Long-Term Effects of the Application of Urban Waste Compost and Other Organic Amendments on Solanum tuberosum L.

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Abstract: Background: In a Mediterranean agrosystem of low productivity, a study was carried out on the effects of municipal solid waste compost (MSWC) compared to other organic and inorganic amendments on the production, quality and yield of three potato varieties (Solanum tuberosum L.) and an advanced clone. Method: Simultaneously, the agronomic and nutritional parameters of the potato crop, the degree of bioavailability and the possible risks of heavy metal contamination were studied. Results: Two stages are observed in the yield and content of macro, micronutrients and heavy metals. The addition of all amendments and especially that of urban waste compost increased potato production and the content of macronutrients, micronutrients and heavy metals in the soils of all varieties, showing a progressive accumulation in tubers. Nevertheless, the performance is not maintained over time with a notable decrease during the second stage of its application. Conclusion: Highlighting the potato clone A7677 not only in its performance but also in the concentration of iron, zinc, copper, essential micronutrients for human consumption and especially for populations deficient in these trace elements.

Keywords: organic amendments; composting; heavy metals; nutrients

1. Introduction

The integrated use of natural resources in the context of sustainable development should be considered, and for that purpose soil management will have a pivotal role in the improvement of agri-food production without compromising soil(s) fertility [1,2]. Agronomical practices have been directed in the last decades to the exploitation of existing resources in order to obtain maximum productivity, with relevant environmental consequences because of the applications of large amounts of agrochemicals and pesticides, decreasing soil biodiversity and fertility [3]. The agricultural use of residues, from cattle of urban origin, in the form of compost could be considered as an alternative that allows the minimization of waste generation by human activities and improves soil(s) fertility.

Nevertheless, the application of organic amendments may have additional potential risks on the environment, derived from its effects on the trophic chains, which are linked to their possible toxicity and persistence in ecosystems. One of the most relevant problems of the applications of compost for agronomical purposes stands on the possible accumulation of heavy metals in the plant tissues by absorption, thus leading to the possibility of being bioavailable to humans and animals.
through its consumption. The chemical forms in which they are found in the organic amendments and their evolution over time once incorporated into the soil will be determinant for metals in plant for the mobility of these pollutants and their degree of assimilation by the crops.

The potato (*Solanum tuberosum* L.) is the third most important food crop worldwide, after rice and wheat [4]. The potato is one of the crops that produce more food per unit of time, water and area, even in more adverse climates in comparison with any other crop. It is also characterized by its extraordinary ability to adapt to different soil and climate conditions, occupying a leading role in the global food chain, and thus being considered by the United Nations Food and Agriculture Organization (FAO) as a food security crop. Likewise, the increase in world population leads to uncertainties in the food supply chain [2,5] and it shows the need for high-yield crops [1,6]. For this purpose, the potato should be marked as one of the crops with greater genetic diversity, with the Germplasm Bank of the International Centre of the Potato (IPC) in Lima (Peru) including more than 7000 accessions of native, wild and improved potato varieties. Therefore, the need for developing new potato varieties with greater nutritional value and durable resistance to diseases is of global importance.

According to the FAO, it is estimated that around 792.5 million people across the world are malnourished, out of which 780 million people live in developing countries [7]. In transitional countries, stunting (shortness for age) and micronutrient deficiencies (iron, vitamin A, and zinc) in children coexist with obesity and nutrition-related chronic diseases (NRCDs), demonstrating the double burden of nutritional disease [8]. The various strands of malnutrition—undernutrition, hidden hunger and overweight—are interwoven in many ways, and there is a triple burden of malnutrition in growing numbers of countries and communities [9]. Biofortification of potatoes would not only increase the nutrient content in the potato, but also their bioavailability, offering a long-term sustainable solution to provide micronutrient-rich crops to people at nutritional risk.

The main objective of breeding programs is to increase productivity by increasing yields, considering that micronutrients deficit is the most widespread nutritional problem in the world today [10]. For this purpose, selecting progenies with resistance to diseases, plant height, and biomass increase, and harvest index has been studied. However, the nutritional composition, especially of micronutrients, was often overlooked. Therefore, it is important to obtain clones, which are not only capable of high yields with resistance to pests and diseases, but also can develop varieties with greater nutritional value, and are more efficient in the absorption of nutrients.

There are few long-term field studies on the effects of the use of municipal solid waste compost (MSWC) in the production and possible contamination by heavy metals in potato cultivation. The main hypothesis considered in this work is that the application of MSWC for potato production should have a relevant effect on the micronutrient content of this crop, thus affecting its effects on human consumption. Therefore, the objective of the long-term field study reported in this work was to explore the use of MSWC as a source of nutrients, comparing it with other organic and inorganic amendments in the production, quality and yield of three potato varieties (*Solanum tuberosum* L.) and an advanced clone on a low productivity Mediterranean agrosystem, determining the agronomic and nutritional parameters of the potato crop, as well as the degree of bioavailability and the possible risks of contamination of heavy metals.

2. Materials and Methods

2.1. Site, Soil and Climate

The long-term study was carried out between 1998 and 2016 on an experimental farm in Tobar (Burgos, Spain) (Figure 1). Tobar shows a continentalized subarid Mediterranean climate, with an average annual rainfall of 639 mm and an average annual temperature between 10.3 and 14 °C. The hottest months (July and August) show average temperatures of 18.6 and 19.1 °C, respectively. The average altitude is 910 m and its geographical coordinates are 42° 29’ 01” North latitude and 3° 56’ 18” West longitude. The soil was characterized as *Typic Calciusteps* [11]. The main soil characteristics are reported in Table 1.
Figure 1. Flow diagram of the experimental field study.

Table 1. Main analytical characteristics of the soil used in this study.

| Physicochemical Properties                   | Soil          |
|----------------------------------------------|---------------|
| Texture (USDA) [12]                          | Loam          |
| Sand (g kg⁻¹DW)                              | 380           |
| Silt (g kg⁻¹DW)                              | 420           |
| Clay (g kg⁻¹DW)                              | 200           |
| Carbonates (g kg⁻¹DW))                       | 101           |
| pH (H₂O)                                     | 7.4           |
| Electrical Conductivity (dS m⁻¹)             | 0.3           |
| Nitrogen (g kg⁻¹DW)                          | 0.9           |
| Organic matter (g kg⁻¹DW)                    | 18.0          |
| Total organic carbon (g kg⁻¹DW)              | 10.4          |
| Cation Exchange Capacity (cmol(+)kg⁻¹)       | 23.0          |

Assimilable macronutrients (mg kg⁻¹DW)

| Nutrient   | Amount (mg kg⁻¹DW) |
|------------|--------------------|
| Phosphorus | 54                 |
| Potassium  | 888                |
| Calcium    | 1830               |
| Magnesium  | 130                |
| Sodium     | 14                 |

Heavy Metals (mg kg⁻¹DW)

| Metal    | Amount (mg kg⁻¹DW) |
|----------|--------------------|
| Iron     | 4860               |
| Manganese| 48                 |
| Zinc     | 10                 |
| Copper   | 3                  |
| Lead     | 3                  |
| Cadmium  | <0.2               |
| Chromium | 4                  |
| Nickel   | 3                  |
2.2. Vegetal Material and Organic Waste Composts

The varieties Agria, Monalisa and Jaerla of *Solanum tuberosum* subspecies *tuberosum* (Ststub) were selected for this study as well as the advanced clone A7677, which came from the crossing of two subspecies Ststub and *Solanum tuberosum* subspecies *andigenum* (Stsand), Table 2. Their selection was done according to production, stability, yield, commercial caliber, shape and size of the tuber, and resistance to the most common potato diseases. The applied MSWC came from the Valdemingomez Urban Waste Treatment Plant (Madrid) and the Villarrasa recycling plant (Huelva), and the different fertilizers and plant residues were provided by local poultry and livestock farms.

Table 2. Species involved and country of origin of four potato tetraploid parents (2n = 4x = 48).

| Variety/Clone | Pedigree              | Species Involved       | Country of Origin |
|---------------|-----------------------|------------------------|-------------------|
| Agria         | Quarta × Semlo         | Ststub × Ststub        | Germany           |
| Jaerla        | Sirtema × MPI 19268    | Ststub × Ststub        | Holland           |
| Monalisa      | Bierma A 1-287 × Colmo | Ststub × Ststub        | Netherlands       |
| Clone A7677   | Aphrodite × IPC ICA    | Ststub × Stsand (Stsand × PL) | Holland-Peru (IPC) |

Abbreviations: *Solanum tuberosum* subsp. *tuberosum* (Ststub); *Solanum tuberosum* subsp. *andigenum* (Stsand); PL: free pollination. IPC: International Potato Center.

The applied organic composites were prepared in the spring of the year prior to sowing, (1–7 April). For that, 16 composting pits were used, according to the modified Indore method [13], divided into 4 pits, for each of the materials to be composted. For MSWC pits, one 3 × 2 × 1.5 m pit was dug where the first layer of chopped legume residues (20 cm thick) was placed. Leaving a part of the pit unfilled to facilitate the turning of the materials. The second layer of municipal solid waste was placed (10 cm thick). Four layers of legume residue (20 cm thick) alternated with 4 layers of urban waste (10 cm thick) were mixed in each well. On each layer of the residue, a layer of a stabilizing agent (calcium carbonate) was applied, uniformly distributed over the entire material (1 cm thick). The process was repeated until a stack of alternating layers was formed until it reached a height of 1.5 m. Wooden rods (10 cm in diameter) were inserted vertically into various parts of the pit. The wooden rods were removed after 3 days, which allowed adequate aeration of the material pile. In addition, on each layer was applied 30 L of water (total 120 L) and finally covered all with a thin layer of legume residue and soil.

In each of the pits, daily temperatures were recorded with geothermometers, at the same time and at different depths. Three turns of the mixture were made until the temperature dropped to 30 °C, which ensured a good supply of oxygen, homogenization and acceleration of the transformation process. The humidity of the material was maintained around 50% to 60%, until its complete maturity. After the thermophilic stage of composting (average 3 months), it could mature for seven months. The same procedure was followed for pits with the cow (CMC), chicken (ChMC) and sheep (SMC) manure. The compost obtained was taken to the field and applied to the plots before sowing or planting, according to the scheme shown in Figure 2. Characteristics of the used composts are reported in Tables 3–6.
Figure 2. Scheme of the block distribution of treatments in the field experiments.

Table 3. Main analytical characteristics of the compost obtained from the mixture of municipal solid waste with legume straw (MSWC) and applied to the soil in the years of study.

| Compost of Municipal Solid Waste with Leguminous Straw (MSWC) | 1998  | 2001  | 2004  | 2007  | 2010  | 2013  | 2016  |
|---------------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Ashes (g kg⁻¹ DW)                                             | 690.0 | 683.0 | 703.0 | 658.0 | 708.0 | 711.0 | 698.0 |
| pH (H₂O)                                                     | 7.0   | 6.9   | 7.1   | 7.1   | 7.3   | 8.3   | 7.1   |
| Electrical conductivity (dS m⁻¹)                             | 2.8   | 2.3   | 1.4   | 2.1   | 2.3   | 2.9   | 2.1   |
| Nitrogen (g kg⁻¹ DW)                                         | 18.9  | 19.3  | 21.3  | 29.6  | 18.7  | 18.4  | 21.9  |
| Total organic carbon (g kg⁻¹ DW)                             | 170.0 | 154.0 | 194.0 | 210.0 | 177.0 | 147.0 | 211.0 |
| Carbon/Nitrogen ratio                                        | 8.9   | 7.9   | 9.1   | 9.0   | 9.4   | 7.9   | 9.6   |
| Total macronutrient (g kg⁻¹ DW)                              |       |       |       |       |       |       |       |
| Phosphorus                                                   | 9.7   | 9.3   | 9.8   | 7.9   | 6.8   | 6.4   | 10.1  |
| Potassium                                                    | 16.9  | 20.1  | 17.9  | 18.8  | 6.3   | 4.1   | 6.6   |
| Calcium                                                      | 46.4  | 48.6  | 44.4  | 73.6  | 71.6  | 68.4  | 73.3  |
| Magnesium                                                    | 1.8   | 1.7   | 1.3   | 3.4   | 3.8   | 4.3   | 4.4   |
| Sodium                                                       | 3.1   | 2.6   | 0.8   | 1.3   | 1.1   | 0.7   | 0.8   |
| Heavy Metals (mg kg⁻¹ DW)                                    |       |       |       |       |       |       |       |
| Iron                                                         | 14787 | 13361 | 9874  | 15889 | 15448 | 15489 | 15380 |
| Manganese                                                    | 250   | 263   | 291   | 468   | 468   | 353   | 306   | 474   |
| Zinc                                                         | 718   | 694   | 706   | 203   | 197   | 200   | 198   |
| Copper                                                       | 468   | 448   | 307   | 110   | 124   | 108   | 69    |
| Lead                                                         | 399   | 316   | 210   | 108   | 120   | 123   | 40    |
| Cadmium                                                      | 1     | <0.2  | 1     | <0.2  | <0.2  | <0.2  | 1     |
| Chromium                                                     | 136   | 128   | 213   | 76    | 63    | 68    | 66    |
| Nickel                                                       | 124   | 104   | 81    | 86    | 60    | 68    | 25    |
Table 4. Main analytical characteristics of the compost obtained from the mixture of cow manure with leguminous straw (CMC) and applied to the soil in the years of study.

| Compost of Mixed Cow Manure with Leguminous Straw (CMC) | 1998  | 2001  | 2004  | 2007  | 2010  | 2013  | 2016  |
|--------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Ashes (g kg\(^{-1}\) DW)                               | 623.0 | 687.0 | 711.0 | 740.0 | 630.0 | 780.0 | 730.0 |
| pH (H\(_2\)O)                                          | 8.3   | 8.1   | 8.0   | 8.4   | 8.1   | 8.3   | 8.0   |
| Electrical conductivity (dS m\(^{-1}\))                | 3.6   | 2.8   | 2.1   | 2.6   | 2.3   | 2.8   | 2.1   |
| Nitrogen (g kg\(^{-1}\) DW)                            | 16.4  | 16.6  | 15.3  | 14.7  | 15.6  | 18.8  | 17.9  |
| Total organic carbon (g kg\(^{-1}\) DW)                | 71.0  | 160.0 | 143.0 | 128.0 | 151.0 | 164.0 | 159.0 |
| Carbon/Nitrogen ratio                                  | 10.4  | 9.6   | 9.3   | 8.7   | 9.7   | 8.7   | 8.9   |
| Total macronutrient (g kg\(^{-1}\) DW)                 |       |       |       |       |       |       |       |
| Phosphorus                                             | 1.1   | 1.3   | 2.3   | 2.9   | 2.1   | 1.9   | 1.3   |
| Potassium                                              | 3.1   | 3.3   | 3.2   | 16.6  | 14.7  | 16.8  | 16.3  |
| Calcium                                                | 7.7   | 7.4   | 7.8   | 19.8  | 11.9  | 18.6  | 17.8  |
| Magnesium                                              | 1.1   | 1.1   | 1.2   | 3.8   | 3.3   | 3.9   | 3.6   |
| Sodium                                                 | 0.6   | 0.8   | 0.4   | 1.6   | 0.9   | 1.1   | 0.4   |
| Heavy Metals (mg kg\(^{-1}\) DW)                       |       |       |       |       |       |       |       |
| Iron                                                   | 2023  | 2827  | 1897  | 2993  | 1266  | 2446  | 2897  |
| Manganese                                              | 303   | 287   | 288   | 329   | 278   | 283   | 297   |
| Zinc                                                   | 71    | 78    | 86    | 133   | 87    | 64    | 91    |
| Copper                                                  | 144   | 193   | 213   | 64    | 66    | 68    | 63    |
| Lead                                                   | 2.7   | 11.0  | 6.0   | 7.0   | 6.3   | 4.0   | 3.3   |
| Cadmium                                                | <0.2  | <0.2  | <0.2  | <0.2  | <0.2  | <0.2  | <0.2  |
| Chromium                                               | 63    | 65    | 67    | 70    | 59    | 70    | 68    |
| Nickel                                                 | 25    | 28    | 26    | 28    | 23    | 17    | 19    |

Table 5. Main analytical characteristics of the compost obtained from the mixture of chicken manure with leguminous straw (ChMC) and applied to the soil in the years of study.

| Compost of Mixed Chicken Manure with Leguminous Straw (ChMC) | 1998  | 2001  | 2004  | 2007  | 2010  | 2013  | 2016  |
|-------------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Ashes (g kg\(^{-1}\) DW)                                   | 628.0 | 630.0 | 713.0 | 729.0 | 698.0 | 741.0 | 736   |
| pH (H\(_2\)O)                                              | 6.8   | 6.7   | 6.4   | 6.9   | 6.8   | 6.7   | 6.3   |
| Electrical conductivity (dS m\(^{-1}\))                    | 2.7   | 2.8   | 2.3   | 3.8   | 2.3   | 2.8   | 2.1   |
| Nitrogen (g kg\(^{-1}\) DW)                                | 17.4  | 20.4  | 29.6  | 38.9  | 28.4  | 33.6  | 38.6  |
| Total organic carbon (g kg\(^{-1}\) DW)                    | 184.0 | 178.0 | 287.0 | 331.0 | 231.7 | 291.3 | 329.4 |
| Carbon/Nitrogen ratio                                      | 10.6  | 8.6   | 9.7   | 8.5   | 8.2   | 8.7   | 9.8   |
| Total macronutrient (g kg\(^{-1}\) DW)                     |       |       |       |       |       |       |       |
| Phosphorus                                                | 4.1   | 3.3   | 3.8   | 6.3   | 5.1   | 4.4   | 5.8   |
| Potassium                                                 | 2.6   | 2.4   | 2.8   | 17.8  | 14.1  | 17.8  | 14.9  |
| Calcium                                                   | 3.4   | 7.6   | 6.8   | 8.7   | 6.6   | 5.1   | 6.3   |
| Magnesium                                                 | 2.9   | 2.3   | 2.8   | 3.9   | 3.1   | 2.8   | 3.6   |
| Sodium                                                    | 0.6   | 0.4   | 0.3   | 0.5   | 0.6   | 0.3   | 0.3   |
| Heavy Metals (mg kg\(^{-1}\) DW)                          |       |       |       |       |       |       |       |
| Iron                                                       | 4900  | 3871  | 4300  | 5489  | 5997  | 5857  | 5400  |
| Manganese                                                 | 267   | 294   | 290   | 324   | 291   | 336   | 343   |
| Zinc                                                       | 79    | 69    | 46    | 40    | 58    | 46    | 59    |
| Copper                                                     | 29    | 40    | 51    | 43    | 48    | 54    | 57    |
| Lead                                                       | 19    | 16    | 12    | 19    | 13    | 11    | 9     |
| Cadmium                                                    | <0.2  | <0.2  | 1.0   | <0.2  | <0.2  | <0.2  | <0.2  |
| Chromium                                                   | 33    | 36    | 31    | 34    | 38    | 43    | 47    |
| Nickel                                                     | 50    | 49    | 54    | 25    | 24    | 23    | 26    |

Table 6. Main analytical characteristics of the compost obtained from the mixture of sheep manure with leguminous straw (SMC) and applied to the soil in the years of study.
2.3. Experimental Design and Sampling

The effects of the treatments of the different composts (MSWC, ChMC, SMC, and CMC), mineral fertilizer (MF), and a control (C), without fertilizer or organic amendment, were studied on each variety of potato from 1998 to 2016. As the potato is a crop that must be planted following a crop rotation procedure, we choose to do it every 3 years. The amendments were added before planting, following the distribution scheme of the treatments (Figure 2). In the years in which the potato was not planted, crops of legumes (1999, 2002, 2005, 2008, 2011 and 2014), corn (2003, 2009 and 2015) or cruciferous (2000, 2006 and 2012) plants were used, without any amendment. The dose used for each of the organic amendments (23 t ha⁻¹) corresponds to the usual amounts of application for this crop [14].

For the plots with MF, the formula of 260-160-100 of nitrogen (N), P₂O₅ and K₂O [Phosphorus (P), Potassium (K)] was chosen. The 50% of nitrogen and all the phosphorus and potassium were applied to the planting, the rest of the nitrogen was applied at the time of hilling. The MF used was urea (46% N), simple superphosphate (18% P₂O₅) and potassium sulphate (50% K₂O, 18% S). In the plots with MF, neither organic sources nor supplemental fertilizers were used. The compost was applied between April 1st and 10th of 1998, 2001, 2004, 2007, 2010, 2013 and 2016. Drip irrigation was used. The plantations were carried out from April 10th to 14th of 1998, 2001, 2004, 2007, 2010, 2013 and 2016. The tubers were harvested manually in the two central rows of each plot 140 days after planting. Forty-eight tubers were randomly collected for the analysis of each plot and were washed with deionized water. The portions of tubers were cut into thinner slices, taking three slices from each section to obtain a sample, which was dried in an oven for 24 h at 80 °C [15]. For the organic amendments, several subsamples of the composted material were randomly taken at different depths to obtain a sample that was dried in an oven for 48 h at 60 °C.
2.4. Analytical Methods

The production of the potato crop was quantified by ton per hectare (t ha⁻¹). The content of macronutrients (nitrogen (N), phosphorus (P) and potassium (K)) in the tuber was measured as grams per kilogram of dry matter (g kg⁻¹DW), and micronutrients and heavy metals by milligrams per kilogram of dry matter (mg kg⁻¹DW). The main chemical properties of soils and compost were determined following official analysis methods [16]. The granulometry was determined by the method of Bouyoucos (1962) [17]. According to Thomas (1996), the pH was measured on mixtures of soil:water = 1:2.5 and compost:water = 1:5 [18]. The electrical conductivity was measured on a 1:5 sample: water extract [19]; total organic carbon and organic matter following the Walkley and Black method [20] and total nitrogen according to Kjeldahl, using a digester equipped with a still [21].

The total elements were determined by digestion of the dried and ground samples with a nitric–perchloric solution. That is, 1 g of sample was weighed, 12 mL of concentrated nitric acid was added. It was then heated at 180 °C in a digester for two hours. Then, it was allowed to cool, transferred to an Erlenmeyer flask, and evaporated to 1 mL in a sand bath. Then, 5 mL of concentrated perchloric acid was added and it was allowed to evaporate to dryness in the same sand bath. The residue was diluted with distilled water and filtered. The sodium (Na), potassium (K) and calcium (Ca) were measured by flame photometry (Eppendorf Lex 6361) and magnesium (Mg), phosphorus (P), iron (Fe), manganese (Mn), zinc (Zn), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni) and lead (Pb) by plasma emission spectrophotometry (Perkin Elmer ICP/-5500).

2.5. Statistical Analysis

The distribution of data was described as mean and standard deviation (SD). The differences among the six treatments by each variety of potato and sampling period were studied, using a randomized block design with 4 repetitions. The treatments were distributed randomized once in units of each block (Figure 2). For the statistical analysis of the experiments, the analysis of variance (ANOVA) was used, and the tests chosen to compare the mean of the treatments of the evaluated variables were the Duncan and Tukey tests. All statistical tests were performed using the Statistical Analysis System (SAS) SAS/STAT® 8.2 software. A p-value < 0.001 was considered as significant.

3. Results

The significant differences in the production and concentration of micronutrient studies after application of M5WC, ChMC, CMC, SMC, MF treatment and control are shown in Figures 3–13. Results show that there were two significant periods in the production of this crop and in the concentration of different micronutrients and heavy metals. The first period ranges from 1998 to 2004 and the second period range from 2007 to 2016.
Figure 3. Evolution of the yield of potato tubers varieties Agria, Monalisa, Jaerla and clone A7677 (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments \((p < 0.001)\). Bars stand for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.

Figure 4. Evolution of the nitrogen content (grams per kilogram of dry matter \((\text{g kg}^{-1} \text{DW})\)) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments \((p < 0.001)\). Bars stand for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.
Figure 5. Evolution of the phosphorus content (g kg⁻¹ DW DW) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments ($p < 0.001$). Bars stands for standard deviations MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.

Figure 6. Evolution of the potassium content (g kg⁻¹ DW DW) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments ($p < 0.001$). Bars stands for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.
Figure 7. Evolution of iron content (mg kg⁻¹DW) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments ($p < 0.001$). Bars stand for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.

Figure 8. Evolution of manganese content (mg kg⁻¹DW) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments ($p < 0.001$). Bars stand for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.
Figure 9. Evolution of zinc content (mg kg⁻¹ DW) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments (p < 0.001). Bars stand for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.

Figure 10. Evolution of copper content (mg kg⁻¹ DW) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments (p < 0.001). Bars stand for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.
Figure 11. Evolution of lead content (mg kg\textsuperscript{-1}DW) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments (p < 0.001). Bars stands for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.

Figure 12. Evolution of chromium content (mg kg\textsuperscript{-1}DW) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments (p < 0.001). Bars stands for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.
Figure 13. Evolution of nickel content (mg kg$^{-1}$DW) in potato tubers of the Agria, Monalisa, Jaerla and clone A7677 varieties (1998–2016) versus the application of compost from different organic amendments. The means with different lowercase letters within each season indicate significant differences between the treatments ($p < 0.001$). Bars stands for standard deviations. MF: mineral fertilizer; ChMC: chicken manure compost; CMC: cow manure compost; MSWC: municipal solid waste compost; SMC: sheep manure compost; C: control.

4. Discussion

The available literature on the long-term yield in potato production with different types of amendments is scarce. Therefore, this study provides, for the first time, information on MSWC as a source of nutrients, in comparison with other organic and inorganic amendments in the production, quality and yield of several potato varieties for a low productivity Mediterranean agrosystem, and the possible risks of contamination of heavy metals.

An initial assessment of results shows a significant increase in potato production with the considered treatments. In the first year, the clone A7677 (54 t ha$^{-1}$), the varieties Agria (51 t ha$^{-1}$) and Monalisa (47 t ha$^{-1}$) have significantly benefited from the MSWC (Figure 3). With the production of the clone and the Agria variety being higher than the European average (48 t ha$^{-1}$) [22]. The MSWC produced the most significant differences compared to other amendments, reaching in some cases almost triple the production of this crop. In 2004, this treatment provided the best yields in all the genotypes, in clone A7677 (71 t ha$^{-1}$), in the varieties Agria (68 t ha$^{-1}$), Monalisa (56 t ha$^{-1}$) and Jaerla (53 t ha$^{-1}$). Nevertheless, a very significant decrease was observed in 2007 campaign for the Agria (40 t ha$^{-1}$) and Monalisa (40 t ha$^{-1}$) varieties, but not in the clone A7677 (76 t ha$^{-1}$) nor in Jaerla (54 t ha$^{-1}$), whose yields increased. In 2010, a significant decline in the yields of all the varieties under MSWC treatment was distinguished in comparison to the other organic amendments, highlighting the clone A7677 whose yield was considerably reduced from 76 to 27 t ha$^{-1}$. The following treatments that provide better productions are the ChMC and the MF. The ChMC provided a second better production of potato with the clone A7677 in the years 2007 (70 t ha$^{-1}$), 2010 (71 t ha$^{-1}$) and 2016 (73 t ha$^{-1}$), followed closely by the MF (64 t ha$^{-1}$). The potato production obtained with the CMC and the SMC is in the same ranges, being higher in the varieties Agria, Monalisa and clone A7677 in the years 2007 and 2016 (43 to 47 t ha$^{-1}$).
4.1. Factors Involved in Increasing Potato Yield

Three main factors should be considered for the yield in potato production, the considered potato varieties, the physicochemical characteristics of the composts, and the edaphological characteristics of the soil. The use of wild and cultivated species as a source of resistance to biotic and abiotic stress is essential. Efficient wild species in the absorption of nutrients from *Solanum tuberosum* subspecies *andigenum*, resistant to the fungus *Phytophthora infestans* and viruses (potato virus A, potato virus X, potato virus Y) with European varieties or lines of *Solanum tuberosum* subspecies *tuberosum* with resistant genes to other types of viruses (potato leaf roll virus) were crossbreed. New clones were created and tested in 1991 in three phases [23], considering the resistance to the relevant viruses, tolerance to root-knot nematode and adaptability to arid and warm climates. Therefore, for this study, the advanced clone of potato A7677 was selected.

The chemical and physicochemical composition of the MSWC varies greatly according to the composting plant and seasonal variations. The humidity of organic amendments was less than 34%, with 40% being the maximum admissible value according to the fertilizer regulations in force in Spain. Furthermore, the CMC was moderately alkaline (pH 7.9–8.4), SMC was slightly alkaline (pH 7.1–7.8) compared to MSWC and ChMC, which are closer to neutrality. It must be emphasized that the compost had a process of washing with salts during the time of processing and storage, therefore the electrical conductivity in the MSWC was slightly saline with a range between 2 to 3 dSm⁻¹, being slightly higher in the others compost. Due to the fact that the MSW from the waste treatment plants, in the different years of study, came out with a range between moderate (4 to 8 dSm⁻¹) and strongly saline (8 to 16 dSm⁻¹), we proceeded to incorporate a greater amount of water (160 L) during the composting process with legumes, favoring the reduction in electrical conductivity, obtaining a slightly saline material (2 to 3 dSm⁻¹) comparable to that of other compost.

Despite the washes carried out, the contents in N and P in the MSWC and ChMC are higher than in the CMC and SMC, and the content in K was higher in the CMC than in the MSWC, ChMC and SMC. This may be due to the rich diet based on proteins and phospholipids of the human population. The P is a mineral that is added to many processed foods to enhance flavor, prevent discoloration, and preserve them [24]. In addition, the content of N in the ChMC is higher compared to the other compost, and we must not forget that the richness of nutrients will depend on the type of animals and their destination, the class and proportion of materials used for the litter of livestock and poultry, housing system, cleaning system, treatment and duration of storage [25].

The Carbon/Nitrogen (C/N) ratio of the materials applied as an amendment is considered as the simplest information on the mineralization capacity of organic material, since the contents of carbon and nitrogen are essential for the life and reproduction of microorganisms [26]. The C/N ratio of the different treatments at the time of their incorporation into the soil was very good with an average range of less than 10, this would indicate a very good transformation of the material with greater stability and with a good reserve of nutrients, which would allow it to be better assimilated by plants, not representing a limitation in the bioavailability of N for crops [27]. The Ca content was relatively higher in MSWC, in comparison with the other composts. The Mg and Na contents were usually lower than Ca and were slightly higher in the MSWC and the ChMC.

4.2. Effect of the Treatments on the Yield and the Mineral Content in the Tubers

4.2.1. Yield

Two stages were observed especially for the MSWC in all the varieties, and mainly clone A7677. The first stage takes place from 1998 to 2007 and is characterized especially by a sustained increase in the yield of potato production and mineral content, with a maximum observed between 2004 and 2007. While in the second stage (2007 to 2016) the yield of potato production and mineral content due to the MSWC decreases to values below the control. Regarding the application of MSWC, although the increase in performance in the first stage shows the effectiveness of the treatment, the sustained decrease in the second phase could be due to the interaction of micronutrients and heavy metals, which could affect the food security chain. In this second stage, the highest yield and mineral
content was produced mainly by the ChMC, CMC and SMC. In general, the MF presented a low yield in the potato production and in the mineral content compared to the MSWC, except in the P content exceeding ChMC in some years. The latter was the second treatment to achieve the best yields. The consecutive applications of these organic amendments have produced a remarkable increase in the content of nutrients in the tubers with respect to the control, indicating increasing availability of nutrients for crops over time. However, the content of heavy metals is worrisome since their absorption and storage in the tissues of plants can be included in the trophic chain of living beings.

4.2.2. Macronutrients

A significant increase in the content of N (43 g kg⁻¹DW), P (9 g kg⁻¹DW) and K (48 g kg⁻¹DW) in the tubers with respect to the controls is inferred. The potato crop is particularly demanding in N, P and K, its quality will depend largely on the variety and the availability of nutrients.

1. Nitrogen.

Between 1998 and 2007, the MSWC has provided the highest N content in the tubers of the varieties Agria, Monalisa and Jaerla, only exceeded by clone A7677 (43 g kg⁻¹DW). In the 1998 to 2016 period, the ChMC is the second treatment to provide a high concentration of N, remaining constant along with the experiments (Figure 4). The highest concentration of N obtained in clone A7677 by the application of MSWC from 2004 to 2007 (43 g kg⁻¹DW) largely exceeds those reported by Cabalceta et al., (2005) [28], Alvarado et al., (2009) [29], Correndo and Garcia (2012) [30], Mahamud et al (2016) [31] and Fernandes et al., 2017 (16.4–22.7 g kg⁻¹DW) [32]. The yield obtained in all the varieties under this treatment (MSWC) may be due to the improvement in the availability of this element in the soil, as a consequence of the amount of nitrogen compounds added to it and the continued mineralization of N, favoring its absorption, higher plant biomass and as a consequence higher storage of this nutrient in its tubers [33].

2. Phosphorus.

The MSWC provides the highest P content in the tubers for the 1998 to 2004 period in the varieties Agria and Monalisa and for 1998 to 2007 in the variety Jaerla and in clone A7677. For 2007 to 2016, MF and ChMC lead to the highest P contents in the tubers (Figure 5). These P contents exceed those reported in the literature by Cabalceta et al., 2005 [28] and Alvarado et al., 2009 [29], and Mahamud et al., 2016 (1.2 to 4.7 g kg⁻¹DW) [31]. The addition of the considered amendments causes decomposition processes carried out by microorganisms, which would produce certain quantities and types of organic acids, siderophores, hydroxyl ions and other compounds [34], which would facilitate the gradual conversion of phosphates and weak retention of these in the solid phase of the soil. Therefore, the increase in the P content due to the compost favored an adequate development of roots, increase in the aerial biomass, improvement in the quantity and quality of the tubers in all the varieties, which resulted in better use of this nutrient by crops, especially under the treatment with the MSWC and ChMC (2004 and 2007).

3. Potassium.

For the 1998 to 2007 period, there was an increase in the K content with MSWC for the Agria, Monalisa and Jaerla varieties, only surpassed by the clone A7677 (48 g kg⁻¹DW) (Figure 6). This K concentration exceeds those reported by Alvarado et al., 2009, Mahamud et al., 2016 [31], Jahanzad et al., 2017 [1] and Fernandes et al., 2017 (25.2–29.8 g kg⁻¹DW) [32]. Potassium is essential for the synthesis of starch and simple sugars and for the translocation of carbohydrates, thus playing a pivotal role in maintaining the vigor and efficiency of the potato plant. Along with N, P is the most necessary mineral for the growth of plants [35]. Furthermore, low K intake is associated with various non-communicable diseases, such as hypertension, cardiovascular diseases, chronic nephrolithiasis, osteopenia, etc. [36]. With the rates observed in this study, the intake of K could be increased, which
would help lower blood pressure and the risk of cardiovascular disease, improve bone mineral density and mitigate the negative consequences of consuming large amounts of sodium.

4.2.3. Micronutrients and Heavy Metals

The studied long-term treatments (1998 to 2016) show highly significant increases in micronutrient content with respect to the controls by consecutive applications of the studied composts (MSWC, ChMC, SMC, CMC and MF) when considering Fe, Mn, Zn, Cu. Additionally, relevant variations on heavy metal content (Pb, Cr and Ni) were inferred.

1. Iron

Iron deficiency represents one of the most serious problems in micronutrient nutrition in humans worldwide [37] and there is a need to increase the amount of bioavailable iron in crops such as potatoes. Values of 15 to 20 mg kg⁻¹DW are considered as a baseline for Fe in potatoes [12]. In this long-term study, for the 1998 to 2007 period, the MSWC provides the highest Fe content in the tubers of the varieties Jaerla, Monalisa and Agria, only exceeded by the clone A7677 (118 mg kg⁻¹DW) (Figure 7). The normal potato content of Fe is in the 50–250 mg kg⁻¹ DW range [38,39], being largely dependent on the considered variety. The highest concentrations of Fe reported in this work (2007) with the MSWC in the Agria variety and the clone A7677 are higher than those reported by The Food Composition Table of The US Department of Agriculture (37.754 mg kg⁻¹DW) [12]. We must bear in mind that the prevalence of anemia is higher in developing countries than in developed countries. Estimates have indicated that approximately half of this is attributed to Fe deficiency [40]. Given that Fe availability in potatoes is high (10%) [41], increasing the concentration of this micronutrient in our potato varieties (biofortification) could favor their intake in populations at risk of Fe deficiency anemia worldwide. In addition, our findings also exceed those reported by Burgos et al., [42] and Brown et al., [38] and are in the range of those by Khan et al. (2017a, 108.1 mg kgDW) [39].

2. Manganese

This element was the only one that shows an increasing trend during all the experiments, for all the treatments and varieties Agria, Jaerla and clone A7677. In the 1998 to 2016 period, MSWC provided the highest Mn content for the varieties Jaerla, Monalisa, Agria and clone A7677 (27 mg kg⁻¹DW), ChMC was the second treatment to achieve a higher Mn content in Jaerla, Agria, Monalisa and clone A7677 (19 mg kg⁻¹DW), Figure 8. These values are within the normal range (20–300 mg kg⁻¹DW) and well below the phytotoxicity limits of 500 mg kg⁻¹DW [43]. Likewise, Mn contents reported in this work exceed those by Baranowska [44], Ali and Al-Qahtani [45] and Fernandes et al. (2017, 6.7–11.5 mg kg⁻¹DW) [32]. Mn is another essential nutrient required in very small amounts in the human body [46]. However, the diet of the population based on cereals such as rice, wheat, cassava and corn contain insufficient amounts of this micronutrient [47]. Increasing the Mn content in tubers (biofortification) can help improve this insufficient intake.

3. Zinc

Another important micronutrient is this essential element because Zn deficit affects more than 30% of the world population [10]. Hence the relevance of crops that can supply Zn in greater quantities [48] such as potatoes, which contributes 2.6% and 3.2% of the daily human dietary requirements of Fe and Zn, respectively [49]. Likewise, Zn regulates the formation of ribosomes, auxins, cellular components and increases the resistance of the plant against drought and diseases [44], thus even mild deficiencies can have serious effects on the health and growth of plants. Even though the concentration of Fe and Zn in the potato is low compared to cereals and legumes, their bioavailability in potatoes may be higher due to the presence of high levels of ascorbic acid, which is a promoter of Fe absorption, and low levels of phytic acid (inhibitor) of the absorption of Fe [41,42]. In this study, for the 1998 to 2007 period there was a sustained increase in the Zn concentration in clone A7677 (34 mg kg⁻¹DW) due to MSWC treatment, leading to a high Zn concentration peak for Jaerla, Monalisa and Agria, Figure 9. These data agree with those found in 2012 by Haynes et al., [13...
to 35 mg kg\(^{-1}\)DW) [50] and André et al., [51] and are larger than those by Burgos et al., [41,42], Alvarado et al., [29], Ali and Al-Qahtani [45], and Baranowska et al. (2017, 19.79–21.34 mg kg\(^{-1}\)DW) [44]. The increase in the concentration of Zn in the tubers obtained in our study (biofortification) would favor its intake in the population at risk of deficiency of this micronutrient [52], since according to Burgos, the concentration of Zn in raw and cooked potatoes does not show significant differences due to their cooking [41].

4. Copper

A sustained increase in Cu content was observed in the 1998 to 2016 period for clone A7677 with MSWC (from 12 to 17 mg kg\(^{-1}\)DW), followed by CMC. For 1998 to 2007, MSWC treatment led to larger Cu contents for the varieties Agria, Monalisa and Jaerla. For the 2007 to 2016 period, the largest Cu content was inferred for CMC treatment with the varieties Agria, Monalisa and Jaerla, Figure 10. The available literature shows very different Cu content in crops depending on the type of soil and crop, although the normal range is 2–7 mg kg\(^{-1}\)DW for the minimum value and 20–30 mg kg\(^{-1}\)DW for the maximum value [43]. The highest concentration of Cu registered in our studies was in 2007 with MSWC for variety Agria and clone A7677. These values are higher than those reported by Correndo and Garcia in 2012 [30], Brown et al., (2014) [53], Pozzatti et al., (2017, 5.4 mg kg\(^{-1}\)DW) [54], Alvarado et al., [29], Ali and Al-Qahtani [45], and Baranowska et al. (2017, 6.23–6.58 mg kg\(^{-1}\)DW) [44]. However, our results are in the range of those obtained by Khan et al. (2017a, 11.83 to 18.03 mg kg\(^{-1}\)DW) [27]. Cu is essential for the proper function of human organs and metabolic processes [55], and Cu deficiency in humans can cause anemia that does not improve with daily intake of Fe from the diet [56]. Increasing the Cu content (biofortification) in tubers can help reduce the high level of anemia worldwide.

5. Lead

In the 1998 to 2016 period, MSWC provides the highest Pb content in the tubers of clone A7677 (6 mg kg\(^{-1}\)DW) and in the varieties Agria, Monalisa and Jaerla, observing a significant and sustained increase. However, in 2010 there was a reduction in the Pb content of 20% in the Agria variety and of 42% in the varieties Monalisa, Jaerla and clone A7677 with respect to 2007. This could be due to several factors, among which we have to take into account the absorption of this element in previous crops (legumes and corn); the organic matter that can increase or decrease the solubility of Pb, depending on its degree of polymerization and soil conditions, cation exchange capacity, pH, interaction with other bioavailable micronutrients and lead content in MSWCs. Pb concentrations compared to our controls increase with all treatments, leading to slightly larger values for SMC and ChMC than for CMC, Figure 11. These values were maintained until the end of our study, being within the range considered normal (5–10 mg kg\(^{-1}\)DW) and well below phytotoxicity levels (30–300 mg kg\(^{-1}\)DW) [43]. The reported results are comparable to those obtained by Ali and Al-Qahtani (2012, 1.51 to 6.19 mg kg\(^{-1}\)DW) [45] in a heavy metal biomonitoring study and with those found in crops of potatoes exposed to irrigation by wastewater contaminated with Pb [39]. On the contrary, they were below those obtained by Tadesse et al., in 2015 [57], Jalali and Meyari in 2016 (19.5 mg kg\(^{-1}\)DW) [58] and Angelova et al. (50 to 54 mg kg\(^{-1}\)DW [59]. It should be remarked that Pb is not necessary for plants and can accumulate affecting different physiological and biochemical functions [60]. Even though the Pb content in our study was not in phytotoxicity ranges, we must consider that the increase in the bioavailable content of Pb could be due to the continuous applications of the different amendments used throughout the study, which was giving us a product with a high content of lead, not suitable for human consumption (0.1 mg kg\(^{-1}\)) [61].

6. Chromium

There was a sustained increase in the Cr content for the 1998 to 2007 period for all the varieties, leading to the highest concentration with MSWC treatment for clone A7677 (20 mg kg\(^{-1}\)DW) and in the varieties Agria, Monalisa and Jaerla. For 2007 to 2016, CMC treatment led to the highest Cr contents in clone A7677 (16 mg kg\(^{-1}\)DW) and the varieties Monalisa, Agria and Jaerla (Figure 12). These values exceed the level considered as normal (0.03–14 mg kg\(^{-1}\)DW), going into the
phytotoxicity range (15 to 30 mg kg⁻¹DW) [43]. Cr is an essential element for the normal metabolism of carbohydrates in animal and human nutrition [62] but for plants, there is no conclusive evidence of their essentiality in the metabolism [62,63]. Additionally, Stasinios et al., (2014) [64] point out that Cr falls into the category of heavy metal, which can be easily taken and bioaccumulated by tubers and food roots. However, it should be remarked that in 2004, the maximum content of Cr affect the yields obtained neither for clone A7677 (71 t ha⁻¹) nor for the varieties Agria, Monalisa and Jaerla. In 2007, there was only a decrease in the yields of the varieties Agria and Monalisa (40 t ha⁻¹) compared to the varieties Jaerla (54 t ha⁻¹) and the clone A7677 (76 t ha⁻¹), which showed a yield increase. These observations could make us suppose that the highest concentration of Cr in the MSWC in this year could have stimulated the growth and productivity of clone A7677 and the variety Jaerla, not showing any change in its morphological structure or in the development of the foliage, which was observed in the Agria and Monalisa varieties, such as the reduction in foliage growth, discoloration of leaves, decrease in plant height, which resulted in a decrease in yield. These results agree with Paiva et al., [65], who proposed that Cr exposure in plants led to healthier conditions compared to control plants. Likewise, Guevara and Montes showed that increased exposure to Cr led to Cr concentration in the potato tubers [66]. Several studies show that there is a clear correlation between the content of this metal in soils and the stimulation of growth and the absorption of underground organs [64].

7. Nickel

MSWC provides the highest Ni content for the 1998 to 2007 period for clone A7677 (20 mg kg⁻¹DW) and in the varieties, Agria and Monalisa and Jaerla, decreasing and then remaining constant for the 2007 to 2016 period (4–9 mg kg⁻¹DW). In contrast, for 2010 to 2016, SMC, ChMC and CMC provide similar Ni contents in the varieties Agria, Monalisa and Jaerla and with the clone A7677, Figure 13. The highest Ni concentration exceeds normal values (0.02 to 5 mg kg⁻¹DW), going into phytotoxic levels (10–100 mg kg⁻¹DW) [43]. The reported results agree with those by Mahmood and Malik [67] but are larger than those by Khan et al., (6.84, 7.93 and 8.71 mg kg⁻¹DW) [39] in potato crops exposed to irrigation by Ni-contaminated wastewater. Ni is considered an essential micronutrient for the growth and development of plants with several metabolic roles [68]. The maximum Ni contents (2007, into the phytotoxic range) were obtained for MSWC treatment in the clone A7677 and in the varieties Agria, Monalisa and Jaerla but they did not affect yields. However, in 2007, it is noted that only yields of the varieties Agria and Monalisa (40 t ha⁻¹) with contents of Ni in tubers of 13 mg kg⁻¹DW declined, compared with the variety Jaerla (54 t ha⁻¹) and the clone A7677 (76 t ha⁻¹) whose yields, on the contrary, increased, despite Ni content of 20 and 8 mg kg⁻¹DW, respectively. These results indicate that Ni has stimulated the growth and development of foliage, which agrees with the positive responses of plant growth in the presence of Ni [48,69]. Nevertheless, the possible Ni toxicity should be considered, with a negative impact on photosynthesis, on membranes permeability, and on the decrease in the micronutrient’s absorption [70].

4.3. Bioavailability of Micronutrients and Heavy Metals

A dynamic equilibrium between metal fractions determines the mobility and bioavailability (more than the total content of metals). The pH, the redox potential, and the quantity and types of Organic Matter (OM) and clays are the most important edaphic factors in their control [71]. The availability of Fe, Mn, Zn, and Cu would be scarce or very restricted in the crops considered in this work because the considered soil is slightly alkaline (pH 7.4) and would explain the low Fe, Zn and Cu concentrations in the control samples. Nevertheless, the application of treatments, especially MSWC, leads to a considerable increase in Fe (56 to 118 mg kg⁻¹DW), Mn (9 to 27 mg kg⁻¹DW), Zn (28 to 34 mg kg⁻¹DW) and Cu (14 to 17 mg kg⁻¹DW). Therefore, adequate amounts of compost applied consecutively to the soils would act very favorably for Fe, Mn, Zn and Cu to be in the rhizosphere, and thus being usable by plants. In addition, soil pH also controls the processes of sorption/desorption and chemical speciation in the soils of Cr and other heavy metals such as Pb and Ni [60]. For slightly alkaline soil, as considered in this work, the availability of these minerals would
be very limited; therefore, the concentration of Pb (0.01 to 0.06 mg kg\(^{-1}\) DW), Cr (0.3 to 1.1 mg kg\(^{-1}\) DW) and Ni (0.11 to 0.16 mg kg\(^{-1}\) DW) in the tubers of the plots that did not receive any contribution of compost would be low.

Consecutive addition of treatments to the soil, especially MSWC, increased Pb (3 to 6 mg kg\(^{-1}\) DW), Cr (15 to 20 mg kg\(^{-1}\) DW) and Ni (12 to 20 mg kg\(^{-1}\) DW) for all varieties, especially clone A7677. These results can be justified considering that the addition of organic matter could specifically affect the solubility and bioaccumulation of metals, generally causing variations in pH and ionic composition of the soil. Additional studies have also proposed that it may be also an indirect consequence of the microbiological activity [60]. Nonetheless, it should be emphasized that plants have an extraordinary capacity to absorb heavy metals depending on the species, shape, concentration and bioavailability of the metals in the soil, as well as on the composition of the OM and the microbiological activity [72]. The mechanism of accumulation of Pb, Cr and Ni still have not been elucidated for S. tuberosum, but involvement of membrane transporters involved in the absorption of Ca, Cd, Mn, Fe, Zn and Cu has been proposed [60].

The reported results show that the compost has increased the concentration of macro, micronutrients and heavy metals in the tubers of all the varieties, due to the greater availability of assimilable forms of these. The reported high Cr and Ni concentrations (in the range of phytotoxicity) do not lead to lower yields in potato production between 2004 and 2007, which is probably due to positive interactions between the absorption of minerals [48,62,69]. Moreover, results reported in this work indicate that the concentrations of heavy metals (Cr, Pb and Ni) are not lethal for the plants, with no visible phytotoxic effects, especially during the first stage with the application of the MSWC (1998 to 2007). Therefore, we could suppose that the plants have developed mechanisms of blockade or of acclimatization to the metallic concentrations (Cr and Ni) that allow them to subsist in these conditions of abiotic stress [64]. The lack of visual perception of phytotoxicity in the studied crops, with high contents of heavy metals (Cr and Ni) in their different organs, can provoke an increase in agri-environmental vulnerability with a potential risk in the food chain, due to the possibility of being bioavailable to humans and animals through their consumption [73].

The decrease in yield from 2007–2010, mainly with MSWC treatment, could be due to the cumulative effect not only of heavy metals but also of micronutrients. The use of organic amendments that involve an application of microelements above the requirements could generate an accumulation of both micronutrients and heavy metals that over time can be toxic to plants [74]. This could be from 2010, where a decrease in plant height, reduction in foliage growth, discoloration of leaves, necrosis, epinasty of young leaves was notorious, little or no flowering and smaller tuber size, which produced a lower yield in potato production (2010 to 2016) with the application of the MSWC compared to the other treatments. This reduction in the yields reached up to 83% in the variety Agria, 81% in the clone A7677, 80% in Jaerla and 78% in the variety Monalisa. In a long-term study, as reported in this work, the composition of the organic amendments is very heterogeneous, depending on the source, origin, and previous treatments that these organic materials received [75].

The results found here confirm once again the need to carry out studies of all the metallic elements that can be considered as components in the waste that we use as organic amendments. Taking into account not only the fact that they can influence the chemical properties of the soil, but also that they are related to a required periodicity, in such a way that what reaches the plants can be controlled, both their edible organs and the remains of the harvest that are normally used as feed for livestock, as well as nutrients for other agricultural productions. It is, therefore, necessary to develop treatments for potentially polluting organic wastes to regulate the total concentrations of toxic metals in different fractions and their percentage contributions to the total metal concentrations [76].

In our study, clone A7677 stands out among all varieties, presenting a rapid growth, adapting very well to the prevailing environmental conditions of soil and climate, achieving excellent results, with all the organic amendments provided, thus showing an efficient cultivar in the acquisition and
use of nutrients especially in the period from 2004 to 2007, particularly with MSWC treatment. Efficiency that could be explained thanks to a system of transporters of high-affinity minerals in the roots [60] and/or to the existence of a rhizospheric effect on soil microorganisms, radical exudates that would provide the necessary energy substrate for the microbiological activity that solubilizes minerals and therefore can be used by these plants [60,77].

The greatest strength of this research is that it is a long-term study with adequate sample size and with adequate controls. Despite observing some levels of phytotoxicity and the soil of Tobar in Spain, the 
Typic Calcispepts, this study shows that the performance increased significantly with the application of all the amendments and especially with urban waste compared to its controls. The newly developed clone outperforms the other varieties considered in terms of performance, but it also shows bioaccumulation after long exposure to compost. The reported results show that compost is an alternative to traditional agricultural practices, but special care and regulation must be developed for long-term exposure considering heavy metal accumulation. The hypothesis established is confirmed by the experimental results, thus showing the relevant effect by the application of MSWC in potato content of micronutrients and heavy metals, which should be considered for practical and safety purposes as well as for the consideration of produced potato for human health issues. The reported results would be of interest to researchers interested in alternative and more sustainable agricultural practices, but also to those working in the fields of heavy metal presence in crops and food chains.

5. Conclusions

The addition of urban waste compost increased the content of macronutrients, micronutrients and heavy metals in the soils in all varieties and especially in clone A7677, showing a progressive accumulation in the tubers. Clone A7677 stands out not only in its performance, adapting very well to the prevailing edaphoclimatic conditions and achieving very good yields with organic amendments, but also in the concentration of iron, zinc, copper, micronutrients essential for human consumption and especially for deficient populations. The Agria, Monalisa and Jaerla varieties follow in production, under treatment with MSWC and especially with MSWC and ChMC. The sustained application of municipal waste compost should be considered with caution considering the reported decrease in yield during the second stage of its application compared to the first stage. The ChMC was the second amendment to provide high yields and mineral content, there were similar yields between the ChMC and the MF. Consequently, we suggest the use of ChMC as a good alternative to conventional fertilization.

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