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A Circular Economy Model to Improve Phosphate Rock Fertiliser Using Agro-Food By-Products

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Abstract: Phosphorus (P) is an essential nutrient for the plant life cycle. The agricultural management of phosphorus is complicated by the inefficient use of phosphorus by plants, consequent environmental losses, and the rapid consumption of slowly renewed phosphate rock (PR). These issues represent a huge environmental burden and jeopardise food production. In this study, we proposed the combination of this fertiliser with food-processing by-products such as olive pomace, barley spent grain, and citrus pomace to increase phosphate rock solubility and the efficient use of P. Phosphate rock, by-products, and mixtures of phosphate rock and by-products were placed into litterbags and buried in sand. Periodically, one replicate per treatment was collected for the destructive measurement of total and water-soluble phosphorus. In parallel, pH, organic matter, and ash content were measured to investigate the mechanisms behind changes in P content. The mixtures' P-release values ranged between 80% and 88%, whereas phosphate rock lost 23% of its P over 30 days. Phosphate rock showed a constant water-soluble P fraction at the four sampling times, whereas the mixtures exhibited a highly water-soluble P fraction that tended to decrease over time. Specifically, citrus pomace led to the significant and rapid release of phosphorus, barley spent grain maintained the highest water-soluble fraction over 30 days, and olive pomace was not the best-performing product but still performed better than pure phosphate rock. Moreover, the increased solubility of phosphate rock in mixtures was significantly ($p < 0.001$) ascribed to the reduction in pH. The results of this experiment are promising for in vivo trials and suggest the possibility of simple and easily achievable solutions for more sustainable production systems and effective P-fertilisation strategies. Proposing such easily applicable and inexpensive solutions can reduce the distance between research achievements and field applications.

Keywords: crop nutrition; organic farming; sustainable agriculture; circular economy; agro-food by-products

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1. Introduction

Although soil may have a high total P concentration, it is barely available because of the ease of formation of insoluble complexes with cations [1]. This makes P the least accessible macronutrient and one of the most deficient nutrients in agricultural soil [2].

Following Liebig's law of the minimum, which has been validated by various experiments [3–6], insufficiency of P in soils becomes a limiting factor for crops in terms of their ability to exploit other nutrients efficiently and to attain optimised growth. To increase yields, overcome P deficiency, and compensate for the retrogradation phenomenon, farmers in the past century have tended to overuse fertilisers [7], causing damage to natural ecosystems [8–10]. Only a small portion of the P used in agriculture is efficiently used for food production, while the rest contributes to eutrophication. Most of the current efforts towards reversing this trend focus on the recovery of P contained in plant residues and the reduction of run-off [11]. A new line of research has successfully explored the potential of chemical strategies to increase phosphorus use efficiency, for example through the use of humic–metal–phosphate acid complexes [12,13]. However, these strategies are not yet available for organic agriculture. In this context, there is a shortage of work and research on increasing the efficient use of available P resources.

For decades now, the most widely used P fertiliser has been phosphate rock, due to its relatively low cost [2,14,15]. Although this resource is renewable, the speed with which it is being consumed is leading to its depletion, and the dominance of a one-way model of use is leading to P accumulation in the environment and an additional burden for ecosystems [16].

To counter the existential challenges that humans are facing, e.g., climate change, resource depletion, and population increases [17], these agricultural trends need to change [18,19]. Sustainable agriculture is an effective alternative to intensification for adaptation to climate change and the improvement of farms' ecosystem services [20]. In particular, sustainable practices in crop nutrition require the integration of traditional and scientific knowledge to innovate [21] and minimise pressures on natural resources without compromising yields and food security.

In this context, numerous co-application techniques have been proposed in the literature, such as the addition of biomasses [22–25], microorganisms [26–28], and inorganic substances to agricultural soils [29–32]. However, many of the proposed solutions are complex and expensive, limiting their practical application at the field level.

In addition to the development of specific mechanisms of action, all these proposed techniques have resulted in higher phosphate rock solubility due to pH reduction [33,34]. Basically, in this experiment, we hypothesise that the acidifying action is due to the waste biomasses' specific action.

On the other hand, following a circular economy model, acidification can be triggered by using waste products and by-products from the agro-food industry, which can lead to the solubilisation of phosphate rock through the direct release of organic acids, the loss of protons, or the production of CO_2 during the decomposition process.

The concept of the circular economy appeared first in Kneese [35] and soon after in Pearce and Turner [36] to describe an economy which turns production waste into inputs. A decade later, after several market events that occurred between 2000 and 2010, the notion began appearing in the industrial and environmental policies of China, Europe, and the United States of America, consecutively [37–39], associated with the aim of minimising dependence on natural resources, decreasing waste, and reducing the life-cycle emissions of economies.

In agriculture, the circular economy model was first promoted in the European action plans and strategies proposed by the European Commission under the EU Green Deal initiative (https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en (accessed on 15 October 2022)). Within this framework, the innovative use of cheap and accessible agro-food waste with no valuable alternative reuse pathway can contribute to the valorisation and sustainable transformation of agriculture with low carbon costs [40].

Therefore, in this study, in contrast to the available literature exploring more expensive co-application methods, we aimed to carry out the co-application of agro-food by-products in an incubation experiment to evaluate their performance in increasing phosphate rock solubility, and to identify the best by-product and the best mixture rate. To this end, we selected three food-processing by-products based on their availability and their chemical characteristics [41]. Agro-food by-products (more generally, waste biomasses) are locally produced, easily available, and often represent a cost due to the need for their disposal. Their valorisation for the fertiliser sector would increase the latter's circularity and contribute to more sustainable agricultural practices.

2. Materials and Methods

This experiment was developed in a field belonging to CIHEAM Bari (Apulia region), in Southern Italy. The incubation of pots was carried out in 2019 during the month of June.

The climate was typically Mediterranean, with a monthly average temperature above 25 °C and the absence of precipitation [42].

All the by-products were locally collected and are representative of the waste biomasses produced during food transformation in the Mediterranean basin. The selected by-products were citrus pomace (C), olive pomace (O), and barley spent grain (B) collected from local transformation sectors. The by-products were placed in a greenhouse until they were completely air-dried and they were ground before their chemical characterisation. They were then brought to the laboratory for the determination of their pH and organic matter and ash contents, as well as their total and water-soluble phosphorus contents. The by-products' chemical characteristics are presented in Table 1.

Table 1. Chemical characteristics of air-dried and ground brewer's spent grain (B), citrus pomace (C), and olive pomace (O).

		B	**C**	**O**
pH	H_2O	5.3 ± 0.1	3.4 ± 0.1	5.5 ± 0.1
Organic Matter	%	96.0 ± 0.1	89.0 ± 0.2	94.0 ± 0.2
Ash	%	4.2 ± 0.1	11.2 ± 0.2	6.2 ± 0.1
Total P	g/kg	12.8 ± 0.4	64.6 ± 5.7	6.3 ± 0.6

The phosphate rock used in this study was provided by TIMAC AGRO Italia (Pheosol line–Fosfonature 26) and was a soft natural rock containing 26% P_2O_5. This commercial product was analysed in terms of its pH, exhibiting a pH of 6.2 ± 0.1.

After chemical characterisation, sand was used to incubate the litterbags containing different treatments. The sand had a slightly alkaline pH (7.9) and low available phosphorus (<6 mg/kg).

The treatments in the litterbags were designated as PR, containing 15 g of phosphate rock; B, C, and O, containing 45 g of each by-product separately; and their mixtures, BPR, CPR, and OPR, with 15 g of phosphate rock and 45 g of each by-product. Three litterbags per treatment were then buried in pots containing only sand, and four pots per treatment were arranged and left in an open field for a total of 30 days. Every 10 days (T1, T2, T3) one litterbag per pot was collected for the destructive analysis of dry weight, pH, organic matter, total P, and water-soluble P. The first chemical analysis (T0) was performed on treatments that had not been incubated. The above-cited parameters were analysed, while the total P was calculated based on the sum of total P contained in the elements included in the treatment.

As for the characterisation of by-products and PR, the pH in the water was measured with a 3:50 w:v ratio and that of organic matter was determined through dry combustion at 550 °C [43]. Total phosphorus was measured colourimetrically after the acid digestion of samples, whereas water-soluble P was quantified colourimetrically from water sample extracts at 1:100 w:v [44].

Data processing was carried out through analysis of variance, and the significance of differences was identified using Fisher's least significant difference (LSD) test at a 5% probability level among treatments. In graphs, the means with significant differences ($p \leq 0.05$) are labelled with different letters, whereas values with no significant differences are not labelled.

3. Results

The pH of the PR treatment did not change across the four observations (from T0 to T3). On the other hand, the other treatments underwent some modifications over time, with few differences between by-products and by-products with phosphate rock (Figure 1). B and BPR exhibited pH values of approximately 5.3 at T0 and 6.7 at T3, C and CPR had values of approximately 3.4 at T0 and 6.1 at T3, and O and OPR had values of approximately 5.5 at T0 and 6.0 at T3. Treatments containing barley spent grain and olive pomace had already reached a pH of 6.0 at the first collection of litterbags (T1), whereas treatments containing citrus pomace only reached a pH value of 6.0 after twenty days (T2).

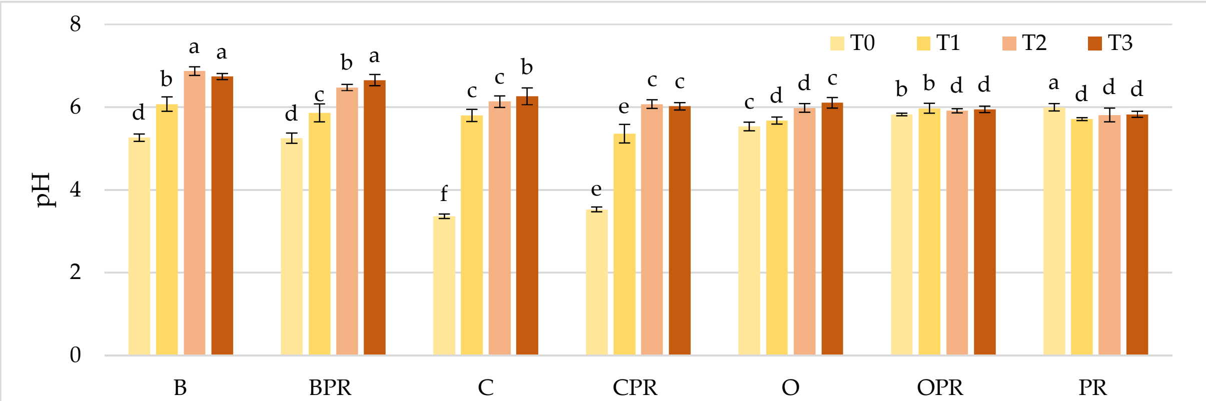

Figure 1. Changes in pH values of different treatments over 30 days. pH values of treatments were compared statistically across the four sampling times, and data with different letters indicate significant differences ($p \leq 0.05$).

Figure 2 shows through a bar graph the organic matter (OM, g) and ash content (Ash, g) per litterbag at each sampling time and, additionally, the trends of weight loss (WL, %). In all treatments, organic matter decreased significantly, whereas ash content did not differ over time. Moreover, the ash content was clearly different between by-products and by-products with phosphate rock. Comparing each by-product and the same by-product with the addition of phosphate rock, the reduction in organic matter content was similar. The only difference was observed in T1 and T2 in the case of the barley spent grain treatments, with BPR having a slightly higher organic matter content than B, and in T2 and T3 in the case of the citrus pomace treatments, which revealed a higher organic matter content in C than in CPR.

In contrast to the reduction in organic matter, the weight loss values followed upward trends. Even in this case, the trends of by-products and by-products plus phosphate rock were similar, with the only significant differences observed in the citrus pomace treatments. Indeed, the weight losses of CPR were constantly lower than those of C and reached 45% at the last sampling time (T3), approximately six percentage points less than C (51%).

Treatments containing only by-products exhibited lower total phosphorus values compared to their PR-added analogues (Figure 3). The PR treatment group exhibited a total phosphorus reduction of about 27 g/kg over a period of 30 days and displayed the highest total phosphorus content. Considering the total phosphorus losses, PR had the lowest loss (23.5%), whereas C had the highest (98.4%); treatments O and B had losses of approximately 80–85%; CPR had a loss of about 70%; and BPR and OPR exhibited losses of approximately 27–30%. Among the by-products, the greatest losses occurred during the first 10 days, with the highest reduction observed for C (96%). In contrast, in the PR treatment group, the total phosphorus reduction was about 9% every 10 days.

Water-soluble phosphorus is a fraction of total phosphorus, and the treatments' trends are alike. Indeed, in treatments containing only by-products, the highest water-soluble phosphorus amount was detected in T0, and this remained steady across the other sampling times. With respect to PR, the highest amount of water-soluble phosphorus was measured in T0, and the solubility in water slowly and constantly decreased over time. Regarding treatments with by-products with added phosphate rock, T0 exhibited the highest water-soluble phosphorus amount, with CPR being more abundant than the others, and unvarying fractions were observed for BPR from T1 to T3. In contrast, a constant reduction in water-soluble phosphorus aliquots was visible for CPR and OPR.

Figure 2. Litterbags' organic matter and ash content (g per litterbag) and weight losses (%) for treatments coupled with common by-products. By-products alone and those with phosphate rock were compared statistically across the four sampling times. Data with different letters indicate significant differences ($p \leq 0.05$).

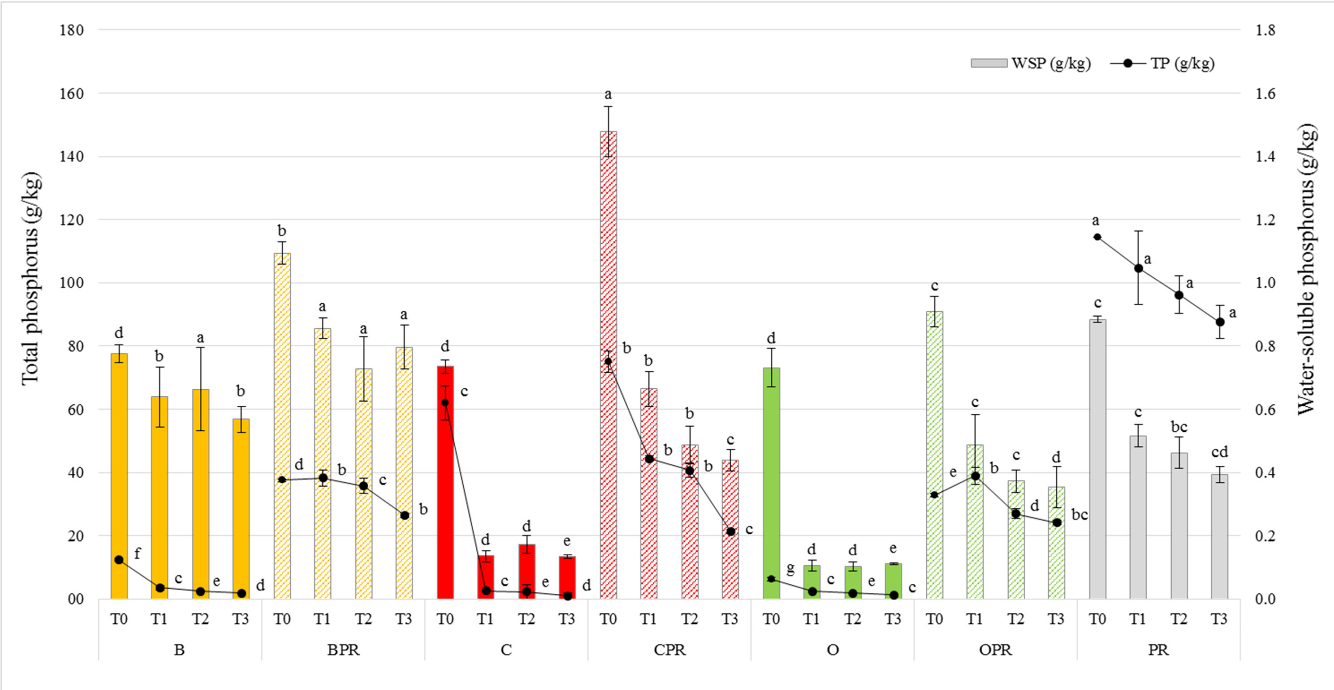

Figure 3. Total phosphorus (trends, g/kg) and water-soluble phosphorus (bars, g/kg) measured in litterbags with various treatments. Statistical comparisons among values for each sampling time were carried out, and data with different letters indicate significant differences ($p \leq 0.05$).

The high correlation coefficients of barley spent grain- and citrus pomace-based treatments indicate the significant ($p < 0.001$) impact of organic matter on pH (Figure 4). On the other hand, the coefficient of determination—which underlined a strong linear relationship in the case of barley spent grain and citrus pomace—was weaker for olive pomace ($R^2 \approx 0.2$).

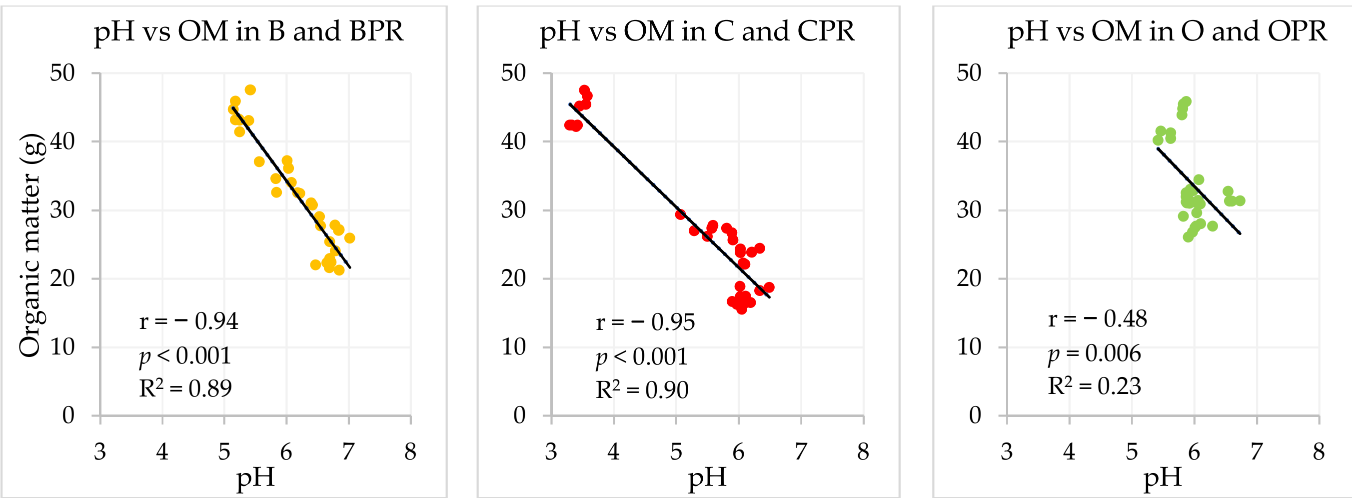

Figure 4. Correlations, significance level, and linear relationships among pH and organic matter (OM) in by-products and by-products plus phosphate rock.

Figure 5 shows that a high correlation was observed between organic matter and weight losses and a low and nonsignificant ($p > 0.001$) correlation was observed between weight losses and ash content. Moreover, the coefficient of determination for organic matter (g per litterbag) and weight loss (%) was approximately 0.8, and a weak relationship was observed for ash content (g per litterbag) and weight loss (%). On the other hand, the diagram on the right of Figure 5 (ASH vs. WL) clearly displays the separation between treatments containing only by-products (light grey circles) and by-products plus phosphate rock (dark grey circles).

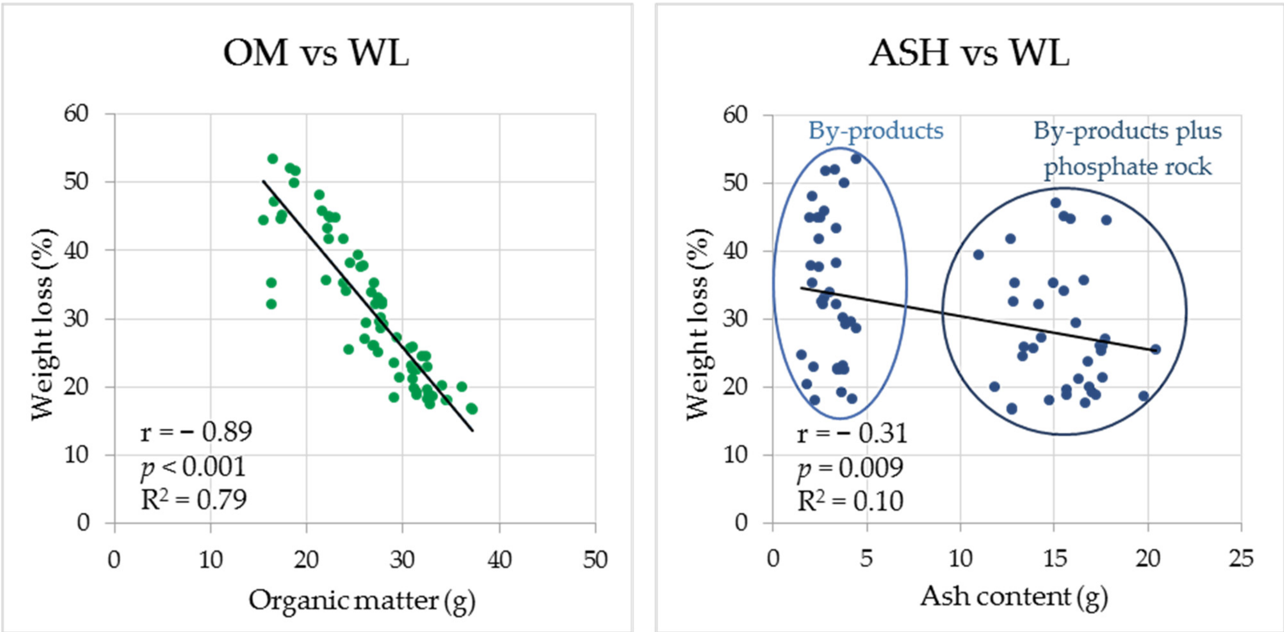

Figure 5. Correlations, significance level, and linear relationships among organic matter (OM) or ash content (ASH) and weight loss (WL).

Table 2 presents the correlation coefficient values, significance levels, and coefficients of determination related to the pH, water-soluble phosphorus (WSP), and total phosphorus (TP) values for each by-product and by-product plus phosphate rock. The pH values of olive pomace plus phosphate rock had the weakest correlation with water-soluble and total phosphorus, whereas BPR and CPR showed a high and significant correlation. The same situation was visible even in the case of coefficient of determination values.

Table 2. Correlations, significance level, and linear relationships among pH, water-soluble phosphorus (WSP), and total phosphorus (TP) for by-products plus phosphate rock.

	pH vs. WSP			**pH vs. TP**			**WSP vs. TP**		
	BPR	**CPR**	**OPR**	**BPR**	**CPR**	**OPR**	**BPR**	**CPR**	**OPR**
r	−0.85	−0.99	−0.58	−0.86	−0.97	−0.58	0.88	0.98	0.97
p	<0.001	<0.001	0.019	<0.001	<0.001	0.019	<0.001	<0.001	<0.001
R^2	0.72	0.97	0.33	0.74	0.93	0.33	0.77	0.97	0.94

4. Discussion

Considering the evolution of the pH values, the treatments that showed the most significant changes were C and CPR. Indeed, the pH varied from acidic to slightly acidic (Figure 1). This specific modification, as well as the more general reduction in acidity observed for all the by-product-based treatments, can be explained in terms of the loss of organic acids naturally present in these by-products [45,46]. The hypothesis of a reduction in acidity due to the loss of organic compounds was corroborated by the linear negative relationships among pH and organic matter shown in Figure 4 and is supported by the findings of Tumbure et al. [47].

The mutual exchange between the contents of litterbags and sand led to a modification of the pH, which reached 6 for all treatments after 30 days. This change was guided by the loss of mass, mostly organic matter (Figure 2) and subsequent weight losses. According to Zukswert and Prescott [48] the biggest reduction in mass occurred in the earliest days, and this happened even in our case, in which the angular coefficients were higher in the interval between T0 and T1 for all the considered treatments (Figure 2). Moreover, the mass loss was mostly ascribable to the organic matter, whereas ash content did not vary over time in any treatments. The treatments that lost the least weight were O and OPR, and this result was consistent with the slight modifications of pH observed for these groups, and this could be due to the high lignin content in olive pomace. Lignin is present in olive pomace [49] and, together with cellulose and hemicellulose, is one of the main compounds of this food-processing by-product. Additionally, this compound is recalcitrant to thermal and physicochemical degradation [50,51], and only a few specific microbial strains can decompose it [52]. In contrast, barley spent grain and citrus pomace treatments exhibited organic matter losses and thus weight losses of about 40% and 50%, respectively. These mass losses could be due to the permeability of the litterbags' tissue [53] and to the interaction of the by-products with external surrounding factors. Indeed, barley spent grain and citrus pomace both exhibit steady interaction with microbial communities—a direct link in the case of barley spent grain because of naturalised microbial charge [54], as well as an indirect connection through the richness in molecules that are attractive for microorganisms [55]. Nevertheless, even in the case of barley spent grain and citrus pomace treatments, there was a consistency in terms of the wide modification in pH values and organic matter reductions, thus supporting the hypothesis of the loss of organic acids.

The modification in terms of weight loss in the PR treatments was negligible and thus is not reported in Figure 2; for all the other treatments, most of the mass losses were organic, and there was a good fit between weight loss and organic matter, with an r-value of approximately 0.9 (Figure 5, left). On the other hand, the correlation of ash content and weight loss was small, and treatments were well distributed over the *Y*-axis and separated on the *X*-axis according to the addition of phosphate rock to by-products. These diagrams together support what was already underlined in Figure 2 regarding the limited losses of ash in comparison with the notable decreases in organic matter content. According to Prescott and Vesterdal [56], the decomposition of plant biomass and its transformation can follow several pathways that depend on external and site-specific conditions. In environments with low amounts of natural organic matter and poor biological activities, such as sand, the decomposition of labile organic matter is fostered by an emphasised priming effect [57]. On the other hand, summer temperatures can play a crucial role in organic matter decomposition. Indeed, Pérez et al. [58] found that after four months, the biomass weight of litterbags decreased by about 2% and that leaf litter decomposition was slower in winter than in the hotter seasons.

Total phosphorus was lower in treatments containing a single by-product; only the C treatment had a high total phosphorus content, but this was mostly labile and was lost during the first 10 days (Figure 3). It is important to underline that the higher level of total phosphorus in OPR at T1 compared to T0 can be justified by the relative loss in organic matter during the first 10 days (already shown in Figure 2). In turn, this led to a reduction in the total mass of the litterbags that did not correspond to a related and coherent loss of phosphorus, with a consequently slowed release in the absence of additives such as microorganisms [59]. On the other hand, by-products plus phosphate rock had high initial total phosphorus contents, and, at T3, BPR had lost 27% of its total phosphorus, and OPR and CPR had lost 30% and 70%, respectively. On the other hand, PR lost about 24% of its initial total phosphorus over 30 days, thus suggesting a good performance of all the mixtures in increasing the solubility of phosphate rock. Relatedly, several studies have documented the adoption of different strategies or practices for increasing phosphate rock solubility, such as the addition of zeolite and pillared clay [31], nanoparticles [32], a combination with acid mine waste [29], co-composting [22], a combination with green waste [23], co-application with manure [24] or other amendments [25], and enrichment with microorganisms [27,28]. The effects of all these strategies were directly or indirectly ascribable to acidifying effects. Indeed, phosphate rock efficacy is higher under acidic conditions, and even artificial combination with an organic acid increases phosphorus solubility [60].

The crucial role of pH in increasing the solubility of phosphorus from phosphate rock was corroborated by the high correlation between pH and TP (Table 2). Moreover, pH significantly ($p < 0.001$) affected WSP, especially in the case of BPR and CPR (Table 2), in which a progressive reduction in pH corresponded to a higher water-soluble fraction. Water-soluble phosphorus dynamics over 30 days mirrored the total phosphorus trends, as underlined by the high positive correlation between TP and WSP shown in Table 2. Despite TP and WSP's high correlation, it is important to highlight that the water-soluble fraction indicates phosphorus that is rapidly available. Therefore, its evaluation, as well as the maintenance of an adequate WSP supply, is crucial for the use of these mixtures in soil–plant systems [61]. In this sense, PR maintained a constant and adequate water-soluble phosphorus fraction. On the other hand, CPR showed the highest phosphorus release from the preparation of the mixture. Moreover, BPR showed a constantly higher WSP over the 30 days. The knowledge regarding these BPR and CPR behaviours can be exploited for the programming of a fertilisation plan in order to tailor phosphorus release to the needs of crops. In contrast, the WSP of OPR was close to that of PR. This result, together with the TP values, suggests that most of the solubilising action occurred in the first 10 days, in which there was a high release of phosphorus.

The results of this experiment confirm the role of pH in increasing the solubility of phosphate rock and underline the potential uses of by-products in combination with this fertiliser and as a substitute for more complex technologies, strategies, and products. The findings contribute to the achievement of more sustainable management of phosphate rock [62] and phosphorus flow [63], and the valorisation of waste biomasses through soil incorporation [64].

At a global level, there is an urgent need to reduce the distance between scientific research achievements and applications [11], but this transfer of knowledge can only be fostered if the proposed solutions are easily applicable and inexpensive; the present work meets these requirements.

5. Conclusions

In this study, we evaluated the combination of phosphate rock with three widely available food-processing by-products at the benchmark level with the aim of increasing the solubility of phosphate rock and the consequent phosphorus release for crop nutrition.

In a simplified environment consisting of litterbags incubated in sand, all the selected by-products showed a high capacity for solubilisation of phosphate rock. The weight losses in litterbags containing only by-products and by-products combined with phosphate rock were mainly caused by losses of organic matter. Two out of three by-products showed a high correlation between pH and organic matter content. Moreover, pH was positively correlated with total phosphorus and water-soluble phosphorus in the litterbags containing mixtures. The combination of phosphate rock with the considered by-products resulted in more solubilised phosphorus than phosphate rock alone after 30 days, and barley spent grain and citrus pomace seemed to be the most promising by-products for field use due to the high correlations observed between pH and total phosphorus.

Indeed, citrus pomace had a high natural phosphorus content and, combined with phosphate rock, produced a great and rapid release of phosphorus (within 10 days). In contrast, barley spent grain maintained the highest water-soluble phosphorus content over the entire experiment. Nevertheless, olive pomace combined with phosphate rock still exhibited better performance than phosphate rock alone, even though the mechanisms of phosphorus solubilisation were not strictly ascribable to pH. Beyond the performances of the single by-products, this study demonstrated the in vitro efficacy of products that must be valorised and that can contribute to strengthening soil organic matter. In addition, the more efficient use of phosphate rock will reduce the squandering of this fertiliser and the related problem of eutrophication. The advantage of this combination is its simplicity and affordability, which can make its practical application more easily adaptable for farm use. In turn, agricultural practices such as this one can be spread widely in order to foster agricultural sustainability.

The limitations of this experimental set-up include the use of a single ratio of partitioning, the limited types of biomasses used, and lack of evidence regarding the mixtures' performances in soil–plant systems. Indeed, this study is the first step towards more complex work which could lead to the development of innovative products for agriculture. The results support the fulfilment of the EU and UN policies aiming towards a more circular agro-food sector and sustainable agriculture.

In this context, the results illustrated in this research add to the scientific literature by highlighting promising by-products for valorisation in crop nutrition, and they should also motivate the scientific community to find simple, easily achievable, scalable, and cheap solutions to support farmers in transitioning to more sustainable production systems. The industrial sector could also build on these results and conduct pre-industrial research to explore the normative, technical, and environmental aspects of incorporating these by-products efficiently into the production process. The benefits extend to the agricultural sector, which needs to innovate to increase nutrient use efficiency, especially in organic agriculture. The outcomes of this study represent the first step in a broader project to explore other potential by-products from local agro-food industries and to test these mixtures in more complex systems, such as soil–plant systems.

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