Biofortification of Sweetcorn with Iodine: Interaction of Organic and Inorganic Forms of Iodine Combined with Vanadium

Marlena Grzanka 1,*; Sylwester Smoleń 1,*; Łukasz Skoczylas 2; and Dominik Grzanka 1

Abstract: Around the world, maize cultivation is an essential part of food systems for humans and animals. Effective reactions against the occurrence of diseases related to the deficiency of elements in the human diet are related to the biofortification of plant species of broad importance, including maize. The enrichment of maize with iodine is difficult due to the poor transport of this element to the plant’s generative organs. In marine algae, vanadium is part of the structure of the enzyme iodine-dependent peroxidase (vHIPO) that catalyzes the uptake of cellular iodine (I) and its volatilization as I₂. The relationship between iodine and vanadium in higher plants, however, is not well-known. The aim of this research was to determine the effect of vanadium fertilization and the interactions of organic and inorganic iodine compounds with vanadium under soil application. In the pot experiment, NH₄VO₃ was applied to the soil in two doses of 0.1 and 1 µmol·dm⁻³ both separately and in combination, with the following iodine compounds: 5-iodosalicylic acid (5-ISA), 2-iodobenzoic acid (2-IBeA), potassium iodide (KI), and potassium iodate (KIO₃). The iodine compounds were also applied independently to vanadium, while in the control combination, fertilization was performed without I and V. Iodine compounds were applied with doses calculated using the molar mass of this element (i.e., 10 µmol·dm⁻³·I). The highest level of iodine accumulation in grains (regardless of fertilization with V) was obtained after the application of organic compounds 5ISA and 2IBeA. A lower dose of vanadium (0.1 µmol·dm⁻³) in combination with KI and KIO₃ increased the accumulation of iodine in leaves, roots, and grains compared to the combination without the additional application of vanadium. The combined application of vanadium in both doses with 2-IBeA most effectively stimulated the transport and accumulation of iodine to the maize grain. Under the combined application of 5-ISA and vanadium (10 µmol·dm⁻³), we observed the stimulating effect of this organic iodine compound on the accumulation of vanadium in the roots as well as the antagonistic effect of vanadium in combination with 5-ISA on the accumulation of iodine in the roots, leaves, and maize grain. Vanadium accumulated mainly in the roots, where the content of this element increased proportionally to its dose. The soil application of 5-ISA increased the total sugar content and vitamin C content in the grain.

Keywords: iodine fortification; organic iodine; inorganic iodine; vanadium; beneficial elements; iodine deficiency; functional food

1. Introduction

Cereal production is strategically important in many countries around the world. On a global scale, grain production is dominated by cereals which constitute about 50% of all crops [1]. Maize is an essential part of the food systems of humans and livestock. In many countries, especially economically undeveloped ones, wheat, rice and maize account for 60% of dietary calories [2].
Cereals, vegetables, and fruits are the main sources of macro- and microelements, phenolic compounds, and vitamins necessary for human and animal organisms to properly function. However, only a balanced and varied diet can effectively prevent the diseases and ailments related to element and vitamin deficiencies [3–5]. The problem of malnutrition and “hidden hunger” is common in several areas of the world [1,6]. The multidisciplinary approaches of scientists and their cooperation in, e.g., the HarvestPlus program, helped to establish the procedures of biofortification programs [5,7]. The biofortification of major crops via micronutrients using agrotechnical solutions is a cost-effective and sustainable approach to solve the deficiencies of these elements in the human diet [1,3,4].

The WHO recommendations to limit iodized table salt consumption intensified research on the effective enrichment and biofortification of crops with iodine [8]. Iodine is essential for the proper functioning of the thyroid gland and the synthesis of hormones (thyroxin-T4 and triiodothyronine-T3) [9–11]. Deficiency of this micronutrient also negatively affects the metabolic pathway responsible for proper development of the brain, reducing the ability to learn, associate, and form memories, leading to a decrease in the intelligence factor [10–12]. The recommended daily amount of this micronutrient is 200–290 µg for pregnant women, 150 µg for adults, 90 µg for children aged 0–5, and 90–120 µg for children from 5 to 12 years old [10,12,13].

Previous research conducted on the iodine biofortification of rice [14] did not yield the expected results, which was explained by the low mobility of iodine in the phloem and, consequently, the low level of grain enrichment [4]. In a previous study on biofortification, the effect of enriching the grains of maize, wheat, and rice with iodine via foliar application was determined, but for maize, this process was less effective than that for wheat and rice [15].

The possibility of iodine transport (after applying inorganic compounds of this element) to the generative parts of plants was also confirmed not only in cereal crops but also in nectarine and plum fruit [16], tomato [17], and strawberry [18]. Most relevant studies were conducted on the effectiveness of enriching plants with different levels of iodine, as well as the methods of iodine application best suited to obtain a biofortification effect. Soil application was studied in the cultivation of wheat, rice, and maize [15]; lettuce [19]; radish; and kohlrabi [20]. Foliar application was conducted in the cultivation of potatoes, tomatoes, nectarines [16], and lettuce [20] along with application via a nutrient solution in hydroponic cultivation [21]. Determining the optimal methods of enriching plants with iodine depending on the cultivation method and the species of the plant being grown involved, almost exclusively, the use of inorganic iodine compounds KI [22] and KI₂O₃ [23–25]. Studies testing organic iodine compounds, however, are rare [26,27]. One groundbreaking approach was to test the application of iodosalicylates and iodobenzoates in research on tomato cultivation [26]. These compounds are iodine derivatives of salicylic acid (SA) and benzoic acid (BeA). In plants, benzoic acid (BeA) is a precursor to SA, which is considered a signaling molecule and plant growth regulator [28]. Organic iodine compounds in which iodine is bound to the phenolic nucleus (5-ISA and 2-IBeA) can be absorbed by the roots of crops. In young tomato plants, the authors tested 5-iodosalicylic (5-ISA), 3,5-diiodosalicylic (3,5-ISA), 2-iodobenzoic (2-IBeA), and 4-iodobenzoic (4-IBeA) acids [26]. Transitions, including possible secondary iodine metabolites, that can arise in maize plants after the use of low-molecular-weight aromatic iodine compounds and their functions in the plant are not well known. In the lettuce, the authors confirmed the presence of endogenous 3,5-diSA, 5-ISA, 2-IBeA, 4-IBeA, and T₃ (triiodothyronine) [21].

The second important aspect is the possible interaction of vanadium on the uptake and accumulation of iodine in plants. Among all plants from individual ecosystems, the most efficient accumulators of iodine are sea algae and brown algae Laminaria digitata, which contain 1% dry matter on average [29]. The iodine uptake by L. digitata seaweed involves the extracellular oxidation of iodide by vanadium-dependent haloperoxidase (vHPO) [30,31]. In seaweed, one of the functions of iodine is to participate in antioxidant mechanisms that protect the surfaces of the capsid and thallus from oxidative stress [29].
The vHPO enzymes play a central role in both the capture of iodine from sea water and volatile hydrogen halides in the synthesis of marine algae [31,32]. Vanadium-dependent iodo-peroxidases (vHPO) facilitate iodine uptake by catalyzing the oxidation of I$^-\,$ to more lipophilic compounds (iodine (I) acid) HIO and subsequently forming molecular I$_2$ which readily diffuses across the cell membranes into the cytosol. The course of the further reduction of HIO or I$_2$ to $I^-\,$ in apoplasts is unknown [29–32]. The presence of an enzyme whose prosthetic group consists of a metal such as vanadium capable of catalyzing the oxidation of halides (Cl$^-\,$, Br$^-\,$, I$^-\,$) in the presence of H$_2$O$_2$ to hypohalogenic acids is unknown in higher plants. The first affirmation of vHPO activity in higher plants was observed in lettuce by Smolen et al. [21].

Vanadium and iodine are well known to be beneficial elements for higher plants. Vanadium’s ability to stimulate positive effects on plants at low concentrations was confirmed, as were the toxic effects of higher doses of vanadium on plants. The biological and physiological properties of V also depend on V’s oxidation state. Vanadium exists in several oxidation states from −1 to +5 [33]. For peppers cultivated in a hydroponic system with the addition of vanadium into the nutrient solution at a concentration of 5 $\mu$mol $\cdot$dm$^{-3}$, V significantly increased the growth of the aerial part of the plant, stimulated the development of flower buds, and accelerated the blooming of the pepper. The contents of amino acids and sugars in the roots and leaves of the pepper were significantly higher after the application of 5 $\mu$mol $\cdot$dm$^{-3}$ of vanadium [34]. The dry matter content of mint roots increased significantly after vanadium application at the corresponding doses of 10, 20, and 40 mg V $\cdot$dm$^{-3}$ [35]. Vanadium caused a decrease in biomass and inhibited the development of the root system in the cultivation of chickpeas, indicating the toxic effect of this element in applicable doses [36]. Application of the vanadium to the nutrient solution at a dose of over 40 mg $\cdot$dm$^{-3}$ was used to retard the growth of Chinese green mustard (B. campestris ssp. Chinensis var. Parachinensis) and tomato [37]. Several studies have confirmed that the accumulation of vanadium is much higher in the roots than in the above-ground vegetative and generative parts of the plant [33,36,37].

The aim of this research was to compare the efficiency of maize grain’s biofortification into iodine depending on the application of various chemical forms of this element, i.e., aromatic organic compounds and inorganic compounds. Moreover, the aim of this study was to determine the effect of vanadium on the uptake and transport of organic and inorganic iodine compounds by maize.

2. Materials and Methods

2.1. Plant Material and Cultivation

The experiments were performed with sweetcorn (Zea mays L. subsp. Mays Saccharata Group) “Zlota Karłowa” (a Polish dwarf variety of maize for amateur farmers) by the Faculty of Biotechnology and Horticulture, the University of Agriculture in Kraków (50°05′04.1″N,19°57′02.1″E). The experiments using sweetcorn were pot studies. Each pot study was conducted in a foil tunnel in heavy mineral soil. Each experiment was repeated twice. The pot experiments were conducted in the spring/summer season during 2018 and 2019. For the pot experiment in mineral soil, seeds were sown into 7 dm$^3$ pots filled with heavy mineral soil, and one plant was cultivated per pot. There were 4 replications used with 3 plants per replication (12 plants per treatment). Organization of the pots in the foil tunnel used randomized blocks. The study plan included fifteen treatments (Tables 1 and 2) of plant treatment with various iodine compounds, including KI, KIO$_3$, 5-ISA, and 2-IBeA, and vanadium in the form of ammonium methavanadate (NH$_4$VO$_3$). The dose of iodine was 10 $\mu$mol I $\cdot$dm$^{-3}$ along with two doses of vanadium: 0.1 $\mu$mol V $\cdot$dm$^{-3}$ ($V_1$) and 1 $\mu$mol V $\cdot$dm$^{-3}$ ($V_2$). The control plants were not fertilized with iodine or vanadium. The first application of iodine and vanadium compounds started four weeks after sowing (in the plant growth phase, BBCH 16-17). The iodine and vanadium compounds were applied to the soil once a week through manual fertigation. Manual watering with solutions of the compounds studied, at a dose of 200 cm$^3$ $\cdot$pot$^{-1}$ (one plant$^{-1}$), was
implemented. We used seven applications of iodine and vanadium compounds through fertigation (Tables 1 and 2). During cultivation, the plants were watered with tap water through a drip irrigation system. Harvesting of the corn cobs was carried out at the full milk maturity stage of the granuloma (BBCH 75). The leaf sheaths were removed from the corn cobs after harvesting. The corn cobs were then counted and weighed successively. After harvest, we measured the heights and weights of the above-ground parts of the plants without corn cobs.

Table 1. Methodological information about application of iodine and vanadium compounds to soil during sweetcorn cultivation in pot experiments.

| Year of Experiment | Sowing Date | Date of First Application of Iodine and Vanadium Compounds | Developmental Phase (BBCH) of First Application | Application Cycle | Date Last Application | Date of Harvest | Amount of Applications |
|--------------------|-------------|----------------------------------------------------------|---------------------------------------------|------------------|----------------------|-----------------|-----------------------|
| 2018               | 8 May 2018  | 8 June 2018                                              | 6–7 leaves                                  | Each 7th day     | 17 July 2018         | 24 July 2018   | 7                     |
| 2019               | 9 April 2019| 22 May 2019                                              | 6–7 leaves                                  | Each 7th day     | 3 July 2019          | 10 July 2019   | 7                     |

Table 2. Design and method of conducting experiment with sweetcorn plants cultivation.

| Treatments | Dose * of Iodine Compounds and Dose of Iodine | Dose * of Vanadium as Ammonium Metavanadate | I and/or V Application from BBCH 16-17 | Amount of Iodine Applied for One Plant (µmol I plant⁻¹) | Amount of Vanadium Applied for One Plant (µmol V plant⁻¹) |
|------------|-----------------------------------------------|--------------------------------------------|----------------------------------------|--------------------------------------------------------|--------------------------------------------------------|
| Control    | - **                                          | - **                                       | -                                      | - ****                                                 | - ****                                                 |
| V₁         | -                                             | 0.1 µM V                                   | 7 times ***                            | - 0.14                                                 | - 0.14                                                 |
| V₂         | -                                             | 1.0 µM V                                   | 7 times ***                            | - 1.4                                                  | - 1.4                                                  |
| KI         | 10 µM (10 µM I)                               | -                                         | 7 times ***                            | 14                                                     | - 14                                                   |
| KI + V₁    | 10 µM (10 µM I)                               | 0.1 µM V                                   | 7 times ***                            | 14                                                     | 0.14                                                   |
| KI + V₂    | 10 µM (10 µM I)                               | 1.0 µM V                                   | 7 times ***                            | 14                                                     | 1.4                                                    |
| KIO₃       | 10 µM (10 µM I)                               | -                                         | 7 times ***                            | 14                                                     | - 14                                                   |
| KIO₃ + V₁  | 10 µM (10 µM I)                               | 0.1 µM V                                   | 7 times ***                            | 14                                                     | 0.14                                                   |
| KIO₃ + V₂  | 10 µM (10 µM I)                               | 1.0 µM V                                   | 7 times ***                            | 14                                                     | 1.4                                                    |
| 5ISA       | 10 µM (10 µM I)                               | -                                         | 7 times ***                            | 14                                                     | - 14                                                   |
| 5ISA + V₁  | 10 µM (10 µM I)                               | 0.1 µM V                                   | 7 times ***                            | 14                                                     | 0.14                                                   |
| 5ISA + V₂  | 10 µM (10 µM I)                               | 1.0 µM V                                   | 7 times ***                            | 14                                                     | 1.4                                                    |
| 2IBeA      | 10 µM (10 µM I)                               | -                                         | 7 times ***                            | 14                                                     | - 14                                                   |
| 2IBeA + V₁ | 10 µM (10 µM I)                               | 0.1 µM V                                   | 7 times ***                            | 14                                                     | 0.14                                                   |
| 2IBeA + V₂ | 10 µM (10 µM I)                               | 1.0 µM V                                   | 7 times ***                            | 14                                                     | 1.4                                                    |

*—The dose of 200 cm³ of iodine, vanadium or iodine + vanadium solution pot⁻¹ (one plant⁻¹) were applied at a single application. **—Without iodine and vanadium fertilization—the natural content of iodine and vanadium in mineral soil to the experiments. ***—7 times every 7 days. ****—The determined iodine and vanadium content (in TMAH and 1 M HCl extracts, respectively) do not allow for estimating the amount of available iodine and vanadium for plants in the soil solution of mineral soil. It is also not possible to accurately estimate the changes in the content of I and V in the soil solution during the whole period of sweetcorn cultivation using other methods of soil extraction.

2.2. Analysis of Dry and Fresh Samples of Roots, Stems, and Leaves

Fresh samples of roots, leaves, and grain were dried at 70 °C (48 h) in a laboratory dryer with forced air circulation. Dried samples of leaves, roots, and grain were ground in a laboratory mill and stored in a plastic bag until analysis of the iodine, vanadium, microelements, and microelements was carried out. The dry weight content in these samples was determined using the oven-drying method at 105 °C.

To determine iodine content, the PN-EN 15111-2008 method was applied with the modifications described in [38] using ICP-MS/MS (iCAP TQ ICP-MS ThermoFisher Scientific, Bremen, Germany). The concentrations of V, P, K, Mg, Ca, S, Cu, Fe, Mn, Mo, and Zn were determined using an ICP-OES spectrophotometer (Prodigy Spectrometer, Leeman...
Labs, New Hampshire, MA, USA) after microwave digestion in 65% super pure HNO₃. Plant samples of 0.5 g dry material were placed in 55 mL TF-disk-modified polytetrafluoroethylene (PTFE) vessels and digested in 10 mL of 65% HNO₃ using a CEM MARS-5 Xpress (CEM World Headquarters, Matthews, NC, USA) microwave digestion system [39].

The samples of fresh grain (milk stage) were then homogenized and total sugars, as a sum of glucose, fructose, and sucrose, were extracted by boiling 96% ethanol (Destylenia ‘Polmos’ Sp. z.o.o., Kraków, Poland). The contents of fructose, glucose and sucrose (and their sum as total sugars) were assessed using the capillary electrophoresis technique with the PA 800 Plus system (Beckman Coulter, Brea, CA, USA). Capillaries of 50 μm and a total length of 60 cm (10 cm for detection) were used. A positive power supply of 15 kV was applied, and the temperature was set at 25 °C. The running buffer solution contained 20.0 mmol·dm⁻³ sorbic acid, 0.20 mmol·dm⁻³ CTAB, and 40 mmol·dm⁻³ NaOH, pH 12.2. [40].

The content of L-ascorbic acid in the grains was analyzed via capillary electrophoresis after the homogenization of 20 g samples in 80 cm³ of 2% oxalate acid (puriss. p.a., Avantor Performance Materials) and further centrifugation for 15 min at 4500 rpm and 5 °C. The supernatants were then filtered through a 0.25 μm cellulose acetate membrane filter and analyzed using a PA 800 Plus capillary electrophoresis system (Beckman Coulter, Indianapolis, IN, USA) with a diode array detector (DAD). We used capillaries of 50 μm i.d. and 365 μm o.d. and a total length of 50 cm (40 cm to detector) and applied a negative power supply of 25 kV. A running buffer solution containing 30 mM NaH₂PO₄ was prepared as proposed in [41] (puriss. p.a., Avantor Performance Materials) with 15 mM Na₂B₄O₇ (puriss. p.a., Sigma-Aldrich, Burlington, MA, United States) and 0.2 mM cetyltrimethylammonium bromide (CTAB) (puriss. p.a., Sigma-Aldrich) (pH 8.80).

### 2.3. Data Analysis

All data were statistically verified using the one-way analysis of variance (ANOVA) module of the Statistica 13.3 PL program at p < 0.05. The significance of differences between the means was estimated using Tukey’s test at p < 0.05.

3. Results

#### 3.1. Plant Biomass and Yield of Corn Cob

The application of iodine and vanadium compounds in each of the applied doses did not have a statistically significant effect compared to the control on the sweetcorn cob yield, the average weight of one cob, and the plant height and weight of the aerial part of a single plant after harvest (Table 3 and Scheme 1).

**Table 3.** Results of growth of sweetcorn plants and yielding parameters of corn cob.

| Treatments      | Yield of All Gained Corn Cobs from One Plant (FMW g Plants⁻¹) | Average Weight of One Corn Cob (FMW g) | Weight of Aerial Part of Single Plant after Harvest of Corn Cob (FMW g) | Height of Aerial Part of the Plant at Harvest (cm) |
|-----------------|---------------------------------------------------------------|---------------------------------------|-------------------------------------------------------------------------|-----------------------------------------------|
| Control         | 323.0 ± 36.21 a                                              | 61.1 ± 6.47 a                         | 295.9 ± 47.82 a                                                        | 168.4 ± 1.64 a                                |
| V₁              | 278.6 ± 37.76 a                                              | 52.9 ± 7.23 a                         | 305.3 ± 29.75 a                                                        | 177.2 ± 3.53 a                                |
| V₂              | 284.4 ± 35.76 a                                              | 56.3 ± 5.99 a                         | 245.0 ± 24.02 a                                                        | 169.0 ± 5.52 a                                |
| KI              | 355.1 ± 26.00 a                                              | 61.6 ± 7.38 a                         | 259.3 ± 20.12 a                                                        | 167.3 ± 9.03 a                                |
| KI + V₁         | 311.2 ± 29.40 a                                              | 57.4 ± 7.35 a                         | 310.2 ± 25.52 a                                                        | 180.0 ± 6.73 a                                |
| KI + V₂         | 310.1 ± 28.21 a                                              | 61.0 ± 8.62 a                         | 264.6 ± 17.71 a                                                        | 170.3 ± 5.86 a                                |
| KIO₃            | 295.0 ± 32.19 a                                              | 58.7 ± 8.57 a                         | 292.3 ± 26.39 a                                                        | 174.9 ± 8.28 a                                |
| KIO₃ + V₁       | 280.6 ± 39.98 a                                              | 54.6 ± 6.82 a                         | 251.7 ± 31.10 a                                                        | 169.0 ± 8.34 a                                |
| KIO₃ + V₂       | 291.5 ± 14.16 a                                              | 58.5 ± 9.11 a                         | 239.0 ± 23.85 a                                                        | 168.1 ± 6.01 a                                |
| 5ISA            | 261.1 ± 21.04 a                                              | 53.8 ± 8.88 a                         | 254.8 ± 43.40 a                                                        | 165.9 ± 10.53 a                               |
| 5ISA + V₁       | 291.1 ± 44.03 a                                              | 57.7 ± 37.37 a                        | 288.5 ± 23.70 a                                                        | 176.4 ± 16.77 a                               |
| 5ISA + V₂       | 254.3 ± 28.61 a                                              | 53.4 ± 6.66 a                         | 228.3 ± 18.05 a                                                        | 164.0 ± 5.46 a                                |
| 2IBeA           | 242.8 ± 43.62 a                                              | 58.3 ± 9.90 a                         | 225.3 ± 12.86 a                                                        | 168.0 ± 7.12 a                                |
| 2IBeA + V₁      | 287.8 ± 36.79 a                                              | 60.7 ± 6.61 a                         | 294.7 ± 41.53 a                                                        | 168.8 ± 7.63 a                                |
| 2IBeA + V₂      | 239.5 ± 34.41 a                                              | 54.9 ± 7.26 a                         | 245.5 ± 16.59 a                                                        | 175.6 ± 5.09 a                                |

Means followed by different letters for treatments differ significantly p < 0.05 (n = 8).
Table 3. Results of growth of sweetcorn plants and yielding parameters of corn cob.

| Treatments     | Yield of All Gained Corn Cobs from One Plant (FMW g/Plants⁻¹) | Average Weight of One Corn Cob (FMW g) | Weight of Aerial Part of Single Plant after Harvest of Corn Cob (FMW g) | Height of Aerial Part of the Plant at Harvest (cm) |
|----------------|---------------------------------------------------------------|----------------------------------------|------------------------------------------------------------------------|-----------------------------------------------|
| Control        | 323.0 ± 36.21 a                                               | 61.1 ± 6.47 a                          | 295.9 ± 47.82 a                                                        | 168.4 ± 1.64 a                                 |
| V₁             | 278.6 ± 37.76 a                                               | 52.9 ± 7.23 a                          | 305.3 ± 29.75 a                                                        | 177.2 ± 3.53 a                                 |
| V₂             | 284.4 ± 35.76 a                                               | 56.3 ± 5.99 a                          | 245.0 ± 24.02 a                                                        | 169.0 ± 5.52 a                                 |
| KI             | 355.1 ± 26.00 a                                               | 61.6 ± 7.18 a                          | 259.3 ± 20.12 a                                                        | 167.3 ± 9.03 a                                 |
| KI + V₁        | 311.2 ± 29.40 a                                               | 57.4 ± 7.35 a                          | 310.2 ± 25.52 a                                                        | 180.0 ± 6.73 a                                 |
| KI + V₂        | 310.1 ± 28.21 a                                               | 61.0 ± 8.62 a                          | 264.6 ± 17.71 a                                                        | 170.3 ± 5.86 a                                 |
| KIO₃           | 295.0 ± 32.19 a                                               | 58.7 ± 8.57 a                          | 292.3 ± 26.39 a                                                        | 174.9 ± 8.28 a                                 |
| KIO₃ + V₁      | 280.6 ± 39.98 a                                               | 54.6 ± 6.82 a                          | 251.7 ± 31.10 a                                                        | 169.0 ± 8.34 a                                 |
| KIO₃ + V₂      | 291.5 ± 14.16 a                                              | 58.5 ± 9.11 a                          | 239.0 ± 23.85 a                                                        | 168.1 ± 6.01 a                                 |
| 5ISA           | 261.1 ± 21.04 a                                               | 53.8 ± 8.88 a                          | 254.8 ± 43.40 a                                                        | 165.9 ± 10.53 a                                |
| 5ISA + V₁      | 291.1 ± 44.03 a                                              | 57.7 ± 7.37 a                          | 288.5 ± 23.70 a                                                        | 176.4 ± 6.17 a                                 |
| 5ISA + V₂      | 254.3 ± 28.61 a                                              | 53.4 ± 6.66 a                          | 228.3 ± 18.05 a                                                        | 164.0 ± 5.46 a                                 |
| 2IBeA          | 242.8 ± 43.62 a                                              | 58.3 ± 9.90 a                          | 225.3 ± 12.86 a                                                        | 168.0 ± 7.12 a                                 |
| 2IBeA + V₁     | 287.8 ± 36.79 a                                              | 60.7 ± 6.61 a                          | 294.7 ± 41.53 a                                                        | 168.8 ± 7.63 a                                 |
| 2IBeA + V₂     | 239.5 ± 34.41 a                                              | 54.9 ± 7.26 a                          | 245.5 ± 16.59 a                                                        | 175.6 ± 5.09 a                                 |

Means followed by different letters for treatments differ significantly $p < 0.05$ ($n = 8$).

Scheme 1. Corn cob at harvest—one from four replications.

3.2. Iodine Accumulation in Sweetcorn Plants

The application of organic and inorganic iodine compounds, both separately and together with vanadium, significantly increased the content of iodine in the roots, leaves, and grains of sweetcorn compared to the control (Figure 1A–C). Based on the effects of the tested iodine compounds (without the application of vanadium), the highest level of iodine enrichment in the grains was obtained with the application of organo-iodine compounds 5-ISA and 2-IBeA (increases of 117% and 110% relative to the control) followed by the inorganic forms KI and KIO₃ (with increases of 70% and 60%, respectively) (Figure 1A). In the leaves, after the application of the organic iodine compounds 5-ISA and 2-IBeA, we observed a lower level of iodine accumulation than that observed after fertilization with KI and KIO₃ (Figure 1B). For roots, the increase in iodine accumulation compared to the control was greatest after the application of 2-IBeA, followed by the application of KI, KIO₃, and 5-ISA (respectively, 124%, 92%, 36%, and 24% higher iodine levels than in the control). In general, the vegetative parts of sweetcorn were characterized by a higher level of iodine accumulation (roots > leaves) than that observed in grains, regardless of the form of iodine applied to the soil (Figure 1A–C).
3.2. Iodine Accumulation in Sweetcorn Plants

The application of organic and inorganic iodine compounds, both separately and together with vanadium, significantly increased the content of iodine in the roots, leaves, and grains (by 2% and 11% in the roots, 17% and 21% in the leaves, and 25% and 32% in the grains, respectively, for doses V1 and V2), compared to the use of only 5-ISA. In the roots, this effect was significant only for the 5-ISA + V1 combination. In roots and leaves, the combined fertilization of 2-IBeA with vanadium in two doses resulted in a significant reduction in iodine content compared to the application of 2-IBeA alone—a reduction of 17% and 5%, respectively, for V1 and V2 in the roots and 16% and 11% for V1 and V2 in the leaves. Meanwhile, in the grain, along with

3.3. The Interaction of Iodine with Vanadium in Individual Parts of the Plant

Under the combined application of KI and ammonium metavanadate at a lower dose (0.1 µmol V·dm$^{-3}$; KI + V1), a significant increase of the iodine content in roots, leaves, and grain was observed (increases of 15%, 28%, and 10%, respectively, compared to KI). An increase in iodine accumulation was also observed in grains after the combined application of KI with a higher dose of vanadium (1.0 µmol V·dm$^{-3}$; KI + V2 versus KI; Figure 1A) (an increase of 10% compared to KI). The application of KI + V2 did not increase the accumulation of iodine in the roots and leaves relative to KI (Figure 1B,C). For plants fertilized with KIO$_3$ + V1, compared to fertilization with KIO$_3$, we observed increased iodine content in the roots (by 3%), leaves (by 7%), and grains (by 11%). A higher dose of vanadium (KIO$_3$ + V2) caused a decrease (7%) in the level of iodine accumulation only in grains. The combined application of iodine in the form of the organic compound 5-ISA with vanadium in two doses (0.1 µmol V·dm$^{-3}$ and 1.0 µmol V·dm$^{-3}$) reduced the level of iodine accumulation in the roots, leaves, and grains (by 2% and 11% in the roots, 17% and 21% in the leaves and 25%, and 32% in the grains, respectively, for doses V1 and V2), compared to the use of only 5-ISA. In the roots, this effect was significant only for the 5-ISA + V2 combination. In roots and leaves, the combined fertilization of 2-IBeA with vanadium in two doses resulted in a significant reduction in iodine content compared to the application of 2-IBeA alone—a reduction of 17% and 5%, respectively, for V1 and V2 in the roots and 16% and 11% for V1 and V2 in the leaves. Meanwhile, in the grain, along with

![Figure 1](image-url)
an increase in the dose of vanadium used together with 2-IBeA, we observed a significant increase in the iodine content—by 14% and 32%, respectively, compared to the application of 2-IBeA alone.

The iodine content in the grain after the application of 2-IBeA + V2 was approximately 180% higher than that in the control and V1 (without iodine fertilization) and 32% higher than that after the application of 2-IBeA and 5-ISA.

3.4. Vanadium Content in Sweetcorn Plants

We found a significant effect of vanadium fertilization on the content of vanadium in the roots, leaves, and grains of sweetcorn when used both separately and together with all applied iodine compounds (Figure 2A–C). In maize grain, we observed significantly higher vanadium content than that in the control for the following combination: \( \text{KIO}_3 + V1 > 5\text{-ISA} + V1 > \text{KI} + V1 = \text{KIO}_3 \) (Figure 2A).

![Figure 2](https://example.com/image)

**Figure 2.** Vanadium contents in grain (A), leaves (B), and roots (C) of maize. Means followed by different letters for treatments differ significantly \( p < 0.05 \) \((n = 8)\). Bars indicate standard error.

The content of vanadium in the leaves was, on average, 60 times lower than that in the roots (Figure 2B,C). In the leaves, all tested combinations with iodine fertilization in the form of \( \text{KIO}_3 \), 5-ISA, and 2-IBeA (but not KI) without vanadium resulted in a significant increase in the content of vanadium compared to the control (Figure 2B). For the application of individual iodine compounds together with vanadium at a lower dose, the level of vanadium accumulation in leaves was observed in the following order: KI,
+ V1 < KIO₃ + V1 < 5-ISA + V1 = 2-IBeA + V1. In total, fertilization with all the tested iodine compounds together with vanadium at a higher dose (V2) significantly increased the accumulation of vanadium in the leaves compared to the application of the iodine compound +V1.

Soil fertilization and ammonium metavanadium were applied separately and together with iodine compounds. We noted that with an increase in the dose of vanadium, there was a significant increase in the level of vanadium accumulation in the roots (Figure 2C) compared to the control (by 83% and 101%). Differences in application-particular iodine percentages without vanadium ranged from 27% for 5-ISA + V2 versus 5ISA to 29% for KIO₃ + V1 versus KIO₃ (Figure 2C). The application of a lower dose of vanadium with 2-IBeA (the 2-IBeA + V1 combination) did not have a statistically significant effect on the content of vanadium in the roots compared to the control object and fertilization with 2-IBeA alone. The highest content of vanadium in the roots was observed when a higher dose of V2 was combined with the application of 5-ISA.

3.5. Content of Total Sugar and Ascorbic Acid in Sweetcorn Grains

The total content of sugars and vitamin C (L-ascorbic acid) in sweetcorn grain significantly depended on the form of iodine and the dose of vanadium applied (Figure 3A,B). Compared to the control, a significant increase in the sugar content of the grain was found only after soil fertilization with 5-ISA and 5-ISA + V1 (by 37% and 36%, respectively; Figure 3A). On the other hand, all the other tested combinations of vanadium and iodine fertilization used with and without vanadium at both doses (except 5-ISA + V2) resulted in a significant reduction of sugar content in maize. This was observed to the greatest extent for the KIO₃ + V2 combination, where a two-fold reduction in sugar content was observed compared to the control. Under the application of KIO₃ and 5ISA, a higher dose of vanadium and fertilization with KIO₃ and 5-ISA, without vanadium, reduced sugar content in the grain was observed. Such relationships were not observed for the fertilization of KI and 2-IBeA under the application of V1 and V2.

After 5-ISA fertilization, the content of vitamin C was significantly higher than that in the control (Figure 3B). The combined application of 5-ISA with vanadium, at both doses, resulted in a significant reduction of vitamin C content in the grains (by 48% and 61%, respectively, for 5-ISA + V1 and 5-ISA) compared to the use of 5-ISA alone (and compared to the control). The application of vanadium alone, at both doses without the application of iodine, reduced vitamin C content in the grain compared to the control. The fertilization of KI with the additional application of vanadium at both doses did not have a significant effect on the vitamin C content in the grain. On the other hand, when using KIO₃, the additional application of V1 and V2 decreased and increased vitamin C content, respectively. However, when fertilizing with 2-IBeA, the use of vanadium increased the content of vitamin C in grain, which was observed to a greater extent with 2-IBeA + V1.

Figure 3. Content of total sugars (A) and ascorbic acid (B) in sweetcorn grain. Means followed by different letters for treatments differ significantly at p < 0.05 (n = 8). Bars indicate standard error.
3.6. Content of Macro- and Microelements and Dry Matter in Maize Plant

The applied iodine and vanadium compounds had various effects on the content of macro- and microelements in the leaves, roots, and grains of sweetcorn (Tables 4 and 5). Generally, all the tested combinations of iodine and vanadium fertilization influenced the observed tendency (statistically significant for some of the combinations) to decrease Ca content in the grain (Table 4) and increase Mn and Fe content in the roots (Table 5). All the tested combinations of iodine and vanadium fertilization caused a significant reduction of Mo content in the grains compared to the control but, at the same time, did not affect the accumulation of Zn in the grains (Table 5).

### Table 4. Contents of Ca, K, Mg, P, and S in grain, leaves, and roots of “Złota Karłowa” sweetcorn.

| Treatment | Grain (% D.W) | Leaves (% D.W) | Roots (% D.W) |
|-----------|---------------|----------------|---------------|
|           | Ca            | Kg             | Mg            | P             | S             | Control | 2.70 ± 0.28 bcd | 1.98 ± 0.15 a | 0.49 ± 0.05 abcd | 0.54 ± 0.03 ab | 0.32 ± 0.03 abcd |
| V1        | 0.020 ± 0.001 cdde | 0.85 ± 0.07 c   | 0.14 ± 0.02 b  | 0.49 ± 0.02 c  | 0.13 ± 0.006 abc |
| V2        | 0.022 ± 0.002 de | 0.79 ± 0.08 abc | 0.13 ± 0.002 ab | 0.48 ± 0.01 bc | 0.13 ± 0.002 abc |
| KI        | 0.013 ± 0.001 abc | 0.77 ± 0.06 abc | 0.12 ± 0.004 ab | 0.45 ± 0.02 abc | 0.13 ± 0.003 abc |
| KI + V1   | 0.020 ± 0.004 cde | 0.82 ± 0.08 bc  | 0.12 ± 0.002 ab | 0.44 ± 0.02 abc | 0.12 ± 0.009 abc |
| KI + V2   | 0.019 ± 0.003 bcde | 0.83 ± 0.07 bc  | 0.13 ± 0.005 ab | 0.47 ± 0.01 bc  | 0.13 ± 0.003 abc |
| KIO3      | 0.016 ± 0.002 abcd | 0.85 ± 0.07 c   | 0.13 ± 0.005 ab | 0.46 ± 0.02 bc  | 0.14 ± 0.004 bc |
| KIO3 + V1 | 0.022 ± 0.003 de | 0.82 ± 0.07 bc  | 0.13 ± 0.003 ab | 0.46 ± 0.02 ab  | 0.14 ± 0.007 abc |
| KIO3 + V2 | 0.016 ± 0.001 abcd | 0.75 ± 0.04 abc | 0.12 ± 0.008 ab | 0.45 ± 0.01 abc | 0.12 ± 0.005 abc |
| 5ISA      | 0.016 ± 0.002 abcd | 0.70 ± 0.02 a   | 0.12 ± 0.009 a  | 0.41 ± 0.02 ab  | 0.12 ± 0.007 abc |
| 5ISA + V1 | 0.011 ± 0.002 ab   | 0.77 ± 0.05 abc | 0.13 ± 0.010 ab | 0.43 ± 0.01 ab  | 0.12 ± 0.008 abc |
| 5ISA + V2 | 0.009 ± 0.001 a    | 0.75 ± 0.04 abc | 0.14 ± 0.003 b  | 0.41 ± 0.02 ab  | 0.10 ± 0.008 a  |
| 2BeA      | 0.012 ± 0.002 ab   | 0.73 ± 0.05 ab  | 0.12 ± 0.006 ab | 0.41 ± 0.02 abc | 0.11 ± 0.007 ab  |
| 2BeA + V1 | 0.017 ± 0.002 bcde | 0.78 ± 0.05 abc | 0.13 ± 0.008 ab | 0.39 ± 0.03 a   | 0.11 ± 0.012 ab  |
| 2BeA + V2 | 0.021 ± 0.002 cde  | 0.81 ± 0.06 bc  | 0.13 ± 0.006 ab | 0.47 ± 0.02 bc  | 0.15 ± 0.004 c   |

Means followed by different letters for treatments differ significantly at \( p < 0.05 \) \((n = 8)\).
Table 5. Contents of Cu, Fe, Mn, Zn, Mo in the grain, leaves and roots of “Złota Karłowa” sweetcorn.

| Treatment     | Grain (mg kg⁻¹ D.W) | Leaves (mg kg⁻¹ D.W) | Roots (mg kg⁻¹ D.W) |
|---------------|---------------------|----------------------|---------------------|
|               | Mo      | Zn      | Mn      | Fe      | Cu      | Mo      | Zn      | Mn      | Fe      | Cu      | Mo      | Zn      | Mn      | Fe      | Cu      |
| Control       | 2.32 ± 0.65 c | 53.59 ± 1.59 ab | 5.36 ± 0.48 bc | 40.13 ± 2.22 cdef | 2.42 ± 0.02 abcd | 7.15 ± 0.25 a | 41.07 ± 5.62 a | 110.01 ± 17.41 cdef | 167.27 ± 11.08 a | 5.12 ± 1.00 ab |
| V1            | 1.09 ± 0.21 ab | 46.39 ± 0.50 ab | 4.76 ± 0.52 abc | 35.61 ± 1.60 abcd | 2.47 ± 0.03 abcde | 6.28 ± 0.35 b | 46.42 ± 3.57 ab | 135.11 ± 10.23 i | 157.96 ± 7.82 a | 5.73 ± 0.65 b |
| V2            | 1.25 ± 0.23 ab | 51.91 ± 2.04 ab | 5.02 ± 0.54 abc | 35.00 ± 1.39 abcd | 3.09 ± 0.13 e | 6.50 ± 0.38 b | 44.19 ± 4.44 a | 7.17 ± 1.11 abc | 41.16 ± 1.50 def | 2.66 ± 0.07 abcd |
| KI            | 1.16 ± 0.23 ab | 43.82 ± 1.49 a | 4.47 ± 0.51 ab | 30.58 ± 1.48 a | 2.24 ± 0.07 a | 6.28 ± 0.35 b | 44.28 ± 4.94 a | 4.59 ± 0.78 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab |
| KI + V1       | 1.46 ± 0.40 ab | 46.86 ± 2.45 ab | 5.16 ± 0.78 bc | 32.88 ± 0.99 ab | 2.68 ± 0.15 abcd | 7.17 ± 1.11 abc | 41.16 ± 1.50 def | 41.88 ± 1.24 ef | 2.30 ± 0.04 abc | 1.95 ± 0.08 abc |
| KI + V2       | 1.21 ± 0.26 ab | 47.83 ± 1.38 ab | 5.45 ± 0.86 c | 34.05 ± 3.12 abc | 2.50 ± 0.03 abcd | 6.41 ± 0.38 b | 44.97 ± 8.12 a | 9.11 ± 1.88 cd | 166.70 ± 8.19 a | 4.88 ± 0.10 ab |
| KIO₃          | 1.07 ± 0.15 ab | 55.75 ± 4.34 b | 5.27 ± 0.62 bc | 35.22 ± 1.62 abcd | 2.48 ± 0.04 abcd | 6.41 ± 0.38 b | 44.97 ± 8.12 a | 9.11 ± 1.88 cd | 166.70 ± 8.19 a | 4.88 ± 0.10 ab |
| KIO₃ + V1     | 1.40 ± 0.32 b | 53.21 ± 3.12 ab | 4.94 ± 0.35 abc | 35.56 ± 1.58 abcd | 2.63 ± 0.08 abcd | 6.41 ± 0.38 b | 44.97 ± 8.12 a | 9.11 ± 1.88 cd | 166.70 ± 8.19 a | 4.88 ± 0.10 ab |
| KIO₃ + V2     | 1.27 ± 0.20 ab | 50.73 ± 2.98 ab | 5.41 ± 0.90 ab | 33.78 ± 2.56 abc | 2.71 ± 0.05 bcde | 6.50 ± 0.38 b | 44.28 ± 4.94 a | 4.59 ± 0.78 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab |
| 5ISA          | 0.61 ± 0.09 a | 45.62 ± 4.45 ab | 4.17 ± 0.84 a | 40.04 ± 2.27 cdef | 2.82 ± 0.14 de | 6.50 ± 0.38 b | 44.28 ± 4.94 a | 4.59 ± 0.78 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab |
| 5ISA + V1     | 1.15 ± 0.18 ab | 46.44 ± 3.24 ab | 4.61 ± 0.84 abc | 41.16 ± 1.50 def | 2.66 ± 0.07 abcd | 6.50 ± 0.38 b | 44.28 ± 4.94 a | 4.59 ± 0.78 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab |
| 5ISA + V2     | 0.91 ± 0.12 ab | 44.19 ± 4.44 a | 4.77 ± 1.11 abc | 41.88 ± 1.24 ef | 2.30 ± 0.04 abc | 6.50 ± 0.38 b | 44.28 ± 4.94 a | 4.59 ± 0.78 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab |
| 2IBeA         | 1.11 ± 0.17 ab | 44.28 ± 3.26 ab | 4.59 ± 0.78 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab | 6.50 ± 0.38 b | 44.28 ± 4.94 a | 4.59 ± 0.78 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab |
| 2IBeA + V1    | 0.88 ± 0.07 ab | 44.77 ± 4.82 ab | 4.95 ± 0.88 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab | 6.50 ± 0.38 b | 44.28 ± 4.94 a | 4.59 ± 0.78 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab |
| 2IBeA + V2    | 1.19 ± 0.18 ab | 53.45 ± 1.71 ab | 4.95 ± 0.41 abc | 42.32 ± 3.46 f | 2.47 ± 0.04 abcd | 6.50 ± 0.38 b | 44.28 ± 4.94 a | 4.59 ± 0.78 abc | 39.63 ± 2.36 cdef | 2.27 ± 0.09 ab |

Means followed by different letters for treatments differ significantly at p < 0.05 (n = 8).

The 5-ISA application stood out from the other combinations. Compared to the control, the use of 5-ISA significantly reduced the content of Ca, P, K, and Mg in the grain by −62%, −16%, −17%, and −14%, respectively (Table 4). After fertilization with 5-ISA alone, without vanadium, we also noted a reduction in the content of Mn in the grain compared to the control (−22%; Table 5). Moreover, in the leaves, after fertilization with...
5-ISA alone, compared to the control, we found a reduction in Mg content (−14% Mg) (Table 4), with the lowest amount related to the lowest Mo content (−41%) (Table 5).

The soil fertilization of plants with vanadium alone at a higher dose (V2) resulted in leaves with the highest content of Ca and Mn (17% and 22% higher than that in the control; see Tables 4 and 5) and grains with the highest content of Cu (28% higher than that in control; see Table 5).

In the roots, fertilization with KI and KI + V1 resulted in the lowest Mg content (−9% and −14% versus the control, respectively), and KI + V2 fertilization yielded the highest value of Mg accumulation (+14% compared to the control) (Table 4). Fertilization with potassium iodide (KI) without vanadium resulted in the lowest K content in the roots (−22% versus the control) (Table 4), the lowest Fe and Cu content in the grain (−24% and −8%, respectively, compared to the control), and the highest Fe in the roots (106% higher than that in the control; see Table 5).

Compared to the control, the applied iodine and vanadium compounds had no significant effect on the content of S in grains, K, Mg, P, and S (Table 4); Fe and Cu (Table 5) in maize leaves; and Ca, P, and S in roots (Table 4).

Compared to the control, there was a significant decrease (−40%) in dry matter content (Table 6) in the roots after 2-IBeA + V2 fertilization and in the leaves after V1 and V2 fertilization (22.6% and 23.4%; KIO$_3$ + V1 21, 5%), as well as under all combinations with 5-ISA and 2-IBeA alone and together with vanadium (23% on average). In grain, only 5-ISA + V2 fertilization caused a significant increase in dry matter content (+11.5%) compared to the control.

### Table 6. Dry matter content in sweetcorn plants part (roots, leaves, grain).

| Treatments       | % Dry Weight |          |          |
|------------------|--------------|----------|----------|
|                  | Roots        | Leaves   | Grain    |
| Control          | 12.03 ± 1.14 b | 25.95 ± 1.73 b | 35.66 ± 2.13 abc |
| V$_1$            | 9.59 ± 0.60 ab | 20.06 ± 0.50 a  | 34.40 ± 1.96 ab  |
| V$_2$            | 9.25 ± 0.66 ab | 19.88 ± 0.76 a  | 36.02 ± 1.63 ab  |
| KI               | 8.79 ± 0.24 ab | 22.15 ± 0.84 ab | 37.41 ± 1.86 abcd|
| KI + V$_1$       | 10.27 ± 0.71 ab | 22.09 ± 0.95 ab | 35.97 ± 1.57 abc |
| KI + V$_2$       | 10.17 ± 2.12 ab | 22.61 ± 0.61 ab | 37.89 ± 2.34 cd  |
| KIO$_3$          | 8.80 ± 0.63 ab | 22.04 ± 1.57 ab | 34.16 ± 1.38 a   |
| KIO$_3$ + V$_1$  | 10.41 ± 0.36 ab | 20.37 ± 0.85 a  | 36.40 ± 1.70 abc |
| KIO$_3$ + V$_2$  | 8.88 ± 0.39 ab | 22.98 ± 2.59 ab | 37.81 ± 0.51 cd  |
| 5ISA             | 9.32 ± 0.55 ab | 22.26 ± 1.14 ab | 37.54 ± 1.10 bcd |
| 5ISA + V$_1$     | 10.24 ± 0.84 ab | 20.67 ± 1.10 a  | 37.26 ± 1.26 abcd|
| 5ISA + V$_2$     | 8.31 ± 0.49 ab | 19.44 ± 1.14 a  | 39.79 ± 0.95d    |
| 2IBeA            | 9.27 ± 0.35 ab | 20.59 ± 0.37 a  | 36.60 ± 1.43 abcd|
| 2IBeA + V$_1$    | 8.47 ± 0.59 ab | 20.51 ± 0.68 a  | 35.87 ± 2.22 abc |
| 2IBeA + V$_2$    | 7.28 ± 0.67 a  | 19.84 ± 0.42 a  | 35.08 ± 1.79 abc |

Means followed by different letters for treatments differ significantly at $p < 0.05$ ($n = 8$).

### 4. Discussion

The toxic effects of iodine applied in the form of iodide (at doses of 10 µmol·dm$^{-3}$ and 100 µmol·dm$^{-3}$) and iodate (KIO$_3$ 100 µmol·dm$^{-3}$) were previously demonstrated in studies on rice biofortification [14]. The authors in [42] applied iodine via fertigation (2.34 mmol·dm$^{-3}$ for KIO$_3$ and 3.01 mmol·dm$^{-3}$ for KI) for the greenhouse cultivation of tomatoes, potatoes, maize, barley and observed the strongly phytotoxic effect of iodine compounds on plants. The authors observed a decrease in the growth of the biomass of these plants. In studies on the soil and foliar application of KI and KIO$_3$ at various doses in the cultivation of maize, wheat, and rice, the authors did not observe significant effects of the tested compounds on plant biomass and grain yield [15]. Other scientific reports indicate the bio-stimulating effect of iodine used at low concentrations, such as increases in
biomass in water spinach [27,32] and spinach [9,43] and increases in the yield of soybeans, rapeseed [4], and strawberry [18].

These studies did not show any negative or phytotoxic effects of organic and inorganic iodine compounds applied to the soil and vanadium fertilization on the growth and development of sweetcorn plants. The applied doses of iodine compounds (10 µmol l·dm⁻³) for all compounds of this element and the doses of vanadium (0.1 and 1 µmol V·dm⁻³) were found to be safe for sweetcorn plants. The soil application of iodine compounds in combination with vanadium (10 and 0.1 µmol V·dm⁻³, respectively) in the early developmental stages of sweetcorn (BBCH 15) significantly increased the root mass. The application of KI, KIO₃, and the organic form 5-ISA significantly increased the height of sweetcorn plants [44].

The stimulating effect of vanadium at low doses was confirmed in the cultivation of peppers [34]. A 5 µmol V·dm⁻³ dose of vanadium increased the plant height, stem diameter, number of leaves and flower buds, volume of roots, and weight of fresh and dry pepper biomass. Higher concentrations of vanadium (i.e., 10 and 15 µmol·dm⁻³ V) had a negative effect on pepper plants [34]. Smoleń et al. [21] conducted an experiment on hydroponic lettuce cultivation using organic (5-ISA and 3,5-diISA) and inorganic (KIO₃) iodine compounds at the same dose of 10 µmol l·dm⁻³ and in combination with four different doses of vanadium (0.05, 0.1, 0.2, and 0.4 µmol V·dm⁻³). The addition of organic iodine compounds to the medium (5-ISA and 3,5-diISA) reduced the size of the lettuce head by 7.5 times compared to the control object, and the object with KIO₃ applied at the same dose. The specificity of hydroponic cultivation is also important, where the iodine compounds are added to the growing medium and supplied throughout the period of growing lettuce. This previous study used seven soil applications for the cultivation of maize.

The soil application of iodine compounds and the combined application of iodine and vanadium in two doses significantly increased the content of iodine in all tested parts of the plant, i.e., roots, leaves, and sweetcorn grain. The strongest enrichment of sweetcorn grain with iodine was achieved by applying the organic compounds 5-ISA and 2-IBeA (analyzing only the effectiveness of the various forms of iodine applied individually without vanadium). The effectiveness of the forms of iodine used and their accumulation varied depending on the part of the plant. In the case of roots, the application of 2-IBeA was found to be the most effective. The distribution according to the efficiency of accumulation was 2-IBeA > KI > KIO₃ > 5-ISA in the roots, KI > KIO₃ > 5-ISA = 2-IBeA in the leaves, and 5-ISA = 2-IBeA > KI = KIO₃ in the grain. In the cultivation of tomato, the dominance of the application of organic forms on the accumulation of iodine in individual parts of the tomato plant was also demonstrated as follows: 4-IBeA > 3,5-diISA > 5-ISA > KI > 2-IBeA > KIO₃ > 2,3,5-triliBeA in leaves and petioles, 2-IBeA > 5-ISA > 2,3,5-triliBeA > 4-IBeA > 3,5-diISA > KI > KIO₃ in roots, and 2-IBeA > KI > 4-IBeA > 5-ISA > 3,5-diISA > KIO₃ > 2,3,5-triliBeA in tomato fruits [17]. In the cultivation of water spinach, the greatest accumulation of iodine was observed after applying the organic compound of iodine as follows: CH₂ICOO⁻ > I⁻ > IΟ₃⁻ [27]. Research on the effectiveness of iodine enrichment in crops has been mainly carried out using inorganic iodine KI and KIO₃. Many studies on crops have demonstrated more efficient iodine intake in the form of KI than KIO₃ [14,18,42,45–47], the latter of which must be reduced to I⁻ before uptake [9,32]. On the other hand, greater iodine accumulation with the addition of KIO₃ than KI was found in the cultivation of spinach [24].

Previous research on plants with the most effective degree of iodine accumulation showed leafy vegetables to be the best biofortification targets [43,48,49]. Cereals, including maize, are the dietary foundation of people in both developing and developed countries. The development of effective methods for enriching cereal plants with iodine will facilitate a wide range of methods to combat “hidden hunger”, diseases caused by iodine deficiency in the diet [50,51]. The biofortification of rice into iodine did not result in any notable increases of iodine content in the grain, likely due to the specificity of iodine transport in the plant which takes place largely through the xylem. The efficiency of enriching the generative parts of the plant with iodine (rice grains) is limited. The iodine content in the
vegetative parts was several times higher than that in the grain [14]. Landini et al. [22] demonstrated the possibility of iodine transport through the phloem in tomatoes, which was confirmed by the significantly higher content of iodine in the fruit (generative parts of the plant) compared to the control. Similar results indicating effective iodine transport to the generative parts were found in the cultivation of tomato [17,42], strawberry [18], rice, and maize [9,15,52].

Vanadium-dependent haloperoxidases (vHPO) are crucial enzymes in the metabolism of brown algal halides (Cl\(^{-}\), Br\(^{-}\), I\(^{-}\)); vanadium-dependent iodoperoxidases play an important role in iodine accumulation [31,32] and antioxidant defence [29]. VHO enzymes play a central role in both the capture of iodine from seawater and the synthesis of volatile hydrogen halides in marine algae [29,31]. Most studies have focused on *Laminaria digitata*, the brown North Atlantic algae considered to be a biogeochemical pump of iodine and bromine from the ocean to the atmosphere and the strongest accumulator of iodine [29,31]. The interactions of iodine and vanadium in higher plants, however, are not yet well known. The present research showed that vanadium in a lower applied dose (0.1 \(\mu\)mol V \(\cdot\) dm\(^{-3}\)) in combination with KI increased the content of iodine in the roots, leaves, and grain. The combined application of KIO\(_3\) with vanadium at a lower dose resulted in more effective transport to the higher parts of the plant, which led to higher iodine content in the leaves and grains compared to the application of KIO\(_3\) alone. Under the combined application of 5-ISA and vanadium (1 \(\mu\)mol V \(\cdot\) dm\(^{-3}\)), we observed a stimulating effect of this organic form of iodine on the accumulation of vanadium in the roots, as well as an antagonistic effect of vanadium in combination with 5-ISA on the accumulation of iodine in sweetcorn. On the other hand, under the combined application of vanadium at both doses (0.1 and 1 \(\mu\)mol V \(\cdot\) dm\(^{-3}\)), 2-IbeA led to the significantly more effective transport of iodine to, and accumulation in, the grains. The most effective application was observed for 2-IbeA + V. Vanadium application at a dose of 0.10 and 0.20 \(\mu\)mol V \(\cdot\) dm\(^{-3}\) V together with the organic form of 3,5-diISA iodine increased the iodine content in lettuce leaves [21].

The ratios of iodine in the roots to leaves and in the roots to the grains for the combinations with organic iodine (2-IbeA + V2, where the iodine content was highest in the grain) and inorganic iodine (KI + V1, where the iodine content was highest in the roots and equally high in the grain) were as follows: for 2-IbeA + V2 30:1 (root: grain), 7:1 (leaf: grain), and 9:1 (root: leaf) for KI + V1; 53:1 (root: grain), 25:1 (leaf: grain), and 2:1 (root: leaf). The difference in the iodine content in the roots after the application of iodine compounds applied individually and in combination with vanadium was several dozen times lower (depending on the combination used) than the iodine content in the kernels of sweetcorn. The iodine accumulation gradient described in the literature is as follows: roots > leaves > stem > fruit > seeds [15,16,53,54]. In the present study, analogous dependencies were obtained for the level of iodine accumulation in the individual parts of the sweetcorn plants.

The reports in the literature on the accumulation of vanadium in various parts of the plant indicate that the roots are characterized by the highest degree of vanadium accumulation and low mobility to the above-ground parts of the plant. The poor reutilization of vanadium into the above-ground parts of plants is well known [35,55,56]. This dependence was also observed for maize. In the roots and leaves of sweetcorn, the content of vanadium increased with an increase in the dose. The concentration of vanadium in the roots was, on average, 50 times higher than that in the leaves. The combined application of 5-ISA with vanadium at a dose of 0.1 \(\mu\)mol \(\cdot\) dm\(^{-3}\) stimulated the accumulation of vanadium in the grains. The same high content of vanadium in the grain observed in 5-ISA + V1 was also observed in KIO\(_3\) + V1. The ratio of vanadium in roots, leaves, and grains for 5-ISA + V2 (the combinations with the highest content of vanadium in the roots and leaves, reflecting low vanadium mobility) were 875:1 (root: grain), 14:1 (leaf: grain), and 57:1 (root: leaf). In maize leaves and roots, the level of vanadium accumulation increased with an increase in dose. This confirms the results obtained in the cultivation of beans [55], pepper [34], and chickpea [36].
The dry matter content in maize leaves was statistically significantly lower in the objects with the application of vanadium (0.1 and 1 µmol V·dm$^{-3}$). In the roots, the application of 2-IBEa + V2 in the soil led to statistically significantly lower dry matter content than that in the control. On the other hand, the application of 5-ISA + V2 in the grain caused an increase in dry matter content compared to the control. In the cultivation of pepper, the dry matter content in leaves, roots, and shoots was significantly higher than that in the control at a dose of 5 µmol·dm$^{-3}$ of vanadium [34] and in the cultivation of beans, for which an increase in the dry matter content was observed with an increase in the dose of vanadium compared to the control [35].

Fertilization with 5-ISA yielded the highest content of sugars and vitamin C in grain, and additional fertilization with vanadium using this iodine compound resulted in a reduction in vitamin C content. For KIO$_3$ used with vanadium, a reduction in sugar content was observed compared to the application of KIO$_3$ only. In the cultivation of pepper, vanadium stimulated an increase of sugar content in the plant leaves [34]. In sugar beet, the sucrose content increased by 28% in plants treated with 10 mmol V·dm$^{-3}$ [57]. The application of KI in the cultivation of lettuce significantly increased the content of fructose at all tested doses, as well as glucose and sucrose (at doses of 20 and 40 µmol·dm$^{-3}$, respectively). KIO$_3$ had a negative effect on the content of fructose, glucose, and sucrose in lettuce leaves.

In many previous studies on the influence of iodine and vanadium (in various forms), different dependencies were observed in terms of the influence of these elements on the functioning of mineral nutrition, i.e., on the macro- and microelements of the plant nutrition process [8,35,58]. With high probability, this result is related to the plant species and the iodine [8] or vanadium doses used [34]. There is no unequivocal relationship between iodine and vanadium on the mineral nutrition of maize plants, which was observed to be specific for each of the iodine compounds used. The combination with the application of 5ISA was different from other combinations. Compared to the control, the application of 5ISA significantly reduced the content of Ca, P, K, Mg, and Mn in the grain and Mg and Mo in the leaves. Despite this result, the nutritional intake of the plants with these ingredients was so high that there were few negative consequences on the growth and development of plants or the yield of corn cobs. The literature data show that iodine may have an antagonistic or synergistic effect on the uptake of macro- and microelements [35]. Smolen and Sady [24] showed increased uptake and accumulation of Mg, Na, Cu, and Fe in spinach cultivation at a dose of 1 mg I·dm$^{-3}$. A higher dose of iodine, 2 mg I·dm$^{-3}$, increased the content of Na, Fe, Zn, and Al in spinach leaves and decreased the content of P, S, Cu, and Ba. The fertilization of KI plants had a negative effect on the content of Ca, Mg, B, and Mn in the leaves of maize plants in sweet maize cultivation at an early stage of development (BBCH 15) [44]. This result was caused by the dilution effect, as KI fertilization enabled the maize plants to grow heavier and longer roots, as well as heavier and taller above-ground parts.

5. Conclusions

The effective biofortification of corn grain into iodine was possible despite the poor mobility of this element into the generative organs of plants, including the grains of cereal plants, as described in the literature. The organic iodine compounds 5-ISA and 2-IBeA produced the strongest enrichment of iodine in sweetcorn grains. The synergistic effect of vanadium on the accumulation of iodine in corn grain was demonstrated after the application of the organic compound 2-IBeA, while the application of vanadium together with 5-ISA presented an antagonist effect on the accumulation of iodine in the grains. Organic 5-ISA and inorganic KIO$_3$, in combination with a lower dose of vanadium, significantly increased the accumulation of this element in the grain. This study confirmed the poor transport of vanadium in plants, as this element was mainly accumulated in the roots of sweetcorn. The application of 5-ISA (without vanadium) significantly influenced the quality parameters of sweetcorn grain, increasing the content of vitamin C and sugars.
Sweetcorn species can thus be considered for iodine biofortification programs. Such programs will allow researchers to incorporate the principles of soil fertilization with iodine in agrotechnical methods for combating iodine deficiency in the diets of people in many regions around the world.

**Author Contributions:** S.S., M.G., conceived and designed experiments; S.S., M.G., D.G., performed element content analyses, data analysis and wrote the manuscript; Ł.S., help with wrote and revised the manuscript. All authors have read and agreed to the final version. All authors have read and agreed to the published version of the manuscript.

**Funding:** The subvention from the Polish Ministry of Science and Higher Education for the University of Agriculture in Krakow.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** We thank all the participants without their contributions this would not have been possible.

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

**References**

1. Khan, M.K.; Pandey, A.; Akkaya, M.S.; Gezgin, S.; Hamurcu, M.; Hakki, E.E. Wheat biofortification—A potential key to human malnutrition. *J. Elem.* **2017**, *22*, 937–944. [CrossRef]
2. Ginter, A.; Szarek, S. Sytuacja Dochodowa Producentów Zboża Na Przykładzie Uprawy Pszenicy. *J. Agribus. Rural Dev.* **2010**, *4*, 29–39.
3. White, P.J.; Broadley, M.R. Biofortification of crops with seven mineral elements often lacking in human diets—Iron, zinc, copper, calcium, magnesium, selenium and iodine. *New Phytol.* **2009**, *182*, 49–84. [CrossRef] [PubMed]
4. Mao, H.; Wang, J.; Wang, Z.; Yan, Y.; Lyons, G.; Zou, C. Using agronomic biofortification to boost zinc, selenium, and iodine concentrations of food crops grown on the loess plateau in China. *J. Soil Sci. Plant Nutr.* **2014**, *14*, 459–470. [CrossRef]
5. Nestel, P.; Bouis, H.E.; Meenakshi, J.V.; Pfeiffer, W. Symposium: Food Fortification in Developing Countries Biofortification of Staple Food Crops. *J. Nutr.* **2006**, *136*, 1064–1067. [CrossRef] [PubMed]
6. Bouis, H.E.; Saltzman, A. Improving nutrition through biofortification: A review of evidence from HarvestPlus, 2003 through 2016. *Glob. Food Sec.* **2017**, *12*, 49–58. [CrossRef] [PubMed]
7. Bouis, H.E.; Hotz, C.; McClafferty, B.; Meenakshi, J.V.; Pfeiffer, W.H. Biofortification: A new tool to reduce micronutrient malnutrition. *Food Nutr. Bull.* **2011**, *32*, 31–40. [CrossRef]
8. Krzepiłko, A.; Zych-Wężyk, I.; Święcilo, A.; Molas, J.; Skwaryło-Bednarz, B. Effect of iodine biofortification of lettuce seedlings on their mineral composition and biological quality. *J. Elem.* **2016**, *21*, 1071–1080. [CrossRef]
9. Gonzali, S.; Kiferle, C.; Perata, P. Iodine biofortification of crops: Agronomic biofortification, metabolic engineering and iodine bioavailability. *Curr. Opin. Biotechnol.* **2017**, *44*, 16–26. [CrossRef]
10. Zimmermann, M.B. The effects of iodine deficiency in pregnancy and infancy. *Paediatr. Perinat. Epidemiol.* **2012**, *26*, 108–117. [CrossRef]
11. Choudhry, H.; Nasrullah, M. Iodine consumption and cognitive performance: Confirmation of adequate consumption. *Food Sci. Nutr.* **2018**, *6*, 1341–1351. [CrossRef] [PubMed]
12. Bath, S.C. The effect of iodine deficiency during pregnancy on child development. *Proc. Nutr. Soc.* **2019**, *78*, 150–160. [CrossRef] [PubMed]
13. Weng, H.X.; Weng, J.K.; Yan, A.L.; Hong, C.L.; Yong, W.B.; Qin, Y.C. Increment of iodine content in vegetable plants by applying iodized fertilizer and the residual characteristics of iodine in soil. *Biol. Trace Elem. Res.* **2008**, *123*, 218–228. [CrossRef] [PubMed]
14. Mackowiak, C.L.; Grossl, R.R. Iodate and iodide effects on iodine uptake and partitioning in rice (*Oryza sativa* L.) grown in solution culture. *Plant Soil* **1999**, *212*, 135–143. [CrossRef] [PubMed]
15. Cakmak, I.; Prom-u-thai, C.; Guilherme, L.R.G.; Rashid, A.; Hora, K.H.; Yazici, A.; Savasli, E.; Kalayci, M.; Tutus, Y.; Phuphong, P.; et al. Iodine biofortification of wheat, rice and maize through fertilizer strategy. *Plant Soil* **2017**, *418*, 319–335. [CrossRef]
16. Caffagni, A.; Pecchioni, N.; Meriggi, P.; Bucci, V.; Sabatini, E.; Acciarri, N.; Ciriaci, T.; Pulcini, L.; Felicioni, N.; Beretta, M.; et al. Iodine uptake and distribution in horticultural and fruit tree species. *Ital. J. Agron.* **2012**, *7*, 229–236. [CrossRef]
17. Halka, M.; Smoler, S.; Czernicka, M.; Klimmek-Chodacka, M.; Pitala, J.; Tutaj, K. Iodine biofortification through expression of HMT, SAMT and SSI genes in *Solanum lycopersicum* L. *Plant Physiol. Biochem.* **2019**, *144*, 35–48. [CrossRef]
18. Li, R.; Liu, H.P.; Hong, C.L.; Dai, Z.X.; Liu, J.W.; Zhou, J.; Hu, C.Q.; Weng, H.X. Iodide and iodate effects on the growth and fruit quality of strawberry. *J. Sci. Food Agric.* **2017**, *97*, 230–235. [CrossRef]
19. Smoleń, S.; Skoczylas, Ł.; Ledwożyw-Smoleń, I.; Rakocy, R.; Kopec, A.; Piątkowska, E.; Bieńkowska-Kopec, R.; Pysz, M.; Koronowicz, A.; Kapusta-Duch, J.; et al. Iodine and selenium biofortification of lettuce (Lactuca sativa L.) by soil fertilization with various compounds of these elements. *Agric. Sci. Pol. Hortorum Cultus* 2016, 15, 69–91.

20. Lawson, P.G.; Daum, D.; Czauderna, R.; Meuser, H.; Härting, J.W. Soil versus foliar iodine fertilization as a biofortification strategy for field-grown vegetables. *Front. Plant Sci.* 2015, 6, 1–11. [CrossRef]

21. Smoleń, S.; Kowalski, I.; Halka, M.; Ledwożyw-Smoleń, I.; Grzanka, M.; Skoczylas, Ł.; Czeńnicka, M.; Pitala, J. Selected Aspects of iodate and iodosalicylate metabolism in lettuce including the activity of vanadium dependent haloperoxidases as affected by exogenous vanadium. *Agronomy* 2020, 10, 1. [CrossRef]

22. Landini, M.; Gonzali, S.; Perata, P. Iodine biofortification in tomato. *J. Plant Nutr. Soil Sci.* 2011, 174, 480–486. [CrossRef]

23. Germ, M.; Stibič, V.; Šircelj, H.; Jerše, A.; Krofic, A.; Golob, A.; Marsič, N.K. Biofortification of common buckwheat microgreens as well as the content of mineral nutrients and heavy metals in spinach plants (Spinacia oleracea L.). *Sci. Hortic.* 2012, 143, 176–183. [CrossRef]

24. Smoleń, S.; Sady, W. Influence of iodine form and application method on the effectiveness of iodine biofortification, nitrogen metabolism as well as the content of mineral nutrients and heavy metals in spinach plants (*Spinacia oleracea L.*). *Biol. Trace Elem. Res.* 2018, 164, 290–306. [CrossRef] [PubMed]

25. Blasco, B.; Rios, J.J.; Sánchez-Rodríguez, E.; Rubio-Wilhelmi, M.M.; Leyva, R.; Romero, L.; Ruiz, J.M. Study of the Interactions Between Iodine and Mineral Nutrients in Lettuce Plants. *J. Plant Nutr.* 2012, 35, 1958–1969. [CrossRef]

26. Halka, M.; Klimek-Chodacka, M.; Smolen, S.; Baranski, R.; Ledwożyw-Smolen, I.; Sady, W. Organic iodine supply affects tomato plants differently than inorganic iodine. *Physiol. Plant.* 2019, 184, 1–16. [CrossRef] [PubMed]

27. Weng, H.X.; Yan, A.L.; Hong, C.L.; Xie, L.L.; Qin, Y.C.; Cheng, C.Q. Uptake of different species of iodine by water spinach and its effect to growth. *Biol. Trace Elem. Res.* 2008, 124, 184–194. [CrossRef] [PubMed]

28. Saxena, I.; Srikanth, S.; Chen, Z. Cross talk between H2O2 and interacting signal molecules under plant stress response. *Front. Plant Sci.* 2016, 7, 1–16. [CrossRef]

29. Tymon, T.M.; Miller, E.P.; Gonzales, J.L.; Raab, A.; Kipper, F.C.; Carrano, C.J. Some aspects of the iodine metabolism of the giant kelp *Macrocystis pyrifera* (phaeophyceae). *J. Inorg. Biochem.* 2017, 177, 82–88. [CrossRef] [PubMed]

30. Verhaeghe, E.F.; Fraysse, A.; Guerquin-Kern, J.L.; Wu, T.D.; Devès, G.; Mioskowski, C.; Leblanc, C.; Ortega, R.; Ambroise, Y.; Potin, P. Microchemical imaging of iodine distribution in the brown alga *Laminaria digitata* suggests a new mechanism for its accumulation. *J. Biol. Inorg. Chem.* 2008, 13, 257–269. [CrossRef]

31. Leblanc, C.; Colin, C.; Cosse, A.; Delage, L.; La Barre, S.; Morin, P.; Fiévet, B.; Voiseux, C.; Ambroise, Y.; Verhaeghe, E.; et al. Iodine transfers in the coastal marine environment: The key role of brown algae and of their vanadium-dependent haloperoxidases. *Biochimie* 2006, 88, 1773–1785. [CrossRef]

32. Medrano-Macías, J.; Leija-Martínez, P.; González-Morales, S.; Juárez-Maldonado, A.; Benavides-Mendoza, A. Use of iodine to biofortify and promote growth and stress tolerance in crops. *Front. Plant Sci.* 2016, 7, 1–20. [CrossRef]

33. Yang, J.; Wang, M.; Jia, Y.; Gou, M.; Zeyer, J. Toxicity of vanadium in soil on soybean at different growth stages. *Environ. Pollut.* 2017, 231, 48–58. [CrossRef] [PubMed]

34. García-Jiménez, A.; Trejo-Téllez, L.I.; Guillén-Sánchez, D.; Gómez-Merino, F.C. Vanadium stimulates pepper plant growth and flowering, increases concentrations of amino acids, sugars and chlorophylls, and modifies nutrient concentrations. *PLoS ONE* 2018, 13, e0201908. [CrossRef] [PubMed]

35. Akoumianaki Ioannidou, A.; Barouchas, P.E.; Kyramariou, A.; Ilia, E.; Moustakas, N.K. Effect of Vanadium on Dry matter and Nutrient Concentration in pennyroyal (*Mentha pulegium*) flower. *Bull. Univ. Agric. Sci. Vet. Med. Cluj-Napoca. Hortic.* 2015, 72, 1–4. [CrossRef]

36. Imtiaz, M.; Ashraf, M.; Rizwan, M.S.; Nawaz, M.A.; Rizwan, M.; Mehmood, S.; Yousaf, B.; Yuan, Y.; Ditta, A.; Mumtaz, M.A.; et al. Vanadium toxicity in chickpea (*Cicer arietinum*) L grown in red soil: Effects on cell death, ROS and antioxidative systems. *Ecotoxicol. Environ. Saf.* 2018, 159, 139–144. [CrossRef]

37. Vachirapatama, N.; Jirakiattikul, Y.; Dicinoski, G.; Townsend, A.T.; Haddad, P.R. Effect of vanadium on plant growth and its accumulation in plant tissues. *Songklanakarin J. Sci. Technol.* 2011, 33, 255–261.

38. Smoleń, S.; Ledwożyw-Smoleń, I.; Sady, W. The role of exogenous humic and fulvic acids in iodine biofortification in spinach (*Spinacia oleracea L.*). *Plant Soil* 2016, 402, 129–143. [CrossRef]

39. Pasławski, P.; Migaszewski, Z.M. The quality of element determinations in plant materials by instrumental methods. *Polish J. Environ. Stud.* 2006, 15, 154–164.

40. Rizelio, V.M.; Tenfen, L.; Da Silveira, R.; Gonzalez, L.V.; Costa, A.C.O.; Fett, R. Development of a fast capillary electrophoresis method for determination of carbohydrates in honey samples. *Talanta* 2012, 93, 62–66. [CrossRef]

41. Zhao, Y.; Zheng, J.; Yang, M.; Yang, G.; Wu, Y.; Fu, F. Speciation analysis of selenium in rice samples by using capillary electrophoresis-inductively coupled plasma mass spectrometry. *Talanta* 2011, 84, 983–988. [CrossRef]

42. Caffagni, A.; Arru, L.; Meriggi, P.; Milc, J.; Perata, P.; Pecchioni, N. Iodine fortification plant screening process and accumulation in tomato fruits and potato tubers. *Commun. Soil Sci. Plant Anal.* 2011, 42, 706–718. [CrossRef]

43. Dai, J.L.; Zhu, Y.G.; Zhang, M.; Huang, Y.Z. Selecting iodine-enriched vegetables and the residual effect of iodate application to soil. *Biol. Trace Elem. Res.* 2004, 101, 265–276. [CrossRef]

44. Grzanka, M.; Smolen, S.; Kovačić, P. Effect of vanadium on the uptake and distribution of organic and inorganic forms of iodine in sweetcorn plants during early-stage development. *Agronomy* 2020, 10, 1666. [CrossRef]
45. Kiferle, C.; Gonzali, S.; Holwerda, H.T.; Ibaceta, R.R.; Perata, P. Tomato fruits: A good target for iodine biofortification. *Front. Plant Sci.* **2013**, *4*, 205. [CrossRef] [PubMed]

46. Zhu, Y.G.; Huang, Y.Z.; Hu, Y.; Liu, Y.X. Iodine uptake by spinach (*Spinacia oleracea* L.) plants grown in solution culture: Effects of iodine species and solution concentrations. *Environ. Int.* **2003**, *29*, 33–37. [CrossRef]

47. Kiferle, C.; Ascrizzi, R.; Martinelli, M.; Gonzali, S.; Mariotti, L.; Pistelli, L.; Flamini, G.; Perata, P. Effect of Iodine treatments on *Ocimum basilicum* L.: Biofortification, phenolics production and essential oil composition. *PLoS ONE* **2019**, *14*, e0226559. [CrossRef] [PubMed]

48. Weng, H.X.; Hong, C.L.; Yan, A.L.; Pan, L.H.; Qin, Y.C.; Bao, L.T.; Xie, L.L. Mechanism of iodine uptake by cabbage: Effects of iodine species and where it is stored. *Biol. Trace Elem. Res.* **2008**, *125*, 59–71. [CrossRef]

49. Voogt, W.; Holwerda, H.T.; Khodabaks, R. Biofortification of lettuce (*Lactuca sativa* L.) with iodine: The effect of iodine form and concentration in the nutrient solution on growth, development and iodine uptake of lettuce grown in water culture. *J. Sci. Food Agric.* **2010**, *90*, 906–913. [CrossRef]

50. Zia, M.H.; Watts, M.J.; Gardner, A.; Chenery, S.R. Iodine status of soils, grain crops, and irrigation waters in Pakistan. *Environ. Earth Sci.* **2015**, *73*, 7995–8008. [CrossRef]

51. Cakmak, I.; Marzorati, M.; Van Den Abbeele, P.; Hora, K.; Holwerda, H.T.; Yazici, M.A.; Savasli, E.; Neri, J.; Du Laing, G. Fate and Bioaccessibility of Iodine in Food Prepared from Agronomically Biofortified Wheat and Rice and Impact of Cofertilization with Zinc and Selenium. *J. Agric. Food Chem.* **2020**, *68*, 1525–1535. [CrossRef]

52. Zou, C.; Du, Y.; Rashid, A.; Ram, H.; Savasli, E.; Pieterse, P.J.; Ortiz-Monasterio, I.; Yazici, A.; Kaur, C.; Mahmoud, K.; et al. Simultaneous Biofortification of Wheat with Zinc, Iodine, Selenium, and Iron through Foliar Treatment of a Micronutrient Cocktail in Six Countries. *J. Agric. Food Chem.* **2019**, *67*, 8096–8106. [CrossRef]

53. Weng, H.X.; Hong, C.L.; Xia, T.H.; Bao, L.T.; Liu, H.P.; Li, D.W. Iodine biofortification of vegetable plants—an innovative method for iodine supplementation. *Chin. Sci. Bull.* **2013**, *58*, 2066–2072. [CrossRef]

54. Budke, C.; thor Straten, S.; Mühling, K.H.; Broll, G.; Daum, D. Iodine biofortification of field-grown strawberries—Approaches and their limitations. *Sci. Hortic.* **2020**, *269*, 109317. [CrossRef]

55. Saco, D.; Martin, S.; San José, P. Vanadium distribution in roots and leaves of *Phaseolus vulgaris*: Morphological and ultrastructural effects. *Biol. Plant.* **2013**, *57*, 128–132. [CrossRef]

56. Anke, M. Vanadium—An element both essential and toxic to plants, animals and humans? *An. la Real Acad. Nac. Farm.* **2004**, *70*, 961–999.

57. Singh, B.; Wort, D.J. Effect of Vanadium on Growth, Chemical Composition, and Metabolic Processes of Mature Sugar Beet (*Beta vulgaris* L.) Plants. *Plant Physiol.* **1969**, *44*, 1321–1327. [CrossRef] [PubMed]

58. Smoleń, S.; Sady, W.; Rozek, S.; Ledwozyw-Smoleń, I.; Strzetelski, P. Preliminary evaluation of the influence of iodine and nitrogen fertilization on the effectiveness of iodine biofortification and mineral composition of carrot storage roots. *J. Elem.* **2011**, *16*, 275–285. [CrossRef]