

Article

Potential for Production of Biochar-Based Fertilizers from Olive Mill Waste in Mediterranean Basin Countries: An Initial Assessment for Spain, Tunisia, and Greece

Evan A.N. Marks ^{1,*}, Vasiliki Kinigopoulou ², Hanene Akrout ³, Ahmed Amine Azzaz ^{4,5}, Charalampos Doulgeris ², Salah Jellali ⁶, Carlos Rad ⁷, Paula Sánchez Zulueta ⁷, Evangelos Tziritis ², Leila El-Bassi ³, Camélia Matei Ghimbeu ^{4,5} and Mejdi Jeguirim ^{4,5}

- ¹ BETA Technological Center, University of Vic–University of Central Catalonia, Carrer de la Laura 13, 08500 Vic, Catalonia, Spain
- ² Soil & Water Resources Institute, Hellenic Agricultural Organisation "DEMETER", 57400 Sindos, Central Macedonia, Greece; v.kinigopoulou@swri.gr (V.K.); ch.doulgeris@swri.gr (C.D.); e.tziritis@swri.gr (E.T.)
- ³ Laboratory of Wastewaters and Environment, Centre of Water Researches and Technologies (CERTE) Technopark of Borj Cedria PB 273, Soliman 8020, Tunisia; hanene.akrout@gmail.com (H.A.); l.elbassi@gmail.com (L.E.-B.)
- ⁴ Mulhouse Institute of Materials Sciences, Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France; amine.azzaz@uha.fr (A.A.A.); camelia.ghimbeu@uha.fr (C.M.G.); mejdi.jeguirim@uha.fr (M.J.)
- ⁵ Université de Strasbourg, F-67081 Strasbourg, France
- ⁶ PEIE Research Chair for the Development of Industrial Estates and Free Zones, Center for Environmental Studies and Research, Sultan Qaboos University, Al-Khoud, Muscat 123, Oman; s.jellali@squ.edu.om
- ⁷ Composting Research Group UBUCOMP, Universidad de Burgos, Faculty of Sciences, Pl. Misael Bañuelos s/n, 09001 Burgos, Spain; crad@ubu.es (C.R.); pszulueta@ubu.es (P.S.Z.)
- * Correspondence: evan.marks@uvic.cat

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Abstract: Olive mill wastes continue to be a management challenge due to the large volumes produced, particularly due to their toxicity and impacts on the environment. Thermal conversion through pyrolysis or hydrothermal carbonization techniques can detoxify wastes while conserving nutrient contents. In this work, we produced up-to-date data on olive mill waste flows in Spain, Tunisia, and Greece and characterized representative samples in the laboratory. Assays of thermal conversion of olive mill wastewaters and solid wastes were also performed to understand biochar yields and final properties, and the total quantities of nutrients contained were estimated. Of particular note were the quantities of potassium in Tunisian wastewaters, representing 0.6% of the total mass and an annual flow of approximately 5000 t, and in the Spanish solid wastes, an average of 1.7% of the total mass is potassium, representing an annual flow of approximately 23,000 t. Concerning phosphorus, Spanish solid wastes had the highest contents (0.1%), double that of other countries' wastes. Annually, olive mill wastes from the three countries are estimated to contain approximately 35×10^3 tons of potassium and 2.6×10^3 tons of phosphorus. With this resource converted to biochar, each year more than 700 km² of soils could be enriched in 0.2% carbon with biochar at an application rate of 7 t ha⁻¹.

Keywords: olive mill solid waste; olive mill wastewater; Mediterranean Basin; biochar; hydrochar; nutrients; carbon



1. Introduction

Mediterranean countries alone produce 97% of the world's olives [1]. In the EU, Spain, Italy, and Greece are three of the most important producers, while Tunisia is one of the largest producers in the Mediterranean Basin. Disposal and handling of large quantities of olive mill wastes (OMWs) remain a critical environmental protection issue, particularly in those countries which have not banned three-phase extraction systems (such as Spain), which leads to what is often uncontrolled disposal of immense amounts of olive mill wastewater (OMWW). The situation is exacerbated by the fact that olive oil production is seasonal, and thus requires huge storage ponds or facilities since processing cannot be spread over time. It was previously estimated that in the Mediterranean approximately 30 Mm³ of OMWW must be handled each year [2]. In all Mediterranean countries, the direct discharge of OMWW into rivers and lakes is strictly forbidden, but in fact, the illegal direct disposal of OMWW into nearby aquatic resources and ecosystems is known to be a common practice. There is still no common EU legislation for OMWW regulation and management; standards, physicochemical parameters, limit, and threshold values for safe disposal are left to individual countries [3]. In Tunisia, the restriction related to the discharge of raw OMWW is defined according to the standard NT.106.002 [4].

The main physicochemical characteristics of OMWW making them a pollutant are their dark color, their strong offensive smell, high acidity, and high values of chemical oxygen demand (COD) and biological oxygen demand (BOD₅), with a COD/BOD₅ ratio between 2.5 and 5, which correspond to recalcitrant organic materials [5], high electrical conductivity [6], high values of solid matter [7], organic compounds (lignins and tannins, associated with dark color), and long-chain fatty acids and phenolic compounds which contribute to their low degradability and their high toxicity to most crops and microorganisms [8–10].

Much research has been carried out on numerous physicochemical methods for treating OMWW, alone or combined, such as oxidation, filtration, centrifugation, flocculation, incineration, coagulation, ultrafiltration, reverse osmosis, ozonation, or photolysis. Many of these approaches are efficient for pollutant removal—namely monophenolic compounds and high organic charge—and consequently quite useful as pretreatment methods, but they are expensive and do not generate valuable sub-products [11]. Furthermore, since conventional olive mill waste-treatment methods have proven to be inadequate and ineffective for removing OMWW pollutants, several studies have been carried out in order to use this waste as a renewable resource and to transform OMWW from a pollutant to organic fertilizer, agricultural water source, or green fuel [12].

Direct application of olive mill waste to soil has been investigated for many years. While useful as an amendment in moderation, studies have also shown that OMWW, due to phenolic contents, can also have a high antimicrobial capacity, being useful for soil sanitation against certain pathogens [13,14]. The high concentrations of phenolic compounds of fresh OMWW lend to toxic and antimicrobial properties that lead to slow microbial degradation of the organic matter in the soil, especially of highly resistant lignocellulosic compounds [15]. Moreover, its high mineral salt content, low pH, and the presence of phytotoxic compounds have a negative effect on soil productivity [16]. Direct application to soil has been reported to cause inhibition of seed germination, genotoxicity effect, and a decrease in phosphatase and fluorescein diacetate hydrolase activities in the soil [17], the latter of these being enzymes which are important indicators of soil microbial activity and a soil's capacity for the mineralization of plant-available nutrients.

Olive mill solid waste (OMSW), otherwise known as olive pomace, contains high potassium concentrations and high organic matter (mainly fibers). Unlike other organic residues that have been proposed for agricultural purposes such as sewage sludge and municipal solid wastes, the concentration of heavy metals in OMSW is almost imperceptible [18]—this is an important factor when considering thermal transformations since these processes concentrate non-volatile components. Nevertheless, several studies have shown that, although it is less phytotoxic than wastewaters, it causes great nutritional imbalances since it modifies the nitrogen cycle in soil due to its high C/N ratio [19]. For this reason, it has been previously considered that the suitability of OMSW as

a soil amendment is enhanced when adding mineral nitrogen, and results show that its mineralization largely depends on the type of soil, being temporarily inhibited in acidic soils [20]. Thus, it has been demonstrated that nitrogen fertilizers should preferably be added along with OMSW, as this technique results in a large increase in soil-available K [21].

In order to avoid negative effects often observed when directly applied to the soil, the recycling of OMSW and their transformation into fertilizer by composting technology has been widely recommended. Composts from OMSW have been shown to serve as adequate organic fertilizers for olive trees or as part of a substrate or growing media [22]. However, the dense and sticky physical texture of OMSW makes it difficult to maintain aerobic conditions inside the material for composting [22]. In addition, other properties like excessive moisture content and the presence of non-easily degradable compounds, fats and polyphenols, make OMSW a difficult substrate for composting [23]. In light of the above, several researchers have developed co-composting procedures for olive mill by-products with many agricultural wastes [24]. Although some of these co-composts showed a satisfying degree of humification and no phytotoxic effect, physical characteristics of OMSW make it difficult to compost by forced aeration systems since different flow paths are generated for the air that dries the material forming aggregates [25]. Moreover, high acidity values reached during co-composting of OMSW may represent a limitation for its soil application [26].

Recently, the production of biochar has been studied as a conversion technology for olive mill wastes—both solid and liquid—to deal with their usual toxicity [27]. Biochar is a C-rich organic material, which is produced during slow exothermic decomposition of biomass under low oxygen conditions and at temperatures \leq 700 °C [28]. Biochars can be used to improve the productive capacities of degraded and low-fertility soils [29,30]. Depending on soil mineralogy, pH, and organic matter, among others, their application can increase soil pH, base saturation, electrical conductivity, available P, exchangeable Ca, Mg, Na, K, and cation exchange capacity [31,32]. Other olive industry biomass sources including olive tree prunings and olive pits have been satisfactorily processed through pyrolysis in order to obtain biochar [33]. However, biochar obtained from olive biomass—as is the case for most other lignocellulosic feedstocks—has low N contents, limiting its fertilizer value [33,34]. Biochar is a good strategy for increasing soil organic carbon contents with long residence times due to its recalcitrant nature. Following pyrolysis, a large proportion of non-volatile total plant nutrients are soluble [35], but following this, mineralization and nutrient release is expected to be slow [36]. In light of the above, recently, a new environmentally friendly strategy was implemented for the valorization and recovery of OMWW, based on the impregnation of wood sawdust with OMWW, followed by drying and slow pyrolysis and leading to the recovery of nutrients contained in OMWW [12]. This strategy does in fact increase N contents of the final biochar in addition to enriching it with macro- and micro-nutrients. With a thermal treatment strategy such as this, the recycling of OMWW in agricultural systems may be improved, with multiple benefits for the environment and soil protection, while promoting the circular economy.

Although the production of biochar is a fairly established technology, at the moment it is not economically competitive compared to the production of fertilizers using other techniques because of its high cost of production and the skilled workforce and amounts of energy that are required [37]. The economics of biochar depend on the availability of advanced technology to produce and optimize co-products based on management objectives. Moreover, the economic feasibility of biochar must contemplate the costs of processing, distribution of the product, and energy generated during the pyrolysis process [38]. However, if long-term carbon sequestration is valued above renewable energy, then more biochar should be produced. Its economic feasibility improves when life cycle costs and environmental impacts are accounted for. This is especially the case when biochar is produced with reference to biomass availability and sustainability and is used as a soil amendment for greenhouse gas emissions reduction [37]. Therefore, in order to maximize the economic outputs and beneficial outcomes, the supply chain including feedstock collection, transportation, pyrolysis plant design and operation, and product recovery need to be optimized [39].

In this study, we highlight the potential of two thermal conversion technologies: on the one hand, conventional pyrolysis for solid fractions, and on the other, hydrothermal carbonization for liquid fractions. The choice between either technique depends generally on the desired quality and the physio-chemical characteristics of the produced chars. Slow pyrolysis (e.g., at 500 °C, a common temperature for high-quality chars) creates a stable carbonaceous product with a relatively high specific surface but with relatively low nutrient content. Chars produced from pyrolysis are known for their carbon sequestration value when applied as a soil amendment [40]. On the other hand, hydrothermal carbonization (HTC), which is conducted at lower temperatures, typically between 140–350 °C, has larger final yields, i.e., more of the mass is conserved as compared to pyrolysis chars (typically less than 60%) [41]. HTC also produces liquid phase liquor which to date has not received much attention as a fertilizing substance but concentrates some nutrients such as potassium (e.g., [42]). Furthermore, it has been shown that resulting carbonaceous materials have high mineral contents which are valuable in agriculture for their slow carbon mineralization and other complementary effects to fertilizer [43]. Moreover, the surface of hydrochars have low pH_{zpc} and high densities of phenolic, carboxylic, and aliphatic groups, contrasting greatly with the properties of pyrolysis chars, which have few aliphatic groups and are more aromatic [35,44].

In the present study, the objectives were to conduct an inventory of olive mill wastes generated in relevant Mediterranean countries and determine the potential for thermal conversion and agricultural applications. To this end, olive mill waste samples were analyzed to estimate the flows of matter and nutrients contained in this immense waste stream. Subsequently, assays were carried out to produce biochar with two thermal treatment technologies—pyrolysis and hydrothermal carbonization—in order to characterize the volumes of chars and HTC liquors which could possibly be generated from this resource, as well as the matter and nutrients also contained therein. Then, we upscaled these values to the country level in order to provide a basis for calculating the flows of matter and nutrients contained in the untreated wastes and thermally treated wastes, which may aid relevant policies and strategies for dealing with the problem of OMW disposal and valorization on the EU and country levels.

2. Materials and Methods

2.1. Olive mill Wastes Inventory and Sampling

The amounts of olive mill wastes generated in Spain, Tunisia, and Greece were determined through consultation of European and national-level databases and local authorities. For this study, we have used the data from 2017. Some wastes and sub-products were theoretically estimated based on published data, depending on the country and olive oil extraction system. For Spain, data on amounts of wastes generated are available publicly [45]. In the case of Tunisia, 10-year estimates for olive mill wastes were provided by the Ministry of Agriculture and Olive Institute. Finally, in the case of Greece, beginning with governmental data for olive oil production [46], known relative proportions of three-and two-phase mills [47], and tons of olive-to-waste conversions based on published studies [48], the amounts of solid and liquid wastes were estimated.

For characterization of wastes generated in each country, composite samples of solid (500 g) and liquid wastes (1 L) were collected. This included four two-phase olive mill solid wastes (OMSWs) from Spain (Valencia region) and two from Greece; one three-phase OSMWs from Tunisia and two from Greece; and one three-phase olive mill wastewater (OMWW) sample from Tunisia and four from Greece (a total of 13 samples); in the case of Greece, the samples represented Northern Greece (Central Macedonia region) and Southern Greece (Peloponnese region). These samples were used for the up-scaling exercise, and the sample number did not confer a high degree of confidence in the estimation of error margins but served as the basis for this initial assessment within the considered countries which can be expanded in the future.

2.2. Physio-Chemical Analysis

The samples were analyzed for their most agronomically relevant physical-chemical properties following the analytical procedures described in [49]: total solids were determined gravimetrically by drying a fresh sample at 70 °C until constant weight. Electrical conductivity and pH were measured on fresh samples, directly in the case of liquid samples, and in 1:5 (w:v) slurries, in the case of solid samples. For total carbon (TC) and total nitrogen (TN), liquid samples were first filtered to remove the largest particles and thereafter measured on an autoanalyzer (TOC-V CSN, Shimadzu Corp., Kyoto, Japan). For solid samples, a sub-sample was taken and dried at 36 0 C for analysis of carbon and nitrogen contents: total C and N were measured on a combustion analyzer (TruSpec, LECO Corporation, St. Joseph, MI); available N was measured by extracting 5 g sample with 20 mL K₂SO₄(1:4), and NO₃⁻ and NH₄⁺ were measured colorimetrically on a segmented flow autoanalyzer (San ++, Skalar, Breda, the Netherlands). All samples were analyzed sequentially for dry matter, organic matter, and ash contents by drying at 35 °C, oxidation in a muffle furnace at 375 °C for 18 h, and 550 °C for 5 h, respectively. Finally, macro- and micro-nutrient contents of samples were evaluated by acid digestion in concentrated HNO₃ in a microwave-assisted digestion apparatus (ETHOS ONE, Milestone, USA) and measurement on an ICP-OES apparatus (GENESIS, SPECTO Analytical Instruments GmbH).

2.3. Biochar and Hydrochar

In order to estimate the potential production of biochar from the waste streams in each country, representative samples of OMWW and OMSW were obtained from a representative three-phase olive mill located in Grombalia, Nabeul city in the north of Tunisia, during the winter season (November-December) of 2018. Solid was naturally air-dried for a week, then stored in bags for further use. Olive mill wastewater (OMWW) was provided from the same olive oil plant, then was stored in hermetic bottles at low temperature (> 4 °C). For biochar production via pyrolysis of OMSW under an inert atmosphere, 3 g of feedstock was placed in an alumina crucible and introduced in a tubular furnace reactor. Then, argon flow was supplied continuously at room temperature for 30 min in order to remove residual oxygen. Afterward, the temperature increased to the setting value (500 °C) at a range of 5 °C/min under nitrogen at a flow rate of 6 N L h⁻¹. The sample was maintained for 1 h at the desired temperature, then cooled naturally under argon flow. The produced biochar was then weighed and stored in a glass flask for further analysis. The HTC of the used OMWW was carried out by using a high-pressure laboratory autoclave (Top Industrie, Vaux-le-Pénil, France). For this assay, 10 mL of OMWW were heated at 200 °C at a constant heating rate and residence time of 10°C/min and 24 h, respectively. After carbonization, the mixture was filtered and the solid phases were dried in an oven at 105 °C overnight and then weighted and stored in glass vials. Produced pyrolysis biochar, HTC hydrochar, and HTC liquid samples were analyzed for total C and N and metal contents as with the raw feedstocks described above. For each material, the mass balance was recorded as the weight before and after pyrolysis, both for solids and liquids. The results on yield and properties of these samples were used to calculate potential biochar production, mass flows, and nutrient contents for each waste stream (full results of biochar production and chemical characteristics are reported in a separate article by Azzaz et al. [44]).

3. Results

3.1. Results of the Analyses of Waste Stream Chemical Properties

After compiling the quantities of wastes generated in each of the three countries and analyzing representative samples, we calculated the estimates of nutrients and matter contained in these waste streams. Country and process-specific averages of the parameters of interest were calculated for each country and waste type, and these were applied to the total waste amounts. The results of laboratory analyses for the chosen parameters are shown in Tables 1–3; these averages are the basis for the up-scaled estimations of matter and nutrients by country and mill extraction system presented in Tables 4–6.

	Spain Two-Phase	Tunisia Three-Phase	Greece Two-Phase	Greece Three-Phase
OMWW TS (% <i>w/v</i>)	-	10.6 (<0.1)	-	5.6 (5.9)
OMSW TS (% dry weight)	30.5 (3)	45 (<0.1)	29.2 (0.8)	47 (3.4)
OMWW C (% <i>w</i> / <i>v</i>)	-	5.17 (0.3)	-	1.94 (1.56)
OMWW N (% <i>w/v</i>)	-	0.23 (0.1)	-	0.1 (0.1)
OMSW C (% dry weight)	54.7 (1.9)	58.9 (0.6)	55.5 (5.1)	60.1 (0.6)
OMSW N (% dry weight)	1.2 (0.4)	1.1 (0.1)	0.8 (0.1)	1.1 (0.1)
OMWW OM ($\% w/v$)	-	8.5 (0.1)	-	7.8 (5.5)
OMWW mineral ash (% w/v)	-	3.1 (0.1)	-	1.3 (0.6)
OMSW OM (% dry weight))	94.7 (1.5)	97.6 (0.5)	95.5 (3)	97.4 (0.4)
OMSW mineral ash (% dry weight)	5.3 (1.5)	2.4 (0.5)	4.5 (3)	2.6 (0.4)

Table 1. Averages and standard deviations (in parentheses) of basic analytical measurements carried out on samples obtained for the study, with standard deviations of measurements of samples of the same type in parentheses. Abbreviations: TS, total solids; C, carbon; N, nitrogen; OM, organic matter; OMWW: olive mill wastewater; OMSW: olive mill solid waste.

Table 2. Averages of macronutrient contents and standard deviations (in parentheses) of the samples obtained for the study, with standard deviations of measurements of samples of the same type in parentheses. All units are mg kg⁻¹ in the case of solid wastes and mg L⁻¹ in the case of liquid wastes.

	Spain Two-Phase	Tunisia Three-Phase	Greece Two-Phase	Greece Three-Phase
OMWW Ca	-	275 (65)	-	96 (32)
OMSW Ca	2578 (497)	12770 (525)	3218 (415)	2226 (111)
OMWW Mg	-	176 (27)	-	48 (12)
OMSW Mg	777 (103)	9998 (44)	486 (46)	391 (55)
OMWW K	-	5549 (769)	-	1782 (59)
OMSW K	17340 (1327)	8991 (364)	7329 (520)	6548 (469)
OMWW Na	-	206 (57)	-	150 (32)
OMSW Na	1834 (184)	2659 (187)	2038 (485)	1000 (195)
OMWW P	-	349 (41)	0	114 (4)
OMSW P	1350 (123)	650 (34)	584 (70)	562 (55)
OMWW S	-	237 (38)	-	80 (14)
OMSW S	930 (168)	1443 (80)	905 (148)	762 (94)

Table 3. Averages of micronutrient contents and standard deviations (in parentheses) of the samples obtained for the study, with standard deviations of measurements of samples of the same type in parentheses. All units are mg kg⁻¹ in the case of solid wastes and mg L⁻¹ in the case of liquid wastes.

	Spain Two-Phase	Tunisia Three-Phase	Greece Two-Phase	Greece Three-Phase
OMWW Al	-	7 (3)	-	10 (3)
OMSW Al	137 (19)	414 (12)	90 (12)	96 (35)
OMWW Fe	-	9 (2)	-	8 (2)
OMSW Fe	175 (26)	472 (27)	100 (13)	117 (6)
OMWW Si	-	14 (41)	-	8 (2)
OMSW Si	104 (7)	189 (7)	88 (10)	88 (12)
OMWW B	-	4(1)	-	2 (2)
OMSW B	31 (5)	24 (3)	18 (5)	17 (3)
OMWW Cu	-	1.3 (0.5)	-	1.6 (0.3)
OMSW Cu	8.7 (0.4)	4.4 (0.9)	6.2 (0.7)	4.8 (1.3)
OMWW Cr	-	0.2 (0.2)	-	0.5 (0.3)
OMSW Cr	4.8 (0.3)	9.1 (0.5)	2.2 (0.1)	2.0 (0.3)
OMWW Mn	-	1.3 (0.1)	-	0.5 (0.1)
OMSW Mn	8.6 (0.9)	11.3 (0.9)	3.6 (0.8)	5.7 (0.8)
OMWW Zn	-	4.2 (0.6)	-	0.9 (0.3)
OMSW Zn	12.1 (1.9)	10.8 (1.4)	10.7 (1.3)	13.2 (1.8)

	Spain Two-Phase	Tunisia Three-Phase	Greece Two-Phase	Greece Three-Phase
OMWW 2017 (1000 m ³)	-	900	-	1499
OMSW 2017 (1000 tons)	4336	450	415	635
OMWW C (1000 tons)	-	46.5	-	29.1
OMWW N (1000 tons)	-	2.1	-	1.0
OMSW C (1000 tons)	746.8	119.3	67.2	179.2
OMSW N (1000 tons)	16.2	2.2	1.0	3.3
Total C (1000 tons)	746.8	165.8	67.2	208.2
Total N (1000 tons)	16.2	4.3	1.0	4.4
OMWW OM (1000 tons)	-	76.5	-	116.9
OMWW mineral ash (1000 tons)	-	27.9	-	19.5
OMSW OM (1000 tons)	1292.5	197.6	115.6	290.7
OMSW mineral ash (1000 tons)	72.5	4.9	5.5	7.6
Total OM (1000 tons)	1292.5	274.1	115.6	407.6
Total mineral ash (1000 tons)	72.5	32.8	5.5	27.1

Table 4. Estimated calculations of annual (2017) flows of the main components of each waste type by country, based on the values obtained in Table 1.

Table 5. Estimated calculations of annual (2017) flows of macronutrients of each waste type by country, based on the values obtained in Table 2.

	Spain Two-Phase	Tunisia Three-Phase	Greece Two-Phase	Greece Three-Phase
OMWW 2017 (1000 m ³)	-	900	-	1499
OMSW 2017 (1000 tons)	4336	450	415	635
OMWW Ca (1000 tons)	-	0.09	-	0.14
OMSW Ca (1000 tons)	3.52	2.30	0.39	0.66
Total Ca (1000 tons)	3.52	2.38	0.39	0.81
OMWW Mg (1000 tons)	-	0.16	-	0.07
OMSW Mg (1000 tons)	1.06	0.18	0.06	0.12
Total Mg (1000 tons)	1.06	0.34	0.06	0.19
OMWW K (1000 tons)	-	4.99	-	2.67
OMSW K (1000 tons)	23.67	1.62	0.89	1.95
Total K (1000 tons)	23.67	6.61	0.89	4.62
OMWW Na (1000 tons)	-	0.19	-	0.23
OMSW Na (1000 tons)	2.50	0.48	0.25	0.30
Total Na (1000 tons)	2.50	0.66	0.25	0.52
OMWW P (tons)	-	313.67	-	170.92
OMWW P (tons)	1842.17	116.98	70.77	167.53
Total P (tons)	1842.17	430.65	70.77	338.45
OMWW S (tons)	-	1298.97	-	119.59
OMSW S (tons)	1269.70	42.66	109.64	227.33
Total S (tons)	1269.70	1341.63	109.64	346.92

pH values for solid samples were between 5 and 6, whereas liquid samples had slightly lower pH, around 4.5. Electrical conductivity values were quite variable both within solid (0.9–4.4 dS m⁻¹) and liquid (1.1–11.7 dS m⁻¹) samples. In liquid samples, this is due to dilution of the wastewaters or management such as flocculation and sedimentation, etc. In solid samples, on the other hand, this may be due to extraction conditions at the plant. As can be expected, electrical conductivity (EC) was highly correlated with ash contents (r = 0.95, p < 0.001, t = 9.8).

	Spain Two-Phase	Tunisia Three-Phase	Greece Two-Phase	Greece Three-Phase
OMWW 2017 (1000 m ³)	-	900	-	1499
OMSW 2017 (1000 tons)	4336	450	415	635
OMWW Al (tons)	-	6.42	-	14.59
OMSW Al (tons)	187.14	74.45	10.86	28.54
<i>Total Al (tons)</i>	187.14	80.87	10.86	43.13
OMWW Fe (tons)	-	7.75	-	12.53
OMSW Fe (tons)	239.14	84.89	12.15	34.84
<i>Total Fe (tons)</i>	239.14	92.64	12.15	47.37
OMWW Si (tons)	-	12.55	-	11.92
OMSW Si (tons)	142.37	33.98	10.66	26.37
Total Si (tons)	142.37	46.53	10.66	38.28
OMWW B (tons)	-	3.90	-	3.07
OMSW B (tons)	42.59	4.32	2.20	5.19
Total B (tons)	42.59	8.22	2.20	8.26
OMWW Cu (tons)	-	1.17	-	2.35
OMSW Cu (tons)	11.88	0.79	0.75	1.40
Total Cu (tons)	11.88	1.96	0.75	3.76
OMWW Cr (tons)	-	0.16	-	0.70
OMSW Cr (tons)	6.55	1.64	0.27	0.60
Total Cr (tons)	6.55	1.80	0.27	1.30
OMWW Mn (tons)	-	1.15	-	0.70
OMSW Mn (tons)	11.74	2.03	0.44	1.70
Total Mn (tons)	11.74	3.19	0.44	2.40
OMWW Zn (tons)	-	3.82	-	1.32
OMSW Zn (tons)	16.52	1.94	1.30	3.94
Total Zn (tons)	16.52	5.76	1.30	5.26

Table 6. Estimated calculations of annual (2017) flows of micronutrients of each waste type by country, based on the values obtained in Table 3.

Olive mill solid wastes had around 55–60% carbon contents and 1% nitrogen contents, giving these materials mid-range C: N values (~50), comparable to corn stalks or woody shrub trimmings. The values for OMSW within and between countries were also very similar with relatively little variability. OMWW C:N values were much lower (~20), which can be expected both because C values were much lower and because nitrate—the most abundant nitrogen species—is highly soluble and will preferentially pass to the liquid phase in a three-phase system. NO₃⁻ was the dominant inorganic species in liquid samples (data not shown), with a large range of 35–2262 mg L⁻¹. NH₄⁺, on the other hand, was barely present in liquid OMWW samples, having a range from below detection limit (BDL) up to 13 mg L⁻¹. In solid samples, nitrate was not detected; the reason for this may be the inhibition of biological nitrification, whereas olive mill wastes contain phenolic substances. NH₄⁺ was present in solid samples, albeit in very small concentrations (BDL-222 mg kg⁻¹). In solid biomass, most nitrogen is contained in the organic matter (0.6–1.8%).

The macro- and micro-nutrient metal content results are shown in Tables 2 and 3. In the case of the three-phase mills, the proportion of metal elements found in the aqueous phase varied greatly, from 1–2% (Al and Fe) to 38% (K). Soluble phosphorus was also in greater concentrations in the solid samples than liquid samples (comparing mass with volume). The quantities of K in Tunisian wastewaters were of particular note, representing 0.6% of the total mass. Regarding the OMSW, K was unequivocally the most abundant nutrient: in the Spanish wastes analyzed, an average of 1.7% of the total mass was K. These OMSWs, when converted to chars, would have their K contents concentrated (increased). The other wastes also had K quantities in the range of 0.7–0.9%. Concerning P, Spanish wastes had the highest contents (0.1%), about double the concentrations in the other solid wastes. As to be expected, the most abundant metal elements in the wastewaters were major nutrient cations, followed not insignificantly by P and S. Extractable P in solid samples was between 260 and

1090 mg kg⁻¹, while in the liquid fractions it was between 3 and 300 mg L⁻¹. Phosphorus typically concentrates in the solid fractions of waste streams since it is associated with organic matter, so this result was expected. The Tunisian waste had relatively high concentrations of alkali earth metals, with the highest concentrations of Ca (1.2%) and Mg (1.0%) among the samples analyzed. The reported Cr values are total chromium, not differentiating between trivalent Cr (III) and hexavalent Cr (VI). The reported values were between 2 and 9 mg kg⁻¹, and the actual concentrations of Cr (VI) were not known.

3.2. Results of Up-Scaling of Flows of Olive Mill Waste Products and Nutrients to Regional Scale

Tables 4–6 show the results of up-scaling the measurements of Tables 1–3 to total mass flows by country and extraction system contained within these wastes. For this, average values for each parameter for each country and waste stream (Tables 1–3) were multiplied by the flows of each waste stream (headers of Tables 4–6). It must be understood that these estimations are based on the particular properties of the test material, whereas olive mill waste properties vary from region to region, and will also be affected by process conditions. Above all, these estimations serve to indicate the large masses and therefore the importance of the nutrients contained in olive mill wastes and of their utility in the circular economy context. Since our up-scaling was undertaken with one material in this first study, the biochar production results reported in greater detail in [44] were compared with other references: concerning biochar yield with the HTC of OMWW, we obtained 40% biochar yield for 200 °C, whereas other authors have reported 30% for 200 °C [50] or 50% [51] for 225 °C. Regarding OMSW biochar yield, we obtained 32.7% for 500 °C while others have reported 29% for 530 °C [52].

When considering Table 4, the amounts of carbon and organic matter are quite appreciable, especially in the case of Spain. Considering total amounts of carbon in the olive mill wastes for these countries, they reach 1.2 Mt, or 2.1 Mt of organic matter, and around 0.14 Mt of mineral ash. Nitrogen, on the other hand, amounts to 25,900 t. Observing Table 5, what is most noticeable is the immense amounts of potassium contained in these waste streams, 35,790 t, or around 26% of all mineral ash. Finally, regarding phosphorus (Table 6), another element critical for plant growth, total flows amounted to 2682 t.

3.3. Potential Biochar Production

Finally, the estimations of biochar production from the considered waste streams were carried out based on the laboratory assays and are shown in Table 7. In this case, all estimated chemical component up-scaled calculations were based on the Tunisian samples used in the carbonization assays (not based on Tables 1–3 above). What is seen is that when pyrolyzing solid waste—considering initial fresh weights—the yield in solid biochar produced at 500 °C was about 10% of the original mass. The pyrolysis of olive pomace at such temperature caused the elimination of volatile matter and the degradation of the lignocellulosic matrix, thus explaining the relatively low final solid yield [53]. With the estimates performed here, the quantities of solid char potentially produced amount to 42.6×10^4 t in Spain, 44.2×10^3 t in Tunisia, and 13.4×10^4 t in Greece. HTC-process liquors, on the other hand, would amount to 37.4×10^4 t in Tunisia and 62.2×10^4 t in Greece. When liquid fractions from three-phase mills are treated with HTC (as expected), very little solid char is produced, around 4%, whereas the remaining mass is HTC liquor (this study was conducted on a weight basis, 1 t liquor is very close to 1 m^3). This solid phase, however, tends to retain the P. In the three-phase systems of Tunisia and Greece, it is seen that over 98% of all P in the waste stream was retained in the solid phases of biochar. It is worth mentioning that the P content in the liquid phase of the OMWW used in HTC in this study was 1.66 mg L^{-1} , whereas following hydrothermal carbonization at 200 °C this quantity decreased to 0.72 mg L^{-1} [44]. In other words, the P contained in OMWW concentrated in the solid phase with HTC. Potassium, on the other hand, was very rich in the HTC liquor. The calculations estimated that for three-phase systems, about 65% of all K in the waste stream is in the liquid (liquor) fraction following HTC.

Table 7. Estimated calculations of annual (2017) flows of biochar which can be potentially produced from olive mill waste flows by waste type, country, extraction technology, carbonization technology, and fraction (solid or liquid). In this case, all estimated chemical component up-scaled calculations are based on the representative Tunisian samples used in the carbonization assays (not based on Tables 1–3 above). Abbreviations: "WW" = wastewater; "SW" = solid waste; "PYR" = pyrolysis, corresponding to biochar generation; "HTC" = hydrothermal carbonization, corresponding to biochar and HTC liquor generation; NA = not available.

	Spain Two-Phase	Tunisia Three-Phase	Tunisia Three-Phase	Tunisia Three-Phase	Greece Two-Phase	Greece Three-Phase	Greece Three-Phase	Greece Three-Phase
WW/SW	SW	SW	WW	WW	SW	SW	WW	WW
Transformation	PYR 500	PYR 500	HTC 200 - solid	HTC 200 - liquid	PYR 500	PYR 500	HTC 200 - solid	HTC 200 - liquid
OMSW/WW (1000 tons/1000 m ³)	4336	450	900	900	415	635	1499	1499
Potentially produced biochar/hydrochar/HTC liquor (1000 tons)	426.3	44.2	15.4	358.3	40.8	93.6	25.6	596.7
C (1000 tons)	325.4	33.8	10.4	NA	31.1	71.5	17.3	NA
N (1000 tons)	4.4	0.5	0.3	NA	0.4	1.0	0.5	NA
Na (tons)	754.5	78.3	3.9	63.7	72.2	165.7	6.6	106.0
K (tons)	7934.9	823.5	51.5	1906.0	759.5	1743.1	85.7	3174.5
Mg (tons)	227.6	23.6	0.5	35.9	21.8	50.0	0.8	59.9
Ca (tons)	727.9	75.5	0.1	16.2	69.7	159.9	0.2	27.0
P (tons)	153.5	15.9	0.5	0.3	14.7	33.7	0.8	0.4

4. Discussion

This study provided up-to-date data on the flows of matter and nutrients contained in olive mill waste, a hugely important food waste stream in Mediterranean countries, where there is increasing political and economic incentives to properly treat and reutilize this resource. On the one hand, if raw olive mill wastes are to be promoted more extensively as a "soil improver," falling under the new European Fertilizer Guidelines (EU 2019/1009) [54], the OMWs were well within limits for Cu (limit 300 mg kg⁻¹) and Zn (800 mg kg⁻¹). Raw wastes also have high mineral contents. In the Spanish wastes analyzed, an average of 1.7% of the total mass was K (the highest of the wastes assessed in this study, whereas the other had K quantities in the range of 0.7–0.9%). This property would probably qualify those particular wastes as "solid organic fertilizer," according to the new EU Fertilizer regulations, which specify that these products must contain minimum 2% by mass total potassium oxide (K_2O ; when applying the conversion factor, this is equivalent to 1.66% K). If considering the OMW as a "soil improver," the OMWs were well within limits for Cu (limit 300 mg kg⁻¹) and Zn (800 mg kg^{-1}) [54]. Furthermore, conversion to biochar is a management option which detoxifies organic contaminants present in the wastes, upgrading their agricultural value both in terms of nutrient availability and carbon sequestration. These OMSWs, when converted to chars, have their K contents concentrated (increased). When considering the large overall amounts of potassium in these waste streams (35,000 t annually, see Table 5 above), it is seen that OMW could be targeted as a source for renewable minerals for agriculture.

Mediterranean soils are characterized by their low organic C contents, typically below 2%, and contents of as low as 0.5% are even common [55]. In the countries considered, any contribution of organic matter is likely to improve soil quality and productivity. How much land surface could be amended with these materials, protecting soil quality and increasing soil available nutrients? To carry out this exercise, we can imagine the goal of increasing soil carbon by 0.4% (such as suggested by the 4p1000 initiative; [56]) by way of land application of these oil milling sub-products. If we consider a standard soil density of 1.3 g cm⁻³, enrichment of the plowed horizon (0–20 cm), this would equate to additions of approximately 17 t ha⁻¹ for OMSW (appx. 60% C) or 13.8 t ha⁻¹ for OMSW biochar (appx. 75% C). By using OMSW (unpyrolyzed dry mass basis), it would be possible to increase C by 0.4% on approximately 45,000 ha in Spain, 7000 ha in Tunisia, and 14,000 ha in Greece. For biochar solid fractions, it is more realistic to consider lower application rates since commonly cited application rates fall in the range of 2–10 t ha⁻¹. Assuming an application rate of 7 t per ha, biochar from these wastes would enrich soil carbon by 0.2% on approximately 50,000 ha in Spain, 6300 ha in Tunisia, and 14,000 ha in Greece. Therefore, due to the recalcitrant nature of biochar, with just two or three subsequent yearly additions it could be possible to reach the goal of 0.4%. Though conversion to biochar allows amendment of less land area, it is important to keep in mind the higher residence times of pyrolyzed materials, which can be on the scale of hundreds to thousands of years, whereas the maximum residence times of raw olive wastes will be at least an order of magnitude lower. To summarize, the potential is that each year more than 700 km² of arable soils in the three countries could be enriched in approximately 0.2% stable carbon in the form of biochar at an application rate of 7 t ha^{-1} .

Emerging research shows that processing liquid wastes with HTC, producing HTC liquor, reduces chemical oxygen demand, produces pyrolytic products with biostimulant properties, such as sorbitol, myo-inositol, glycerol, and galactitol [44], and helps concentrate minerals in the solid fraction [57,58]. This is the alternative to traditional management—direct land application of both liquid and solid fractions—which can cause problems of high oxygen demand, phytotoxicity, and salinity. Countries still employing three-phase mills must manage huge quantities of wastewater, containing, among other elements, large quantities of P and K [59]. Recovery of waste stream nutrients is a strategy for avoiding larger nutrient losses from the processing of limited, critical nutrients such as phosphorus [60], and improving the nutrient status of Mediterranean soils. One result of this study is to see that thermal treatment will concentrate a portion of the soluble P in the solid phase following treatment [58]. On the other hand, it is seen that following HTC the liquid phase is significantly

enriched by potassium during the process, as shown in Table 7 and also described in our related work [44]. This fact must be taken into account when considering sub-products and fertigation uses with this resource, and it may aid in strategies for use of these mineral-rich wastewaters, avoiding consumption of mined sources (potash) which has its own notable environmental impact, costs, and losses in processing.

This study estimated total masses of olive mill sub-products to be valorized, their properties, and the agricultural land area which can be positively impacted by improved management of problematic wastes. The aim was to quantify this potential for measurable advancements in soil protection and carbon sequestration in agricultural soils through a circular economy approach. Future studies can build upon this work by considering a wider range of olive mill wastes and undertaking similar carbonization experiments with more materials and larger-scale plants in order to obtain improved estimates for these countries and the wider Mediterranean Basin.

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