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Article

A Multidisciplinary Approach to *Posidonia oceanica* Detritus Management (Port of Sperlonga, Italy): A Story of Turning a Problem into a Resource

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Abstract: Ports are affected by a high rate of sedimentation that requires frequent dredging of the seabed to restore bathymetric levels. In some cases, the sediments consist of a large amount of leaves of phanerogams (e.g., *P. oceanica*) that must be treated differently from what is required by the Italian law on sediments (Ministerial Decree No. 173/2016), since soils cannot be treated either as sediment or as waste. About one meter of the sediment cores collected in the Port of Sperlonga consisted of organic waste derived from a different stage of seagrass decomposition. To optimize the management, the decomposed organic detritus was characterized from physical-chemical (content of nutrient and pollutants), ecotoxicological and mechanical (microtensile, microscopic structure) points of view, to define different management solutions for the final disposal. The results of this study describe the characteristics of this type of organic detritus, highly present in Mediterranean coastal ecosystems, and allow a better definition of different possible solutions to valorize this resource instead of disposing it in an organic waste landfill. The search for environmentally friendly options for waste management is of particular interest in terms of the green economy, and the reduction of CO_2 emissions as an indirect effect obtained by improving waste recycling.

Keywords: *Posidonia oceanica* leaves; sedimentary organic detritus; sediment dredging (M.D. 173/2016); waste management; recycling; waste valorization

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Citation: Renzi, M.; Guerranti, C.; Anselmi, S.; Provenza, F.; Leone, M.; La Rocca, G.; Cavallo, A. A Multidisciplinary Approach to *Posidonia oceanica* Detritus Management (Port of Sperlonga, Italy): A Story of Turning a Problem into a Resource. *Water* **2022**, *14*, 2856. https://doi.org/10.3390/w14182856

Academic Editor: Guangyi Wang

Received: 14 August 2022
Accepted: 8 September 2022
Published: 13 September 2022

1. Introduction

Ports are important structures of great economic importance on the coasts; increasing human activities lead to severe pollution of sediments by organic chemicals and inorganic elements [1–3]. Sediment dredging is widespread due to rapid sedimentation rates and the need to keep access channels and port berths functional [4]. The potential negative impacts of these activities are multiple and widely discussed by the literature [5–8]. In Italy, for the exposed reasons, dredging is regulated by a specific law that aims to classify the materials to be treated and to define their management (M.D. 173/2016; Regulation laying down the procedures and technical criteria for the authorization of the dumping of excavated material from the seabed onto shoreline [9]). In general, Italian ports are characterized by soft soils composed mainly of small particles of silt and clay (<2–20 µm Ø), although ports with sandy soils are, also, reported [10]. As far as we know, there is no record in the scientific literature of bottoms characterized by a dominant presence of biological deposits, nor is there any evidence of appropriate management strategies. The port of Sperlonga (Lazio, Italy) is an exception, where bottoms to a thickness of about

1–1.5 m are covered with decomposing leaves of *Posidonia oceanica* mixed with a small amount (<10%) of sand and thinner sediment particles. *Posidonia oceanica* is an endemic seagrass of the Mediterranean Sea, where it forms extensive meadows from the surface to a maximum depth of about 40 m [11,12]. In the marine area of Sperlonga, there is a large amount of healthy *P. oceanica* meadows [13], which form a continuous accumulation of dead leaves in the port basin during marine sea storms. These meadows are one of the most important ecosystems of the Mediterranean coast in terms of primary production and biodiversity [14].

Various uses are being considered for sediments deposited in the port area, such as an alternative to permitted landfilling and for natural resource recovery, such as beach nourishment [15]. However, the presence of massive biological detritus from foliage layers poses an obstacle to the characterization of the underlying sediment and, in perspective, a problem for the dredging process. More recently, *Posidonia oceanica* wastes have been considered as a resource in several studies and have been investigated mainly, but not only, for their suitability as a source for the extraction of microcrystalline cellulose [16–18], opening new perspectives for the reuse of these biomasses, with the aim of supporting a better sustainability of human activities by reducing the wastes sent to landfills, which contribute to the overall CO_2 footprint in ports and shipping [19].

The objective of this study is to investigate possible alternative uses for the dead leaves of *Posidonia oceanica* that need to be removed from port bottoms instead of being disposed of as wastes in landfills. The aim is to explore alternative uses that are compatible with the need for environmentally and economically sustainable management of the port system. A sustainability that is also sought in the European Community's Horizon 2030 guidelines [20]. The activities listed below included the chemical and ecotoxicological characterization of a representative quantity of *P. oceanica* leaves and the study of their physical and mechanical properties to provide a knowledge base that will allow the development of alternative management hypotheses.

This study examined the following potential uses:

- Transfer of organic material to recycling leaves as input matrix in composting or anaerobic digestion plants to produce soil amendments according to national legislation and literature application [21,22].
- Extraction of active ingredients for phytocosmetic, medicinal and pharmaceutical applications as described in the literature [23].
- Production of engineering materials (e.g., insulating products for the construction industry, especially for roofs and floors, due to their thermal insulating and fireproof properties).
- Production of biocomposites as natural products obtained by combining different raw materials to obtain an environmentally friendly final product with excellent performance.

To obtain this information, a chemical-physical characterization of the material was carried out to evaluate its suitability for one or more of the above applications. The list of evaluations performed, and their specific purpose are given below:

- Determination of chemical pollutants (according to M.D. 173/2016 [9]) to evaluate the compatibility of the raw material as a substrate for the extraction of molecules of cosmetic and pharmaceutical interest for the production of compost and for underground experiments and reuse in the adjacent marine areas.
- Determination of macronutrient contents (i.e., TOC, TN, TP) to determine potential for composting/soil amendment production and/or their reuse in situ.
- Ecotoxicological impacts on marine species exposed to leaf biomass elutriates to assess environmental impacts associated with in-situ reuse (e.g., seashore burial or offshore dispersal above 3MN).
- Determination of their structural and mechanical properties of leaves waste.

2. Materials and Methods

2.1. The Study Area

The port of Sperlonga is embedded in a high-quality ecological environment: the Natura 2000 site IT6000014 "Seabed between Terracina and Lago Lungo" [24], located at about 2500 m altitude in the northwest, where the presence of stable and dense meadows of *Posidonia oceanica* and *Pinna nobilis* is documented. Deposits of *P. oceanica* leaves in various stages of decomposition are found along the entire shoreline near the port area and are transported to the port basin by storm surges and ocean currents [25]. During the above characterization work, carried out in accordance with the Italian M.D. 173/2016 [9] for sediment characterizations, it was found that the sediment to be treated is under a layer of organic detritus with an inhomogeneous thickness and distribution between 0.30–1.30 m, mainly composed of submerged banquettes of *Posidonia oceanica* leaves, which have both a wide distribution throughout the basin and a different stage of decomposition.

2.2. Sampled Detritus

Leaf detritus in various stages of decomposition was collected from sediment cores of Sperlonga during soil characterization sampling (Figure 1).

Figure 1. Example of a sediment core collected from bottoms in Sperlonga Port.

The collected leaves were homogenised and about 2 kg of representative material was divided into two different aliquots, one for "fresh weight" (w.w.) analysis and the other for analysis after drying in an oven at 40 °C (±1 °C, "dry weight," d.w.). All anthropogenic residues in the sample were removed by *Posidonia oceanica* leaves before performing the analyses.

2.3. Physical-Chemical Analyses

Physical and chemical analyses of the collected detritus were performed according to the methods listed in Table 1. Analyses were performed on both wet detritus and detritus dried at 40 °C to determine standard parameters that may influence the potential use of this resource. Macronutrients (total organic carbon-TOC, total nitrogen-TN, total phosphorus-TP), chemicals (metals and metalloids, aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, persistent organic pollutants such as polychlorinated biphenyls, pesticides, organotin) were measured.

Table 1. Physical-chemical analyses performed on leaves both on fresh tissues (wet weight "w.w.") and dried tissues at 40 °C (dry weight "d.w."). In this table, variables and their abbreviations, methods, measurement units and limit of quantifications (LOQ) are reported.

	Variable	Abbreviation	Method	Units	LOQ
Nutrients	Total organic carbon	TOC	UNI EN 15936:2012	%	0.3
	Total nitrogen	TN	UNI EN 15407-2011	%	0.1
	Total phosphorous	TP	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	2.5
Metals and metalloids	Aluminum	Al	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	1
	Arsenic	As	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	0.5
	Cadmium	Cd	UNI EN 16174-2012 + UNI EN 16171-2016	mg/kg	0.03
	Chromium	Cr	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	1
	Chromium VI	Cr VI	CNR IRSA 16 Q 64 Vol 3 1986	mg/kg	0.1
	Iron	Fe	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	1
	Mercury	Hg	UNI EN 16174-2012 +UNI EN 16171-2016	mg/kg	0.03
	Nickel	Ni	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	1
	Lead	Pb	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	1
	Copper	Cu	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	1
	Vanadium	V	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	0.5
	Zinc	Zn	EPA 3051 A 2007 + EPA 6010 D 2018	mg/kg	1
Hydrocarbons	Acenaphthylene	At	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Benzo(a)anthracene	BaA	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Fluoranthene	Fluo	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Naphthalene	Nap	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Anthracene	A	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Benzo(a)pyrene	BaP	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Benzo(b)fluoranthene	BbF	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Benzo(k)fluoranthene	BkF	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Benzo(*g*,*h*,*i*)perylene	BghiP	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Acenaphthene	Acn	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Fluorene	Flur	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Phenanthrene	Phe	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Pyrene	Py	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Dibenzo(*a*,*h*)anthracene	DahA	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Chrysene	Cr	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Indeno(1,2,3-c,d)pyrene	I(1,2,3)P	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	1
	Hydrocarbons C > 12	C > 12	EPA 3550 C 2007 + EPA 8015 C 2007	mg/kg	5
POPs	Polychlorinated biphenyls	PCB	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	0.1
	Pesticides	-	EPA 3545 A 2007 + EPA 8270 E 2018	µg/kg	0.1
	Organotin	BTs	ICRAM (2001)-App. 1	µg/kg	1

2.4. *Ecotoxicological Tests*

Ecotoxicological tests were performed on both elutriates (1:4 p/v) from wet and dried leaves according to the methods listed in Table 2. Elutriates were prepared by mechanical shaking at 150 rpm for 1 h. Tests were performed with both unfiltered and elutriates filtered at 0.45 µm. The species tested were selected according to the Italian law (M.D.

173/2016 [9], list of species reported in the Table 2.3 of the cited decree). This type of matrix does not allow solid phase tests (type I); therefore, tests were performed with two type II species (*Phaeodactylum tricornutum*, growth inhibition after 72 h of exposure; *Paracentrotus lividus*, spermiotoxicity after 20 min of exposure), and one type III species (*Paracentrotus lividus*, embryotoxicity after 72 h of exposure). All tests were performed according to standardized methods using UNI EN ISO 10253: 2017 for the algal species, and EPA/600/R-95-136 August 1995, sections 15 and 16 + ISPRA no. 11/2017, for the fertilization and larval development tests with *Paracentrotus lividus*. Further details on methods are reported in Table 2. Positive and negative controls were used to verify the quality of analyses. Negative controls were performed with natural, prefiltered seawater (0.45 micron), while positive controls were performed with reference toxicants. In positive controls, the algal inhibition test includes potassium dichromate ($EC_{(r50)}$: 9.28–26.46%) as the reference toxicant. Tests with *Paracentrotus lividus* were conducted with copper nitrate trihydrate at different EC_{50} values for larval development (EC_{50} = 22.60–68.34 μg/L) and fertilization (EC_{50} = 21.69–68.18 μg/L). Filtered natural seawater was used as a negative control in all tests; nutrients were also added in the case of the algal test. The negative controls were considered satisfactory if the recorded effects were <20% at the end of the test. The positive controls were considered acceptable if the recorded EC_{50} values were within the acceptable range of variation specified by the method.

Table 2. Ecotoxicological tests performed on elutriates of leaves both on fresh tissues (wet weight "w.w.") and dried tissues at 40 °C (dry weight "d.w."). In this table, species tested, methods, measured endpoint and effects, and measurement units are reported for both acute and chronic assays. QA/QC section of this table reports the performances on both positive and negative controls. All controls resulted acceptable as specified by the followed method.

Methods	Acute Toxicity (Type II)		Chronic Toxicity (Type II)		Chronic Toxicity (Type III)	
Species	*Paracentrotus lividus*		*Phaeodactylum tricornutum*		*Paracentrotus lividus*	
Method	EPA/600/R-95-136/s16 + ISPRA 11/17		UNI EN ISO 10253:2017		EPA/600/R-95-136/S15 + ISPRA 11/17	
Endpoint	Fertilization inhibition		Growth inhibition		Embryotoxicity	
	20 min		72 h		72 h	
Unit	%		%		%	
QA/QC	**Average**	**SD/range**	**Average**	**SD/range**	**Average**	**SD/range**
Negative control	13.3	1.5	0.0	2.1	9.0	1.0
Positive control	40.06	(35.98–44.59)	23.15	(20.63–25.99)	33.08	(28.93–37.83)

2.5. Ultrastructural and Mechanical Analyses

Microanalyses on leaves were performed using a high-resolution scanning electron microscope (FESEM) (Merlin II, Zeiss, Jena, Germany) with a combined EDS/WDS microanalyzer optimized to obtain high energy resolution quantitative and qualitative elemental analysis. Moreover, the FESEM is equipped with both secondary and backscattered electron detectors for image analysis up to sub-nanometric resolution (inLens detectors) and a charge compensator for analysis of nonconducting and unprepared samples. By using this microanalytical platform it is possible to characterize the microstructures, morphology, and elemental composition of samples. In addition, X-ray diffraction analysis (XRPD, Rigaku, Smartlab, Tsuen Wan, Hong Kong) and microtensile mechanical strength analysis (Gatan 5 kN, Figure 2) were performed to correlate mechanical tensional strength (stress/strain diagrams) parallel to the growth direction of the blade and cellulose crystallinity.

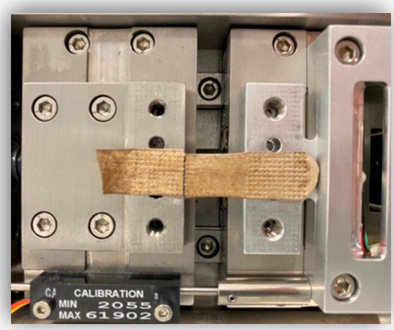

Figure 2. Leaf of *P. oceanica* on the microtensile stage.

2.6. Quality Assurance and Quality Control

This study was performed by a UNI EN ISO/CEI 9001 and UNI EN ISO/CEI 17025 certified laboratory ensuring high levels of control on analyses. Analyses were performed according to standardised official methods (UNI EN ISO, ICRAM, EPA, APAT) in compliance with UNI EN ISO/CEI 17025 guidelines. BsRC (Accredia Lab. N. 1715L) performed chemical and ecotoxicological analyses. The ultrastructural and mechanical analysis (FE-SEM, XRPD, microtensile tests) was performed by the Centre of Excellence CERTEMA (Tuscany). The QA/QC technique included blank tests for chemical analysis, the use of standard reference materials, and positive and negative controls.

Ecotoxicological tests (liquid phase, Type II, and Type III according to Table 2.3 reported in M.D. 173/2016); both positive and negative controls were performed to ensure data quality. Obtained values during positive and negative controls are reported in Table 2 (section QA/QC). Concerning the inhibition of algal growth, negative control was 0% ± 3.63%. Spermiotoxicity showed a negative control of 5.0% ± 2.6%, while embryotoxicity of 0% ± 2.65%.

3. Results

3.1. Macronutrients

The content of macronutrients in leaves (i.e., TOC, TN, TP), which may be important contributors to the marine trophic network, was determined on both the fresh and dried biomass (Table 3). Data for the fresh sample are reported as both dry weight (d.w.) and fresh weight (f.w.). It should be noted that the drying process concentrates the TP contained in the leaf residues, while the TOC content decreases, falling from 25.4% to 18.9% in the fresh sample. This difference could be due to the loss of the labile carbon fraction in favour of the refractory fraction (cellulose and lignin), which tends to persist after drying and naturally has a longer decomposition time in the environment of the labile organic matter, which consists of sugars and rapidly biodegradable polymers. A high percentage of the organic matter consists of refractory substance (e.g., cellulose, and lignin).

Table 3. Physical-chemical analyses on leaves both on fresh tissues (wet weight "w.w.") and dried tissues at 40 °C (dry weight "d.w."). Methods and LOQ are reported in Table 1.

		Fresh Leaves		Dried Leaves
		w.w.	**d.w. (Converted Values)**	**d.w.**
TOC	%	16.6	25.4	18.9
TN	%	0.22	0.34	0.59
TP	mg/kg	128	195	700

3.2. Pollutants

The complete results of the analyses are given in Table 4. Chemical characterization of the material revealed that almost all metals are quantified in the analysed tissues. On the contrary, most pesticides, and Σ BTs, are in concentrations lower than the limit of quantification-LOQ (see Table 1 for specific LOQ). DDT and its degradation compounds (DDD; DDE) in both -ortho and -para forms, are measured at levels below 0.5 µg/kg. It is interesting to note that Σ PAHs are higher in fresh tissues than in dried ones, whereas Σ PCB are comparable and always below 4.0 µg/kg. It is noteworthy that the drying process significantly reduced the organic contaminants in fresh tissue in terms of PAHs, PCBs, and organophosphorus pesticides. In contrast, dried tissue showed higher levels of metals and metalloids.

Table 4. Physical-chemical analyses on leaves both on fresh tissues (wet weight "w.w.") and dried tissues at 40 °C (dry weight "d.w."). Methods and LOQ are reported in Table 1.

		Fresh Leaves		Dried Leaves
		w.w.	**d.w. (Converted Values)**	**d.w.**
Al	mg/kg	1362.4	2080	1810
As	mg/kg	4.86	7.42	9.02
Cd	mg/kg	0.14	0.22	0.19
Cr	mg/kg	7.2	11.0	9.1
Fe	mg/kg	2581	3940	5380
Ni	mg/kg	8.9	13.6	20.1
Pb	mg/kg	3.8	5.8	7.1
Cu	mg/kg	4.4	6.7	15.7
V	mg/kg	15.2	23.2	32.2
Zn	mg/kg	16.2	24.7	30.8
C > 12	mg/kg	15.7	23.9	92.1
BaA	µg/kg	28.8	44	<1
Fluo	µg/kg	34.1	52	11
A	µg/kg	3.1	4.8	<1
BaP	µg/kg	34.7	53	5.4
BbF	µg/kg	41.9	64	<1
BkF	µg/kg	17.0	26	<1
BghiP	µg/kg	23.6	36	4
Phe	µg/kg	10.5	16	6.3
Py	µg/kg	28.2	43	8.6
DahA	µg/kg	4.2	6.4	<1
Cr	µg/kg	32.8	50	4.8
I(1,2,3)P	µg/kg	22.3	34	2.9
Total PAH	µg/kg	281	429	43.3
PCB 28 + PCB 31	µg/kg	0.10	0.19	<0.1
PCB 52	µg/kg	0.10	0.23	<0.1
PCB 101	µg/kg	0.40	0.57	0.29
PCB 118	µg/kg	0.20	0.29	<0.1
PCB 138	µg/kg	0.60	0.84	0.48
PCB 153	µg/kg	0.60	0.91	0.47
PCB 180	µg/kg	0.30	0.48	0.24
Total PCB	µg/kg	2.30	3.50	1.48
DDD o,p′ + p,p′	µg/kg	0.2	0.3	<0.1
DDE o,p′ + p,p′	µg/kg	0.3	0.4	0.5
DDT o,p′ + p,p′	µg/kg	0.1	0.2	0.2

Notes: Chemicals resulted always lower than LOQ are not reported in this Table and are the following: form metals (Cr VI and Hg); for polycyclic aromatic hydrocarbons (At, NaP, Acn, Flur); for PCBs (77, 81, 126, 128, 156, 169); for BTs (monobutyltin, dibutyltin and tributyltin); for pesticides (Aldrin Dieldrin, Endrin, alpha, beta, gam BHC, cis-trans Chlordane, HCB, Heptachlor epoxide).

3.3. Ecotoxicity

Ecotoxicological tests show that elutriate (1:4 w/v; tested as 100%) from fresh tissue shows an inhibition of algal growth of 7.08% ± 2.53%; a similar trend is reported from dried tissue (6.60% ± 2.98%), indicating no significant toxicity, and a similar behavior when leaves are treated; levels of less than 10–15% inhibition are considered negligible toxicity. The test with unfiltered elutriates showed 100% growth inhibition of algae. Spermiotoxicity of elutriates (1:4 w/v; tested as 100%) from fresh tissue showed a percentage inhibition of fertilization of 6.3% ± 1.5% (Abbott correction = 1.4%); when elutriates are tested at 50% dilution, a percentage of 1.7% + 0.6% (Abbott = 0%) is recorded. In contrast, elutriates from dried tissue showed 100% activity at both 100% and 50% dilutions, highlighting the toxicity of dried leaves and the lack of toxicity of fresh leaves. No differences were observed when comparing filtered and unfiltered elutriates. A similar trend is reported for embryotoxicity, where tests with elutriates (1:4 w/v; tested as 100%) from fresh tissue give 5.0% ± 1.53% (when tested at 50% of dilution, 3% ± 2%); but even in this case, elutriates from dried tissue tested at both 100% and 50% of dilution show toxicity at 100%. No differences were observed when comparing filtered and unfiltered elutriates.

3.4. Mechanical Analyses

Micro Tensile Strength Testing. The tensile strength test, performed on several significant replicates of leaf remnants, shows a different response of the tested material. The results show that the highest resistance value in Newtons is obtained in dried leaves (over 30 N resistance) and not in fresh leaves (<20 N resistance), which are not as strong as dried leaves.

FESEM mechanical-structural analysis. The High Resolution (InLens) secondary electrons micrographs obtained by FESEM show the presence of abundant voids in the fresh leaves, in contrast with the more structural compaction revealed in the dried ones (Figure 3).

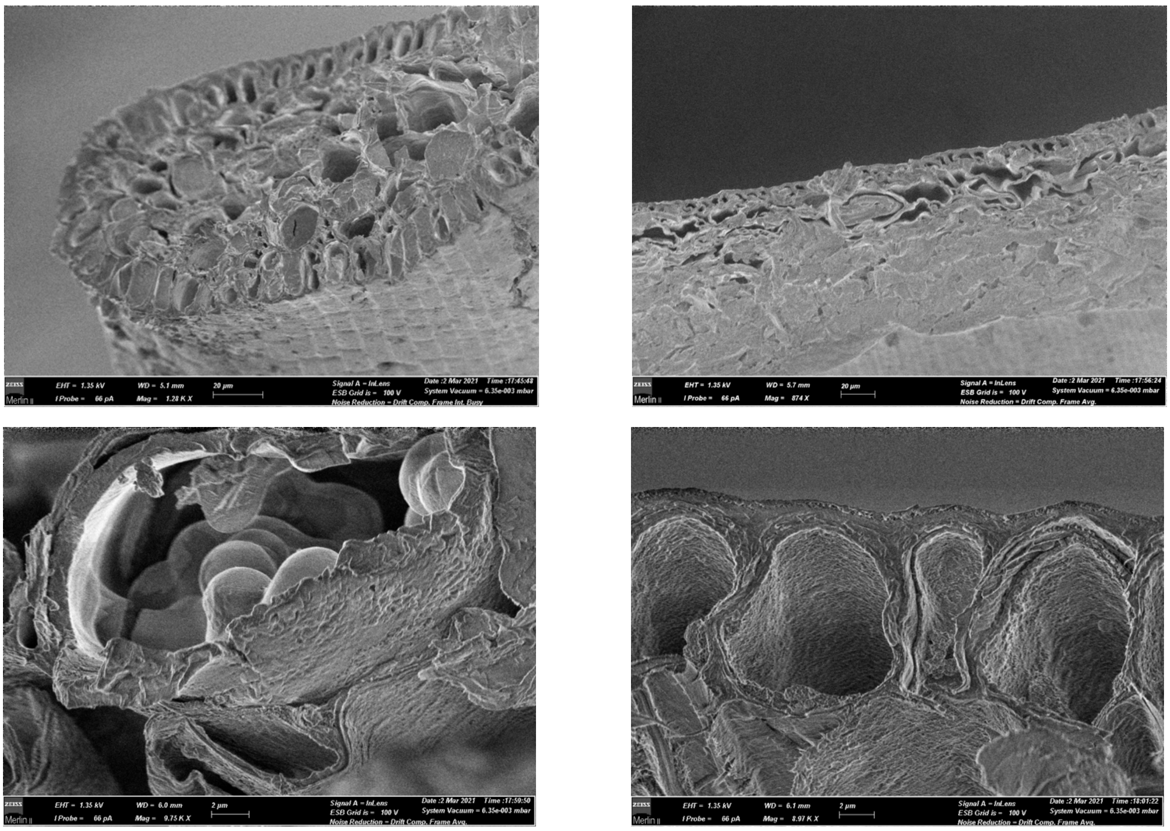

Figure 3. *Posidonia oceanica* dried leaves under field Emission scanning electron microscope (FESEM, Zeiss). Leaves are reported at different dimensional levels to highlight the filling process.

XRD diffractometry. Based on the XRD results, the crystallinity index can be calculated according to Tarchoun et al. [18]. This index was 3.0% for fresh and 4.6% for dry leaf. This suggests that the higher tensile strength found for dried leaves corresponds to higher crystallinity of the microcellulose present in the leaf. Peak 27.37 means dried salt and the crystal formation is aligned along the growth axis of the leaf. The halite peak (NaCl) is observed; the peak indicates that the sodium chloride is aligned along the 1-1-1 crystallographic plane (Figure 4).

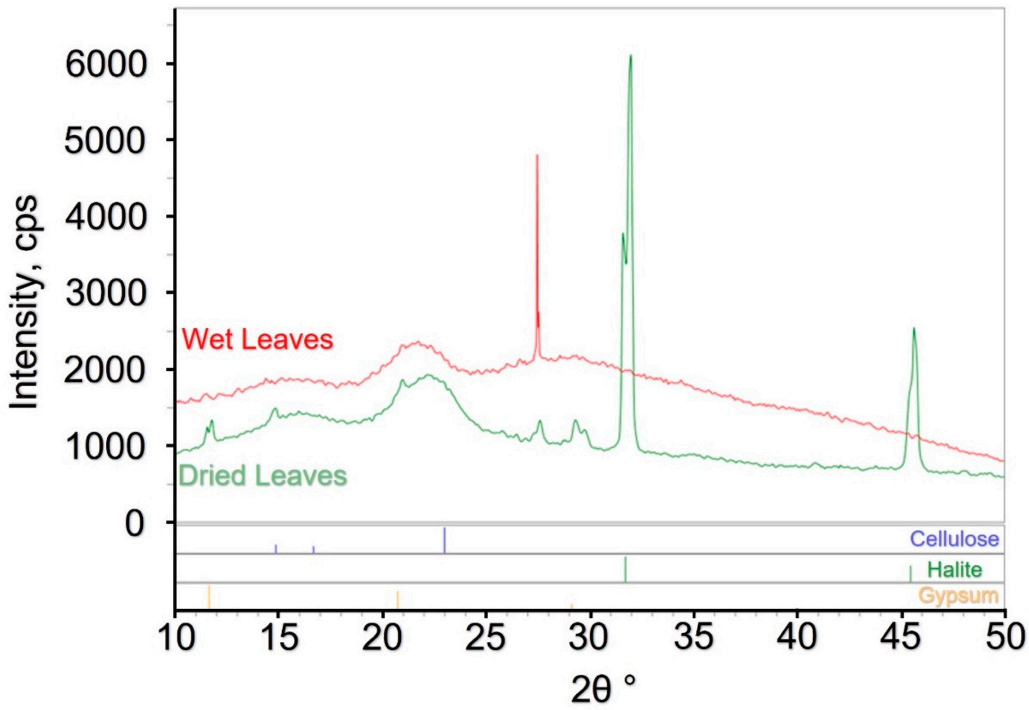

Figure 4. Automated multipurpose x-ray diffractometer (XRD, Rigaku, Smartlab) comparison of the diffractometric results (XRD).

4. Discussion

The Italian National Institute for Environmental Protection and Research (ISPRA) has carried out some projects to evaluate possible alternative solutions for the management of stranded *P. oceanica banquettes*; among the possible management projects, the measures to remove the deposited leaves are the most interesting in the specific case, since the storage area (port area in the port of Sperlonga) must be cleaned of biomass. Among the possible options considered in the ISPRA projects [26], the results obtained in this study could provide a useful basis for public and private founders to select the most promising among them and produce prototypes from leaves that can be tested in field conditions. In this way, the utilization of natural biomass waste can be improved allowing the development of a less impacting human society. Some of the potential applications considered are discussed in this study.

Medicine and phyto-cosmetics. The literature shows that many studies are performed on macroalgal biomasses to extract active molecules useful in medicine, cosmetics, and phyto-treatments [27,28]. Many lignin-rich tissues have been used to extract molecules of particular interest to the pharmaceutical industry, such as olive pressing waste [29] and chestnut hedgehog [30]. Applications in this field for *P. oceanica* leaves are reported in the ISPRA guidelines and could include potential chemicals for the treatment of diabetes mellitus and hypertension [31], extraction and marketing of natural bioactive compounds for the production of anti-cellulite products (iodine content), antioxidants, depigmentation agents, immunostimulants, anti-inflammatory agents (presence of polyphenols, including chicory acid, caffeic acid and ferulic acid), antioxidants (presence of flavonoids), and nutrients (presence of essential fatty acids and sesquiterpenes). The Marine Protected Area of the Egadi Islands has launched a project (named Egadi Cosmesi) to use the active ingredients contained in *Posidonia oceanica* collected in the Egadi Islands in cosmetics [32].

Manufacts and other products for buildings. Use of stranded *Posidonia oceanica* to produce insulating products, especially for roofs and floors, due to its thermal insulating and fireproof properties; recycling of stranded *Posidonia oceanica* together with construction and demolition waste to produce cement concrete mixes. For example, a Greek start-up company (named PHEE) has developed a new material consisting of a thin film of dead leaves of *Posidonia oceanica* and biological resins. The material is patented, high quality, lightweight, water and UV resistant. The start-up company can produce objects for various purposes and is testing the material for some interior design applications [33].

Biocomposites. These are certainly the most promising applications. Biocomposites are natural products obtained by combining different raw materials to obtain an environmentally sustainable product with excellent performance. It is a further development of composites produced according to the same principle but using synthetic matrices. Only biodegradable elements are combined, such as natural fibers with natural polymers. Although in some cases their processing requires special techniques, the use of natural fibers and polymers manages to attract the interest of the market and compete with the more traditional materials. Depending on the materials used for the combination, it is possible to obtain composites in agglomerated, fibrous, or porous form, and it is also possible to use them from recycling. Several other applications of *Posidonia oceanica* are currently being studied or tested, particularly in the form of fibers as reinforcement in composites for the manufacture of products in the supply chains for green building, textiles, and household items. Horticulture, environmental and coastal remediation, etc. In order to consider the deposition of *Posidonia oceanica* leaves as reuse and not as waste, Legislative Decree No. 75 (Circular 8838/2019) [22] provides that the concessionaire/manager may decide to deliver the organic material to recycling plants. In this case, the seagrass residues can be used as input matrix in composting or anaerobic digestion plants to produce soil improvers in accordance with Legislative Decree No. 75 [22]. In addition, the same Legislative Decree regarding fertilizers, provides for the use of algae and marine plants among the organic matrices that can be used as inputs to plants to produce soil amendments. Several projects have been or are being implemented in different regional and local contexts, which can serve as a reference for the implementation of similar initiatives in Lazio. For example, the research project carried out by the Caript Foundation, the Research Institute of Terrestrial Ecosystems of the National Research Council (CNR-Iret) and the Zelari farm in Pieve a Nievole (PT) [34] demonstrated that it is possible to recover materials considered as waste, such as dredged sediments and stranded marine plant remains, and use them as an alternative growth substrate to peat for nursery production.

Based on the results reported in the present study, it was possible to make some considerations on possible uses of considered wastes. The use of leaves for energy production by the extraction of oil to produce biodiesel is evaluated by the literature [35]. Nevertheless, performance of oil extraction from *P. oceanica* leaves and performance resulted in a low efficiency of oil extraction that do not allow a sufficient yield to develop and industrial process [35,36]. For this reason, in this study the oil extraction performance was not evaluated. The possibility of using this resource to produce cosmetics, phyto-molecules, and chemicals for medicinal applications is closely related to the presence of impurities. Indeed, any process for extracting chemicals from leaves may also contain impurities that cannot be removed in a further purification process, or only at great expense, when the process is no longer economical. To evaluate this occurrence, principal organic and inorganic pollutants are evaluated in this study. Metals and metalloids are commonly present in plant organisms that accumulate them in leaf and root structures at high levels ([37] and references cited) and could be accumulated form polluted environments [38]. Levels measured in this study increased during drying process highlighting that metals are fixed to cellulose structure and not in solution in cellular cytosol. This behavior is reported in the literature by the vegetal cells of many algal species which tend to effectively capture metal cations by biosorption fixing them to the cellulose of the wall [28]. The fact that the metals are bound to cellulose and not solubilized in the cytosol makes theoretically conceivable an extraction process of active molecules that does not also extract the metals and that produces extracts with low levels of these contaminants. Nevertheless, fresh tissues are also polluted by organic chemicals. The interesting aspect is represented by the fact that the drying process substantially reduces the organic contaminants present in the fresh tissue, as observed by levels of PAHs, PCBs and organophosphorus pesticides recorded in this study on both fresh and dried leaves. Unfortunately, the better matrix for the extraction of biomolecules of industrial and cosmetic interest is represented by fresh tissues that resulted enriched by organic pollutants. Due to the high presence of refractory substance, it is reasonable to assume that most of the chemicals detected remain adsorbed to it and that their turnover process is slow, producing low bioavailability. For these reasons, based on obtained results, the use of this resource as a vegetable compost could be evaluated. In fact, with reference to L.D. 75/2010 [22], the threshold limits of heavy metals are significantly higher than the concentrations found in the foliar debris analyzed. Nevertheless, the total content of chloride, also, highlighted by XRD measures shall be accurately consider avoiding soil salinization effects [39]. The possibility of reusing leaf biomass in situ to restore coastal dunes or feed local food webs needs to be carefully considered given the small but measurable amounts of organic contaminants that have been detected. The best matrix in this case is certainly the dehydrated leaves, which contain fewer organic compounds than the fresh leaves. However, the metal content could lead to local accumulation of contaminants after the organic matter of the leaves has been fully mineralized in sediments at the site where they were buried due to the affinity of both metals and metalloids to sedimentary TOC and silts [10]. Phyllosilicates and TOC concentrated in clay (<2 μm) and fine silts (2–20 μm); due to their chemical affinity metals and metalloids tend to accumulate pollutants at high concentrations [40].

Ecotoxicological impacts resulting from potential disposal of leaves by spreading beyond 3 NM and the effect of natural leaching of leaves buried along the seashore for coastal restoration activities (dune restoration, anti-erosion barriers formation, trophic webs feedings) were carefully evaluated in this study by conducting ecotoxicological tests on the species and larval stages most exposed to the effects of toxicity both using unfiltered elutriates (simulating shadowing effect on phytoplankton communities of floating leaves) and filtered elutriates of both fresh and dried leaves. Floating leaves produce a shading effect that may affect phytoplankton productivity. In this study, 100% growth inhibition was observed after 72 h of exposure of the tested algal cells. Even though the shading effect is rather natural and cannot be considered as an impact, it changes the discourse on the distributed quantities and the areas of the marine ecosystem affected by the shading effect of the distributed biomass. The residence time of the same at the surface of the water column should also be carefully evaluated to assess the tolerance of such type of management. About use buried leaves in coastal areas, the results reported in this study show an ecotoxicological effect on fertilization and the early developmental stages of sensitive key species of marine ecosystems [41–43]. Although negligible effects were found with fresh sample material, dried leaves showed significant effects on the species tested, likely due to chemical byproducts released from leaf debris during the drying process that strongly inhibit both fertilization and development of *P. lividus*. Results on fresh leaves also suggest that chemicals recorded in such tissues resulted not to be bioavailable.

Finally, from a mechanical point of view, the dried leaves have better performance then wet ones to form fiber part in construction aggregates or interior materials. The major cellulose crystallinity and the orientation of crystals along phloem and xylem of dried leaves improve the yield stress. The salt and sulfate compounds content determined by XRD measurements requires coupling materials that are not disturbed by calcium sulphate (gypsum) due to the calcium/silicate reaction with the lime of the cement (e.g., no reinforced concrete, yes to polymer-based mixtures). Nevertheless, the micrographs show

how the mineral phases are distributed along the inner part of leaves structural channels avoiding the contact with other components.

Since the pollutant content, nutrient values, and ecotoxicological effects are not of interest for this type of use, this could be the more appropriate and concrete way to reuse these wastes, since the cost of pretreatment or pretreatment required before use is lower.

5. Conclusions

The results of this study are important for making decisions about recycling organic waste in coastal areas. This is critical for ports and harbors where large amounts of organic matter are deposited, making dredging expansive and difficult.

Cosmetic and pharmaceutical uses are not the better solution for this type of specific waste, just as remaining in the port area has determined the accumulation of organic chemicals that could be extracted and collected into chemicals of specific interest, making the entire process difficult, expensive, and less attractive to industry. The dispersion of large amounts of *P. oceanica* leaves into the environment is verified by an experimental trial to measure the effective dispersion of measured amounts of chemical substances in the environment during the mineralization process of the organic matter. Due to the high content of refractory material, it can be assumed that most of the detected chemicals are adsorbed on this material and their turnover process is slow, resulting in low bioavailability of the pollutants.

Legislative Decree 75/2010 (reorganization and revision of regulations on fertilizers), thresholds defined for metals and metalloids are significantly higher than the concentrations recorded in this study, therefore remove chlorine, it is conceivable the use of this resource as a soil conditioner (compost).

Mechanically, the dried leaves have the optimal conditions to form the basis for construction aggregates or interior finishing materials. The chloride content present requires coupling materials that do not experience degradation of calcium sulfate (gypsum) by the reaction of calcium silicate with the lime in cement (e.g., no reinforced concrete, yes to polymer-based mixes). A pilot study should be envisaged to make an overall assessment of the feasibility of the measures and a cost-benefit estimate based on experimental results aimed at defining the best choice of different local contexts, management methods, technologies and specific skills that can be structured in production systems and circular economy.

An important future perspective for this research is the improvement of microchemical and microstructural analyses. For example, the content of salt and sulfate compounds determined by XRD measurements requires further research to reveal the rule of the cement reactions like the ettringite formation and sulfate attack.

Author Contributions: Conceptualization, M.R. and A.C.; methodology, C.G., M.L., S.A., F.P. and A.C.; validation, A.C. and C.G.; formal analysis, M.R.; investigation, S.A., F.P. and A.C.; resources, M.R. and G.L.R.; data curation, S.A. and F.P.; writing—original draft preparation, C.G.; writing—review and editing, M.R. and A.C.; supervision, project administration, funding acquisition, M.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by ASSING SpA, grant number RG05100022021.

Data Availability Statement: Original data are available on request.

Acknowledgments: Authors are grateful to Porto di Sperlonga which allowed researchers during sampling and collection of samples.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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