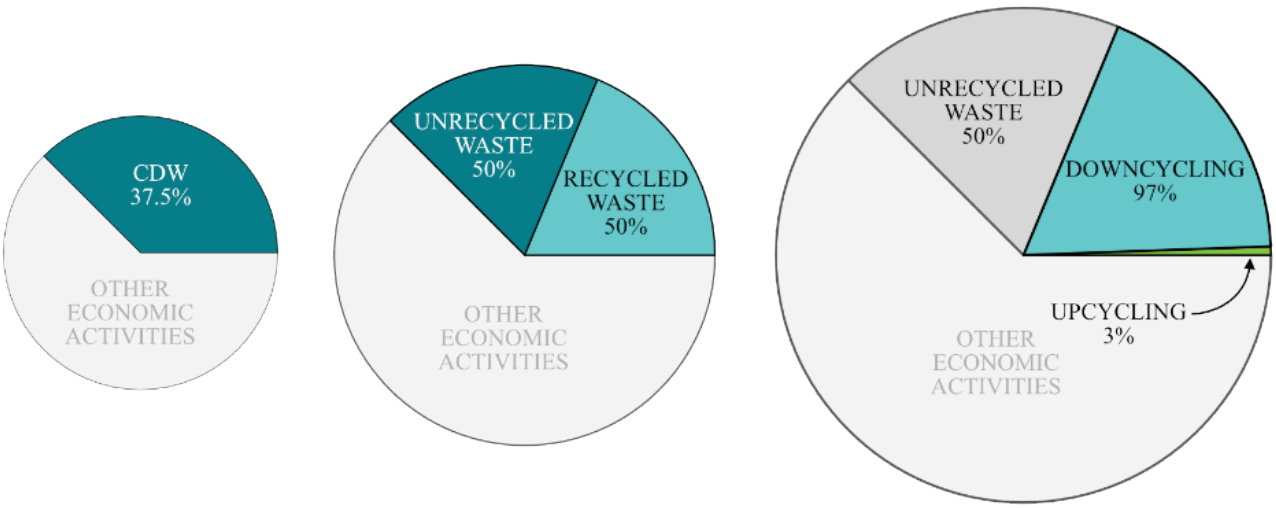

Figure 2. European CDW recycling statistics.

1 Data referred to the production and operational components.
2 The World Population Prospect 2022 estimates that the world population will reach 9.7 billion in 2050 [3].
3 Data extracted in January 2023.
4 The percentage is meant relative to the weight of the waste.
5 Data updated to 09/30/2021. Data refer to public rubble only. Public rubble is defined as "materials resulting from the partial or total collapse of public and private buildings caused by the seismic events, as well as materials resulting from the demolition activities of unsafe buildings ordered by the municipalities affected by the seismic events or other competent entities."

hand, in the Marche region, debris predominantly composed of aggregates (98%), once selected and crushed, has been transformed into recycled aggregates to be used for the construction of road sub-bases, embankments, etc. [7]. On the other hand, provisional works components, mainly of the wood type, have high circular potential, due to their homogeneous sections and absence of chemical treatment. The life cycle of these elements currently ends in landfills or as biomass, also involving the release of CO2 accumulated over time from the wood. Finally, to date there are no shared procedures, at the regulatory and operational level, aimed at the streamlining and efficiency of the recovery process, the reuse of this material directly in the post-earthquake reconstruction, and the definition of protocols capable of considering, from the design stages, the continuation of the life cycle of building components following selective demolition, with the consequent formation of new business models.

DIGITALIZATION AS A STRATEGY FOR THE IMPLEMENTATION OF CIRCULAR PROCESSES

In this scenario, the digitalization of the AEC industry, especially in the emergency context, assumes a crucial role. The urgency to adopt responsible strategies for the design, production and management of the built environment leads to considering *data* as the raw material underlying the entire supply chain. The collection and management of data makes it possible to read and interpret the criticalities of building processes throughout the entire life cycle of architectural artifacts, and to implement multi-criteria optimization strategies. It is no coincidence that technological developments in the AEC industry, during the 4th industrial revolution, have been primarily concerned with data, addressed in the nuances of design, production and management of the built environment.

The main novelty in the design field is represented by an approach involving the extension of human capabilities through the use of computers, defining a new design philosophy known as *procedural design* (PD) [8]. The main difference, compared to traditional design, is the development of a set of rules and processes that produce a geometric and/or informational output from the transformation and management of data [9]. Through PD, designers are able to deal dynamically with data complexity, made manageable through the use of algorithms, in a precise and efficient manner.

In the field of building management, numerous tools have been developed that fall under the label of *Building Information Modeling* (*BIM*). The term stands for the "*use of a shared digital representation of a built asset to facilitate design, construction and operation processes to form a reliable basis for decisions*" [10]. The BIM methodology was born in response to the problem of the *MacLeamy curve* (Figure 3) within the construction history: moving forward in the life cycle of a building artifact, the impact of new choices on the project decreases, while the costs associated with those choices increase. The BIM methodology operates a shift of effort in the design phases, where choices determine a strong impact on the project while minimizing costs. Through a digital simulation of the building process, potential issues are anticipated as early as the design and pre-design phase [11].

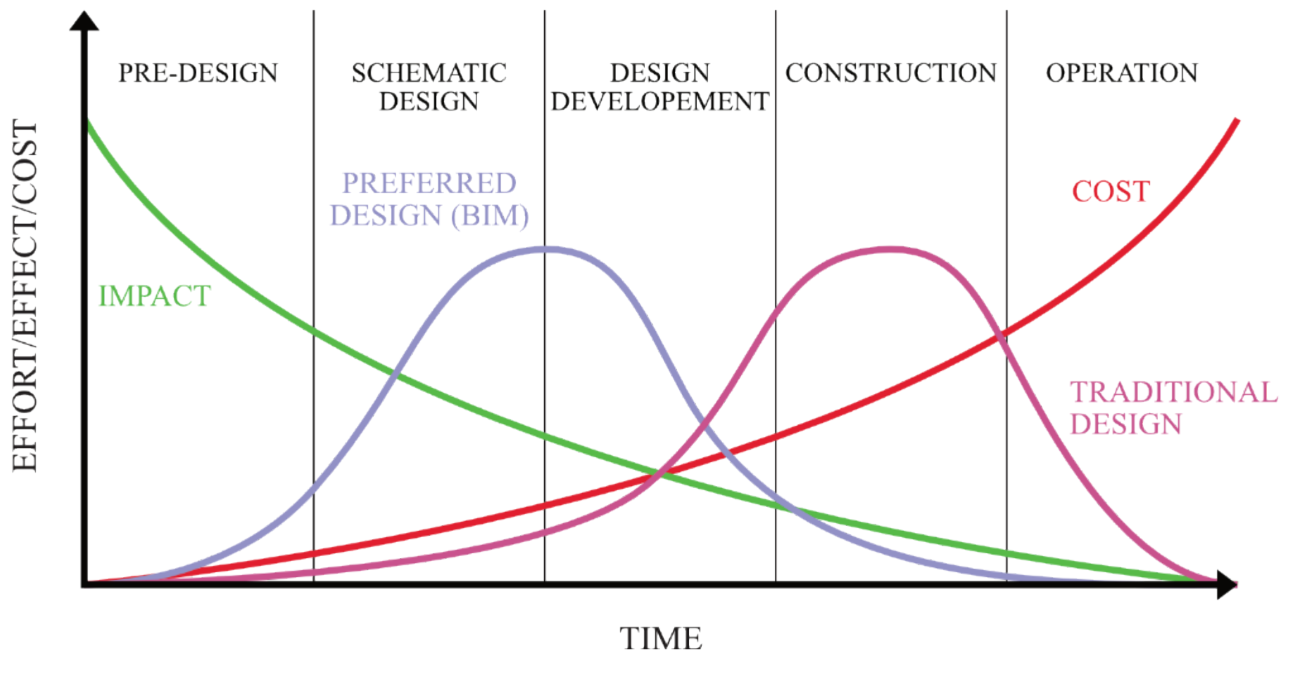

Figure 3. MacLeamy curve adapted to BIM.

The BIM methodology has many advantages in terms of economic and environmental sustainability, but it is currently marked by theoretical and practical limitations. BIM appears to be applicable mainly to new buildings, demonstrating significant shortcomings toward existing artifacts, especially historical ones. The geometric representation of such artifacts is not easy, thus also limiting the information potential of the building system. Despite efforts toward so-called *openBIM*[6], such tools are also unable to guarantee a constant information flow in the exchange of data between software. This shortcoming leads to disruptions in operational workflows, reducing the effectiveness of the goals set by the BIM methodology. In addition to issues related to computer tools, which are currently limited to extremely sectoral stages, the absence of a unified, shared, and comprehensive methodology poses a main limitation.

Such a described cultural context thus creates significant difficulties for designers and stakeholders when attempting to address the sensitive issue of circularity in relation to the digitalization processes in the AEC industry.

RESEARCH OBJECTIVES AND PHASES

The current research of the authors, carried out at School of Architecture and Design of the University of Camerino (Italy), define an operational methodology aimed at implementing digital processes for circularity in the AEC sector, with a focus on post-earthquake emergency contexts. The research focus is on the sustainability implications of the formation of a new market that can attract opportunities and investments. By defining planning strategies and digital tools and procedures, the research aims to facilitate the reuse of building elements from post-earthquake demolition and reconstruction operations. For provisional works, the research provides the integration of such procedures as early as the immediate post-installation phase. The research also aims to provide alternative solutions for both streamlining upcycling procedures for construction waste and facilitating post-earthquake reconstruction operations through a concrete economic boost. Constant discussion with administrations, local authorities and economic actors are key factors to immerse the research within the dynamics that characterize the AEC sector. The use of IT tools is conducted following the perspective of interoperability and responsiveness, in order to limit the loss of data during the various stages of research, optimizing the workflow in terms of timing and accuracy of operations. The final output of the research consists of a cloud database, a *digital material bank* (*DMB*), of informed building elements from post-earthquake selective demolition operations that can be reused in the construction market as a secondary raw material, while defining strategies to facilitate new business models. The research mainly involves three phases:

- state of the art analysis and market surveys;
- development of methodology;
- pilot design application

Analysis and market surveys

The first step of the research involves a market survey, with a focus on the Italian and regional AEC industry in the post-earthquake context. The survey aims at understanding the potential and interest that digitalization processes for circularity exert, and will exert, within the construction supply chain. This phase consists of collecting a large amount of data in order to accurately describe the current and projected situation of the circularity market in the AEC sector. The dialogue with stakeholders (local authorities, companies, economic actors) is pivotal to analyze the opportunities, benefits, and large-scale applicability of circularity processes. In addition, the research analyzes the current legislative and administrative apparatus to assess the level of depth and criticality of circularity processes within the post-earthquake demolition and reconstruction scenario. Moreover, the research addresses the application and management limitations currently found in digitalization processes. These limitations include IT issues (software and hardware), interoperability, cloud data, traceability, certifications, etc. This first phase takes place with parallel insights regarding the topic of circularity in AEC, with a focus on international academic developments and applications conducted on the built environment.

Methodological development

Data acquisition

The first task of the methodological development is the identification of strategies for acquiring the information of the building elements, from the post-earthquake demolition operations, that make up the DMB. The data to be acquired are: the identity of the building elements, geometry, typology, materials, weight, chemical and physical characteristics, architectural and geographical location (to be integrated with *GIS* systems), and information related to the production, installation, and management of the elements. The retrieval of such information is also addressed through analysis of data from existing databases using programming tools. Related to geometric surveying, the topic of photogrammetry (*Structure from Motion*) is integrated in the workflow, including the subsequent processing and management of point clouds using algorithmic support for classification, segmentation, etc.

6 "openBIM extends the benefits of BIM (Building Information Modeling) by improving the accessibility, usability, management and sustainability of digital data in the built asset industry. At its core, openBIM is a collaborative process that is vendor-neutral. openBIM processes can be defined as sharable project information that supports seamless collaboration for all project participants. openBIM facilitates interoperability to benefit projects and assets throughout their lifecycle." [12]

Building elements analysis

Once the data are collected, the building elements are subjected to analysis to understand their state of preservation (Figure 4). The analyses cover the mechanical strength of the elements, the state of deformation, the presence of aesthetic imperfections and deteriorating conditions, etc. The analyses are conducted in an automated manner using *VPL* (*Visual Programming Language*) computational tools. The analyses aim at defining the economic value of the objects, as well as understanding the degree and contexts of reusability.

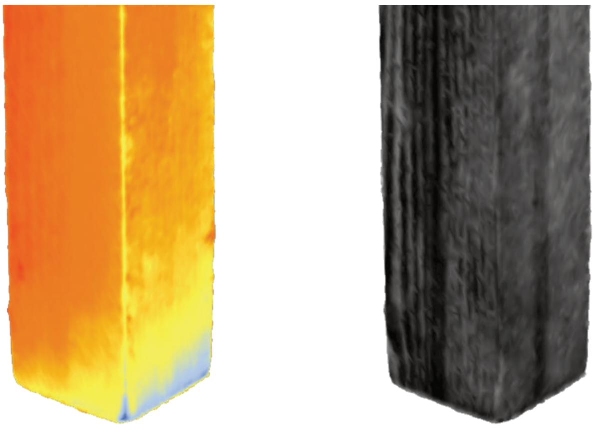

Figure 4. Analysis detail of a building element for deformation (left) and texture quality (right).

***BIM* compiling**

The collected geometric and descriptive data need to be represented within platforms capable of synthesizing and organizing the different categories of information. BIM tools are be used for this phase, developing procedures to automate the compilation of information and the conversion of meshes, obtained from 3D scans, into *Brep* (*Boundary Representation*), the native geometric typology of the main BIM software. Connection tools between BIM and VPL tools are used. The outcome of this phase is a *digital twin*, i.e. a digital alter ego of the database of real elements (Figure 5).

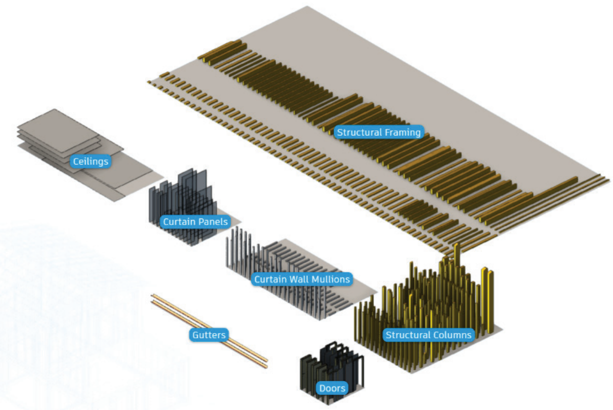

Figure 5. Digital twin of the building elements.

Life cycle assessment

Within the circularity dynamics for the AEC sector, *life cycle assessment* (LCA)[7], plays a key role in simulating their environmental footprint, in terms of CO2 equivalent, from the extraction of the raw materials to the decommissioning and/or reuse. The goal of this phase is to develop decision-making strategies to optimize the use of building elements in the AEC industry for a responsible and sustainable design approach. This operation contributes to the creation of comparative models between conventional and circular practices.

Dashboard and reports

The data collected and processed in the previous phases need refinement aimed at making such data readable and interpretable in a clear and effective manner. Therefore, strategies are developed, both on the IT and communication level, for producing interactive reports and dashboards (Figure 6). A high degree of interoperability among the tools

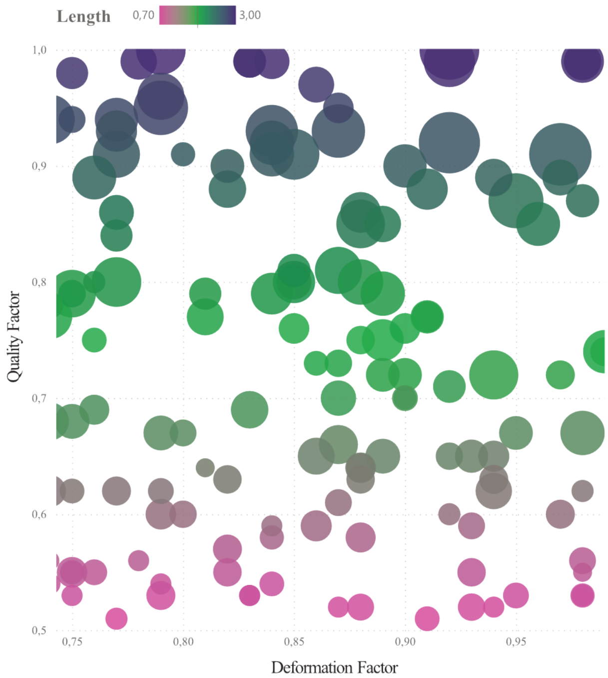

Figure 6. Interactive dashboard of the digital material bank.

7 LCA is defined as "a technique for assessing the environmental aspects and potential impacts associated with a product." [13].

involved is maintained in this phase as well, so any kind of updates from previous phases will be responsively reflected in the reports. The outcome of this phase composes an initial finished and autonomous product, which can also be summarized by means of technical data sheets and certifications, to be submitted to the attention of the stakeholders to obtain feedback about possible investment interests.

Cloud database

The next step of the research is the *cloud* publication of the DMB generated in the previous steps. The main challenge is the programming of a bidirectionally interactive database, so that any changes can be updated simultaneously on both the digital twins and the cloud database itself. Strategies are planned to track updates and to manage the usability, accountability, and security levels of the database.

Worksites

The operations described so far involve an initial transition from the physical to the digital world, converting building elements into a condensed dataset within a fully digitized database. The next step is to return research within the physical world in order to develop strategies that can be traced back to the worksite domain. These include the use of *RFID* (*Radio Frequency Identification*) technologies and *QR codes* that can be physically applied to the building elements of the database, also with the support of augmented and virtual reality technologies, in order to visualize and edit the data associated with the elements.

Design applications

As a conclusion of the research, it is proposed to verify the applicability of the system by carrying out a pilot architectural project. The design of the pavilion will be done by taking into consideration only the database building elements, which can be considered as secondary raw material, from the post-earthquake selective demolition operations. The design will be addressed with the aim of *loop algorithms* which operate successive iterations to select from the database, for each design architectural element, the most suitable building element for design purposes. The architectural product will again trigger circular procedures: its component building elements will re-enter the database with updated information to be reused in the future.

Comparative models

Finally, comparative models between traditional and circular approach are conducted to highlight the benefits of the latter in terms of environmental impact, economic savings, waste generation and opportunities for local governments and businesses.

The research is currently in the first of three planned years of the Ph.D. program in Architecture, Design and Planning at the International School of Advanced Studies of the Camerino University, curriculum in Innovation Design - Design for environmental sustainability and for process and product innovation. In addition, a baseline trial of the entire process of digitizing construction waste was initiated in order to understand the constraints, requirements, objectives and data crucial for methodological development. Future research developments will involve theoretical and practical insights into the individual steps of the methodology, which will be interspersed with milestones that can be configured as stand-alone products.

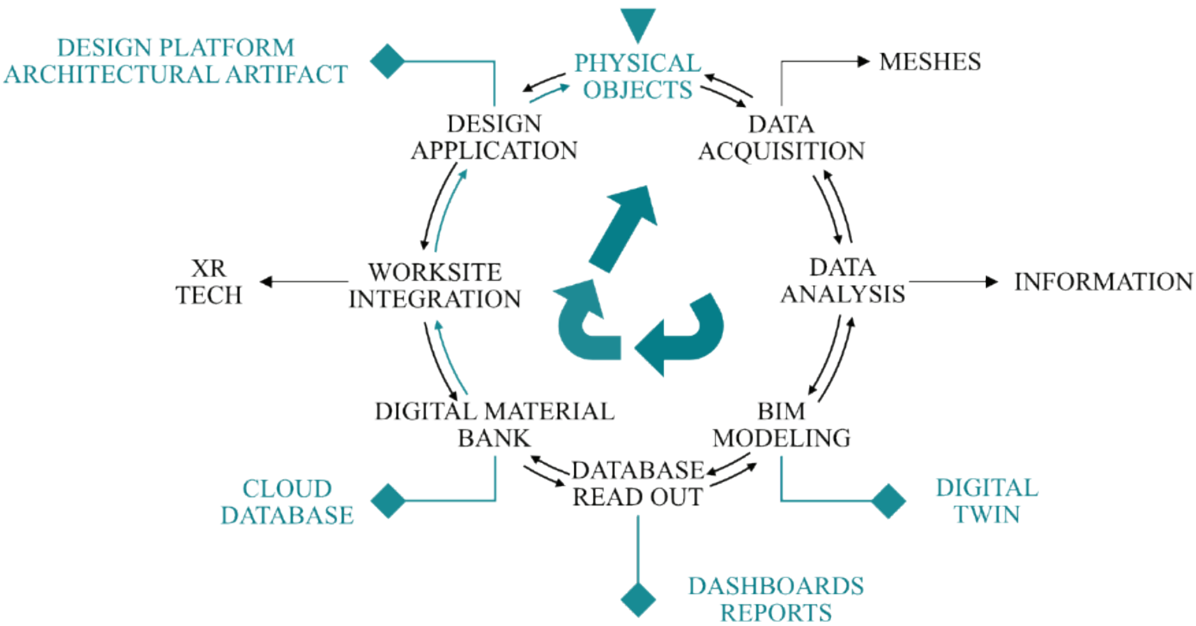

Figure 7. Methodology summary diagram.

FIELD OF APPLICATION AND EXPECTED OUTCOMES

Demolition and reconstruction operations after the 2016 Central Italy earthquake is identified as the scope of application, with a focus on the situation in the Marche region. The proposed methodology provides numerous advantages for local governments and companies operating in the AEC industry, as well as benefits in terms of environmental sustainability. The research provides a system for the upcycling of construction and demolition waste and in which the elements to be used for provisional works are produced, processed, certified, and installed following certain planned procedures in such a way that they are considered, from the earliest stages of their life cycle, as elements that can potentially be reused in the future as secondary raw material. It would thus open up the possibility for companies to purchase materials in advance at a subsidized price since they are reusable only after dismantling. In addition, such a system is convenient for local governments as they would be able to benefit from economic subsidies that can be reused directly in safety and post-earthquake reconstruction works. Finally, the reuse of such building material leads to a significant reduction in waste production and greenhouse gas emissions. However, the proposed methodology is applicable in a variety of contexts, not necessarily emergencies, and to the entire caseload of technological units and building materials.

The main limitations of the research relate to the difficulties of incorporating this methodology within the European and national regulatory framework. A reform in this sense is auspicable in order to fulfill the paradigms of Architecture 4.0 for circularity processes in the construction sector, not only for new construction. From an IT point of view, the geometric and informational representation of certain categories of building elements (e.g. aggregates) remains uncertain to date. In addition, tools for converting point clouds, derived from photogrammetric surveys, into BIM objects need further development to ensure a high level of automation of the process itself. Possible future scenarios for the advancement of the research project involve the integration of artificial intelligence within the process. The use of AI and Computer Vision can potentially automate the entire process of acquiring the different layers of information (geometric, material, presence of degradation). Such acquisition represents today the most time-consuming and complex operation in terms of accuracy. Thus, AI contribution could be a winning strategy to augment design and management capabilities in the construction industry, within the circularity framework.

CONFLICT OF INTEREST

The authors declare no potential conflicts of interest regarding the research, authorship and/or publication of this article.

DATA AVAILABILITY

The data used to support the findings of this study are included within the article.

AUTHOR’S CONTRIBUTIONS

All authors are contributed equally to bring out this article.

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Review Article

Recycling domestic sewage sludge to agricultural and farming areas in line with Sustainable Development Goals (SDG)

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ABSTRACT

Corresponding to the rapid increase in population, the increase in the number of domestic wastewater treatment plants, as well as the increase in domestic sludge levels above acceptable levels, pave the way to utilize sewage sludge in a variety of different applications and usage areas. Using sewage sludge in agriculture, landscape plant cultivation, and other agricultural areas has a number of advantages, including the ability to make rational use of waste without damaging the environment as well as delivering fertilizer benefits to the plant due to the high organic matter content of the wastewater sludge. Aside from these advantages, the most serious drawbacks of waste sewage are pathogenic bacteria, heavy metal contamination, and the presence of potentially hazardous compounds. The use of existing waste in the soil in appropriate proportions and in methods that are compatible with ecological life, on the other hand, will contribute to the fertilization of agricultural areas, providing an alternative to the fertilizer industry. The Sustainable Development Goals (SDGs), also known as the Global Goals, are a global call to action to end poverty, safeguard the environment, and guarantee that everyone lives in peace and prosperity. It is expected that this research will help to promote awareness about the reuse of waste within the context of a sustainable environment, as well as shed light on the application of sewage sludge to agricultural fields in accordance with the Sustainable Development Goals. Furthermore, the support for sewage sludge recycling in agricultural regions for long-term development goals is shown.

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INTRODUCTION

Rapid increases in the world population have expedited the economic and technical advancements taken by human beings, resulting in a rapid depletion of our planet's natural resources. Because our resources are finite, exhaustion and deprivation are unavoidable consequences of our existence. The natural balance of the environment, which humanity uses thoughtlessly and rudely, has deteriorated over time, and this situation has caused irreversible detrimental consequences.

Today, the subject of waste management is a critical concept that is being explored and stressed in a variety of disciplines [1]. Projects and studies on this subject have been increasing, especially recently. The most significant cause for this is a decrease in the ecosystem's tolerance for wastes as a result of climate change. In fact, as a result of the careless release of waste and toxic substances into the environment, the ecological system has begun to worsen significantly around the world [2]. This scenario has developed into a problem that must be addressed at this point, and it has impacted

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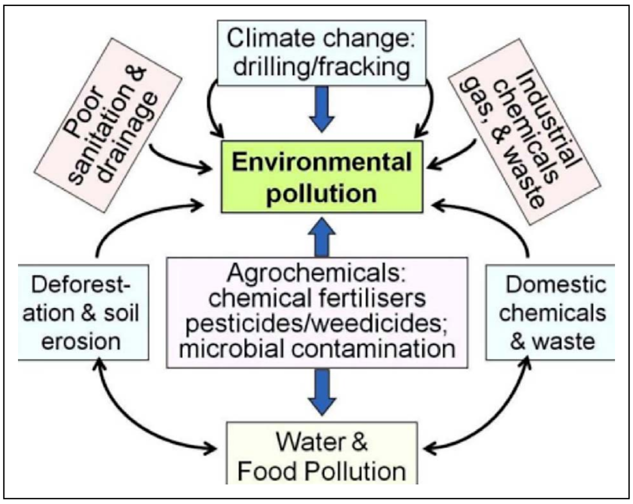

Figure 1. Agrochemical-related environmental pollution [4].

every phase of ecological life as well as the substance of ecosystems in the process. We know that the scenario in which we use our ecological assets carelessly and allow waste to decompose in their natural surroundings without thinking about the harms caused by the waste has extremely negative repercussions for ourselves, our environment, and the entire ecosystem. We started to pay for the price, starting from sea species that are dealing with plastic and other pollution, as well as polar bears that are having difficulties finding a home as a result of global warming in the polar regions, to the plastic in the deepest parts of the oceans and traces of pollution in the most remote places of the earth that have not been touched by humans, as well as the loss of many living species around the world.

Human beings, who are responsible for an increase in pollutant concentrations around the world, damage the ecosystems in which they live by disposing of their waste in urban areas. As can be seen in Figure 1, the source and focal point of many environmental pollution is human. Chemicals and non-organic products used in agriculture and industry to increase productivity cause environmental pollution and cause serious damage to the ecosystem. Harmful pollutants also clog the pores of the soil that provide water and air permeability. With the effect of water and wind erosion, pollutants cause soil and water pollution by moving from their place to another place. Soil pollutants can be decomposed both chemically and by microorganisms living in the soil and turn them into harmless compounds. The products released as a result of decomposition pollute the water, soil and air by passing from the soil solution to the groundwater by washing and adsorbed in the soil. This situation threatens the health and life of the biological environment [3].

Wastewater is created at a high rate in urban areas with a large number of residents. Water treatment plants for domestic wastewater make sure that the sewage water that we release into rivers, lakes, and seas is treated under the standards set forth in the regulations and that it is released into these environments in a manner that does not harm the ecological life that exists therein. This is very important for the sustainability of the environment. There is, however, a significant amount of waste created at the facility's outflow, and the treatment and disposal of this waste is a significant challenge.

Increasing the number of treatment facilities has become more important in recent years in order to mitigate the environmental harm caused by domestic and industrial waste. A growing number of people are opting to transfer domestic waste to the soil environment that is utilized for farming and agricultural purposes in order to prevent re-pollution and manage the nutritional content of these wastes.

In order to properly define the outputs created as a consequence of industrial and domestic activities as "waste," it is necessary to first determine whether they can be used as an input element in another process or production. Utilizing waste as an input to another business allows the waste to serve as a resource for the other business and to be recycled back into the system.

The move from an unsustainable linear economy to a circular economy, which we might define as sustainable and environmentally friendly, has accelerated in recent years around the world. Taking this into consideration, it has now been widely accepted around the world to include all types of waste into the economy, both in the form of a symbiotic relationship and through recycling.

The use of biological treatment sludge, which is a byproduct of a domestic treatment plant, in agricultural regions helps to the formation of living spaces on land by promoting the goals of responsible production and consumption, which is in line with sustainable development goals. The aim of our study; It is the disposal of the waste sludge, which is a waste and formed at the exit of the wastewater treatment plant, without harming the nature. While doing this, it is to be able to use it safely in agricultural areas by making use of the rich organic content and fertilizer feature of the waste sludge. The use of a waste element for the purpose of benefiting the nature again and moreover, serves the concept of sustainability. The contribution of this situation to all SDGs related to the environment is discussed one by one.

SUSTAINABLE DEVELOPMENT GOALS (SDG)

Sustainability Concept

Sustainability is one of the most widely used concepts today, owing to the high demand for raw resources and the ongoing quest for answers to the massive growth in the volume of environmental waste that has occurred in recent years all over the world. Although the word "sustainability," which has been used especially since the 1980s and comes from the Latin word "Sustinere," has different meanings in dictionaries yet, essentially, it means to provide, maintain, keep, support [5].

One can state that in the early periods of the 19^{th} century, the sustainability concept was expressed perceptibly in the literature, and it emerged about renewable resources such as agriculture, forests, and fisheries as a specific notion [6].

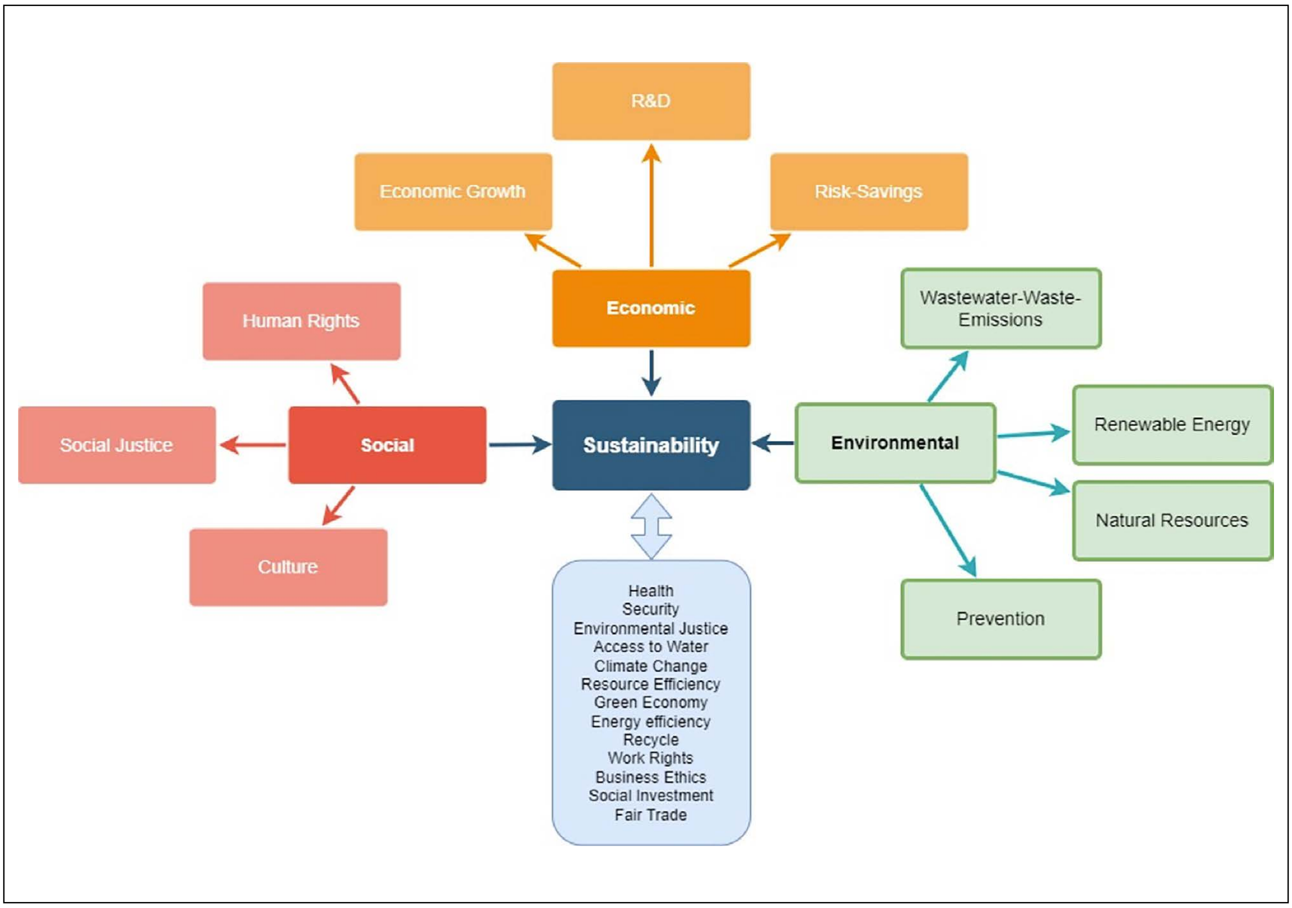

Figure 2. The concept of sustainability and its components.

The sustainability of something can mean its current state of existence or capacity to renew itself. Based on this definition of the word, the notion of sustainability has been applied in the sense of leaving future generations with a world that is sustainable in terms of environmental, economic, and social conditions (Fig. 2).

As can be seen in Figure 2, it is clear that the concept of sustainability is closely tied to economic, social and environmental factors. In order to achieve sustainability, each element supports each other. According to the sustainable development approach, if a coordination between the environment and economic policies is ensured, an improvement in the social structure will also occur. In this context, it is possible to talk about three dimensions of sustainable development that can be defined as economic sustainability, social sustainability and environmental sustainability. The first of these dimensions includes participation and a strong civil society, the second includes the stability of economic capital, and the third includes meeting human needs, conserving natural resources and promoting human well-being [7].

The United Nations' report Our Common Future, issued in 1983, had a significant impact on the definition of the word sustainability. According to the research, sustainability is defined as meeting our daily requirements and developing without jeopardizing nature's and future generations' capacity to meet their own needs.

Sustainability Concept

The problem of sustainable development and sustainability is a critical one on the academic and policy agendas today. It is well known that the subject of sustainable development and sustainability has an interdisciplinary structure that encompasses a broad range of issues in terms of environmental, economic, and social dimensions, as well as pragmatic and political aspects that are accompanied by a solution-oriented standpoint.

The term sustainability has been defined by different sources since its inception. However, due to the fact that this phenomenon is multifaceted, comprehensive and holistic; It is obvious that it is a complex concept that is not easily understood and needs to be explored and developed in depth.

The most common definition of sustainable development is the one by the World Commission on Environment and Development in 1987. According to this definition, development is about 'meeting the needs of the present without compromising the ability of future generations to meet their own needs' [8].

The approach to sustainable development emphasizes the need for increasing economic growth while also taking a protective stance against environmental degradation by placing a high priority on environmental concerns. In brief, for the last quarter-century, efforts have been made to balance the negative consequences of expanding economic ac-

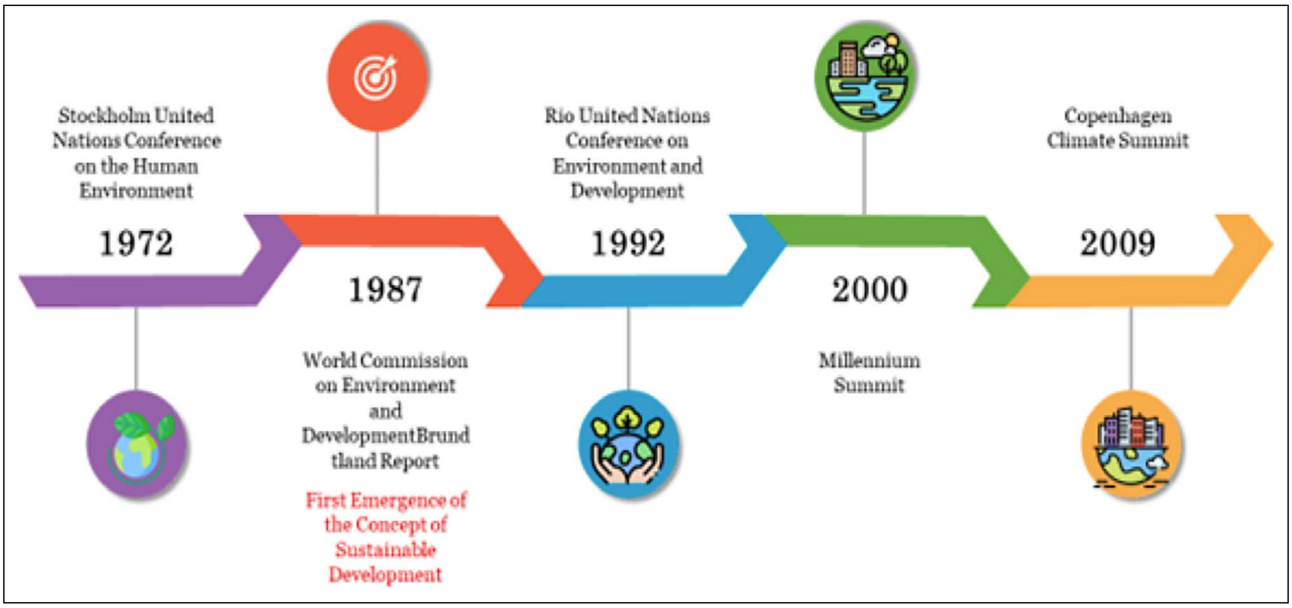

Figure 3. Chronology of agreements on the environment and the first emergence of the concept of sustainable development.

tivity on the environment throughout the world with the "sustainable development" model of growth. As a result of the fact that "we do not have a spare planet" and that yet another planet where humans may dwell has not yet been located. According to the data of the International Energy Agency (IEA), in 2013, the fact that renewable energy sources such as wind and solar surpassed natural gas assets while becoming the world's second-largest natural resource for electricity generation after coal, and the decrease in the average amount of greenhouse gas emissions per capita by 15% in all OECD countries and 26% in EU countries during the 1990-2016 period (OECD STATEUROSTAT, 2018) were two serious examples of the steps taken towards sustainable development [9].

In order to guarantee that human activities do not destroy the earth's land, air, and water resources, the concept of ecological integrity must be adhered to. Ecosystems are presumed to have a limited regeneration capacity as well as a carrying capacity. When combined with population expansion, overconsumption, increasing pollution, and depletion of natural resources, it poses a threat to the integrity of the ecosystem. Human actions have the potential to have substantial negative consequences for the natural environment, including, but not limited to, destruction of biodiversity, depletion of the ozone layer, accumulation of greenhouse gases, waste management, and deforestation, among other things. If the natural environment is threatened, important and necessary resources for human survival such as air, water, and food will be jeopardized as well [10]. With this approach, it is important to protect ecosystem integrity through efficient natural resource management, to use non-renewable resources efficiently, to respect nature and biological diversity, to prioritize global environmental commitment, to prioritize recycling, and to avoid the release of dangerous and polluting substances into the environment.

History And Scope Of Sustainable Development Goals

The concept of sustainable development, which is defined as a "development model that meets current needs without jeopardizing future generations' ability to meet their own needs," was made popular by the World Commission on Environment and Development's Our Common Future report, also known as the Brundtland Report, published in 1987. The Sustainable Development Goals (SDGs), in other words, the Global Goals, are a global call to action to end poverty, safeguard the environment, and guarantee that everyone lives in peace and prosperity (Fig. 3).

The Sustainable Development Goals (SDGs) are moving forward in a spirit of cooperation and pragmatism in order to sustainably enhance living for future generations by making the right decisions now. All countries are given clear advice and objectives to implement in accordance with their priorities and the global environmental issues they face. The Sustainable Development Goals has an inclusive agenda. It addresses the root causes of poverty and unites us to make positive changes for both people and our planet [11].

UNDP Administrator Helen Clark said that supporting the 2030 Agenda is UNDP's top priority and also declared the following "The Sustainable Development Goals provide us with a mutual plan and agenda to address some of the heavy challenges our world is facing, such as poverty, climate change, and conflict (Fig. 4). UNDP has the experience and expertise to help countries make progress and achieve sustainable development." A road map for sustainable development has been established up to the current day as a result of various world summits conducted in the previous 30 years, countless researches, and action plans [12].

Türkiye put the concept of sustainable development on its agenda in 1996, following the United Nations (UN) Conference on Environment and Development in Rio in 1992, and incorporated it in its Development Plans and several

Figure 4. Sustainable development goals [13].

policy documents in the years that followed. Besides the Development Plans, Türkiye's sustainable development agenda now includes sectoral global and thematic national policy and strategy papers that incorporate the notion of sustainability. After all of these, Sustainability in the 10th Development Plan has been one of the key concepts shaping this development plan and also became the dominant theme. The 2030 Agenda for Sustainable Development, which was agreed upon by world leaders and signed by 193 nations, was adopted at the United Nations (UN) Sustainable Development Summit in September 2015. The 2030 Agenda, which accepts the eradication of poverty in all of its forms as an integral part of sustainable development and brings together efforts to tackle climate change with economic and social development issues, was developed as a follow-up to the Millennium Development Goals (MDGs) set in 2000, as well as goals that are even more ambitious. The 2030 Agenda aims to include all societies in efforts to decrease poverty and improve wellbeing throughout the world, safeguard cultural and social values, and avoid or even prevent environmental degradation. Social and environmental issues like gender equality, observing the needs of disadvantaged groups, limiting food waste, trying to combat desertification and drought, and protecting biodiversity, as well as economic problems like economic growth, technological development, employment, and industrialization, have been introduced to the agenda of sustainable development in this emerging global development approach. The Sustainable Development Goals (SDGs) have been defined as part of

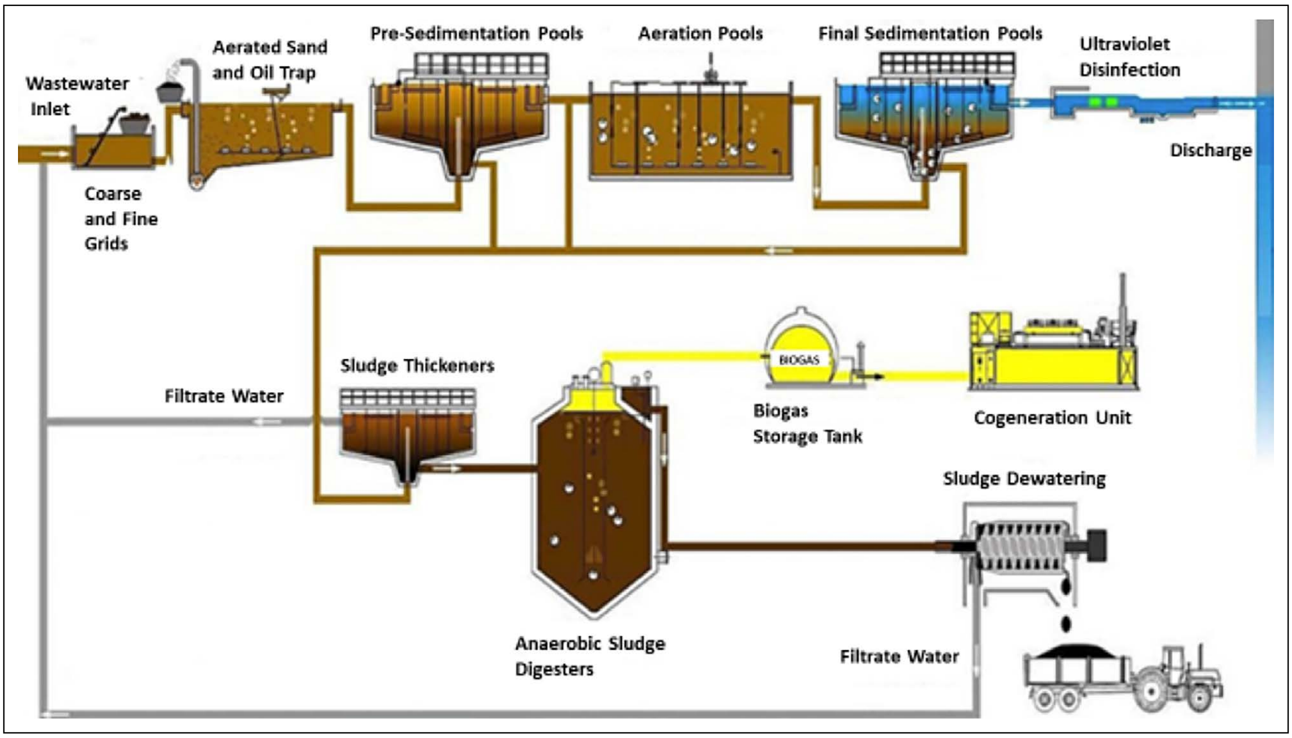

Figure 5. Classic domestic wastewater treatment plant model [15].

the 2030 Agenda, which aims to move the global development trajectory toward a more sustainable path, and a total of 17 Sustainable Development Goals (SDGs) have been identified. The main purpose of SDGs is to work to ensure that no country is left behind in the development process during the period of 2015-2030; it is with the motto of "leaving no one behind." The Sustainable Development Goals (SDGs) include 169 goals and span the economic, social, and environmental components of sustainable development. They have a broader scope than the Millennium Development Goals (MDGs) and go beyond the MDGs by addressing the universal need for development. There is a strong foundation for the SDGs that is based on the achievement and momentum of development achieved by the Millennium Development Goals. "Türkiye's Current Situation Analysis Project within the Scope of Sustainable Creation Objectives" focuses on the development of policy, law, institutional framework, and project concerns for Türkiye in the context of sustainable development goals. Within the scope of the study, the existing status of Türkiye was analyzed for each SDG in light of the results and observations collected; gaps and areas that needed improvement were identified.

FARMING AND AGRICULTURAL APPLICATIONS OF DOMESTIC TREATMENT SLUDGE

An Overview Of Domestic Sewage Sludge

The tremendous growth in population, as well as technological developments and industrialization, has resulted in the contamination of freshwater supplies worldwide. For this reason, wastewater treatment plants using various treatment techniques were designed [14].

Given the presence of potentially hazardous constituents in domestic wastewater, disposal into lakes or rivers is only permitted after it has been cleansed and only under the conditions stated in the legislation.

Solids that are converted into a settleable sedimentable or floatable form from drinking water and wastewater as a result of physical, chemical, and biological treatment processes can be defined as sludge. Sewage sludge is a mixture of particles and liquids that happens during the treatment of water and wastewater. Because of their nature, sewage sludge must be purified before disposal and, if left untreated, can cause environmental damage. They require treatment due to high concentrations of organic matter, nutrients, pathogenic microorganisms, and a high concentration of water in their composition [15].

As can be seen in the flowchart; there are two different types of sludge: chemical waste sludge, which is released as a result of physical treatment in the preliminary settling unit in the facility, and biological waste sludge, which is released as a result of biological treatment from the final settling unit (Fig. 5).

It is appropriate to use biological waste sludge released from the final settling unit in agriculture and agricultural areas. The reason why this sludge is preferred is that it is stabilized sludge free from pathogens. Since biological waste sludge is a fertilizer additive, it can be used in all kinds of agricultural products grown.

Before being disposed of, the sludge from the treatment facilities must be treated. The best method for treating and storing sludge discharged from wastewater treatment facilities is determined by the quality of the waste-

Figure 6. Erzurum domestic wastewater treatment plant sludge images.

water, the chemicals utilized, and existing legislation. Because the disposal of treatment sludge will be regarded as a cost for the facility, the expenditure associated with this should be addressed while establishing the facility, and the design of the facility should be carried out in accordance with this consideration. Costs will vary according to the size of the facility and local conditions.

As can be seen in Table 1; sewage sludge will contain organic compounds, dyes, metal salts, alkalis, phenols, oxidizers, sulfates, oils, hydrocarbons, acids, Cd, Pb, As Fe, Al, Hg, Co, Cu, Cr, organic phosphorus, and nitrogen, depending on the type of industrial structure it was generated [16].

Treatment sludge is rich in heavy metals, pathogenic bacteria, viruses, and toxic chemicals. There are a variety of treatment procedures that are used to clean the treatment sludge, which is generated in large quantities every year, and the aim is to do it in a manner that is safe for human and environmental health (Fig. 6). Developing innovative disposal strategies for the effective and useful use of treatment sludge has become more important in the field of sustainable environmental management [18].

Considering that sewage sludge has a polluting effect, it should be applied carefully to the areas where ornamental plants are grown. Inspections on the subject must be carried out sensitively by complying with the regulations on this subject. Considering the biodegradability of waste sludge and the health hazards arising from its use, there are certain restrictions on the use of treatment sludge in soil in the "Regulation on the Use of Domestic and Urban Treatment Sludges in Soil" of the Ministry of Environment and Forestry dated 03.08.2010 and numbered 27661. Waste sludge may contain toxic organic compounds, heavy metals, pathogenic microorganisms and eggs of parasitic organisms that are harmful to the environment in certain amounts. Biological, chemical (heat) treatments and long-term storage etc. of treatment sludge. The effects are significantly reduced by undergoing appropriate procedures. In addition, sewage sludge can be used as a soil conditioner in soils with low productivity potential [19].

Table 1. Some physical and chemical properties of an average stabilized sludge [17]

Parameters	Unit	Analysis result
Total aluminum	mg/kg	2575
Total nitrogen	mg/kg	3,75
Total copper	mg/kg	15,81
Total iron	mg/kg	5252
Total phosphorus	mg/kg	3715
Total cadmium	mg/kg	0,77
Total lead	mg/kg	9,33
Total nickel	mg/kg	41,04
Total organic matter	%	74,99
Total pH	mg/kg	7,34
Total potassium	mg/kg	1081
C/N	–	11,6
Salt	(μS/cm)	1194

Application of Domestic Sewage Sludge to Soil Environment

The sludge management system should be addressed simultaneously with the design of wastewater treatment plants. As a result, it is vital to building a sustainable sludge management system that incorporates the potential for land usage as well as energy conversion in accordance with the features of the wastewater treatment plant being constructed (Fig. 7) [20].

Different amounts of sludge with distinct characters are released from each unit of the domestic wastewater treatment plant. In addition to being unstable, the sludge produced from the pre-settlement ponds has a high concentration of pathogenic microorganisms. Therefore, it is not suitable for land use. The wastewater is treated biologically in the final settlement ponds, and the sludge generated here is stable and free of pathogenic microorganisms at a high pace, resulting in a stable and pathogen-free sludge. Sewage sludge suitable for field applications is 'Biological Treatment Sludge' released from the final settlement pond.

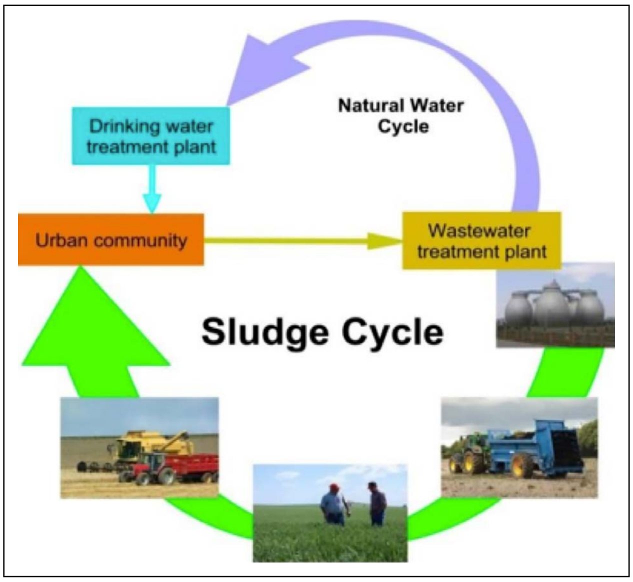

Figure 7. Sludge cycle [20].

Before the biological treatment sludge is released to the soil for any purpose, it is necessary to remove the moisture from it. This sludge should be spread out on a clean outdoor surface and allowed to dry for 2-5 days in the sun for this use. Consequently, the sun's UV rays will both dry and purify the sludge, removing any potentially harmful microbes that may be present in the resulting sludge.

Sewage sludge generated during the treatment of urban wastewater is classified as non-hazardous waste under the "Waste Management Regulation" Annex-IV list issued in the Official Gazette dated 02.05.2015 and numbered 29314 and named with 19 08 05 waste code.

Sludge produced from Wastewater Treatment Plants has a wide range of reuse possibilities. When content analyzes are identified and conform with the permissible limits stipulated in the rules, they can be used in the cultivation of forage crops (clover, sainfoin vetch, oat, clover) and cereal crops (wheat, barley, rye, corn) in agricultural regions. It can also be used in parks, green areas and refuges, and ornamental plant cultivation, as well as in the creation of artificial forest areas, the upgrade of pasture areas, and the conversion of barren lands to the most suitable areas (agricultural land, pasture area, forest).

Although the amount of sewage sludge varies by area and treatment method, most studies estimate that it is high in organic matter, phosphorus, and nitrogen, and it may be released into the soil in a controllable way [21].

Environmentally friendly sludge disposal methods are very costly and time-consuming. It also requires expertise and knowledge. Using sludge for land compared to other disposal methods has been very common recently. Because sewage sludge contains a high amount of organic matter and nutrients (N, P, K) for plant growth, this content stimulates plant yield in the land [22].

Treatment sludge, the amount of which is rising by the day, should be disposed of properly to avoid causing environmental issues. Various methods have been tried for years for sludge disposal, and a great deal of research has been put forward. One of the approaches that are stressed in terms of its contribution to the economy is the disposal of treatment sludge by applying it to the soil. Both sludge disposal and economic advantage in agricultural production may be reached through the use of sewage sludge with acceptable features as an organic fertilizer and soil regulator. It is now common practice to offer treatment sludge with adequate qualities to agricultural areas. When sewage sludge is applied to agricultural land, it delivers the final disposal step and allows the plant nutrients in the sludge to enter their natural cycles in the soil [23].

Wastewater is cleaned to the highest level possible from pathogens and hazardous compounds in its content after going through physical, chemical, and biological treatment procedures. And the obtained sludge may be disposed of in an environmentally friendly manner by using it as a habitat in agriculture, biological repair processes, landscaping, and plant cultivation [17].

Agricultural regions, rehabilitation of unusable degraded areas, artificial forest areas, and sludge storage places can all benefit from treatment sludge. All land use aims at providing more treatment of sewage sludge. Using sunshine, soil bacteria, and the drying impact, many harmful microorganisms and poisonous organic compounds in the sludge are eliminated [24].

The disposal of sludge by land use has become an attractive option used worldwide. As a result, determining the compatibility of sludge in terms of harmful and carcinogenic compounds is critical in order to make informed decisions about its application in agricultural settings [25].

The disposal of treatment sludge via soil is one of the most notable procedures in terms of its contribution to the economy among the several disposal options available. The fact that the disposal option being considered is both cost-effective and easy to apply is a significant advantage. Both wastewater management and treatment sludge, which is its output, is very important [26].

Sewage sludge, which may be disposed of by planting it in agricultural regions, forest areas, degraded park gardens, and grass areas, has been employed in a variety of fields recently, including land recreation, urban landscape, and sapling production [27–29].

Numerous research has demonstrated that applying sewage sludge and compost at certain rates promotes plant growth, soil physical qualities, and useable nutrient levels. Nitrogen, phosphorus, and potassium are the primary nutrients that enable sludge to be utilized as a fertilizer [30].

The fact that certain sewage sludges have beneficial agricultural qualities while others have detrimental impacts on the environment and human health precludes their uncontrolled application in agricultural regions. As negative effects, heavy metals such as manganese, copper, zinc, cobalt, chromium, lead, nickel and cadmium, salts, toxic organic chemicals, and pathogenic microorganisms can be listed. On the other hand, because treatment sludge cannot be obtained constantly or homogeneously at certain times, it is prohibited from being used directly or converted into a commercial product. In short, the qualities of the sludge coming out of different facilities are different, and this can also change the effect of the sludge on yield and usage areas. As a result, before the treatment sludge is applied to the soil, its composition must be identified by the analysis, and for this aim, various treatment sludges should be tested on soil samples to find the most appropriate dosages [31].

Sewage sludge is biological sewage sludge that is created during biological treatment, which is the last output element of a domestic wastewater treatment plant. A large number of nutrients may be found in biological sewage sludge, and these elements are extremely beneficial to plant growth as well as having fertilizer value. However, besides this, there are pathogenic microorganisms, harmful chemicals, and heavy metals in the sewage sludge. This condition raises concerns regarding the amount of sewage sludge that should be applied to the soil environment. As a result, in order to identify the optimal dose of sewage sludge in sewage sludge uses, experiments in micro fields were conducted first, followed by macro-level studies using the optimum sewage sludge dose.

In recent research, the effects of increasing treatment sludge (0, 2.5, 5, 7.5, and 10%) usage on the yield of the corn plant, various soil qualities, the root and above-root sections of the corn plant, as well as changes in length and diameter have been examined. The applications statistically increased root wet and dry yields, above-root fresh and dry yields, plant height, and diameter of the corn plant in all treatments. Although the sludge improves several plants and soil features when treatment sludge (supplied from Hatay province-Iskenderun district's biological treatment facility) is applied in various ratios to the soil, it is not suitable for use in agricultural areas due to the extremely high salt concentration of it [32].

It was discovered in a recent study that by mixing sewage sludge with different soil types and applying them in varied proportions to the carrot plant's growth medium in a pot, it was possible to examine how the plant developed and how much heavy metal is absorbed. Results showed that sludge application significantly affected soil pH, organic matter (OM), electrical conductivity (EC), potassium (K), and phosphorus (P). After the sludge application, the content of heavy metals such as lead (Pb), cadmium (Cd), nickel (Ni), and chromium (Cr) increased in the soil and plant. The sludge application positively affected carrot growth. The maximum fresh weight (66.3 g plant-1) in 30% sewage sludge application and maximum dry unit weight (5.61 g plant-1) in 50% sewage sludge application were recorded [22].

Again, in a recent study, it was aimed to determine the effect of the stabilized sewage sludge on the yield and nutrient intake of the tomato plant by drying and applying it at different doses (0% (control), 1%, 2%, 3%, 4%, 5%, and chemical fertilization). The maximum yield was observed in the application of the most treated sludge (5%). As 5% sludge was applied, an increase in the dry weight of the root, stem, and green portions of the plant of about 187%, 254%, and 132% was seen, respectively, when compared to the control. On average, the yield of plants developed as a result of basic chemical fertilization was comparable to 1% treatment sludge application [26].

In research in which sewage sludge was applied at various rates to the pot of tomato plants, fruit mass was found to be greatest in pots treated with 20% sludge compared to all other treatments. The yield of tomato fruit was determined as control <10%<30%<20%. The absence of appropriate nutrients in the control and 10% sludge treated pots slowed tomato development, but the toxicity of the 30% sludge applied pot suppressed tomato growth. The development of the pot was optimal when 20% sludge was added [33].

Domestic waste sludge provides benefits to plants, agricultural fields, and agricultural practices because of its content. Literature has also proven that sewage sludge creates a fertilizer effect for the plant. Due to the chemicals, heavy metals, and pathogenic microorganisms present in sewage sludge, the dosage administered is critical. As demonstrated by studies, it will not help the plant if applied in excess of what is necessary and will have a detrimental effect on the soil and the plant if applied in excess of what is necessary. The aforementioned studies were carried out to determine the optimum dosage of micro-level waste sludge. The optimal dose of waste sludge found via the tests may be safely administered at the macro level to agricultural and farming areas.

3. AN EXAMINATION OF THE SUITABILITY OF SEWAGE SLUDGE FOR AGRICULTURAL AREAS İN CONFORMANCE WITH SUSTAINABLE DEVELOPMENT GOALS

The Sustainable Development Goals (SDGs) that our government has set for 2030 cover a wide range of themes, from individual education to the social obligations we should undertake. These goals outline how we should prioritize individuals, society, nature, and each living creature. Sustainable development goals, which are meticulously crafted to ensure the long-term viability of nature and its transfer to future generations, include a list of adaptable, dynamic, and current issues that may be included in any subject.

Using sewage sludge in agriculture and farming indirectly contributes to the environmental SDGs? (Goal 6-7-9-11-12-13-14-15) while especially directly contributing to 12th and 15th goals. With this ecologically friendly process, sewage sludge may be disposed of without causing harm to the ecosystem, and waste can be minimized within the framework of Responsible Consumption and Production. Additionally, utilizing treatment waste as an input in natural areas allows the sustainable and effective management of natural resources within the context of the Life on Land goal (Fig. 8).

Figure 8. SDGs that stand out in environmental issues.

Sustainable Development Goals; Goal 11 (Sustainable Cities And Communities)

It is known that more than half of the world's population lives in cities. The concept of sustainable city, which has recently become one of the most important concepts around the world; deals with the increase of urbanization, the development of the economy, the ability to cope with the increasing environmental problems with rapid population growth and the protection of the ecosystem. Creating a city that is beneficial to the environment, nature and people and meets the needs of future generations is the main task of Sustainable Cities and Communities [34].

Sustainable Development Goals; Goal 11 (Sustainable Cities and Communities) is to make cities and human settlements inclusive, safe, resilient and sustainable. In line with this purpose, the sustainable use of waste from the treatment system in the city as a raw material for another system is directly related to Goal Target 11.6. This goal target is defined as "by 2030, reduce the adverse per capita environmental impact of cities, including by paying special attention to air quality, municipal and other waste management" [35].

Goal target 11.a "support positive economic, social and environmental links between urban, peri-urban and rural areas by strengthening national and regional development planning" is emphasized to support economic and environmental relations. Recycling of domestic waste sludge to agricultural and agricultural fields is directly related to this goal target.

Target goal 11.b "By 2020, substantially increase the number of cities and human settlements adopting and implementing integrated policies and plans towards inclusion, resource efficiency, mitigation and adaptation to climate change, resilience to disasters, and develop and implement, in line with the Sendai Framework for Disaster Risk Reduction 2015-2030, holistic disaster risk management at all levels" is another important goal in this regard. The reuse of domestic waste sludge in a circular economy is directly compatible with the resource efficiency included in this goal target. In addition, this process indirectly affects adaptation to climate change, reducing climate change.

Sustainable Development Goals; Goal 12 (Responsible Consumption And Production)

According to research released by the United Nations Population Fund, if the world population hits 11 billion in 2050, we would require the equivalent of three planets to support present lifestyles and provide the necessary natural resources.

One of the most critical stages toward attaining sustainable development is decreasing the use of natural resources, the consumption of harmful substances, and the waste and pollution generated by these activities across the whole production and consumption process.

Türkiye has a multitude of policies, legislation, institutional structures, and practices aimed at achieving responsible production and consumption, and when the objectives are analyzed individually, a large national capacity emerges. However, the need for a more comprehensive approach to sustainable management and effective use of natural resources, chemical management, cleaner manufacturing/eco-efficiency practices, and research and development activities persists.

Through a number of measures, including particular legislation and international agreements on the management of environmentally damaging products, Sustainable Development Goal 12 supports more sustainable consumption and production practices [35].

Goal target 12.2 "By 2030 achieve sustainable management and efficient use of natural resources" which is included in Goal 12, can be related to this issue. Again, the treatment process can be associated with goal target 12.4 "By 2020, achieve the environmentally sound management of chemicals and all wastes throughout their life cycle, in accordance with agreed international frameworks, and significantly reduce their release to air, water and soil in order to minimize their adverse impacts on human health and the environment".

Goal 12 highlights the sustainable management of resources and waste, sustainability reporting, sustainable public procurement and promoting tourism. Sustainable consumption and production ensures the effective use of resources and reducing waste production, increasing the quality of life together with economic activities. In short, it aims to "do more and better with less".

Within the framework of Goal 12 Goals; The biological waste sludge of the domestic wastewater treatment plant is recycled to the nature. It will be prevented that the waste harms the ecological life. waste sludge; It will make a financial contribution to the fertilizer industry by providing fertilizer support to agriculture and agricultural fields. Sustainable economy will be supported by bringing the fertilizer value of the waste sludge into the circular economy.

Sustainable Development Goals; Goal 15 (Life On Land)

In the last 50 years, 60% of the world's ecosystems have been disrupted, their food chains and material flows have been interrupted, and many living species have faced extinction. Today, this situation continues to reduce our natural resources at an alarming rate.

According to the 2019 Global Assessment Report on Biodiversity and Ecosystem Services, approximately 1 million animal and plant species are in danger of extinction within 10 years.

The primary needs identified within the scope of this purpose are to monitor indicators in a variety of critical areas, such as local/sectoral adaptation and climate risk plans, in addition to standard indicators, to promote efficient water use in agriculture, to protect agricultural lands, to rehabilitate meadow/pasture areas, to counteract erosion, and to detect risks early and to develop novel techniques for difficulties such as drought-resistant species selection in agriculture and livestock production.

Its objectives within the scope of terrestrial life are: to protect, restore and support the sustainable use of terrestrial ecosystems; ensuring sustainable forest management; combating desertification; stopping and reversing land degradation; to prevent the loss of biodiversity. In this framework, the use of waste sludge as fertilizer in all kinds of green areas and agricultural areas will be a great step towards the sustainability of the ecosystem, green areas and forests targeted in Article 15. Thus, it will contribute to the plant life and ecosystem on land. As explained above; recycling of waste sludge into nature, not only ensures the disposal of a waste without causing environmental pollution, but also contributes to the production by adding fertilizer to the agricultural fields. Thus, in our agricultural country, it is predicted that this effect will be beneficial to the whole eco-life and economy, with the revival of agriculture with a cost-free fertilizer.

CONCLUSIONS

The main theme of the Sustainable Development Goals is constituted by the elimination of inequalities, the reinforcing of economic growth and employment; improving the air quality in cities and populated neighborhoods; improving the quality of urban life; working to ensure the industrialization of the world; safeguarding ocean and ecosystems; generating more renewable energy; combating climate change; promoting sustainable production and consumption; and enhancing human rights.

In line with the Sustainable Development Goals, the use and disposal of sewage sludge from urban wastewater treatment plants as a raw material for another system in the city is directly related to SDGs.

By using the wastes of treatment plants as renewable raw materials in different systems; it can be said that SDG 11 (Sustainable Cities and Communities) directly contributes to the creation of cities that are beneficial to the environment, nature and people, and that also meet the needs of future generations. In addition, by using this method in the city, it is possible to develop safe, sustainable methods that are inclusive of cities and human settlements.

Following the Sustainable Development Goals, it is intended that residential sewage sludge, which is considered trash, would be used in agricultural regions to enhance soils and for other purposes such as agriculture, landscaping, and other landscaping. It also aims to benefit the plant as fertilizer by recycling a significant quantity of waste that has been left to nature in an uncontrolled manner without ensuring suitable conditions, to prevent damage to the environment caused by the waste, and to obtain the greatest possible benefit from it. Furthermore, sewage sludge will be able to participate in the fertilizer industry as a result of this application, and no extra fertilizer will be required. For this purpose, agricultural use of sewage sludge is directly related to the 12th article of SDGs.

Adding domestic sewage sludge to the soil can improve the soil's quality and deliver fertilizer effects, which will be critical in enhancing agricultural lands. Thus, by implementing responsible production and consumption, agricultural regions will be expanded, and the production sector will thrive. In addition, by creating larger green areas, we will be enabling the sustainability of the environment. In this direction, the agricultural use of sewage sludge is directly related 15th article of SDGs.

Efforts geared towards the goal are needed to ensure and promote the sustainable use and preservation of ecosystems. Sustainable development goals will contribute to leaving a cleaner and greener planet for future generations by assuring that ecosystems, which are at a particularly vulnerable stage, are influenced by production and consumption activities in the most favorable way. Exorbitant volumes of sludge are created, particularly in wastewater treatment facilities, while assuring that the whole city's wastewater (domestic and industrial) is treated and returned to the water environment. The eco-friendly disposal of this sludge conforms with all of the Sustainable Development Goals in its entirety. As a result, we should make global efforts to encourage the recycling of sewage sludge from urban wastewater treatment facilities to agricultural and farming areas.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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