



Article A Life Cycle Analysis to Optimally Manage Wasted Plastic Pesticide Containers

Georgios Garbounis¹, Helen Karasali² and Dimitrios Komilis^{1,*}

- ¹ Department of Environmental Engineering, Democritus University of Thrace, 67132 Xanthi, Greece; ggkarmpo@env.duth.gr
- ² Laboratory of Chemical Control of Pesticides, Benaki Phytopathological Institute, Kifissia, 14561 Athens, Greece; e.karassali@bpi.gr
- * Correspondence: dkomilis@env.duth.gr; Tel.: +30-2541079391

Abstract: Wasted Plastic Pesticide Containers (WPPC) represent the end-of-life cycle of used agrochemicals. Optimal treatment of these containers is necessary to protect both human health and the environment. In Europe, WPPC are typically rinsed after use and landfilled along with commingled Municipal Solid Waste (MSW). There seems to be no Life Cycle Assessment (LCA) methodology in the international literature to compare the environmental impacts of the WPPC management methods. The goal of this work was to perform an LCA to quantify the environmental impacts of seven alternative scenarios to treat and dispose of Wasted Plastic Pesticide Containers and rank them according to their environmental footprints. Thirty-one WPPCs were sampled, triple-rinsed and an analysis of their residual active pesticide was performed. Those residuals amounts were included in the LCA when assembling the WPPC unit. The scenario in which WPPC are separately collected and recycled resulted in the lowest net environmental impacts. Scenario 5 (50% recycling and 50% incineration) and scenario 6 (50% recycling and 50% landfilling) were the next environmentally optimal technologies, while the landfilling scenario resulted in the highest environmental impacts. A sensitivity analysis was performed, using different impact assessment methods, different transportation distances and different types of landfills and incinerators. The residual pesticide amount did not alter the ranking of the management scenarios. Triple rinsing was found to render all wasted containers as non-hazardous wastes.

Keywords: pesticide; wasted plastic pesticide containers; life cycle assessment; recycling; incineration; pesticide packaging

1. Introduction

1.1. Pesticide Use and Impacts

Farmers around the world apply pesticides to mitigate the impacts of crop pests. Insects and fungi can cause crop damage that affects the farmers' income [1]. Several studies indicate that the behavior of farmers, external circumstances (i.e., political and economic issues) and technological factors (i.e., agricultural environment and equipment conditions) can influence pesticide usage [2].

In 2008 the usage of pesticides was estimated at two million tonnes worldwide. The USA, Europe and the rest of the world consume 24%, 45% and 25% of the total amounts of pesticides, respectively [3]. Global pesticide application has increased from 2.3 million tonnes of active ingredient, in 1990, to 4.1 million tonnes in 2016 [4]. In the US, pesticide usage particularly organophosphates has decreased since 1992 by more than 40%, but the used pesticides have become more potent. At the same time, worldwide, pesticide (herbicides in particular) use seems to have an upward trend [5]. Despite the doubling of Plant Protection Products (PPP) since 1980, their environmental impact is significantly reduced due to the use of more specialized PPPs and more advanced application technologies [6].



Citation: Garbounis, G.; Karasali, H.; Komilis, D. A Life Cycle Analysis to Optimally Manage Wasted Plastic Pesticide Containers. *Sustainability* 2022, 14, 8405. https://doi.org/ 10.3390/su14148405

Academic Editors: Paolo S. Calabrò and Daily Rodriguez Padrón

Received: 13 June 2022 Accepted: 5 July 2022 Published: 8 July 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). According to the Food and Agriculture Organization (FAO), more than 500,000 tonnes of unused and obsolete pesticides need proper management.

When pesticides are used on crops, a considerable part of residues remaining in soil is absorbed by plants [7]. Less than 0.1% of the pesticides applied on plants finally reach their target. Thus, a considerable amount of those potentially hazardous chemicals, are transferred to the environment where they can be a hazard to public health and to environmental compartments such as soil, surface, ground water and the atmosphere [8].

Pesticides in the soil move through drainage, leaching or runoff, increasing the extent of pollution [9]. The United Nations Environment Protection (UNEP) reports that 9 out of the 12 most persistent organic pollutants (POPs) are pesticides [10].

The substantial use of pesticides causes severe negative environmental impacts [1]. Health problems on farmers [11], environmental deterioration [12], resistance to pests [13] and presence of residues on agricultural products [14] are the most important of those impacts. Moreover, pesticides could be hazardous to birds, fish and non-harmful insects. Studies have reported that 76 pesticide residues are found in topsoil around Europe. Around 83% of the European soils contained one or more pesticide residues [15]. Pesticides have been also found in surface water, rivers and lakes throughout Europe rendering them a threat to aquatic organisms [16].

Humans are exposed to pesticides through different environmental pathways (soil, water, air and food). Pesticides can enter the body via inhalation, ingestion and skin contact causing serious deterioration to human health, such as diabetes, reproductive disorders, neurological dysfunction, cancer and respiratory disorders [17]. There is a need to keep farmers aware of the safety measures to be employed during the use of pesticides. Environmental organizations, farmers and pesticide manufacturers must take initiatives to reduce the hazard of pesticides. At the same time, governments should apply stricter regulations for the efficient and targeted application of pesticides [16].

Several review papers have investigated the associations between pesticide exposure and cancer risk [18]. In 2012, 193,460 fatalities were recorded across the world due to pesticide poisoning. The International Code of Conduct on Pesticide Management ('Code of Conduct') provides best practices of pesticide use to decrease risks to human health and the environment [4]. The FAO publishes manuals on how to prevent accumulation of the disposed pesticides and the resulting empty containers. It is costly to clean up obsolete pesticide disposal sites, as the management cost seems to range from USD 3 to 5 per kg or L of pesticide. Management methods include repackaging, transportation, incineration and landfilling [19].

1.2. Wasted Plastic Pesticide Containers' Management Worldwide

This work will focus on the plastic wasted pesticide containers, as this is the majority of the containers. According to the European Waste Catalogue (EWC), WPPC is a packaging waste and is listed as a hazardous waste that belongs to the 15 01 10* category, that is "packaging containing residues of or contaminated by hazardous substances". An important source of polluted water with pesticides is the rinsate produced after cleaning empty pesticide containers. Therefore, a suitable treatment of the Wasted Plastic Pesticide Containers (WPPC) is necessary to prevent generation of such polluted wastewater. Reusing WPPC for domestic purposes has been identified as a health risk especially in developing countries. WPPC represent the end of the life cycle of agrochemicals and need to be well rinsed [20] prior to treatment/disposal. However, farmers are often unwilling to clean and destroy empty containers, due to lack of knowledge. In addition, the uncontrolled disposal of the rinsate could be an additional environmental threat.

Farmers can return WPPC to chemical companies for reuse but this option does not appear to be financially feasible. Therefore, reuse of pesticides, high-temperature incineration, chemical treatment and landfilling are possible disposal methods according to the International Group of National Associations of Manufacturers of Agrochemical Products. As several pesticides are being either banned, withdrawn or restricted, container reuse seems to be unfeasible [21]. At the same time, burning empty pesticide containers in open fires or dumping empty containers should be prohibited. On the other hand, safe incineration techniques and safe landfilling require adequate knowledge of pesticide chemistry and local hydrology, respectively [22].

With regard to soils contaminated with pesticides, bioremediation seems to be the most efficient approach [23]. A biological process to degrade pesticides and decontaminate empty pesticide containers could be a proper WPPC management method. In developing countries, farmers dispose of pesticide containers in water canals, streams or nearby vegetation. For example, a study in Pakistan reported that a great proportion of farmers (53%) disposed of WPPC into the environment uncontrollably. At the same time, 18% of those WPPC were reused for household purposes. Similarly, 44% of the farmers in Papua New Guinea dispose of WPPC into fields and bushes, 12% bury them in the ground, 9% discard them into streams, 9% burn them in open fires, 6% reuse them for home purposes and the rest reuse them for other purposes. A total of 14% of the farmers in Costa Rica and 19% in Uganda simply discard pesticide residues into rivers and reuse the WPPC to wash clothes, carry vegetables and even store water [24]. East Africa Rift (EAR) zone countries, such as Ethiopia, Tanzania, Kenya, and Uganda, carry obsolete pesticides to Europe for incineration [19]. In Ghana, 53% of the farmers burn WPPC, 25% bury them and the rest find alternative uses [25]. In Greece, 30.2% of the farmers dump WPPC (and any residual remaining in the container) next to the crops, 33.3% dispose of them near or into irrigation canals and streams and 17.9% burn WPPC in open fires [22]. Additionally, in some developing countries, empty WPPC may be used for storage of fuel or even food and water [21]. Table 1 presents the different WPPC management practices in some countries.

Table 1. Different WPPC management practices worldwide.

Country	Uncontrolled Disposal (%)	Reuse (%)	Uncontrolled Burial (%)	Uncontrolled Burning (%)
Ghana	N/A ¹	22	25	53
Greece	63.5	N/A	N/A	17.9
Pakistan	53	18	N/A	N/A
Papua New Guinea	53	26	12	9

¹ Not available.

Ineffective management for the disposal of obsolete pesticides has been reported in China, India [26] and in most developing countries. Incineration seems to be the prevalent management option for disposal of obsolete pesticides [27], but the releases of toxic chemicals such as hexachlorobenzene (HCB), dioxins and furans is detrimental to the environment. Cement kilns could be an environmentally sound alternative to controlled incineration for obsolete pesticides in developing countries [28]. According to the WHO and the Food and Agriculture Organization (FAO), the most appropriate management method would be to return WPPC back to the manufacturer for destruction through hightemperature incineration [24]. In Ethiopia, 1000 tonnes of obsolete pesticides, including WPPC, have been transported over the period 2006–2007 to incineration facilities in England and Germany [29].

The efficiency of the management system of WPPC depends on training, control and traceability [30]. As technologies for waste management are improving, it is necessary to assess the most optimal forms of treatment of WPPC [31]. The European Crop Protection Agency has proposed triple rinsing of WPPC as a special waste management practice prior to container treatment and disposal. It is a simple and effective method and aims to keep the contents of the active substance of the residual liquid in the container below the threshold limits. The contaminated rinsate is returned back to the spraying tank and is applied again on the crops. WPPC that contains residual pesticide with a very toxic active substance at a concentration higher than 0.1% of its total weight (residual liquid + container), then it is listed as a hazardous waste [32]. If low levels of the active substance of the pesticide are

achieved after triple rinsing, then the WPPC would likely belong to the 15 01 02 (plastic packaging) category of the European Waste Catalogue.

A large number of methods and tools for assessing environmental impacts have been developed. Life cycle assessment (LCA) started to be applied on waste around 1990 [33]. LCA investigates the environmental aspects and potential impacts throughout a product's life (i.e., from cradle to grave) [34]. LCA is widely used as a decision support tool (DST) for effective waste management aiding to find the most appropriate alternative waste management methods [35]. A reliable LCA can be performed only when system boundaries and inventory data are well understood and acquired. For a successful implementation of the LCA models, accurate inventory data (ideally local data) and system boundaries must always be carefully considered [31].

For example, LCA was used as a decision support tool in the State of Rio de Janeiro to evaluate the management of lubricating oil plastic containers, comparing recycling to incineration with energy generation (waste-to-energy). Incineration is a treatment widely used in many countries, as an alternative management to landfilling [36].

The chemical residuals contained in empty WPPC is a necessary knowledge when performing LCAs. Such information does not exist in the international literature and for this reason residual analyses were performed here to determine the remaining pesticide residues in the rinsed WPPC [37]. This analytical methodology could be employed in routine analysis, thus supporting a proper evaluation of the agricultural solid waste according to EU regulations.

1.3. Gaps in Knowledge and Research Objectives

To the knowledge of the authors, there seems to exist no life cycle assessment (LCA) methodology in the international literature to compare the environmental impacts of different WPPC management methods. The current work, therefore, represents the first effort to determine those impacts, and rank alternative WPPC treatment and disposal technologies. Seven (7) WPPC management technologies were evaluated and compared using LCA tools. The technologies (methods) were: landfilling, recycling, incineration and a combination of the above. Comparison among the seven methods in terms of resource and energy use can provide enough information for policy makers to support their decision on the optimal WPPC management scheme per region or country. The methods were ranked according to their overall environmental footprints using a standard LCA environmental impact assessment methodology.

2. Materials and Methods

2.1. Sampling of Empty Plastic Pesticide Containers

Thirty-one (31) wasted (empty) plastic pesticide containers were randomly collected with the aid of local farmers who, right after preparing the spraying solution, provided the empty containers to us (prior to triple rinsing). The sampling period was one working week (5 days) during the summers of 2020 and 2021. During those weeks, an equal number of containers was collected daily from a WPPC disposal site near the city of Drama (North Greece). All the sampled containers were then triple rinsed in a consistent way with tap water, as required by the current Hellenic legislation for such containers prior to disposal. The rinsate was returned to the spraying tank and was applied back to the crops. During the summer period, farmers apply herbicides and fungicides on crops in order to protect them from fungi and weeds; thus, WPPC were readily available for our research purposes. The sizes of the sampled WPPC ranged from 0.4 to 3 L. The containers were then immediately transported (via express courier) to the Benaki Phytopathological Research Institute (BPI) in Athens (Greece) for residual pesticide analysis, which is described below.

2.2. Reagents Used during Pesticide Analysis

2.2.1. Analytical Standards

High purity analytical standards of cyflufenamid (99.2%), difenoconazole (99.5%), folpet (99.5), florasulam (99.5%), mandipropamid (99.2%), pinoxaden (99.5%), quizalofop-P-ethyl (98.5%) and 2.4 D-2-ethylhexyl ester (99.1%) were purchased from ChemService (USA), while clopyralid (99.5%) and cloquintocet-mexyl (99.5%) were obtained from Dow AgroSciences. Analytical standards of fluopyram (99.66%) were purchased from Dr Ehrenstorfer, oxathiapiprolin (98.9%) from Corteva AgriSciences. Methanol of HPLC grade was purchased from Fischer Scientific (Loughborough, UK), acetone (pesticide residue grade) from Carlo Erba (Cornaredo, Italy) and acetonitrile of HPLC grade from Merck (Darmstadt, Germany).

2.2.2. Stock and Working Solutions

Individual pesticide stock solutions (1000 μ g mL⁻¹) were prepared by gravimetric weighing of the high purity analytical standards and dilution by the appropriate solvent. For Gas Chromatographic analysis (GC), acetone (quizalofop-P-ethyl, trifloxystrobin, fluopyram and 2.4 D-2-ethylhexyl ester) was used, while for High Performance Liquid Chromatography (HPLC) either acetonitrile (pinoxaden, pyraclostrobin, florasulam, clopyralid, cloquintocet-mexyl, cyflufenamid, folpet, mandipropamid and oxathiapiprolin) or methanol (difenoconazole) were used. Working solutions of the individual stock solutions were prepared in the range of 0.1 μ g mL⁻¹ to 500 μ g mL⁻¹. The working solutions were used for establishing the chromatographic system's precision through repeatability testing and by accounting for the linearity of the analyte response. Stock and working solutions were kept in amber volumetric flasks at -40 °C in the dark.

2.3. Chromatographic Analysis

2.3.1. Analytical Techniques

The analysis of the containers was based on their rinsing with water and applying the most suitable analytical technique for the individual active substance. Two analytical techniques were engaged in their analysis, the High-Performance Liquid Chromatography (HPLC) with Diode array detector (DAD), and the Gas chromatography (GC) with flame ionization detector (FID). The HPLC system used in the analysis was a Shimadzu UFLC instrument (Shimadzu, Japan) equipped with a column oven (CTO-20A), a Diode array detection system (SPD-M20A), an autosampler (Sil-20AC) and a degasser (DGU-20As). System control and data analysis was carried out using the LabSolution software (Shimadzu, Japan). The GC system employed in the analysis was a Shimadzu GC-2010 PLUS instrument (Shimadzu, Japan), equipped with a Flame Ionization Detection system, a split/splitless injector operated in the splitless mode and an autosampler (AOC-20i). System control and data analysis was performed by the GC LabSolution software (Shimadzu, Japan).

2.3.2. High-Performance Liquid Chromatography

HPLC/DAD: HPLC analysis was performed for all the HPLC-amenable analytes: pyraclostrobin, clopyralid, florasulam, pinoxaden, cloquintocet-mexyl, folpet, oxathiapiprolin, difenoconazole, cyflufenamid and mandipropamid. Chromatographic separation for pyraclostrobin, pinoxaden, cloquintocet-mexyl, mandipropamid, difenoconazole and cyflufenamid and was achieved on a Phenomenex Luna C18 250 × 4.6 mm × 5 μ m (film thickness), maintained at 40 °C. The optimum mobile phase for the chromatographic separation of pyraclostrobin, pinoxaden, cloquintocet-mexyl, and mandipropamid was acetonitrile: water (25:75 *v/v*) with the addition of 1 mL acetic acid. The flow rate of the mobile phase was maintained at 1.2 mL min⁻¹. The chromatographic separation of difenoconazole and cyflufenamid was achieved with acetonitrile: water (60:40 *v/v*) and the flow rate of the mobile phase was set at 1 mL min⁻¹. The detection wavelength set at 275 nm for

pyraclostrobin, 244 nm for pinoxaden and cloquintocet-mexyl, 230 nm for mandipropamid and 210 nm for difenoconazole and cyflufenamid.

Clopyralid and florasulam were separated with intersil-phenyl chromatographic column 4.6 × 250 mm × 5 μ m (film thickness), maintained at 40 °C. The optimum mobile phase for their chromatographic separation was acetonitrile: water (60:40 v/v) with the addition of 0.1% phosphoric acid. The flow rate of the mobile phase was set at 1.2 mL min⁻¹, while the detection wavelength was set at 260 nm for florasulam and 285 nm for clopyralid.

Folpet and oxathiapiprolin were separated with a C_8 chromatographic column 4.6 × 150 mm × 3.5 µm (film thickness), retained at 40 °C. The mobiles phases, A and B, were 1.36 gr KH₂PO₄ which was dissolved in 1 L water, the pH of the solution was adjusted to 2.5 with phosphoric acid and acetonitrile, respectively. The flow rate was 1 mL min⁻¹ and the column gradient consisted of 60% eluent A and 40% eluent B where it remained for 10 min. Next, at 10.01 min it was changed to 40%, where it remained for 25 min. At 25.01 the gradient was returned to the initial conditions (60% vol. A), where it maintained up to the end of the analysis at 30 min. Quantification was performed at 260 nm.

2.3.3. Gas Chromatography

GC/FID: GC analysis was performed for all the GC-amenable analytes: quizalofop-P-ethyl, 2.4 D-2-ethylhexyl ester, fluopyram and trifloxystrobin. The chromatographic separation for all five compounds was achieved with a DB-1 chromatographic column, 30 m \times 0.53 mm \times 1.5 µm film thickness. Injector and detector temperatures were set at 250 °C and 300 °C, respectively. For the determination of quizalofop -P-ethyl and 2.4 D-2-ethylhexyl ester the oven temperature program was programmed as follows: initial temperature was set at 230 °C for 1min, raised to 280 °C (5 °C min⁻¹) for 10 min. For the determination of fluopyram and trifloxystrobin the oven temperature program was programmed as follows: initial temperature was set at 200 °C (10 °C min⁻¹) for 5 min.

2.4. LCA Methodology

Life Cycle Assessment (LCA) is an internationally standardized analysis technique. It quantifies environmental, health impacts and resource depletion issues that are associated with products or services [38]. It takes into account impacts through a product's life cycle: from the extraction of resources, through production, use, and recycling, up to the disposal of waste. Life Cycle Assessment is eventually a decision support tool (DST). It has been widely used in various fields. It addresses the environmental impacts throughout a product's life cycle. According to ISO 14040/14044, the four phases of an LCA study are: (1) goal and scope definition; (2) inventory analysis; (3) impact assessment; and (4) interpretation and discussion of results.

The goal and scope definition phase determine the objective and purpose of the LCA study and the corresponding system boundaries. The inventory analysis phase includes the collection of the input/output data that are necessary for our study. The impact assessment phase converts inventory data into indicator scores by using a life cycle impact assessment method. The interpretation summarizes and discusses the results of the impact assessment phase and sets the basis for conclusions, recommendations and decision-making [39].

2.4.1. Goal and Scope Definition and Functional Unit

The goal of this work was to assess the environmental impacts (or burdens) of seven alternative technologies (or methods) to manage the WPPC via LCA. The functional unit of the study was 1 tonne (1 Mg) of generated WPPC. Figure 1 presents the system boundaries of the study that starts with the collection of WPPC and includes waste transportation, waste treatment (recycling, incineration) and final disposal (landfilling) of those waste. Raw materials and energy are referring to the management of the WPPC only, and do not include materials and energy associated with the production of the pesticides and of the

containers. For example, the raw materials in this system would include the fuel used to transport the WPPC to the treatment/disposal facility or materials used to operate the WPPC treatment/disposal facilities. In a similar manner, the input energy refers to the energy needed to operate the facilities that are treating the WPPC, the transport, etc. In all management scenarios, WPPC are considered to have been first triple rinsed prior to entering the treatment/disposal facilities.

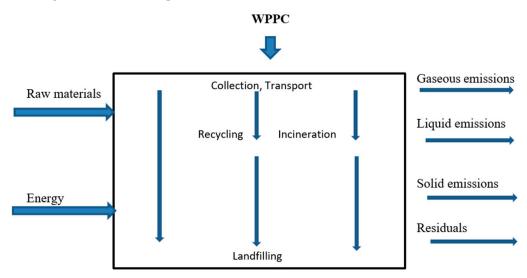


Figure 1. System boundaries to treat 1 tonne (functional unit) of WPPC.

In this study, the following waste treatment technologies are modeled so that to calculate and rank their net environmental impacts. In all cases, the generation node of the WPPC is the city of Drama, which was the location from which the sampling of the containers took place. All waste treatment and disposal facilities (landfill, incinerator, recycling facility) are located at the same site at a 160 km distance from the city of Drama. In all scenarios (except in landfilling and incineration), WPPC are collected as a separate stream and then transported with dedicated vehicles to the treatment/disposal facilities mentioned in Table 2.

Table 2. Alternative scenarios to manage WPPC via LCA (% on a per wet weight basis of WPPC generated).

Scenario	L	R	Ι	Comments
1	100%	0%	0%	WPPC are disposed of to an MSW sanitary landfill site along with commingled MSW. The stream entering the MSW landfill has the composition described in Table 3. It is noted that this scenario partially represents the current WPPC management scenario in Greece.
2	0%	100%	0%	WPPC, as a separate stream, are transported to a recycling plant that refines and processes WPPC to convert them to HDPE pellets.
3	0%	0%	100%	Wasted Plastic Pesticide Containers are transported to a mass-burn MSW incinerator facility, where they are incinerated along with commingled municipal solid waste.
4	50%	0%	50%	Half of the WPPC are transported to a landfill site and the other half to an MSW incineration plant.
5	0%	50%	50%	Half of the WPPC are transported to a recycling plant and the other half to the MSW incineration plant.
6	50%	50%	0%	Half of the WPPC are transported to a landfill site and the other half to the recycling plant.
7	33.3%	33.3%	33.3%	A shared treatment in all three facilities.

L: Landfilling, R: Recycling, I: Incineration.

2.4.2. Description of the Scenarios

In order to analyze the effects of the use of different WPPC management technologies, seven scenarios were assessed. The alternative scenarios under study are shown in Table 2.

Solid Waste Components	% w/w
Biowaste	45.2
Paper	24.2
Plastics	15
Wood	5.0
Glass	4.1
Ferrous metals	2.6
Textile	2.5
Non-Ferrous metals	1.1
WPPC ¹	0.29

Table 3. MSW composition for commingled MSW entering the landfill and the mass-burn MSW incinerator (as input in SimaPro[®] under the assembly function).

¹ WPPC were calculated as a fraction of the MSW generated by the municipality of Doxato in northern Greece based on a WPPC generation rate of 5.4 kg farmer⁻¹ y⁻¹ [40] and the official Greek MSW composition and generation rates described in the Solid Waste National Plan of 2020. This fraction refers only to WPPC; therefore, a large fraction of wasted HDPE based plastics is included in the plastics category.

2.4.3. Life Cycle Inventory

The life cycle inventory (LCI) is the critical part in any life cycle study. Original data were gathered from the literature [35] and the EcoInvent 3.0 database as it was not feasible to acquire original data from pesticide manufacturing companies. The environmental impacts were calculated according to the ReCiPe v.1.12 assessment method.

Road transportation contributes to the environmental impacts as part of the collection and transport of WPPC to the treatment facilities and the landfill. In this study, it is assumed that the recycling plant, the incinerator and the landfill are located at the same region and there will not exist any considerable differences in transport emissions and the LCA results. The unit process for the transport is selected from the Ecoinvent 3-consequential-Unit project in SimaPro[®] 'Transport, freight, lorry 16–32 metric ton, EURO5".

The MSW landfill selected here represents a typical municipal waste landfill, for commingled MSW, with surface and basic sealing, that abides to the European limits for waste landfill emissions. It includes biogas treatment, leachate treatment, sludge treatment and deposition. Average landfill depth and area were 30 m and 40,000 m², respectively.

The selected recycling plant converts the HDPE derived WPPC to HDPE pellets after refining and cleaning, and was selected from the Ecoinvent3-consequential unit project.

The incineration plant represents an average European mass-burn Waste-to-Energy plant (WtE) for the thermal treatment of commingled municipal solid waste (MSW). It includes wet and dry flue gas treatment and NO_x removal technologies.

2.4.4. Life Cycle Impact Assessment

The assessment method chosen was the ReCiPe Endpoint (H) 1.12 version Europe Recipe H/H which normalizes impacts to scores per average European citizen. That is, all scores are divided by a reference situation score, to produce a non-metric unit (Pt) to evaluate the impact of a process or a product. The score is represented on a point scale (Pt), where a point (Pt) is the annual environmental load (i.e., whole production/consumption undertakings in the economy) of an average European citizen. The method includes 17 impact categories: climate change human health, climate change ecosystems, ozone depletion, terrestrial acidification, freshwater eutrophication, human toxicity, photochemical oxidant formation, particulate matter formation, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, ionizing radiation, agricultural land occupation, urban land occupation, natural land transformation, metal depletion and fossil depletion. The above are mid-point indicators too, that are reported in addition to the three end-point indicators (damage to human health, damage to ecosystems, damage to resource availability) normally reported by the aforementioned ReCiPe method. A major limitation of the study is related to the fact that EcoInvent uses average European data to assess impacts that may differ from local (Greek) data or any other specific country/region, for that matter. The electricity mix used

in this work to calculate electricity consumption and credit calculation was based on an average value from EU-27 (for 2002), as included in SimaPro[®], for a typical incinerator facility, namely: 32% nuclear, 19% hard coal, 17% natural gas, 11% lignite, 10% hydro, 6% fuel oil and 5% other. The mix for the heat export from the incinerator was based on an EU 27 District Heating Mix 2002, namely: 40% Natural gas, 34% hard coal, 10% Biomass, 7% lignite, 6% fuel oil and 3% peat. In the case of landfilling, SimaPro[®] considers that an average MSW landfill recovers biogas as follows: 17% flaring, 21% energy recovery with the remaining 62% being fugitive emissions. For the landfill that accepts solely plastic waste (that was examined under a sensitivity analysis), the distribution of landfill biogas is: 22% flaring, 28% energy recovery and the remaining 50% is fugitive emissions

2.4.5. Interpretation and Sensitivity Analysis

The interpretation comprises of the evaluation of results. A sensitivity analysis is necessary to check the reliability of the results by making variations in assumptions, methods and inputs data. In this section a sensitivity analysis was performed by using alternative impact assessment methods to observe variations on results. ReCiPe Endpoint (H) 1.12 version Europe Recipe H/H was the main one used throughout the project; however, for sensitivity analysis, three others alternative methods were used, namely: (i) IMPACT 2002+ v. 2.12, (ii) Ecological Scarcity 2013 v.1.03 and (iii) ILCD 2011 Midpoint+ v1.08. As part of the sensitivity analysis, the transportation distance in scenario 2 was changed from 160 km to 650 km, which is the driving distance between the city of Drama and Athens (capital of Greece). This change aimed to observe the effect of transportation on the LCA results.

2.4.6. Composition of MSW Used in All Scenarios

One of the key aspects when making an LCA for any type of waste, is to define the composition of the waste mixture in which the component that is investigated belongs to. In this research, we considered approaches with regard to the composition of the stream entering the landfill, the incinerator and the recycling facility.

- (i) WPPC are part of the commingled MSW stream with the composition included in Table 3 (which is typical for Greece considering no separate collection of biowaste). WPPC were represented by the "HDPE" component when defining the MSW composition in SimaPro[®]. The WPPC percentage in the commingled MSW stream (0.29% w/w) was calculated using WPPC and MSW generation data from the prefecture of Drama in Greece [37]. In this approach, the landfill type used in SimaPro[®] was an average MSW European (EU-27) landfill with biogas utilization and leachate treatment. In a similar manner, the incinerator used is a typical EU-27 MSW incineration facility that accepts commingled MSW with the composition included in Table 3.
- (ii) WPPC are treated as an individual stream with a composition of 100% HDPE (including the residual pesticides). In this case, the landfill type (monofill) used in SimaPro[®] was the "Landfill of plastic waste EU27" whilst the incinerator type used was the "Waste incinerator of plastics (PE, PP, PS, PB), EU-27S". In the case of recycling specifically, WPPC are considered to always enter the recycling facility as a single stream after separate collection. The recycling facility designated in SimaPro[®] was the "Recycling of HDPE" type.

3. Results and Discussion

3.1. Quantification of Active Substances in WPPC

The residual active substance contained in all WPPC analyzed in this work are presented in Table 4. Results are expressed on a per unit mass basis (mg of substance per kg of the net mass of WPPC without the residual liquid). In addition, the total mass of the residual active substance that was measured in each WPPC is presented.

Active Substance	Mass of Tripled Rinsed (as Received) WPPC (g)	Content of Active Substance ¹ (mg/kg of as Received WPCC).	Mass of Active Substance Contained in the WPPC (mg)	Remaining Ingredients as a Percentage of the Weight of as Received WPCC (% w/w)
Pyraclostrobin	112 ± 1.87	2.47 ± 1.55	0.272 ± 0.172	0.000247 ± 0.000155
Pinoxaden	98.8 ± 0.211	0.966 ± 0.737	0.0963 ± 0.0738	0.0000966 ± 0.0000737
Cloquinticet-mexyl	98.8 ± 0.211	1.00 ± 0.556	0.0993 ± 0.0562	0.000100 ± 0.0000556
Clopyralid	40.8 ± 0.395	206 ± 95.2	8.42 ± 3.96	0.0206 ± 0.00952
Florasulam	40.8 ± 0.395	1.62 ± 0.567	0.0665 ± 0.0230	0.000162 ± 0.0000567
Quizalofop-P-ethyl	207 ± 0.321	7.67 ± 4.46	1.62 ± 0.935	0.000767 ± 0.000446
2.4 D EHE	98.1 ± 0.378	321 ± 144	31.3 ± 14.0	0.0321 ± 0.015
Folpet	103 ± 0.435	771 ± 854	76.7 ± 85.5	0.0771 ± 0.0862
Oxathiapiprolin	103 ± 0.435	34.1 ± 30.0	3.38 ± 2.96	0.00341 ± 0.00577
Mandipropamid	107 ± 0.850	2970 ± 305	327 ± 30.6	0.297 ± 0.0306
Fluopyram	69.4 ± 0.404	3810 ± 3090	263 ± 215	0.381 ± 0.310
Trifloxystrobin	69.4 ± 0.404	3380 ± 2790	230 ± 189	0.338 ± 0.276
Difenoconazole	60.8 ± 0.808	12.9 ± 17.3	0.790 ± 1.05	0.00129 ± 0.00173
Cyflufenamid	60.8 ± 0.808	6.20 ± 8.49	0.379 ± 0.519	0.00062 ± 0.000849

Table 4. Residual active substances and hazard potential of the sampled WPPC.

¹ Analyses were performed at the Benakion Phytopathological Institute (BPI), Means \pm Standard Deviations are based on *n* = 3; all values are expressed with a precision of 3 significant digits.

The most contaminated containers were found to be those with Mandipropamid (hazard statement codes: H400 and H410), Fluopyram (H411) and Trifloxystrobin (H317, H400 and H410). For those specific three substances, the hazard threshold limits are 25%, 25% and 10% w/w, respectively [41,42], which are concentrations much higher than the concentrations measured here. The next four less contaminated containers were the ones with Chlopyralid (not classified with regard to its hazard), 2.4 D EHE (H302, H317, H400, H410), Folpet (H317, H319, H332, H351, H400) and Oxathiapiprolin (H400, H410). The three latter compounds had hazard threshold limits equal to 10%, 1% and 25%, respectively. The seven remaining compounds (Pyraclostrobin, Pinoxaden, Cloquinticet-mexyl, Florasulam, Quizalofop-P-ethyl, Difenoconazole, Cyflufenamid) were at very low concentrations (<0.001% w/w), far below any threshold limits. Therefore, none of the WPPCs analyzed here are hazardous wastes, as all concentrations of the residual active substances were below hazard threshold limits. This finding agrees with the ones of Briassoulis et al. [32], who also found that the residual amounts of the pesticides in the WPPCs were below hazard threshold limits. The findings also indicate that triple rinsing is effective to render the WPPC as non-hazardous wastes.

Both the masses of WPPC and the masses of active residual substance were input into the LCA software SimaPro[®] to make the LCA.

3.2. Life Cycle Analysis of WPPC Alternative Management Methods

The impact assessment method used by the LCA software was the ReCiPe v.1.12. Europe ReCiPe H/H method refers to the normalization values of Europe with the weighting set that belongs to the hierarchist perspective. The results of the analysis are presented through diagrams and tables, in which the positive values indicate environmental burdens and the negative values indicate environmental benefits.

3.2.1. Scenario 1: 100% Landfilling (along with Commingled Municipal Solid Waste)

Figure 2 illustrates the scores for each impact category for the 100% landfilling scenario. On the environmental burden side, fossil depletion causes the largest impact, equal to 1.69 Pt. Fossil depletion is associated with the operation of the landfilling equipment that typically combust diesel fuel. Climate change human health, climate change ecosystems and particulate matter formation contribute to environmental burden with 0.641 Pt, 0.541 Pt and 0.265 Pt, respectively. The climate change related impacts are traditionally associated

with both the operation of landfilling equipment, that generate fossil CO_2 , as well as to the methane fugitive emissions that can escape the landfill biogas recovery system (the default value of which is 60% for a typical MSW landfill in SimaPro[®]). The other less important impact categories are human toxicity (0.141 Pt), agricultural land occupation (0.113 Pt), metal depletion (0.104 Pt), urban land occupation (0.0671 Pt) and ionizing radiation (0.000312 Pt). The final score of this analysis was 3.61 Pt, which being a positive value indicates a net environmental burden.

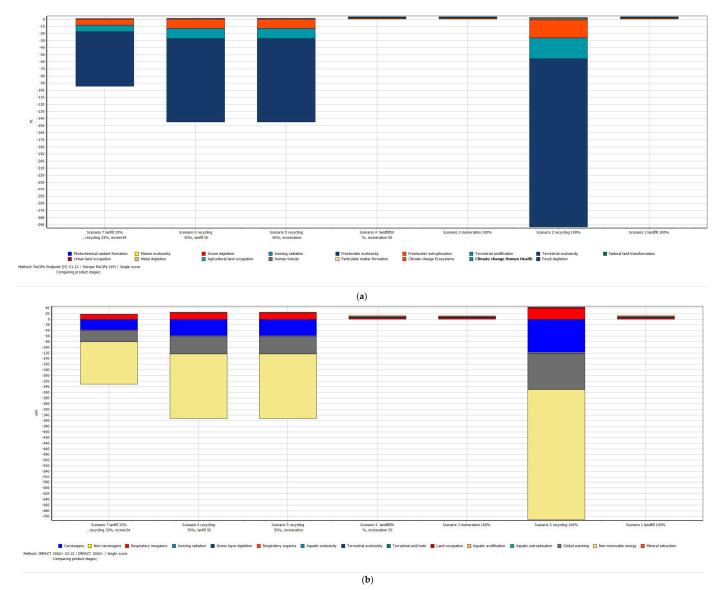


Figure 2. Comparison of the seven alternative management methods for WPPC: (**a**) using ReCiPe Endpoint (H) v.1.12; (**b**) using IMPACT 2002+ v.2.12 method.

3.2.2. Scenario 2: 100% Recycling (as a Single Stream after Separate Collection)

Figure 2 depicts the impacts per category for the 100% recycling scenario. As shown, recycling results in an environmental benefit with a score of -292 Pt, which are distributed per major impact as follows: fossil depletion (-237 Pt), climate change human health (-29.8 Pt) and climate change ecosystems (-25.2 Pt). The fossil depletion contributes the most in the benefit from this scenario, since recycling of HDPE can substitute the corresponding virgin material (oil) to make new containers. It is mainly the benefit in fossil depletion that makes recycling overall attractive. On the other hand, the main negative impacts/environmental burdens (2.47 Pt) associated with recycling are human toxicity

12 of 18

(1.87 Pt), metal depletion (0.38 Pt) and agricultural land occupation (0.22 Pt). As a result of the above, the final net score of the recycling scenario is -290 Pt, which indicates that recycling has the lowest environmental footprint among all scenarios examined here.

3.2.3. Scenario 3: 100% Incineration (along with Commingled MSW)

The final net score for the 100% incineration scenario is 3.42 Pt and its distribution can be seen in Figure 2. The positive value of Pt for this scenario indicates a net environmental burden when incineration WPPC, as part of the commingled MSW. Fossil depletion causes the largest impact, being equal to 1.63 Pt. Fossil depletion is associated with the operation of the MSW incinerator that typically consumes crude oil and hard coal. Climate change Human health, climate change ecosystems and particulate matter formation contribute to the overall environmental burden with 0.581 Pt, 0.49 Pt and 0.255 Pt, respectively. The climate change related impacts are associated with both the operation of the MSW incineration facility, that generate fossil CO_2 . The other less important impact categories are human toxicity (0.141 Pt), agricultural land occupation (0.113 Pt), metal depletion (0.0867 Pt), urban land occupation (0.0671 Pt) and natural land transformation (0.0406 Pt).

3.2.4. Scenario 4: 50% Landfilling and 50% Incineration

In this scenario, fossil depletion causes the largest impact, being equal to 1.66 Pt. Fossil depletion is associated with the operation of the landfilling equipment and MSW incinerator that typically consumes crude oil and hard coal. Climate change human health, climate change ecosystems and particulate matter formation contribute to environmental burden with 0.611 Pt, 0.516 Pt and 0.26 Pt, respectively. The final score of this analysis was 3.52 Pt, which being a positive value indicates a net environmental burden.

3.2.5. Scenario 5: 50% Recycling and 50% Incineration

In this scenario, the major environmental benefit resulted from fossil depletion (-118 Pt) followed by climate change (human health) (-14.6 Pt) and climate change ecosystems (-12.3 Pt). Negative impacts are 1.01 Pt and are attributed to human toxicity. The high environmental benefit (-118 Pt) associated with fossil depletion is attributed the recycling of HDPE, for the reasons stated in Section 3.2.2.

3.2.6. Scenario 6: 50% Recycling and 50% Landfilling

The final score of -143 Pt for recycling 50%–landfilling 50% scenario is distributed according to Figure 2. The highest benefits were associated with fossil depletion (-118 Pt) followed by climate change human health (-14.6 Pt) and climate change ecosystems (-12.3 Pt). Negative impacts due to human toxicity and metal depletion result in 1.01 and 0.242 Pt, respectively.

3.2.7. Scenario 7: 33.3% Landfilling, 33.3% Recycling, 33.3% Incineration

On the environmental burden side, human toxicity causes the largest impact, which results in 0.712 Pt. Agricultural land occupation and urban land occupation contribute to environmental burden by 0.148 and 0.109 Pt, respectively. Fossil depletion results in the highest environmental benefit namely -77.1 Pt. Climate change human health and climate change ecosystems contribute to environmental benefits by -9.43 and -7.96 Pt, respectively.

3.3. Comparison of Alternative Management Methods of WPPC

The comparison of all scenarios per impact category is presented in Table 5. The largest negative impact from scenario 1 is due to fossil depletion that is associated with the operation of the diesel based landfilling equipment and the methane fugitive emissions. During recycling (scenario 2), metal depletion is the main environmental negative impact (i.e., positive Pt) and is associated with the use of iron and manganese needed during the construction of the recycling facility. Scenario 2 leads to the most negative Pt values for

the fossil depletion impact, explained by the fact that recycling of the HDPE of WPPC substitutes the same amount of the corresponding virgin material (oil).

Impact Category	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6	Scenario 7
Fossil depletion	USD	1.74	-244	1.68	1.71	-121	-121	-79.3
Climate change Human Health	DALY ¹	4.32×10^{-5}	$-200 imes 10^{-5}$	3.91×10^{-5}	4.11×10^{-5}	-98.4×10^{-5}	-98.2×10^{-5}	$-63.5 imes10^{-5}$
Particulate matter formation	DALY	$1.79 imes 10^{-5}$	-4.66×10^{-5}	$1.72 imes 10^{-5}$	$1.75 imes 10^{-5}$	-1.47×10^{-5}	-1.43×10^{-5}	$-3.63 imes10^{-6}$
Climate change Ecosystems	species.yr ²	$2.45 imes 10^{-7}$	-1.14×10^{-5}	$2.21 imes 10^{-7}$	$2.33 imes10^{-7}$	-5.57×10^{-6}	-5.56×10^{-6}	$-3.60 imes10^{-6}$
Photochemical oxidant formation	DALY	$4.58 imes10^{-9}$	$-2.86 imes10^{-7}$	$4.46 imes 10^{-9}$	$4.52 imes 10^{-9}$	$-1.41 imes10^{-7}$	$-1.41 imes10^{-7}$	$-9.14 imes10^{-8}$
Terrestrial acidification Marine ecotoxicity Freshwater ecotoxicity Terrestrial ecotoxicity	species.yr species.yr species.yr species.yr	$\begin{array}{c} 5.91 \times 10^{-10} \\ 6.50 \times 10^{-11} \\ 2.31 \times 10^{-10} \\ 2.98 \times 10^{-9} \end{array}$	$\begin{array}{c} -2.11\times 10^{-8} \\ 7.69\times 10^{-10} \\ 3.72\times 10^{-9} \\ 3.24\times 10^{-9} \end{array}$	$\begin{array}{l} 5.54\times10^{-10}\\ 6.49\times10^{-11}\\ 2.30\times10^{-10}\\ 2.98\times10^{-9} \end{array}$	$\begin{array}{c} 5.73\times10^{-10}\\ 6.49\times10^{-11}\\ 2.30\times10^{-10}\\ 2.98\times10^{-9} \end{array}$	$\begin{array}{c} -1.03\times 10^{-8}\\ 4.17\times 10^{-10}\\ 1.98\times 10^{-9}\\ 3.11\times 10^{-9}\end{array}$	$\begin{array}{c} -1.03\times 10^{-8}\\ 4.17\times 10^{-10}\\ 1.98\times 10^{-9}\\ 3.11\times 10^{-9}\end{array}$	$\begin{array}{c} -6.59\times 10^{-9} \\ 2.97\times 10^{-10} \\ 1.38\times 10^{-9} \\ 3.07\times 10^{-9} \end{array}$
Freshwater eutrophication	species.yr	$3.98 imes 10^{-10}$	$1.21 imes 10^{-8}$	$3.13 imes 10^{-10}$	$3.56 imes10^{-10}$	$6.23 imes10^{-9}$	$6.28 imes 10^{-9}$	$4.25 imes10^{-9}$
Ozone depletion	DALY	$1.34 imes10^{-8}$	$4.28 imes 10^{-8}$	$1.32 imes 10^{-8}$	$1.33 imes 10^{-8}$	$2.80 imes10^{-8}$	$2.81 imes 10^{-8}$	$2.30 imes10^{-8}$
Natural land transformation	species.yr	$1.83 imes10^{-8}$	$8.04 imes10^{-8}$	$1.83 imes10^{-8}$	$1.83 imes10^{-8}$	$4.94 imes10^{-8}$	$4.94 imes10^{-8}$	$3.88 imes 10^{-8}$
Urban land occupation	species.yr	$3.03 imes10^{-8}$	$8.83 imes 10^{-8}$	$3.03 imes 10^{-8}$	$3.03 imes 10^{-8}$	$5.93 imes 10^{-8}$	$5.93 imes 10^{-8}$	$4.94 imes10^{-8}$
Agricultural land occupation	species.yr	$5.12 imes10^{-8}$	$9.93 imes10^{-8}$	$5.12 imes 10^{-8}$	$5.12 imes 10^{-8}$	$7.52 imes 10^{-8}$	$7.52 imes 10^{-8}$	$6.71 imes10^{-8}$
Ionizing radiation Human toxicity Metal depletion	DALY DALY USD ³	$\begin{array}{c} 2.10\times 10^{-8} \\ 9.49\times 10^{-6} \\ 0.106 \end{array}$	$\begin{array}{c} 1.27\times 10^{-8} \\ 126\times 10^{-6} \\ 0.391 \end{array}$	$\begin{array}{c} 1.86\times 10^{-8} \\ 9.49\times 10^{-6} \\ 0.0892 \end{array}$	$\begin{array}{c} 1.98\times 10^{-8} \\ 9.49\times 10^{-6} \\ 0.0978 \end{array}$	$\begin{array}{c} 6.46 imes 10^{-7} \\ 6.78 imes 10^{-5} \\ 0.240 \end{array}$	$\begin{array}{c} 6.48\times 10^{-7} \\ 6.78\times 10^{-5} \\ 0.248 \end{array}$	$\begin{array}{l} 4.34\times 10^{-7} \\ 4.79\times 10^{-5} \\ 0.194 \end{array}$

Table 5. Life cycle characterization results per impact category per scenario.

¹ DALY: Disability Adjusted Life Years, which an index used by the World Bank and WHO to express the damage to human health that leads to years lost (death) and years of disability. ² species.yr: the loss of species over a certain area during a year. ³ USD: the extra costs involved for future metal and fossil extraction; all values expressed with a precision of 3 significant digits.

Figure 2 also compares the seven alternative WPPC management technologies when applying the ReCiPe v1.12 method. Scenario 2 (100% recycling) has the lowest environmental footprint, followed by scenario 5 (50% recycling-50% incineration) and scenario 6 (50% recycling–50% landfilling). Scenario 1 (landfilling) has the highest negative environmental impacts (i.e., highest positive Pt) and is the worst scenario. Negative Pt values (i.e., environmental benefits) associated with fossil depletion in scenarios 2, 5, 6 and 7 were due to the savings of energy as a result of the substitution of crude oil and natural gas by the recycled HDPE and biomass is partly incinerated in the incineration facility. In particular, in the scenarios that involve recycling, the savings are attributed to the fact that a secondary waste (HDPE) is used instead of oil to generate new HDPE. The positive Pt value of fossil depletion in scenarios 1, 3 and 4 is due to the consumption of fossil fuels such as crude oil and hard coal needed during the operation of the incinerator and the landfill. Fossil carbon dioxide (generated by diesel equipment) and biogenic methane emissions have an important impact on climate change ecosystems and climate change human health (scenario 1). The latter is due to the fugitive emissions that range from 50% to 62%, according to the default values included in SimaPro® for sanitary landfills. Scenario 2 (100% recycling) presents human toxicity as the main negative impact, due to manganese and arsenic releases to groundwater. Human toxicity positive Pt values, in scenario 3, is caused by manganese and lead emissions. The environmental burden (positive Pt values) of the particulate matter formation impact category in scenario 3 (100% incineration) is caused due to PM, nitrogen oxide and sulfur dioxide emissions emitted by the MSW incinerator. The positive Pt values (environmental burdens) of the metal depletion impact category, in scenario 2, is a result of the consumption of iron, manganese and nickel needed to construct the recycling facilities. The same explanation applies to the natural land transformation impact due to the deforestation that can occur when constructing those facilities.

3.4. Sensitivity Analysis

A sensitivity analysis was performed, using different impact assessment methods, to control the robustness of our results. Figures 2 and 3 indicate the environmental impacts by using ReCiPe v.1.12, IMPACT 2002+ v. 2.12, Ecological Scarcity 2013 v.1.03 and ILCD 2011

Midpoint+ v1.08 method. It is important to note that no significant changes were observed in the results. Table 6 actually shows that all the alternative environmental impact methods resulted in the same ranking of the seven WPPC technologies as these were ranked with the initially chosen Recipe method.



(b)

Figure 3. Comparison of the seven alternative management methods for WPPC: (**a**) using Ecological Scarcity 2013 v.1.03 method; (**b**) using ILCD 2011 Midpoint+ v1.08 method.

Table 6. Ranking of the seven WPPC management scenarios according to four different impact assessment methods.

Impact Assessment Method	Ranking of the Seven Management Technologies According to their Pt Scores			cores			
	1st	2nd	3rd	4th	5th	6th	7th
ReCiPe v.1.12	2 (-290)	5 (-143)	6 (-143)	7 (-93.3)	3 (3.42)	4 (3.52)	1 (3.61)
IMPACT 2002+ v.2.12.	2 (-668)	5 (-328)	6 (-328)	7 (-212)	3 (12.1)	4 (12.3)	1 (12.4)
Ecological Scarcity 2013 v.1.03	2 (-971)	5 (-468)	6(-468)	7 (-297)	3 (35)	4 (35.2)	1 (35.5)
ILCD 2011 Midpoint+ v1.08	2 (-88.2)	5 (-40.6)	6 (-40.5)	7 (-24.3)	3 (7.06)	4 (7.17)	1 (7.27)

Number indicates the scenario and the value in the parenthesis that follows includes the Pt score of the corresponding scenario; 1st is the scenario with the lowest environmental footprint (best scenario) and 7th is the most impactful scenario (worst scenario). As scenario 2 (recycling) has the largest benefits in all impact assessment methods, another sensitivity analysis was performed by increasing the transportation distance in that scenario. The goal of this change was to calculate the effect of the transportation distance on the impacts. The results of that additional sensitivity analysis are included in Figure 4. Figure 4 indicates that as the transport distance increases from 160 km to 650 km (i.e., a 300% increase), the climate change and the fossil depletion impact increase by around 4% and 2%, respectively, due to the additional emissions of carbon dioxide, dinitrogen monoxide, as a result of the increased diesel consumption.

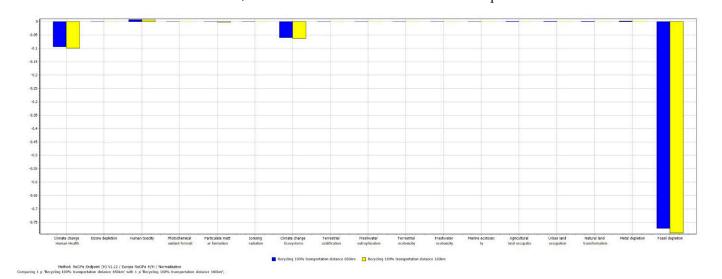


Figure 4. Results of sensitivity analysis with different transportation distances (160 and 650 km).

An additional sensitivity analysis run was performed by excluding the residual amounts of chemicals measured in this work from the wasted containers during the assembly phase in SimaPro[®]. That is, the active pesticide substances mentioned in Table 4 were set equal to zero. The goal was to check the magnitude of the effect of those residual pesticide amount (measured after triple rinsing of the WPPC) on the LCA results. The new LCA results were exactly similar to the ones when the pesticide amounts had been included. This indicates that the residual pesticide amounts are practically zero and have no effect on the environmental impacts calculated by SimaPro[®] for all seven scenarios.

An additional analysis was performed by changing the "MSW landfill" and "MSW incineration" within SimaPro[®] to "landfill for plastics" and to "incinerator for plastics", respectively. The idea of this change was to investigate the case in which the WPPC containers are directed, as a single stream (100% HDPE) that is separately collected to the above final nodes that aim to treat solely plastics (and not as part of commingled MSW). In this case, the ranking of the seven scenarios was found to be the same as the one shown in Table 6. However, there were differences in the Pt values calculated. Specifically, those changes are included in Table 7.

Table 7. Comparison of total Pt per scenario according to the composition of the treated waste stream.

Scenario (Ranked from Best to Worst)	Total Pt When WPPC Are Treated as Part of Commingled MSW in MSW Landfill and MSW Incinerator	Total Pt When WPPC Are Treated as Single Stream in Landfill for Plastics and Incinerator for Plastics
2	-290	-290
5	-143	-178
6	-143	-139
7	-93.3	-114
3	3.42	-65.3
4	3.52	-26.9
1	3.61	11.6

The results of Table 7 indicate that when WPPC are separately collected and treated as a single stream, the environmental impacts are reduced (lower Pt) in all scenarios that involve incineration (scenarios 3, 4, 5, 7) compared to when WPPC are treated along with commingled waste. The largest Pt score change is observed in scenario 3 (incineration) in which the operation of the "incinerator for plastics" results to less environmental impacts (–65.3 Pt) compared to the commingled MSW incinerator (3.42 Pt) that has even positive Pt. This is likely explained by the fact that an incinerator for plastics has stricter air monitoring specifications than the commingled MSW incinerator. No changes are observed in scenario 2 (recycling), since WPPC were considered to be treated as a separate stream in that scenario during the basic analysis.

4. Conclusions

The study was conducted to determine the environmentally optimal WPPC management method through the application of life cycle assessment (LCA). WPPC were considered to be part of the commingled MSW stream when landfilled or incinerated. On the other hand, they were considered to treated as a single stream during the recycling scenario with a prerequisite of a separate collection scheme. Based on the results of the study, the ranking of the scenarios with regard to their environmental footprint (from best to worst using the total Pt scores) are as follows:

- Scenario 2, in which WPPC are 100% recycled via separate collection, is the most environmentally friendly technology to treat WPPC (LCA score achieved: -290 Pt).
- Scenarios 5 (50% recycling and 50% incineration) and scenario 6 (50% recycling and 50% landfilling) are the next best technologies (LCA score –143 Pt for both).
- The scenario that consists of 33.3% landfilling, 33.3% recycling and 33.3% incineration (LCA score -93.3 Pt) is ranked fourth. The scenarios that comprise 100% incineration (LCA score 3.42 Pt) and the scenario with 50% landfilling and 50% incineration (LCA score: 3.52 Pt) follow in descending order.
- The highest environmental burdens (i.e., least desirable scenario) occur in the base scenario that includes 100% landfilling (LCA score 3.61 Pt). Therefore, sanitary landfilling of WPPC should be significantly reduced and, at the same time, recycling and incineration should be included in the management of WPPC, with priority to the former.
- The triple rinsing of the WPPCs that were analyzed here rendered them as nonhazardous wastes, as the concentrations of all active substances were far below their hazard threshold limits. In addition, according to the LCA, the calculated environmental impacts of all seven management methods were not affected by those low pesticide residual concentrations measured in the WPPCs.

The presented methodology used European data, so despite its application to Greece, the ranking of the seven scenarios may apply to other European countries too. A limitation of this study is that a financial analysis was not performed. Therefore, a Life Cycle Costing (LCC) should be additionally conducted to determine the financial ranking of the above seven management scenarios. Future research can target on other PPP derived wastes, such as the wasted greenhouse plastic films that may also contain pesticide residues. Additionally, additional research can evaluate the levels of the pesticide residues after single, double or multiple rinsing to compare it with the typical triple rinsing.

Stakeholders and policy makers can take into account the results of this study to design a sustainable WPPC management system.

Author Contributions: Conceptualization, G.G. and D.K.; methodology, G.G., H.K. and D.K.; investigation, G.G., H.K. and D.K.; data curation, H.K. and G.G.; writing—original draft preparation, G.G. and D.K.; writing—review and editing, G.G. and D.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors wish to acknowledge Fotis Cheimonakis and Dimitrios Mpreskas (farmers) for their assistance during the sampling of WPPC.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Widawsky, D.; Rozelle, S.; Jin, S.; Huang, J. Pesticide productivity, host-plant resistance and productivity in China. *Agric. Econ.* **1998**, *19*, 203–217.
- Pan, Y.; Ren, Y.; Luning, P.A. Factors influencing Chinese farmers' proper pesticide application in agricultural products—A review. *Food Control* 2021, 122, 107788. [CrossRef]
- 3. Abhilash, P.C.; Singh, N. Pesticide use and application: An Indian scenario. J. Hazard. Mater. 2009, 165, 1–12. [CrossRef] [PubMed]
- Van den Berg, H.; Gu, B.; Grenier, B.; Kohlschmid, E.; Al-Eryani, S.; Sergio da Silva Bezerra, H.; Nagpal, B.N.; Chanda, E.; Gasimov, E.; Velayudhan, R.; et al. Pesticide lifecycle management in agriculture and public health: Where are the gaps? *Sci. Total Environ.* 2020, 742, 1–10. [CrossRef] [PubMed]
- 5. In the U.S. and the World, Pesticide Use Is Up. Available online: https://www.panna.org/blog/us-and-world-pesticide-use (accessed on 2 July 2022).
- Riemens, M.; Allema, B.; Bremmer, J.; Apeldoorn, D.V.; Bai, Y.; Kempenaar, C.; Reinders, M.; Wenneker, M. The Future of Crop Protection in Europe, 1st ed.; Scientific Foresight Unit (STOA): Brussels, Belgium, 2021; pp. 9–104.
- Parween, T.; Jan, S.; Mahmooduzzafar, N.; Fatma, T.; Siddiqui, Z.H. Selective effect of pesticides on plant—A review. *Food Sci. Nutr.* 2016, 56, 160–179. [CrossRef]
- 8. Pimentel, D. Amounts of pesticides reaching target pests: Environmental impacts and ethics. *J. Agric. Environ. Ethics.* **1995**, *8*, 17–29. [CrossRef]
- 9. Hamza, R.A.; Iorhemen, O.T.; Tay, J.H. Occurrence, impacts and removal of emerging substances of concern from wastewater. *Environ. Technol. Innov.* **2016**, *5*, 161–175. [CrossRef]
- Zhang, M.; Zeiss, M.R.; Geng, S. Agricultural pesticide use and food safety: California's model. J. Integr. Agric. 2015, 14, 2340–2357. [CrossRef]
- 11. Rola, A.C.; Pingali, P.L. *Pesticides, Rice Productivity, and Farmers' Health: An Economic Assessment,* 1st ed.; International Rice Research Institute: Manila, Philippines, 1993; pp. 55–60.
- 12. Snelder, D.; Masipiquena, M.; De Snoo, G. Risk assessment of pesticide usage by smallholder farmers in the Cagayan Valley (Philippines). *Crop Prot.* 2008, 27, 747–762. [CrossRef]
- Tabashnik, B.E.; Gassmann, A.J.; Crowder, D.W.; Carriere, Y. Insect resistance to Bt crops: Evidence versus theory. *Nat. Biotechnol.* 2008, 26, 199–202. [CrossRef]
- 14. Carvalho, F.P. Agriculture, pesticides, food security and food safety. Environ. Sci. Policy 2006, 9, 685–692. [CrossRef]
- 15. Silva, V.; Mol, H.G.J.; Zomer, P.; Tienstra, M.; Ritsema, C.J.; Geissen, V. Pesticide residues in European agricultural soils—A hidden reality unfolded. *Sci. Total Environ.* **2018**, *653*, 1532–1545. [CrossRef] [PubMed]
- 16. Rani, L.; Thapa, K.; Kanojia, N.; Sharma, N.; Singh, S.; Grewal, A.S.; Srivastav, A.L.; Kaushal, J. An extensive review on the consequences of chemical pesticides on human health and environment. *J. Clean. Prod.* **2021**, *283*, 1–33. [CrossRef]
- 17. Kesavachandran, C.N.; Fareed, M.; Pathak, M.K.; Bihari, V.; Mathur, N.; Srivastava, A.K. Adverse Health Effects of Pesticides in Agrarian Populations of Developing Countries. *Rev. Environ. Contam. Toxicol.* **2009**, 200, 33–52. [PubMed]
- 18. Oddone, E.; Modonesi, C.; Gatta, G. Occupational exposures and colorectal cancers: A quantitative overview of epidemiological evidence. *World J. Gastroenterol.* **2014**, *20*, 12431–12444. [CrossRef]
- 19. Lohaa, K.M.; Lamoreea, M.; Weissb, J.M.; De Boera, J. Import, disposal, and health impacts of pesticides in the East Africa Rift (EAR) zone: A review on management and policy analysis. *Crop Prot.* **2018**, *112*, 322–331. [CrossRef]
- Salem, A.B.; Chaabaneb, H.; Lahbibb, N.; Salghic, R.; Fattoucha, S. Management of phytosanitary effluent: Rinsing and decontamination of empty pesticide containers by bio-detergent. *Crop Prot.* 2019, 116, 142–155. [CrossRef]
- Dalvie, M.A.; London, L. Unwanted agricultural chemicals in Stellenbosch: Need for public health intervention. S. Afr. J. Sci. 2001, 97, 309–312.
- 22. Damalas, C.A.; Telidis, G.K.; Thanos, S.D. Assessing farmers' practices on disposal of pesticide waste after use. *J. Sci. Total Environ.* 2007, 390, 341–345. [CrossRef]
- 23. Silambarasan, S.; Abraham, J. Kinetic studies on enhancement of degradation of chlorpyrifos and its hydrolyzing metabolite TCP by a newly isolated Alcaligenes sp. JAS1. *J. Taiwan Inst. Chem. Eng.* **2013**, *44*, 438–445. [CrossRef]
- 24. Mehmood, Y.; Arshad, M.; Mahmood, N.; Kachele, H.; Kong, R. Occupational hazards, health costs, and pesticide handling practices among vegetable growers in Pakistan. *Environ. Res.* **2021**, 200, 111340. [CrossRef] [PubMed]
- 25. Yeboah, F.K.; Adingo, S.; Xue-Lu, L. Arable Land Pollution in Ghana: A Look at Agrochemical Plastic Waste Handling among Farmers. *Asian J. Environ. Ecol.* 2021, *16*, 42–48. [CrossRef]

- 26. Kumar, S.; Mukherjee, S.; Chakrabarti, T.; Devotta, S. Hazardous waste management system in India: An overview. *Environ. Sci. Technol.* **2008**, *38*, 43–71. [CrossRef]
- 27. Felsot, A.S. Options for cleanup and disposal of pesticide wastes generated on a small scale. *J. Environ. Sci. Health B* **1996**, 31, 365–381. [CrossRef]
- Karstensen, K.H.; Kinh, N.K.; Thang, L.B.; Viet, P.H.; Tuan, N.D.; Toi, D.T. Environmentally sound destruction of obsolete pesticides in developing countries using cement kilns. *Environ. Sci. Policy* 2006, *9*, 577–586. [CrossRef]
- 29. Haylamicheal, I.D.; Dalvie, M.A. Disposal of obsolete pesticides, the case of Ethiopia. Environ. Int. 2009, 35, 667–673. [CrossRef]
- 30. Shu, H.; Zhang, P.; Chang, C.C.; Wang, R.; Zhang, S. Agricultural Waste. Water Environ. Res. 2015, 87, 1256–1285. [CrossRef]
- 31. Damgaard, A.; Christensen, T.H. Implementation of Life Cycle Assessment Models in Solid Waste Management. Ph.D. Thesis, Technical University of Denmark, Copenhagen, Denmark, 2010.
- Briassoulis, D.; Hiskakis, M.; Karasali, H.; Briassoulis, C. Design of a European agrochemical plastic packaging waste management scheme—Pilot implementation in Greece. *Resour. Conserv. Recycl.* 2014, 87, 72–88. [CrossRef]
- Morrisseya, A.J.; Browne, J. Waste management models and their application to sustainable waste management. *Waste Manag.* 2004, 24, 297–308. [CrossRef]
- Finnveden, G.; Johansson, J.; Lind, P.; Moberg, A. Life cycle assessment of energy from solid waste—Part 1: General methodology and results. J. Clean. Prod. 2005, 13, 213–229. [CrossRef]
- 35. Koci, V.; Trecakova, T. Mixed municipal waste management in the Czech Republic from the point of view of the LCA method. *Int. J. Life Cycle Assess.* **2011**, *16*, 113–124. [CrossRef]
- Oliveira, M.C.; Magrini, A. Life Cycle Assessment of Lubricant Oil Plastic Containers in Brazil. Sustainability 2017, 9, 576. [CrossRef]
- 37. Brinco, J.; Ribeiro, A.B.; Cardoso, J.; Da Silva, M.G. Monitoring pesticides in post-consumer containers by GC/TOFMS and HPLC/DAD after the triple rinse method. *Int. J. Environ. Anal. Chem.* **2022**, 1–12. [CrossRef]
- European Commission—Joint Research Centre—Institute for Environment and Sustainability. International Reference Life Cycle Data System (ILCD) Handbook—General Guide for Life Cycle Assessment—Detailed Guidance, 1st ed.; Publications Office of the European Union: Luxembourg, 2010; pp. 275–276.
- Sun, S.; Ertz, M. Life cycle assessment and Monte Carlo simulation to evaluate the environmental impact of promoting LNG vehicles. *MethodsX* 2020, 7, 101046. [CrossRef] [PubMed]
- 40. Garbounis, G.; Komilis, D. A modeling methodology to predict the generation of wasted plastic pesticide containers: An application to Greece. *Waste Manag.* 2021, 131, 177–186. [CrossRef]
- 41. Northern Ireland Environment Agency. *Hazardous Waste: Interpretation of the Definition and Classification of Hazardous Waste,* 2nd ed.; Land and Resource Management Unit: Belfast, Ireland, 2008; pp. 20–26.
- 42. Environmental Protection Agency. *Waste Classification List of Waste & Determining if Waste is Hazardous or Non-Hazardous*, 1st ed.; Environmental Protection Agency: County Wexford, Ireland, 2019; pp. 40–43.