Micronutrients in the Soil and Wheat: Impact of 84 Years of Organic or Synthetic Fertilization and Crop Residue Management

Santosh Shiwakoti 1,2, Valtcho D. Zheljazkov 2,* , Hero T. Gollany 3, Markus Kleber 2, Baoshan Xing 4 and Tess Astatkie 5

1 Department of Crop and Soil Sciences, Washington State University, Pullman, WA 99164, USA
2 Department of Crop and Soil Science, Oregon State University, Corvallis, OR 97331, USA
3 USDA Agricultural Research Service, Columbia Plateau Conservation Research Center, Adams, OR 97810, USA
4 Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA 01003, USA
5 Faculty of Agriculture, Dalhousie University, Truro, NS B2N 5E3, Canada

* Correspondence: Valtcho.jeliazkov@oregonstate.edu; Tel.: +1-541-737-5877

Abstract: Crop residues are an important source of plant nutrients. However, information on the various methods of residue management on micronutrients in soil and wheat (Triticum aestivum L.) over time is limited. A long-term (84-year) agroecosystem experiment was assessed to determine the impact of fertilizer type and methods of crop residue management on micronutrients over time under dryland winter wheat-fallow rotation. The treatments were: no N application with residue burning in fall (FB), spring (SB), and no residue burn (NB); 45 kg N ha\(^{-1}\) with SB and NB; 90 kg N ha\(^{-1}\) with SB and NB; pea vines; and farmyard manure (FYM) and a nearby undisturbed grass pasture (GP). Wheat grain, straw, and soil samples from 1995, 2005, and 2015 were used to determine tissue total and soil Mehlich III extractable Mn, Cu, B, Fe, and Zn, and soil pH. After 84 years, extractable Mn and B in the top 10 cm of soil decreased in all plots, except for B in FYM and SB. The FYM plots had the highest extractable Mn (114 mg kg\(^{-1}\)) in the top 10 cm soil; however, it declined by 33% compared to the GP (171 mg kg\(^{-1}\)). Extractable Zn in the top 10 cm of soil increased with FYM while it decreased with inorganic N application in 2015; however, total Zn in grain increased by 7% with inorganic N (90 kg ha\(^{-1}\)) application compared to FYM application. The results suggest that residue management had similar impact on soil micronutrients. Inorganic N and FYM application can be integrated to reduce micronutrient losses from cultivation.

Keywords: boron; copper; iron; manganese; residue burn; zinc

1. Introduction

Micronutrient deficiencies are a serious problem affecting food production worldwide [1]. With the advent of high yielding and high grain/straw ratio wheat varieties, micronutrient deficiencies are not uncommon in wheat. Since soil micronutrient concentrations are relatively low, they need to be mobilized by roots. High-yielding varieties may have lower micronutrient accumulations in tissues than low-yielding ones due to root biomass formation lagging the increases in aboveground biomass [2]. Micronutrients are important not only for improving crop yields and the sustainability of crop production, but are also important for human health and have a role in overcoming micronutrient deficiencies [3]. For example, zinc deficiency affects over two billion people worldwide, and iron deficiency contributes to about 800,000 deaths annually [4]. Although micronutrients play important roles in agriculture and human nutrition, knowledge of the effect of agricultural practices...
on micronutrient dynamics in soil and wheat is limited. Thus, it is important to explore the impacts of agricultural management practices on micronutrient availability and their accumulations in widely consumed food crops.

Micronutrients in soil and crop are influenced by fertilization and cropping practices [5]. Cropping practices such as crop residue incorporation in soil result in an accumulation of micronutrients along with macronutrients. On the other hand, nutrient losses occur via volatilization to some extent when crop residues are burned [6]. Micronutrients are mostly added to the soil through organic amendments such as manure and green manures, whereas micronutrient addition through commercial fertilizer is not well documented and is in many instances neglected [3]. Many studies have reported that farmyard manure (FYM) increases soil micronutrient availability [7]. However, excess FYM application can lead to Zn precipitation with PO$_4^{2-}$, H$_2$PO$_4^{-}$, or HPO$_4^{2-}$ anions and decrease Zn mobility in soil [7]. The dynamics of micronutrient availability to crops shifts with changes in pH, soil organic matter (SOM), nutrient interactions, and nutrient responses to long-term fertilization [7]. For example, high soil pH decreases Cu, Zn, and Fe availability due to precipitation [3]. In long-term experiments, SOM [8] and different fertilization treatments [7] can exert a significant impact on micronutrients. Continuous application of ammonium fertilizers will decrease the soil pH which, in turn, will increase the availability of micronutrients, except molybdenum (Mo). Similarly, organic materials added to the soil produce chelating agents such as phenols, phenolic acids etc., which can increase Fe and Mn availability. In contrast, SOM has little to no effect on Cu availability [9].

Micronutrient availability is also affected by macronutrient application rates [9]. A high N rate increased the concentration of available Cu, Zn, Fe, and Mn, while a shortage of potassium (K) increased the availability of the same nutrients [10]. Morgounov et al. [11] suggested that management of N fertilizer could affect accumulation of grain micronutrient and found a strong positive relationship between Fe, Zn, and protein content in spring wheat. Xue et al. [12] found increased micronutrients in grain and straw of maize by optimized N fertilizer application rates when compared to lower or zero N supply. In contrast, several researchers found that high N fertilization rates had little to no effect on grain micronutrients [13,14]. These contrasting reports make the role of inorganic N and FYM on micronutrient dynamics debatable. A long-term field study could provide insights into micronutrients dynamics as a function of crop residue incorporation (burned vs. unburned) with inorganic N or organic amendments (FYM or pea vine).

The Crop Residue Experiment (CR-LTE) is the oldest long-term agricultural experiment (dating back 84 years) at the Columbia Basin Agricultural Research Center and can provide useful data on the effect of wheat residue management on micronutrient availability in soil and micronutrient accumulation in wheat grain and straw over time. The conceptual approach of our study consists of comparing micronutrients in soil samples (four depths: 0–10, 10–20, 20–30, and 30–60 cm) and in wheat grain and straw samples from 1995, 2005, and 2015 among the CR-LTE plots, and to determine the trend of micronutrient dynamics over 20 years. In addition, soil micronutrients from CR-LTE plots were compared with those from adjacent long-term undisturbed grass pasture (GP). This comparison demonstrated nutrient changes in the soil after 84 years of cultivation in CR-LTE. The objectives of this study were to quantify the effects of different crop residue management methods on soil micronutrient availability and micronutrient accumulation in wheat grain and straw over time, and to suggest practices to maintain and improve efficient nutrient cycling and resource base preservation in the dryland of the Pacific Northwest (PNW) and possibly in other regions with similar environmental conditions.

The CR-LTE was established in 1931 with the hypothesis that application of inorganic N could replace use of FYM and pea (*Pisum sativum* L.) vine (PV) and could also alleviate detrimental effects of residue burning. It was assumed that application of inorganic N would increase wheat biomass and, following return of biomass to the soil, more nutrients would be released through the mineralization of organic matter. Our objective was to test the following to determine if the hypothesis assumed 84 years ago can still be accepted.
(1) Inorganic N application (NB45, NB90, SB45, or SB90) increases or maintains the concentration of Mn, Zn, Cu, Fe, and B in soil over time compared with the application of FYM or PV.

(2) The spring residues burned plots with inorganic N application (SB45 or SB90) have similar or greater concentrations of Mn, Zn, Cu, Fe, and B in soil than no burn plots with inorganic N application (NB45 or NB90) over time.

(3) The concentrations of Mn, Zn, Cu, Fe, and B in wheat grain and straw are greater or similar in NB45, NB90, SB45, or SB90 plots to those in FYM and PV application plots.

(4) The concentrations of Mn, Zn, Cu, Fe, and B in wheat grain and straw are similar or greater in the SB45 or SB90 than those in the NB45 or NB90.

2. Materials and Methods

2.1. Site Descriptions and Treatments

The CR-LTE was established at the Columbia Basin Agriculture Center (CBARC), 15 km northeast of Pendleton, OR (45°42’ N, 118°36’ W, elev. 438 m asl) on a well-drained Walla Walla silt loam soil in 1931. Annual precipitation averages 437 mm, with 90% of precipitation between November and June [15]. The 81-year (1932–2012) maximum and minimum average annual temperatures were 17.4 °C and 3.06 °C respectively [16]. The soil contains 18% clay, 70% silt with pH 6.1–7.0, and has a cation exchange capacity of 18 cmol, kg⁻¹ in the upper 20 cm depth.

The study has an ordered block of two identical series (1400 and 1500) of nine treatments with two replications. Each series represents a wheat or a fallow phase of the winter wheat 14-month fallow (WW-F) rotation. This experiment does not have randomized treatments; however, extensive investigation of these soil samples and yield data has revealed no biases [17]. The individual plots are 11.6 m by 40.2 m, and are offset by 1 year to collect wheat yield and biomass data annually. Since the establishment of these experiments, various wheat varieties have been grown. The wheat cultivars grown since 1992 are: Malcolm from 1992 to 1995, Stephens from 1996 to 2005, and ORCF102 from 2006 to 2015.

The nine treatments are: fall burning of wheat residue without inorganic N (FB); spring burning of wheat residue without inorganic N (SB), 45 kg ha⁻¹ (SB45), and 90 kg ha⁻¹ (SB90); no burning of wheat residue without inorganic N (NB0), 45 kg ha⁻¹ (NB45) and 90 kg ha⁻¹ (NB90); and no burning of wheat residue with manure (FYM); or with pea vine (PV) incorporation. The results from these nine treatments were compared with the adjacent long-term (undisturbed since 1931) grassland pasture (GP) to determine the changes from the management practices. The GP is a 46 by 109 m plot that has no tillage history other than occasional mowing and may hence serve as a proxy for native grassland [18]. Bluebunch wheatgrass (Agropyron spicatum var. ‘Secar’) and Idaho fescue (Festuca idahoensis var. ‘Joseph’) are the dominant grass species in the GP.

Organic amendments were applied just prior to plowing in the spring of the fallow year; manure (FYM), at a rate of 11.2 Mg ha⁻¹ yr⁻¹ (47.5% DM, 0.85 Mg C ha⁻¹, and 70 kg N ha⁻¹ yr⁻¹), and PV at a rate of 1.12 Mg ha⁻¹ yr⁻¹ (87.8% DM, 0.41 Mg C ha⁻¹ yr⁻¹, and 18.5 kg N ha⁻¹ yr⁻¹). Urea-ammonium nitrate (UAN) was applied one week before seeding wheat in SB and NB treatments in October. Wheat stubble was left undisturbed after harvest and burned in September for FB, or in late March-early April for SB, SB45, and SB90. After burning, the soil was left undisturbed between burning and plowing for 195 days for FB while the soil was left undisturbed for 5 days in SB treatment. Glyphosate was used to control weeds in wheat stubble. After the burning and addition of organic amendments, the field was moldboard plowed 20 cm deep. Plots were seeded with wheat at 90 kg ha⁻¹ before 2002 using a John Deere (JD 8300) drill, while a Case IH 5300 disc drill has been used to plant wheat at 92 kg ha⁻¹ thereafter.
2.2. Soil Sampling and Laboratory Analysis

Soil cores from 1995, 2005, and 2015 were used in this study. We used archived soil from 0–10 cm, 10–20 cm, 20–30 cm, and 30–60 cm soil depths and plant samples (wheat straw and grain) from 1995 and 2005. The 2015 soil samples were collected in the summer of 2015. A truck-mounted Giddings Hydraulic Probe (Giddings Machine Company, Inc., Windsor, CO, USA) with a steel sampling tube (internal diameter 3.6 cm) was used to sample the soils after the wheat harvest. Soil samples collected from north-central and south-central positions in each plot were composited and used in our study. The cores were placed inside the oven at 105 °C for 24 h. The oven-dried soils were roller milled for four hours. Wheat grain and straw were removed from the center of each plot, dried at 60 °C, ground, and dry washed [19]. The Mehlich III extraction method [20], also known as the “universal extractant”, was used at the Central Analytical Lab (Oregon State University, Corvallis, OR, USA) to extract micronutrients because of its improved efficiency and suitability to the broad range of soil types, such as acidic, neutral, and basic soils [21,22]. Additionally, the archived samples were limited and Mehlich III provided the option of multiple element analysis from a single extract. The soils, and grain and straw samples were then analyzed for the available micronutrients using an inductively coupled plasma-optical emissions spectroscopy (ICP-OES, Model # 2100 DV, Waltham, MA, USA). The detection limits for each extractable micronutrients and detailed statement of purpose of the ICP-OES used is provided in Appendix A (Tables A1–A3). The CBARC station provided the soil pH data, which were measured in a 1:2 soil to 0.01 M CaCl₂ solution using pH electrodes after 30 min equilibrium time.

2.3. Statistical Analysis

Repeated measures analysis (RMA) of a split-plot design with two-blocks was conducted to determine the effect of the factors (Year, Treatment and Depth) on Mehlich III extractable Mn, Cu, Zn, B, and Fe in soil. Year (1995, 2005, and 2015) was used as the whole plot factor, with treatments (10 levels: GP, NB, SB45, SB90, NB45, NB90, FB0, SB0, FYM, and PV) as the subplot factor, and responses were measured repeatedly at four soil depths (0–10 cm, 10–20 cm, 20–30 cm, and 30–60 cm). In RMA, since independence assumption is likely to be violated, the Akaike Information Criterion was used to determine the most appropriate co-variance structure and was incorporated in the model using the Mixed Procedure of SAS [23]. For significant ($p$-value < 0.05) effects, multiple means comparisons were made to compare the least squares means of the corresponding treatment combinations. Letter groupings were generated using a 5% level of significance for the main effects and using a 1% level of significance for interaction effects.

For the total concentrations of Mn, Cu, Zn, B, and Fe in grain and straw, a split-plot design with two blocks was used; year (1995, 2005, and 2015) was the whole-plot factor and treatment was the subplot factor. Multiple means comparisons were carried out for the significant effects ($p$-value <0.05) by comparing the least squares means of the corresponding treatment combinations. Letter groupings were generated using a 5% level of significance.

3. Results and Discussion

Mehlich III extractable Mn, Cu, B, Zn, and pH in soil were influenced by the 84 years of cultivation and residue management methods in the CR-LTE (Table S1). Due to a technical problem, we were not able to determine Fe in the GP soil samples; however, Fe for CR-LTE samples was analyzed. Detailed depth, year, and treatment analysis (three-way interaction) of Mehlich III Mn, B, and Zn in soil are found in Tables S2–S4. Only significant results are discussed here.

The availability and uptake of micronutrients were largely determined by soil pH. Soil pH in the 0–10 cm and 10–20 cm soil depths was significantly influenced by the treatments over time (Figure S1). Plots with high N application rates of inorganic N fertilizer had lower soil pH than the rest of the CR-LTE plots, which is in line with a recent study from the same research station but in different
Only FYM application maintained soil pH after 84 years of cultivation compared to the soil pH of GP plots, possibly due to the replenishment of basic cations through manure application.

3.1. Mehlich III Extractable Manganese (Mn) in Soil

The concentration of Mn in the top 10 cm of soil decreased over time in all the CR-LTE plots (Figure 1). Among the CR-LTE plots, the concentration of Mn in the top 10-cm soil depth was significantly higher in the FYM and PV plots in 2015 than at the same depth in the rest of the plots (Table S2). Therefore, we refute our first hypothesis for Mn that inorganic N application (NB45, NB90, SB45 or SB90) increases or maintains the concentration of Mn in soil over time compared to FYM and PV. The higher amount of extractable Mn in the FYM or PV plots can be attributed to organic matter (OM) addition through manure or pea vines. Soil OM complexes Mn in soil and increases the mobility and availability of Mn [24]. Inorganic N fertilizer application may also increase the Mn availability, which may be due to the low pH resulting from the continuous use of inorganic N fertilizer; the solubility of Mn increases with the decrease in pH [25]. However, lower Mn in the N fertilized plots was observed in this study. The possible reason for low Mn with N fertilization may be due to the greater wheat yield and greater Mn removal in these plots compared with that in the other CR-LTE plots. There were no differences in soil Mn concentration between the SB and NB plots. Therefore, we accept our second hypothesis for Mn in soil that SB45 or SB90 have greater or similar soil concentrations of Mn than NB45 or NB90 over time.

![Figure 1. Mehlich III extractable manganese dynamics in upper 10-cm soil surface over 20 years in the Crop Residue Long-term Experiment (CR-LTE), Adams, OR. NB = No burn, SB = spring burn, FB = fall burn, GP = grass pasture, FYM = farmyard manure, and PV = pea vine. 0, 45, 90 accompanied by NB, SB, and FB represents rates of N applied at 0 kg ha⁻¹, 45 kg ha⁻¹, and 90 kg ha⁻¹, respectively. Means sharing the same letter are not significantly different at 5% significance level.](image)

Despite greater Mn in the FYM plots than the rest of the CR-LTE plots, FYM (114 mg kg⁻¹) plots lost Mn (33%) in the upper 10 cm of soil compared to GP (171 mg kg⁻¹) after 84 years of cultivation (Figure 1 and Table S2). Undisturbed GP with high SOM promoted the availability of most of the micronutrients [5]. Significant positive correlation between SOM and micronutrient cation availability is well documented [26,27]. The result from this study corresponds well to a study by Sanchez et al. [28] who found decline in extractable Mn after 8 years of clearing of the forest for cultivation.
3.2. Mehlich III Extractable Boron (B) in Soil

Extractable B in the upper 10 cm of soil consistently decreased over the 20 years in the CR-LTE plots (Figure 2). After 84 years of cultivation, no differences between treatments were observed for B concentration in the top 10 cm of soil (Figure 2 and Table S3); however, the inorganic N fertilized plots had greater B in 1995 in the upper 20-cm soil depths than the plots that received no inorganic N (Table S3). This can be attributed to the low pH in inorganic N fertilized plots, since B is more available in acidic soil. Apparently, soil pH was not the only factor responsible for greater B in 1995 in those plots because the B concentration did not differ among CR-LTE plots in 2005 and 2015 when inorganic N fertilized plots still had lower soil pH compared to other CR-LTE plots (Figure S1). Therefore, the results suggest that there were other factors that controlled the B availability in soils. The observed low B results could be due to the depletion of B in soil because of the continuous removal of B with wheat harvest without replenishment. There were no differences in extractable B between burn (SB) and no burn (NB) plots and hence, we accept the second hypothesis that inorganic N application in residue burn plots (SB45 or SB90) have similar or greater concentrations of B in soil than in NB plots with inorganic N application (NB45 or NB90) over time.

![Figure 2](image-url)  
**Figure 2.** Mehlich III extractable boron dynamics in upper 10-cm soil surface over 20 years in Crop Residue Long-term Experiment (CR-LTE), Adams, OR. NB = No burn, SB = spring burn, FB = fall burn, GP = grass pasture, FYM = farmyard manure, and PV = pea vine. 0, 45, 90 accompanied by NB, SB, and FB represents rates of N applied at 0 kg ha\(^{-1}\), 45 kg ha\(^{-1}\), and 90 kg ha\(^{-1}\), respectively. Means sharing the same letter are not significantly different at 5% significance level.

The role of SOM in B availability is not well understood. Several reports have shown a positive relation of SOM to B availability, whereas others found a negative relation between B availability and SOM accumulation [29]. Despite having greater SOM in the GP [30], in 1995, B in the top 10 cm of soil was markedly lower in the GP (0.17 mg kg\(^{-1}\)) than in the CR-LTE treatments (Table S3). In addition, B was below detection limits in the GP at all the studied soil depths, except for the 0–10 cm in 1995 (Table S3). According to Srivastava and Gupta [24], SOM tightly retains B which can account for the lower B found in GP and in organic amended treatments (i.e., FYM or PV) of this study.
3.3. Mehlich III Extractable Zinc (Zn) in Soil

Extractable Zn in the 0–10 cm soil depth was similar for the CR-LTE treatments in 1995 and 2005 (Table S4). However, in 2015, zinc was greater in the FYM than the other CR-LTE treatments at all the studied depths except for the 30–60 cm depth (Table S4). This suggests the effect of residue management has started to manifest. The observed change in extractable soil Zn refutes the first hypothesis that inorganic N application (NB45, NB90, SB45 or SB90) increases or maintains the concentration of Zn in soil over time compared to FYM or PV. In 2015, the concentration of Zn in the top 10 cm of soil declined with inorganic N application (Figure 3A), possibly due to Zn precipitation in the presence of a high concentration of soil phosphorus (P) in these plots. Zinc availability did not decrease significantly in the CR-LTE plots after cultivation for 84 years (Table S4). These results agree with those by Sanchez et al. [28] who reported relatively constant Zn in 8 years after cultivation in the rainforest of Peru. Extractable Zn in the 0–10 cm soil depth of the GP plots was higher than under CR-LTE treatments in 1995 and 2005 (Table S4) and was comparable to Zn in the FYM plots in 2015 (Figure 3A). The formation of soluble complexes and poor retention on the surface of SOM may be attributed to the greater extractable Zn in the GP plots [31].

![Figure 3. Mehlich III extractable zinc (A) and copper (B) dynamics in upper 10-cm soil surface after 84 years of Crop Residue Long-term Experiment (CR-LTE) in Adams, OR. NB = No burn, SB = spring burn, FB = fall burn, GP = grass pasture, FYM = farmyard manure, and PV = pea vine. 0, 45, 90 accompanied by NB, SB, and FB represents rates of N applied at 0 kg ha\(^{-1}\), 45 kg ha\(^{-1}\), and 90 kg ha\(^{-1}\), respectively. Means sharing the same letter are not significantly different (\(p > 0.05\)).](image)

3.4. Mehlich III Extractable Copper (Cu) in Soil

Extractable Cu was significantly \((p < 0.05)\) affected by the interaction of year and treatment (Table S5). In 1995, copper was lower in the GP (2.68 mg kg\(^{-1}\)) than in the NB90 plots (4.02 mg kg\(^{-1}\)), was comparable among all CR-LTE treatments in 2005, but was lower in GP than all CR-LTE plots in 2015 when averaged over the soil depths (Table S5). These results are in agreement with that of Fan et al. [32] who reported increased Cu following 160 years of cultivation. Copper binds strongly to both soluble and insoluble SOM; however, low molecular weight (<1000 MW) fractions of soluble organocomplexes of Cu like those in FYM and sewage sludge improve the availability of Cu in soils and plant uptake [33]. This could be the reason for low available Cu in the GP plots (average: 2.71 mg
kg$^{-1}$) in this study and relatively higher Cu in the FYM plots (average: 3.21 mg kg$^{-1}$). In 2015, all plots had similar Cu concentrations in the 0–10 cm soil depth, except in the GP and NB plots (Figure 3B). Therefore, we accept our first and second hypothesis for Cu in soil that (1) inorganic N application (NB45, NB90, SB45 or SB90) increases or maintains the concentration of Cu in soil over time compared to FYM or PV, and (2) the residue burned plots with inorganic N application (SB45 or SB90) have greater or similar concentrations of Cu in soil than no burn plots with inorganic N application (NB45 or NB90) over time.

3.5. Total Micronutrient Accumulation in Wheat Grain and Straw

Over the 84 years, total Zn and Mn in wheat grain were affected by the treatments whereas no main effects of treatments were observed for total Zn and Mn in straw (Table S6).

The concentrations of Zn in grain were comparable among the FYM (15 mg kg$^{-1}$), SB90 (16 mg kg$^{-1}$), and NB90 (16 mg kg$^{-1}$) plots and were significantly ($p < 0.05$) higher than in the FB (12 mg kg$^{-1}$), SB (13 mg kg$^{-1}$), SB45 (12 mg kg$^{-1}$), NB (13 mg kg$^{-1}$) (Figure 4A). Therefore, we accept our third hypothesis for Zn in grain that the concentration of Zn is similar or greater in inorganic N applied plots than in FYM or PV plots. This result suggests that higher N rates have a positive effect on Zn accumulation in wheat grain, which can be explained by the fact that low N availability in soil negatively affected the chelate levels and reduced chelates led to a reduction of translocation of Zn to grain [34]. According to Srivastava and Gupta [24], Cu is mutually antagonistic with Zn and competes for the common carrier sites, and hence inhibits the uptake of Zn. However, the results from this study do not agree with the latter statement because higher availability of Cu in soil did not affect Zn accumulation in the grain. The possibility of this disagreement could be attributed to the increased OM production in high N fertilizer rate and FYM plots compared to no N or low N rate plots, since OM can form simple complexes with Zn to increase its availability [24].

Figure 4. Total zinc (A) and manganese (B) dynamics in wheat grain after 84 years of the Crop Residue Long-term Experiment (CR-LTE) in Adams, OR. NB = No burn, SB = spring burn, FB = fall burn, FYM = farmyard manure, and PV = pea vine. 0, 45, 90 accompanied by NB, SB, and FB represents rates of N applied at 0 kg ha$^{-1}$, 45 kg ha$^{-1}$, and 90 kg ha$^{-1}$, respectively. Means sharing the same letter are not significantly different ($p > 0.05$).
The accumulation of Mn in wheat grain was influenced by the residue management methods and increased N fertilization rate in this study (Figure 4B). The NB45 and NB90 plots had greater Mn in grain than FYM or PV plots. Therefore, we accept our third hypothesis regarding Mn in grain that the concentration of Mn in grain is similar or greater in inorganic N applied plots than in FYM or PV plots. Svecnjak et al. [35] reported greater Mn in wheat grain with increased N rate, which is in line with our result. However, the mechanism involved in Mn uptake by N application is still not known. Also, Mn in grain was significantly greater in NB plots with inorganic N compared to SB plots with inorganic N application (Figure 4B). Total Mn in grain was greater in the NB45 (31 mg kg\(^{-1}\)) and NB90 (34 mg kg\(^{-1}\)) plots than in the SB45 (28 mg kg\(^{-1}\)) and SB90 (32 mg kg\(^{-1}\)) plots, respectively (Figure 4B). Therefore, we refute our fourth hypothesis for Mn in grain that concentration of Mn in grain is greater or similar in SB45 or SB90 than NB45 or NB90 plots.

4. Conclusions

This study reports long-term impacts of manure, pea vine, inorganic N application, and residue management (either burned or unburned) on micronutrient dynamics at four soil depths and in wheat straw and grain over 20 years (1995, 2005, and 2015) for the CR-LTE plots which have been in dryland WW-F since 1931. Overall, the results indicate that Mehlich III extractable Mn and B declined considerably, whereas Mehlich III extractable Cu increased over time compared to the GP. This study revealed that none of the CR-LTE treatments curbed micronutrient (except Cu) declines over time. However, micronutrients declined at lower rates with FYM and/or with inorganic N application, suggesting that the combination of inorganic N with FYM application could reduce micronutrient declines over time. Comparison of the extractable micronutrients with total soil micronutrients and then exploring the changes in available micronutrients brought by the treatments of the CR-LTE could have strengthened the output of this study. Decreased soil pH with N fertilization and increased OM application could play important roles in increasing micronutrients in soil and wheat under the dryland WW-F cropping system.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4395/9/8/464/s1, Figure S1: Effect of residue management on soil pH over time in the 0–10 cm and 10–20 cm soil depths, Table S1: ANOVA table for the main and interaction effects of year, treatment and depth on the concentration of Mehlich III extractable manganese, copper, boron, zinc, iron, and soil pH in the Crop Residue Long-Term Experiment, Table S2: Mean concentration of Mehlich III extractable manganese obtained from the 120 combinations of treatment, year and depth (cm) after 84 years for the Crop Residue Long-Term Experiment, Table S3: Mean concentration of Mehlich III extractable boron obtained from the 120 combinations of treatment, year, and depth (cm) after 84 years of the Crop Residue Long-Term Experiment, Table S4: Mean concentration of Mehlich III extractable zinc obtained from the 120 combinations of treatment, year and depth (cm) after 84 years of the Crop Residue Long-Term Experiment (CR-LTE), Table S5: Mean concentration of Mehlich III extractable copper obtained from the 30 combinations of treatment and year after 84 years of the Crop Residue Long-Term Experiment (CR-LTE), Table S6: ANOVA table of the main and interaction effects of year and treatment on the accumulation of Mn, Cu, B, Fe, and Zn in the grain and straw of wheat in the Crop Residue Long-Term Experiment.

Author Contributions: V.D.Z. came up with the idea, conceptualization and the methodology. In addition, V.D.Z. was involved with editing and revision of the paper; S.S. collected, analyzed the samples, and prepared the original draft; T.A. did the statistical analysis; H.T.G. analyzed the carbon, nitrogen and sulfur of soil and wheat tissue for the study and was involved in the review and edit of the manuscript; M.K. and B.X. reviewed and edited the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.
Appendix A

Table A1. Mehlich-III soil extraction protocols for Central Analytical Laboratory, Oregon State University, Corvallis, OR, USA.

| Reagents                                                   |
|------------------------------------------------------------|
| ➢ Ammonium Fluoride (NH$_4$F) fw = 37.037 g mol$^{-1}$      |
| ➢ Ethylenediaminetetraacetic acid dihydrate (EDTA) mw = 372.24 g mol$^{-1}$ |
| ➢ Deionized (DI) water                                     |
| ➢ Ammonium Nitrate (NH$_4$NO$_3$) fw = 80.04 g mol$^{-1}$ |
| ➢ Glacial Acetic acid (CH$_3$COOH) 17.4 M, mw = 60.05 g mol$^{-1}$ |
| ➢ Nitric Acid (HNO$_3$) 15.9 M, fw = 63.01 g mol$^{-1}$  |
| ➢ Elemental standards (1000 ppm; Ca, Mg, P, K; B, Fe, Mn, …) |

**Mehlich-III Stock Solution (3.75M NH$_4$F, 250mM EDTA)**

➢ Weigh 13.89 g NH$_4$F and 9.306 g EDTA dihydrate in a weigh boat and add to a 100 ml volumetric flask

➢ Dilute to 100 ml using DI water

**Mehlich-III Extractant (250 mM NH$_4$NO$_3$, 15 mM NH$_4$F, 1.0 mM EDTA, 13.0 mM HNO$_3$, 200 mM acetic acid)**

➢ Weigh 20 g NH$_4$NO$_3$ in a weigh boat and add to a 1L volumetric flask

➢ Using an adjustable pipette, add 4 ml of the Mehlich-III stock solution, 11.5 ml glacial acetic acid, and 0.82 ml HNO$_3$ to the flask

➢ Dilute to 1L using DI water

➢ Add a magnetic stir bar to the flask

➢ Stir and heat on low until all NH$_4$NO$_3$ is dissolved

➢ Cover and store in the refrigerator; use quickly (within 10 days)
Table A2. Inductively coupled plasma-optical emissions spectroscopy protocols for Central Analytical Laboratory, Oregon State University, Corvallis, OR, USA.

| Summary |
|----------------------|
| ➢ ICP-OES is used to analyze liquid samples for elemental composition. |
| ➢ Matrix-matched standards and a method blank are made and analyzed to produce a calibration curve. |
| ➢ Samples are introduced into the system using an autosampler. It will take approximately a half hour to prepare the machine for analysis. |
| ➢ Each sample and calibration standard will take approximately 1.5 minutes per element being analyzed, plus one minute for washing (all automatic). |
| ➢ A minimum of 5 ml is needed for any analysis, and more is needed if many elements are being analyzed, up to a maximum of 14 ml in the sample tube. |
| ➢ Preparing the instrument to shut down will take approximately twenty minutes. |

| Equipment |
|-----------|
| ➢ PerkinElmer 2100 DV |
| ➢ Chiller |
| ➢ Argon tank |
| ➢ Nitrogen tank |

| Reagents |
|----------|
| ➢ DI water |
| ➢ 10 ppm Mn solution |
| ➢ ICP standard solutions |
| ➢ 5% nitric acid |

Table A3. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) detection limits.

| Element      | Detection limits (µg/L) |
|--------------|-------------------------|
| Boron (B)    | 1                       |
| Copper (Cu)  | 0.4                     |
| Iron (Fe)    | 0.1                     |
| Manganese (Mn)| 0.1                    |
| Zinc (Zn)    | 0.2                     |

All detection limits were determined using elemental standards in dilute aqueous solution and are based on a 98% confidence level (3 standard deviations).
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