EFFECTS OF COPPER AND ZINC-OXIDE NANOPARTICLES ON GROWTH AND PRODUCTIVITY OF *Solanum lycopersicum* L. and *Phaseolus vulgaris* L.

BY

AKANBI-GADA, MARIAM ABIOLA

16/68ES001

B. Sc. (ABU), M. Sc. (ILORIN)

A THESIS SUBMITTED TO THE DEPARTMENT OF PLANT BIOLOGY, FACULTY OF LIFE SCIENCES, UNIVERSITY OF ILORIN, ILORIN, NIGERIA, IN FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF DOCTOR OF PHILOSOPHY (PH.D.) DEGREE IN PLANT BIOLOGY

MAY, 2021

CERTIFICATION

I certify that this work was carried out by Mrs. Akanbi-Gada, Mariam Abiola in the Department of Plant Biology, Faculty of Life Sciences, University of Ilorin, Ilorin, Nigeria, under my supervision.

_____ _____

Prof. P.O. Fatoba **Date**
Supervisor

APPROVAL PAGE

This thesis has been read and approved as having met the requirement of the Department of Plant Biology and Postgraduate School, University of Ilorin, Ilorin, Nigeria, for the Award of Doctor of Philosophy (Ph.D.) Degree in Plant biology.

Prof. P.O. Fatoba **Supervisor**	**Date**
Prof. K.S. Olorumaiye **Head of Department**	**Date**
External Examiner	**Date**

DEDICATION

This thesis is dedicated to Allah (SWT) for providing the means to this end; to the memory of my late father; Alhaji Akanbi Abubakar and my mother; Alhaja Adijat Akanbi

DECLARATION

I, Akanbi-Gada, Mariam Abiola (Matric Number - 16/68ES001) declare that this thesis entitled ”effects of copper and zinc-oxide nanoparticles on growth and productivity of *Solanum lycopersicum* L. and *Phaseolus vulgaris* L. is the result of a study carried out by me under the supervision of Prof. P.O. Fatoba in the Department of Plant Biology, University of Ilorin, Ilorin, Nigeria. I confirm that this thesis presents the results of my findings and that its contents are entirely my ideas unless otherwise stated with appropriate referencing. This thesis has not been submitted to any University nor is it before any other University for consideration for the Award of a Doctor of Philosophy (Ph.D.) degree in Plant Biology.

_____

AKANBI-GADA, M.A.

ACKNOWLEDGEMENTS

I give special praise to Allah (SWT) for providing the means to this end. May the peace and blessings of Allah (SWT) be on the holy Prophet of Islam, Muhammed (SAW). My profound and sincere gratitude goes to my supervisor, Prof. P.O. Fatoba for his professional, positive and constructive criticism of this research. Permit me sir to use your language: ‘’the unrecognised are also important’’; it is very hard for me to realize that I, a nobody am gradually becoming some body that is recognised. You knew where I was coming from, you gave me preference, encouragement and you supported me like I am your daughter. You help me realized my father’s vision over my life, though it was not easy. In my father’s word ‘I say thank you sir’’ and may the rest of your years on earth be better than your past and may you have a happy ending (amen). Your words of encouragement was the driving force that birthed the success that is been recorded today. Whenever the going becomes tough your words was the balm that soothes my aching heart, please accept my gratitude and appreciation because this is the best way I can do it.

This acknowledgement will not be complete if I failed to recognise my mentors. First of all; Prof. K.S Olorunmaiye, he gave me the idea of coming for Ph.D. In his words; ‘’Mrs Bridge like he always call me, do you know that the beauty of your master’s degree is not complete until you do your Ph.D’’. After series of phone calls from him, I finally came for my P.h.D. Sir; my story is sweet today because you believed in me. I will forever be grateful to you sir.

My second mentor is Dr C.O. Ogunkunle, sir thank you for been there. You gave me courage whenever it mattered most. You played the role of a friend and a mentor perfectly well and I say thank you for helping me in my research as well as my career. Doors of opportunity shall always be opened to you and God almighty shall answer all your open and secret prayers (amen). Dr Kehinde Olawepo (a rare gem), thanks also for all the beautiful ideas that birthed

the success been recorded today. You have been so helpful. God almighty shall always answer when you need help and call on him (amen).

My sincere gratitude further goes to the Head of the Department of Plant Biology, Prof. K.S Olorunmaiye, for his positive criticism and encouragement throughout my studies in the University of Ilorin, while also thanking other Lecturers in the Department of Plant Biology, who have impacted my life in one way or the other: Prof. O. T. Mustapha, Prof. A. A. AbdulRahaman, Prof. E. O. Etejere (retired), Prof. J. A. Morakinyo (retired), Prof. F. A. Oladele (Late), Dr. B. U. Olayinka, Dr. D. Animasaun, Dr. S. Oyedeji, Dr. (Mrs) K. A. Abdulkareem, Dr. A. A. Lateef, Dr. T. Garuba, Mr F.O. Egbedo, Dr. G. S. Olahan, Mr Sagaya and Mr. S. B. Adeyemi, you all mean so much to my academic progression. Furthermore, my immense gratitude goes to my internal supervisor in person of Dr Adebayo (late) of Chemistry Department, University of Ilorin, Ilorin Nigeria. May Allah (SWT) grant repose for your soul and may he grant you aljanat fridaous (amin). I will not forget to thank the non-academic staff of the Plant Biology Department: Mr A. B. Ibrahim, Mr S. Adebayo, Mr Bolu Ajayi, Mr A. O. Olawoyin, Mrs. N.O Suleman, Mrs I. A. Babatunde Mr. C. O. Onele, Mr. S. O. Akin, Mr. I. O. and Salimon. In addition, I will not fail to appreciate the wonderful people at the Botanical garden of Plant Biology, University of Ilorin in person of Mr. Abdullahi and Baba Abu; you are all appreciated. May the good lord reward you all.

To my parents; late Alhaji Akanbi Abubakar and Alhaja Adijat Akanbi, thank you for the beautiful virtue of patience you impacted in me without which this success would have become impossible.

To my husband, Alhaji Ladi Gada; thank you for your support and understanding. Thank you for the opportunity given me to show my talents. May we enjoy the result of this hard work in good health and abundance of wealth (amen).

To my children, thanks for been my pillar of strength. Aisha Gada; thank you for your maturity, you are always my "liver'' whenever my "liver" fails me. Thanks for always telling me that "though it may rain today the sun will definitely shine tomorrow" and for holding forth for me at home whenever I am not around. To Ameen Gada; I say thank you for the editing, correction and typesetting of this thesis. Without your support, the task would have been strenuous and tedious. To AbdulWalliy (the prayer warrior of the house) and Mohammed Gada (baby of the house) thank you for your prayers and encouragement. May Allah (SWT) grant you all beneficial knowledge fiduniyah walihairat (amin).

To my siblings; Mummy Faridat, Dr Kolapo, Mummy Islamiyat, Mummy Hanif, Taiye and Kehinde Akanbi, thanks for all the time you have supported me financially, morally and spiritually. One love will keep us together In Sha Allah (Omo iya dunni).

My special appreciation also to the wonderful Science Staff of Adeta Secondary School, Ilorin; in person of Mrs Zubair, Mr Musa, Mr Bashir, Mrs Abdulraheem, Mrs Shittu, Mr Shittu, Mrs Oukunle, Mrs Shoremekun, Mrs AbdulWahab, Mrs Sanni, Mr Ajadi, Mr Azeez and my dear friend Mrs Lawal of the humanity department, Government Day Secondary School Adeta.

To my friends and colleagues at the department of Plant and Environmental Biology Kwara State University, Malete: Dr Mrs Saliu, Mr Adio, Dr Mrs Oke, Dr Mrs Adepoju, Mrs Sidiq and Dr john, thanks so much for your support and encouragement.

To my colleagues in the struggle Abdulwasiu Opadokun, Mrs Oloyede and others; let us keep hope alive by striving hard to achieve a great feat as we have always desired. Finally to one of our Masters student at Kwara State University, Malete, Nigeria: Mr Najmdeen Abiodun

Bolaji, May Allah strengthen you the more and show you beneficial way to your dream (you are one in a million).

ABSTRACT

Plants growth and productivity require copper and zinc-oxide in small quantity but these nutrients are not readily available to plants. Nanotechnology may be helpful in the effective delivery of these nutrients. This study investigated the effects of engineered nanoparticles of copper (CuNPs) and zinc-oxide (ZnONPs) as well as bulk copper (bCu) and zinc-oxide (bZnO) on the growth and productivity of *Solanum lycopersicum* L. (tomato) and *Phaseolus vulgaris* L. (bean). The objectives of the study were to determine the effects of CuNPs, ZnONPs, bCu and bZnO on the: (i) growth performance of tomato and bean: ii) chlorophyll contents of tomato and bean; iii) responses of the enzymatic and non-enzymatic antioxidants in tomato and bean; (iv) starch and protein content of tomato and bean; and (v) bioaccumulation potentials of tomato and bean.

Four seeds of tomato and bean were planted separately in 96 pots each containing 1.7 kg of sandy loam soil pre-treated with 0 (control), 300, 600 and 1000 mg/kg of CuNPs, ZnONPs, bCu, and bZnO. Growth parameters were measured with metre rule, chlorophyll content with Acetone incubation method, enzymatic and non-enymatic antioxidants with U-V Spectrophotometer, starch and protein contents of were determined following standard methods. Data were analysed using two-way Analysis of variance and means were separated using Duncan Multiple Range Test at $p \leq 0.05$.

The findings of the study were that:

i. ZnONPs, CuNPs, bCu and bZnO treatments promoted larger leaf areas (3.00-14.83 cm^2) than the control (1.87-2.04 cm^2) and the largest leaf area in tomato was promoted by 300mg/kg of ZnONPs (4.93-12.71 cm^2). The number of leaves was highest in 300mg/kg of CuNPs (10.33-14.00) in beans. All treatments in tomato had higher number of leaves (3.00-14.83) than the control (2.67-2.99);

ii. chlorophyll a, b and total chlorophyll were more in control of bean (2.04, 2.73 and 3.20 mg/g) respectively than in 300mg/kgZnONPs (1.20, 0.10 and 1.23 mg/kg) and similar trend of 1.10,1.40 and 1.45 mg/g) in the control compared to (0.27. 0.37 and 0.56 mg/kg) recorded in 300mg/kgZnONPs of tomato;

iii. 300mg/kgCuNPs significantly ($p \leq 0.05$) increased ascorbic acid (highest) in bean 14.50% and 119.5% in tomato, while lycopene contents by 538.00% in bean and 967.00% in tomato and 1000mg/kgZnONPs significantly increased lycopene contents in tomato by 385.5%. Ascorbate peroxidase and superoxide dismutase significantly ($p \leq 0.05$) decreased respectively in bean by 242.00'% and 448.56% while it was54% and 493.93% in tomato; starch (4.20% and 40.15%) in bean and tomato; protein (44.93% and 70.15%) contents in the seed of bean and fruit of tomato respectively were higher in control than treatments; and

iv. Zinc was most bioaccumulated (305.00 mg/kg) in 1000mg/kgZnONPs while copper bioaccumulated 206.25 mg/kg in 1000mg/kgCuNPs in bean. Highest zinc bioaccumulation (312.50 mg/kg) was recorded in 1000mg/kgZnONPs and highest copper bioaccumulation (106.25 mg/kg) was recorded in 300 mg/kgCuNPs in tomato.

The study concluded that CuNPs and ZnONPs increased the growth, bioaccumulation potentials, non-enzymatic antioxidants but reduced enzymatic antioxidant, starch and protein contents of bean and tomato. The study recommended that 300 and 600 mg/kg of CuNPs and ZnONPs should be used in the cultivation of tomato and bean.

TABLE OF CONTENTS

TITLE PAGE		i
CERTIFICATION		ii
APPROVAL PAGE		iii
DEDICATION		iv
DECLARATION		v
ACKNOWLEDGEMENTS		vi
ABSTRACT		x
TABLE OF CONTENTS		xi
LIST OF FIGURES		xvi
LIST OF TABLES		xvii
CHAPTER ONE		1
INTRODUCTION		1
1.1	Background to the Study	1
1.2	Cowpeas (*Phaseolus vulgaris*) L.	3
1.3	Tomato (*Solanum lycope rsicum* L.)	4
1.4	Effects of Nanoparticles on the Growth and the Development of Plants	5
1.5	Statement of Research Problem	6
1.6	Justification of the Study	7
1.7	Aim of the Study	7
1.8	Objectives of the Study	7
1.9	Contributions and Significance of the Study	8
CHAPTER TWO		9
LITERATURE REVIEW		9
2.1	Nanoparticles and nanotechnology	9

2.2 Gold (Au) nanoparticles 13

2.3 Silver (Ag) nanoparticles 14

2.4 Cadmium (Cd) nanoparticles 16

2.5 Titanium oxide (TiO_2) nanoparticles 17

2.6 Zinc/zinc oxide (Zn/ZnO) nanoparticles 18

2.7 Copper and copper oxide (Cu/CuO) nanoparticles 20

2.8 Tomatoes (*Solanium Lycopersicum* L.) 21

2.9 Beans (*Phaseolus vulgaris* L.) 23

2.10 Bulk Copper and Zinc/Zinc-Oxide on Plant Growth and Developments 25

CHAPTER THREE 28

MATERIALS AND METHODS 28

3.1 Source of Materials and Description of the Varieties 28

3.2 Characterization of Nanoparticles 28

3.2.1 Field Scanning Electron Microscopy 28

3.2.2 Analysis of Carbon, nitrogen and oxygen 29

3.3 Determination of the size of Nanoparticles 29

3.4 Determination of the physico-chemical parameters of the soil 29

3.5 Experimental design 30

3.6.1 Leaf length 31

3.6.2 Leaf breadth 31

3.6.3 Leaf area 31

3.6.4 Number of leaves 31

3.6.5 Stem girth 32

3.6.6 Chlorophyll content determination 32

3.7 Determination of productivity parameters of beans and tomatoes 33

3.7.1 Day to flowering 33

3.7.2 Day to fruiting 33

3.7.3 Number of fruits or pods per plant 33

3.7.4 Number of seeds per pod 33

3.7.5 Number of seeds per plant 33

3.7.6 Fresh weight 34

3.7.7 Dry matter 34

3.8 Non enzymatic and enzymatic antioxidants of bean and tomato 34

3.8.1 Non enzymatic antioxidant 34

3.8.2 Determination of ascorbic acid content 34

3.8.2.1 Determination of total carotenoids: lycopene and beta-carotene 34

3.8.3 Determination of enzymatic antioxidant activities 35

3.8.3.1 Determination of ascorbate peroxidase (APX) 35

3.8.3.2 Determination of Catalase activities (CAT) 35

3.8.3.3 Determination of Superoxide dismutase (SOD) 36

3.9 Stress attributes determination 36

3.9.1 Determination of malondialdehyde (MDA) 36

3.9.2 Determination of hydrogen peroxide 37

3.9.3 Determination of Proline 37

3.10 Biochemical constituents of tomatoes and beans 38

3.10.1 Determination of protein 38

3.10.2 Seed starch 38

3.10.3 Determination of copper and zinc contents 39

3.10.4 Statistical analysis 39

CHAPTER FOUR 40

RESULTS 40

4.1 Characterization of the nanoparticles used 40

4.2 Physico-chemical parameters of the soil used for the experiment 45

4.3 Leaf lengths of beans 45

4.4 Leaf breadth in beans 54

4.5 Leaf Area in Beans 60

4.6 Number of leaves in beans 62

4.7 Stem girth in beans 72

4.8 Leaf lengths in Tomato 77

4.9 Leaf Breadths in tomato 83

4.10 Leaf area (cm^2) in tomato 88

4.11 Number of leaves in tomato 93

4.12 Stem girth in Tomato 98

4.13 Chlorophyll content in Beans during 2 and 4 WAP 2017 103

4.14 Chlorophyll content in Beans during 2 and 4 WAP 2018 104

4.15 Chlorophyll content in Tomato during 2 and 4 WAP of 2017 cropping season 114

4.16 Chlorophyll content in tomato during 2 and 4 WAP of 2018 cropping season 115

4.17 Flowering and fruiting in Bean plants during 2017 and 2018 cropping season 124

4.18 Seed morphology in Beans during 2017 and 2018 cropping season 134

4.19 Fruit morphology in tomato fruit 144

4.20 Fresh and dry weights of beans 154

4.21 Non enzymatic antioxidant of bean during 2017 and 2018 cropping season 164

4.22 Enzymatic antioxidants in Bean and Tomato during 2017 and 2018 cropping seasons 183

CHAPTER FIVE 224

DISCUSSION, CONCLUSION AND RECOMMENDATION 224

5.1 Discussion 224

5.2 Conclusion 230

5.3 Contribution to Knowledge 230

5.4 Recommendations 232

REFERENCES 233

LIST OF FIGURES

Figure 1:	FESEM micrograph of nCu particles used for the experiment at (a) high and (b) low	41
Figure 2:	Energy-dispersive X-ray spectroscopy (EDX) of nCu nanoparticles	42
Figure 3:	FESEM micrograph of nZnO nanoparticles used for the experiment at (a) high and (b) low magnifications.	43
Figure 4:	Energy-dispersive X-ray spectroscopy (EDS) of nZnO particles	44
Figure 5:	Bean plants	250
Figure 6:	Tomato plants	251
Figure 7:	Bean and tomato plants	252
Figure 8:	Bean plant showing the pod and the inflorescence	253

LIST OF TABLES

Table 1:	Physico-chemical parameters of copper nanoparticles	47
Table 2:	Physico-chemical parameters of zinc oxide nanoparticles	48
Table 3:	Physicochemical parameters of the soil used	49
Table 4:	Effects of nanoparticles and bulk particles (nCu and ZnO) on leaf length (cm) of beans for 2017 cropping season.	50
Table 5:	Interactive effect between metal salts and various concentrations on the leaf length of beans for 2017 cropping season	51
Table 6:	Effects of nanoparticles and bulk particles (nCu and ZnO) on leaf length of beans (cm) during 2018 cropping season.	52
Table 7:	Interactive effect between metal salts and various concentrations on the leaf length (cm) of beans during 2018 cropping season	53
Table 8:	Effects of nanoparticles and bulk particles (Cu and ZnO) on leaf breadth (cm) of beans during 2017 copping season.	56
Table 9:	Interactive effect between metal salts and various concentrations on the leaf breadth (cm) of beans during 2017 cropping season	57
Table 10:	Effects of nanoparticles and bulk particles (Cu and ZnO) on leaf breadth (cm) of beans during 2018 cropping season.	58
Table 11:	Interactive effect between metal salts and various concentrations on the leaf breadth (cm) of beans during 2018 cropping season	59
Table 12:	Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf area (cm^2) of beans during 2017 cropping season.	64
Table 13:	Interactive effect between metal salts and various concentrations on the leaf area (cm^2) of beans during 2017 cropping season	65
Table 14:	Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf area (cm^2) of beans during 2018 cropping season	66
Table 15:	Interactive effect between metal salts and various concentrations on the leaf area (cm^2) of beans during 2018 cropping season	67
Table 16:	Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of leaves of beans during 2017 cropping season	68
Table 17:	Interactive effect between metal salts and various concentrations on the number of leaves of beans during 2017 cropping season	69

Table 18: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of leaves of beans during 2018 cropping season 70

Table 19: Interactive effect between metal salts and various concentrations on number of leaves in beans during 2018 cropping season 71

Table 20: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stem girth (cm) of beans during 2017 cropping season 73

Table 21: Interactive effect between metal salts and various concentrations on stem girth (cm) of beans during 2017 cropping season 74

Table 22: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stem girth (cm) of beans during 2018 cropping season 75

Table 23: Interactive effect between metal salts and various concentrations on stem girth (cm) of beans during 2018 cropping season 76

Table 24: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf length (cm) of tomato during 2017 cropping season 79

Table 25: Interactive effect between metal salts and various concentrations on leaf length of tomato during 2017 cropping season 80

Table 26: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf length (cm) of tomato during 2018 cropping season 81

Table 27: Interactive effect between metal salts and various concentrations on leaf length (cm) of tomato during 2018 cropping season 82

Table 28: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf breadth (cm) of tomato during 2017 cropping season. 84

Table 29: Interactive effect between metal salts and various concentrations on leaf breadth (cm) of tomato for 2017 cropping season 85

Table 30: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf breadth (cm) of tomato during 2018 cropping season. 86

Table 31: Interactive effect between metal salts and various concentrations on leaf breadth (cm) of tomato for 2018 cropping season. 87

Table 32: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf area (cm^2) of tomato during 2017 cropping season. 89

Table 33: Interactive effect between metal salts and various concentrations on leaf area (cm^2) of tomato during 2017 cropping season. 90

Table 34: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf area of tomato during 2018 cropping season. 91

Table 35: Interactive effect between metal salts and various concentrations on leaf area (cm^2) of tomato for 2018 cropping season. 92

Table 36: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of leaves of tomato during 2017 cropping season 94

Table 37: Interactive effect between metal salts and various concentrations on number of leaves in tomato during 2017 cropping season 95

Table 38: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of leaves in tomato during 2018 cropping season 96

Table 39: Interactive effect between metal salts and various concentrations on number of leaves of tomato during 2018 cropping season 97

Table 40: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stem girth (cm) of tomato during 2017 cropping season 99

Table 41: Interactive effect between metal salts and various concentrations on stem girth (cm) of tomato during 2017 cropping season 100

Table 42: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stem girth (cm) of tomato during 2018 cropping season 101

Table 43: Interactive effect between metal salts and various concentrations on stem girth (cm) of tomato during 2018 cropping season 102

Table 44: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of beans 2 WAP during 2017 cropping season 106

Table 45: Interactive effect between metal salts and various concentrations on the chlorophyll (mg/g fw) content of beans at 2 WAP during 2017 cropping season 107

Table 46: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of beans 4 WAP during 2017 cropping season 108

Table 47: Interactive effect between metal salts and various concentrations on the chlorophyll (mg/g fw) content of beans at 4 WAP during 2017 cropping season 109

Table 48: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of beans 2 WAP during 2018 cropping season 110

Table 49: Interactive effect between metal salts and various concentrations on the chlorophyll (mg g fw) content of beans at 2 WAP during 2018 cropping season 111

Table 50: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/ g fw) content of tomato 4 WAP during 2018 cropping season 112

Table 51: Interactive effect between metal salts and various concentrations on the chlorophyll content of beans at 4 WAP for 2018 cropping season 113

Table 52: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of tomato 2 WAP during 2017 cropping season 116

Table 53: Interactive effect between metal salts and various concentrations on the chlorophyll (mg g fw) content of tomato at 2 WAP for 2017 cropping season 117

Table 54: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of tomato 4 WAP during 2017 cropping season 118

Table 55: Interactive effect between metal salts and various concentrations on the chlorophyll content of tomato at 4 WAP during 2017 cropping season 119

Table 56: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of tomato 2 WAP during 2018 cropping season 120

Table 57: Interactive effect between metal salts and various concentrations on the chlorophyll (mg/g fw) content of tomato at 2 WAP during 2018 cropping season 121

Table 58: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of tomato 4 WAP during 2018 cropping season 122

Table 59: Interactive effect between metal salts and various concentrations on the chlorophyll (mg/g fw) content of tomato at 4 WAP during 2018 cropping season 123

Table 60: Effects of Nanoparticles and bulk particles (Cu and ZnO) on flowering and fruiting (days) of bean for 2017 cropping season. 126

Table 61: Interactive effect between metal salts and various concentrations on flowering and fruiting of bean for 2017 cropping season 127

Table 62: Effects of Nanoparticles and bulk particles (Cu and ZnO) on flowering and fruiting (days) of bean during 2018 cropping season. 128

Table 63: Interactive effect between metal salts and various concentrations on flowering and fruiting (days) of bean for 2018 cropping season 129

Table 64: Effects of Nanoparticles and bulk particles (Cu and ZnO) on flowering and fruiting (days) of tomato for 2017 cropping season. 130

Table 65: Interactive effect between metal salts and various concentrations on flowering and fruiting (days) of tomato for 2017 cropping season 131

Table 66: Effects of Nanoparticles and bulk particles (Cu and ZnO) on flowering and fruiting of tomato during 2018 cropping season. 132

Table 67: Interactive effect between metal salts and various concentrations on flowering and fruiting (days) of tomato during 2018 cropping season 133

Table 68: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of pod per plant during 2017 and 2018 cropping season. 136

Table 69: Interactive effect between metal salts and various concentrations on number of pod per plant during 2017 and 2018 cropping season. 137

Table 70: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of seed per pod during 2017 and 2018 cropping season. 138

Table 71: Interactive effect between metal salts and various concentrations on number of seed per pod during 2017 and 2018 cropping season. 139

Table 72: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of seed per plant during 2017 and 2018 cropping season. 140

Table 73: Interactive effect between metal salts and various concentrations on number of seed per plant bean during 2017 and 2018 cropping season. 141

Table 74: Effects of Nanoparticles and bulk particles (Cu and ZnO) on pod length of beans during 2017 and 2018 cropping season. 142

Table 75: Interactive effect between metal salts and various concentrations on number of seed per plant of bean during 2017 and 2018 cropping season 143

Table 76: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of fruit per plant tomato during 2017 and 2018 cropping season. 146

Table 77: Interactive effect between metal salts and various concentrations on number of fruit per plant of tomato during 2017 and 2018 cropping season. 147

Table 78: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of seed per fruit of tomato during 2017 and 2018 cropping season. 148

Table 79: Interactive effect between metal salts and various concentrations on number of seed per fruit of tomato for 2017 and 2018 cropping season. 149

Table 80: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of seed per plant of tomato during 2017 and 2018 cropping season. 150

Table 81: Interactive effect between metal salts and various concentrations on number of seed per plant of tomato during 2017 and 2018 cropping seasons. 151

Table 82: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fruit length of tomato during 2017 and 2018 cropping season. 152

Table 83: Interactive effect between metal salts and various concentrations on fruit length of tomato during 2017 and 2018 cropping season. 153

Table 84: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fresh and dry weights (g) of beans during 2017 cropping season. 156

Table 85: Interactive effect between metal salts and various concentrations on fresh and dry weights (g) of beans during 2017 cropping season. 157

Table 86: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fresh and dry weights (g) of beans during 2018 cropping season. 158

Table 87: Interactive effect between metal salts and various concentrations on fresh and dry weights (g) of beans during 2018 cropping season 159

Table 88: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fresh and dry weights (g) of tomato during 2017 cropping season. 160

Table 89: Interactive effect between metal salts and various concentrations on fresh and dry weights (g) of tomato for 2017 cropping season. 161

Table 90: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fresh and dry weights (g) of tomato during 2018 cropping season. 162

Table 91: Interactive effect between metal salts and various concentrations on fresh and dry weights (g) of tomato during 2018 cropping season. 163

Table 92: Effects of Nanoparticles and bulk particles (Cu and ZnO) on ascorbic acid (mg/100 g fw) content of bean during 2017 and 2018 cropping season. 167

Table 93: Interactive effect between metal salts and various concentrations on ascorbic acid content of bean for 2017 and 2018 cropping season. 168

Table 94: Effects of Nanoparticles and bulk particles (Cu and ZnO) on total carotenoid content of bean during 2017 and 2018 cropping season. 169

Table 95: Interactive effect between metal salts and various concentrations on total carotenoid content (mg/100 g fw) of bean during 2017 and 2018 cropping season. 170

Table 96: Effects of Nanoparticles and bulk particles (Cu and ZnO) on lycopene (mg/100 g fw) content of bean during 2017 and 2018 cropping season. 171

Table 97: Interactive effect between metal salts and various concentrations on lycopene content (mg/100 g fw) of bean during 2017 and 2018 cropping season. 172

Table 98: Effects of Nanoparticles and bulk particles (Cu and ZnO) on Beta-carotene content (mg/100 g fw) of bean during 2017 and 2018 cropping season. 173

Table 99: Interactive effect between metal salts and various concentrations on Beta-carotene content (mg/100 g fw) of bean for 2017 and 2018 cropping season. 174

Table 100: Effects of Nanoparticles and bulk particles (Cu and ZnO) on content of ascorbic acid (mg/100 g fw) of tomato during 2017 and 2018 cropping season. 175

Table 101: Interactive effect between metal salts and various concentrations on ascorbic acid content (mg/100 g fw) of tomato during 2017 and 2018 cropping season. 176

Table 102: Effects of Nanoparticles and bulk particles (Cu and ZnO) on total carotenoid (mg/100 g fw) content of tomato during 2017 and 2018 cropping season. 177

Table 103: Interactive effect between metal salts and various concentrations on total carotenoid (mg/100 g fw) content of tomato during 2017 and 2018 cropping season. 178

Table 104: Effects of Nanoparticles and bulk particles (Cu and ZnO) on lycopene content of tomato during 2017 and 2018 cropping season. 179

Table 105: Interactive effect between metal salts and various concentrations on lycopene content of tomato during 2017 and 2018 cropping season. 180

Table 106: Effects of Nanoparticles and bulk particles (Cu and ZnO) on Beta-carotene (mg/100 g fw) content of tomato during 2017 and 2018 cropping season. 181

Table 107: Interactive effect between metal salts and various concentrations on Beta- carotene content of tomato during 2017 and 2018 cropping season. 182

Table 108: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of ascorbate peroxidise (APX) (µml/mg) of bean during 2017 and 2018 cropping seasons. 188

Table 109: Interactive effect between metal salts and various concentrations antioxidant enzyme activities of ascorbate peroxidise (APX) (µml/mg) of bean 2017 and 2018 cropping seasons 189

Table 110: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of ascorbate peroxidise (APX) (µml/mg) of tomato during 2017 and 2018 cropping seasons. 190

Table 111: Interactive effect between metal salts and various concentrations antioxidant enzyme activities of ascorbate peroxidise (APX) (µml/mg) of tomato during 2017 and 2018 cropping seasons. 191

Table 112: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of catalase (CAT) (µml/mg) in bean during 2017 and 2018 cropping seasons. 192

Table 113: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of catalase (CAT) (µml/mg) in bean during 2017 and 2018 cropping seasons. 193

Table 114: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of catalase (CAT) (µml/mg) in tomato during 2017 and 2018 cropping seasons. 194

Table 115: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of catalase (CAT) (µml/mg) in tomato during 2017 and 2018 cropping seasons. 195

Table 116: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of superoxide dismutase (SOD) (µml/mg) in bean during 2017 and 2018 cropping seasons. 196

Table 117: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of superoxide dismutase (SOD) (µml/mg) in bean during 2017 and 2018 cropping seasons. 197

Table 118: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of superoxide dismutase (SOD) (µml/mg) in tomato during 2017 and 2018 cropping seasons. 198

Table 119: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of superoxide dismutase (SOD) (µml/mg) in tomato during 2017 and 2018 cropping seasons. 199

Table 120: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attribute or activities of malondialdehyde (MDA (µml/mg) in bean during 2017 and 2018 cropping seasons. 200

Table 121: Interactive effect between metal salts and various concentrations on stress attributes or activities of Malondialdehyde (MDA) (µml/mg) in beans during 2017 and 2018 cropping seasons. 201

Table 122: Effects of Nanoparticles and bulk particles (Cu and ZnO) on enzyme activities or attributes of malondialdehyde (MDA) (µml/mg) in tomato during 2017 and 2018 cropping seasons. 202

Table 123: Interactive effect between metal salts and various concentrations stress attributes or activities of Malondialdehyde (MDA) (µml/mg) in tomato during 2017 and 2018 cropping seasons. 203

Table 124: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attribute or activities of hydrogen peroxide (H_2O_2) (µml/mg) in bean during 2017 and 2018 cropping seasons. 204

Table 125: Interactive effect between metal salts and various concentrations on stress attribute or activities of hydrogen peroxide (H_2O_2) in bean during 2017 and 2018 cropping seasons. 205

Table 126: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attribute or activities of hydrogen peroxide (H_2O_2) (µml/mg) in tomato during 2017 and 2018 cropping season. 206

Table 127: Interactive effect between metal salts and various concentrations on stress attributes or activities of hydrogen peroxide (H_2O_2) (µml/mg) in tomato during 2017 and 2018 cropping seasons. 207

Table 128: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attributes or activities of proline (µml/mg) in bean during 2017 and 2019 cropping seasons. 208

Table 129: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of proline (µml/mg) in bean during 2017 and 2018 cropping seasons. 209

Table 130: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attributes or activities of proline in tomato during 2017 and 2018 cropping season 210

Table 131: Interactive effect between metal salts and various concentrations on stress attributes or activities of proline (µml/mg) in tomato during 2017 and 2018 cropping season 211

Table 132: Effects of Nanoparticles and bulk particles (Cu and ZnO) on starch (mg/100 g fw) content in bean during 2017 and 2018 cropping seasons. 212

Table 133: Interactive effect between metal salts and various concentrations on starch (mg/100 g fw) content in bean during 2017 and 2018 cropping seasons. 213

Table 134: Effects of Nanoparticles and bulk particles (Cu and ZnO) on starch (mg/100 g fw) content in tomato during 2017 and 2018 cropping season 214

Table 135: Interactive effect between metal salts and various concentrations on starch (mg/100 g fw) content in tomato during 2017 and 2018 cropping season 215

Table 136: Effects of Nanoparticles and bulk particles (Cu and ZnO) on protein (mg/100 g fw) content in bean during 2017 and 2018 cropping season 216

Table 137: Interactive effect between metal salts and various concentrations on protein (mg/100 g fw) content in bean during 2017 and 2018 cropping seasons. 217

Table 138: Effects of Nanoparticles and bulk particles (Cu and ZnO) on protein (mg/100 g fw) content in tomato during 2017 and 2018 cropping seasons. 218

Table 139: Interactive effect between metal salts and various concentrations on protein (mg/100 g fw) content in tomato during 2017 and 2018 cropping season 219

Table 140: Effects of Nanoparticles and bulk particles (Cu and ZnO) on copper and zinc content (mg/kg) in bean during 2017 and 2018 cropping seasons. 220

Table 141: Interactive effect between metal salts and various concentrations on copper and zinc content (mg/kg) in bean during 2017 and 2018 cropping seasons. 221

Table 142: Effects of Nanoparticles and bulk particles (Cu and ZnO) on copper and zinc content (mg/kg) in tomato during 2017 and 2018 cropping season 222

Table 143: Interactive effect between metal salts and various concentrations on copper and zinc (mg/kg) content in tomato during 2017 and 2018 cropping seasons. 223

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Nanoparticles are particles with a size of 1 to 100 nanometers (Batista et al., 2015; EPA, 2007). A particle is a small entity that, in terms of transport and properties, functions as a full unit in nanotechnology, diameters are used to further categorize them (Tyagi, 2013). Fine particles have a size range of 100 to 2,500 nm, whereas coarse particles have a size range of 2,500 to 10,000 nm. Ultrafine particles are the same as nanoparticles, which have a size range of 1 to 100 nm (Taylor *et al*., 2013). Nanoparticles could be used in a variety of fields, including medicine, optics, and electronics, therefore there's a lot of research going on about them (Himanshu, 2013).

The term "nanoparticle" is commonly used to refer to inorganic materials rather than individual molecules. The term "nanoparticles" and "ultrafine particles" are used interchangeably since, in the 1970s and 1980s, when the first comprehensive foundational investigations using nanoparticles were being conducted in the United States and Japan, the two terms were used interchangeably (Granqvist *et al*., 1976) and they were dubbed "ultrafine particles" (UFP) as part of an ERATO project (Hayasi *et al*., 1997). However, before the National Nanotechnology Initiative was started in the United States in the 1990s, the new term "nanoparticles" had become more popular (Niklasson *et al*., 1999). Nanoparticles can have size-related features that differ dramatically from fine particles or bulk materials (Buzea *et al*., 2007).

Nanoclusters have a small size distribution with at least one dimension between 1 and 10 nanometers. Agglomerates of ultrafine particles, nanoparticles, or nanoclusters make up nanopowders. Nanocrystals are single crystals with a diameter of a few nanometers or single-

domain ultrafine particles with a diameter of a few nanometers (Taylor *et al*., 2013). Nanoparticles have a lengthy history, despite their association with modern science.

Nanoparticles have been utilized by artisans in Mesopotamia since the ninth century to create a glistening look on the surface of pots (Klaus *et al*., 2016)

Nanoparticles are of tremendous interest to scientists because they act as a link between bulk materials and atomic or molecular structures. A bulk material's physical properties are constant regardless of its size, while size-dependent traits are frequently found at the nanoscale. As a result, as a material's size approaches the nanoscale and the proportion of surface to volume of a material becomes substantial, its properties alter.

The percentage of the surface in bulk materials larger than one micrometer (or micron) is tiny in comparison to the volume in the bulk of the material. The enormous surface area of the material, which outweighs the contributions made by the small bulk of the substance, is thus largely responsible for the fascinating and often unexpected features of nanoparticles.

Nanotechnology is used in nanoagriculture to increase plant yields for food, fuel, and other purposes. There is a significant knowledge gap on the impacts of nanoparticles on rice, tomatoes, corn, and other food crops, according to researchers (Lombi *et al*., 2012; Nadiminti *et al*., 2013). Engineered nanoparticles (ENs) accumulate and are absorbed differently depending on the type of plant, the chemical content, and the size of ENs (Nevious *et al*., 2012). Engineered nanoparticles can also be taken up and accumulated by some plants (Nevious *et al*., 2012). Plant cell interactions with ENs alter plant gene expression and associated biological pathways, affecting plant growth and development (Ghormade *et al*., 2011). ENs can have a wide range of impacts on different plant species depending on their form, size, chemical composition, concentration, surface structure, aggregation, and

solubility, as well as plant developmental phases, manner, and duration of exposure (Radiman *et al*., 2011).

1.2 Cowpeas (*Phaseolus vulgaris*) L.

Cowpeas are a major food legume crop in Asia, Africa, southern Europe, and Central and South America. Cowpeas, a drought-tolerant and warm-weather crop, are well-suited to the tropics' drier parts, where other food legumes struggle. It can also fix atmospheric nitrogen through its root nodules, and it thrives in poor soils with more than 85% sand, less than 0.2 percent organic matter, and low phosphorus levels (Singh *et al*., 2003). It also tolerates shade and can be intercropped with maize, millet, sorghum, sugarcane, and cotton (Singh et al., 2003). Cowpeas are therefore a key part of traditional intercropping systems, particularly in the intricate and sophisticated subsistence farming systems of Sub-Saharan Africa's dry savannas (Blade *et al*., 2005). Cowpea haulm (dry stalks) is a lucrative by-product in these systems and is used as feed (Kureh *et al*., 2005). The cowpea (Vigna unguiculata) is one of several species of the genus Vigna, which is widely cultivated. *V. textilis*, *V. pubescens*, and *V. sinensis* are the four recognized subspecies, three of which are cultivated.

Phaseolus vulgaris, popularly known as the common bean or kidney bean, is an annual herbaceous plant of the Fabaceae family (legume or bean family) that originated in Central and South America but is now farmed in many parts of the world for its edible beans (Peltry *et al.*,2014). Green beans are abundant in vitamins B and C, as well as dietary fiber and different minerals like iron (Fe), magnesium (Mg), phosphorous (P), and potassium (K). Green beans are frequently purchased in canned or frozen form.

1.3 Tomato (*Solanum lycope rsicum* L.)

Tomatoes are one of the most popular fresh vegetables in the developed world.It is one among the world's most economically significant crops (Amini *et al*., 2005).

It's also commonly utilized as a raw material in the culinary industry to make derivative products like purees and ketchup. Tomatoes are also the most popular vegetable in the Mediterranean diet, which is proven to be good for health, especially when it comes to chronic degenerative disorders (Leonardi *et al.,* 2000). Chemical constituents such dry matter, Brix degree, acidity, single sugars, citric and other organic acids, and volatile chemicals have all been used to evaluate tomato fruit quality (Christensen *et al.,* 2006). Tomatoes are one of the world's most valued and widely consumed veggies.

Tomato cultivars differ in fruit size, shape, flavor, color, and skin and flesh firmness, and each cultivar is desirable for being fertile and disease resistant. Tomatoes must also be resistant to transportation circumstances in order to meet market demands and customer preferences, as large-fruit salad-type tomato varieties are becoming more popular.

Tomatoes and tomato-based products are a major agricultural crop in many parts of the world. Tomato juice, paste, puree, ketchup, sauce, and salsa make up more than 80% of all tomatoes farmed worldwide (Kimberly *et al*., 2010). Organic acids, sugars, dietary fibre, pectic compounds, proteins, lipids, minerals (potassium, phosphorus, sulphur, magnesium, calcium, iron, copper, and salt), vitamins (B1, B2, B3, C, provitamin A, I, and H), and antioxidant carotenoids (lycopene, β-carotene) abound in tomato fruit (USDA, 2013). Due to the fact that vegetables are so important in the human diet, the flavor of tomatoes and their products is primarily determined by lycopene, β-carotene, and ascorbic acid, all of which have daily recommendations of 400-500 grams and 140-150 kg of vegetables per year, including 25-32 kg of tomatoes for an adult human (Kadar, 1999; Viskelis, 2005).

Nanotechnology, a new and intriguing branch of science, allows for advanced research in a variety of fields, and nanotechnological breakthroughs could lead to new biotech and agricultural applications. Nanotechnology is developing study in the fields of electronics, energy, medicine, and life sciences, including reproductive science and technology, conversion of agricultural and food wastes to energy and other useful by products via enzymatic nanobioprocessing, chemical sensors, water cleansing, disease prevention, and treatment in plants utilizing various nanocides (Carmen *et al.*, 2003; Nair *et al*., 2010).

Although fertilizers are critical for plant growth and development, the majority of fertilizers applied to plants are rendered ineffective owing to a variety of causes, including leaching, photolysis, hydrolysis, and decomposition (Ahmed, 2019). As a result, it's critical to reduce nutrient losses during fertilizer application while also increasing crop output by utilizing innovative applications made possible by nanotechnology and nanomaterials. Nanofertilizers or nano-encapsulated nutrients may have qualities that are beneficial to plants, such as the ability to release nutrients on demand and Chemicals/fertilizers that influence plant development are released in a regulated manner, and target activity is increased (DeRosa *et al*., 2010; Nair *et al*., 2010).

1.4 Effects of Nanoparticles on the Growth and the Development of Plants:

Depending on the qualities of Nanoparticles, they interact with plants, creating a variety of morphological and physiological changes. The chemical composition, size, surface coverage, reactivity, and, most critically, the dose at which Nps are effective affect their efficacy (Khodakovskaya *et al*., 2012). Both positive and negative effects on plant growth and development have been observed by researchers (Akanbi-Gada et al., 2019 a&b, Hussein et al., 2002, and Zhao et al., 2012), and the influence of engineered nanoparticles (ENps) on plants is dependent on the composition, concentration, size, physical and chemical properties

of ENps, as well as plant species (Ma *et al*., 2010). The effectiveness of Nps is determined by their concentration and varies between plants. Some researchers have looked into using plant seeds and tree bark to make nanoparticles (Kuppusamy *et al.,* 2016).

Although nanomaterials increased seed germination in plants, they can have negative consequences in other situations (Lombi *et al*., 2012).

The dose of nanoparticles in diverse media, their chemical and physical properties, and the mechanisms that allow them to pass through cellular membranes and cell walls are all investigated in these cases. Specific features of nanoparticles that may be related to their positive and negative impacts, as well as the process behind nanoparticle trophic transports, are required (Nevius *et al*., 2012). Furthermore, present application procedures must be evaluated in order to improve nanomaterial efficiency on future targets. Further research into the potential hazards associated with the usage of nanomaterials, as well as their potential negative impacts, is required (Foss *et al*., 2009).

1.5 Statement of Research Problem

Concerns on the impact of nanoparticles (Nps) on living corganisms have grown as their manufacturing and use has expanded. Copper and zinc oxide nanoparticles can be potentially used as fertilizers, fungicides, or insecticides (Selivanov and Zorin, 2001; Sreenivasulu, 2012). The dangers and benefits of the many engineered nanomaterials into the environment are now the subject of intense debate (copper and zinc oxide inclusive) (USEPA, 2007).

However, it is not well understood yet if their effects are different from those of Cu and ZnO bulk materials. Because of the growing interest in the influence of Nps, metal and metal oxide Nps are receiving special attention particularly Cu and ZnO. Nanostructured Zinc oxide and copper fertilizers can improve nutrient efficiency through mechanisms like targeted

delivery and slow or regulated nutrient release (Chinnamuthu and Boopathi, 2009). In response to environmental stimuli and biological demand, they may precisely release their active ingredients. Limited reports underline positive or no adverse effects of Cu and ZnO nanoparticles on higher plants and the association of nanoparticles with edible plants, as well as their potential consequences for the food chain

1.6 Justification of the Study

Nigeria's population is growing at an alarming rate, so there is need to scale up food production to meet up with this increase. Hence there is need to look for other alternative sources of improving crop yield aside from using fertilizer which is known to be a double edge sword as it improves food produvtivity at the same time pollutes the environment and underground water aquifers as leachates. Nanotechnology is a new branch of science that has recently gained a lot of attention and it promises to give smart and controlled release /delivery of nutrients to plants. Furthermore, Ecotoxicological impact of Cu and ZnO nanoparticles is not well documented especially on food crops like tomato and beans, this study therefore sought to find out if the interaction of Cu and ZnO nanoparticles will be positive or negative on the test plants.

1.7 Aim of the Study

The aim of the research was to assess the effects of bulk particles and nanoparticles; Zinc oxide (ZnO) and Copper (Cu) on the growth and productivity of tomatoes (*Solanum Lycopersicum* L.) and beans (*Phaseolus vulgaris* L.).

1.8 Objectives of the Study

The specific objectives were to determine the effects of ZnONPs, CuNPs, bCu, and bZnO on the:

i) growth performances of tomatoes and beans;

ii) chlorophyll content of tomatoes and beans ;

iii) yield attributes of tomatoes and beans;

iv) enzymatic and non enzymatic antioxidants activities in beans and tomatoes;

v) starch and protein constituents of beans and tomatoes and

vi) bioaccumulation potential of both beans and tomatoes

1.9 Contributions and Significance of the Study

At the end of this research work, it is hoped that the work will give an insight into the effects of nanoparticles on the growth and productivity of some economic plants and thus will provide baseline information about the effects of nanoparticles on tomatoes and beans. It will also serve as reference point to other intending researchers who wish to carry out research in Environmental Biology using nanoparticles.

CHAPTER TWO

LITERATURE REVIEW

2.1 Nanoparticles and nanotechnology

Researchers in plant science and other fields may use nanotechnology to create new tools for incorporating nanoparticles into plants that can enhance existing functions and incorporate new ones (Cossins *et al*., 2014). The role of nanoparticles (Nps) in plant growth and development, as well as plant mechanisms, has been a recent focus in plant science.

Biogenic production of metal oxide nanoparticles from plants, particularly zinc oxide nanoparticles (ZnO Nps) received global attention due to its applications in medicines and agriculture. Zinc oxide nanoparticles are reported efficiently to provide protection over a wider UV spectrum than any molecular UV-absorber, photo catalytic degradation of environment pollution, biocompatibility in drug delivery mechanisms and as nanofertilizers and nanopesticides (Devalapally *et al.,* 2007; Kulkarni and Muddapur). Nanoparticles have been successfully synthesized using extracts from a wide variety of plant species (Shekhawati *et al.,* 2014). Different methods of particle characterization and its potential applications in medicine are widely discussed by many researchers (Fatoki *et al*., 2012; Kuppusamy *et al.,* 2014 and Zhang *et al*., 2008).

Engineered nanoparticles (ENPs) have been widely used in the fields of medicine, agriculture (nano-fertilizers and nano-pesticides), manufacturing, electronics, and energy production due to their high surface to volume ratio and greater numbers of atoms at the particle surface (Bandyopadhyay *et al.,* 2013; Gardea- Torresdey *et al*., 2014; Ghormade *et al*., 2011). The global nanotechnology market is expected to surpass $3 trillion by 2020, according to estimates (Venkatesan *et al*., 2004).

Due to their possible applications in microelectronics, semiconductors, optical system processing, and optics, hybrid ENPs, such as doped and coated nanomaterials (NMs), have gained increased attention in recent years (Ozgur *et al*., 2005 ; Dhiman *et al*., 2012). Commercially accessible silane coupling agent (KH550) coated ZnO NPs and alumina doped (Al2O3) ZnO NPs are two significant hybrid NPs used in detectors and optoelectronic devices (Zhang *et al*., 2010 ; Thandavan *et al*., 2015), Preparation of novel polymer inorganic nanocomposites is also included, among other things (Abdolmaleki *et al*., 2012). High reactivity and biocompatibility are two grounds for concern about possible biota toxicity.

The risk of ENP exposure in the atmosphere has increased as development and usage have risen rapidly (Mukherjee *et al*., 2013). The environmental health and safety of these newer hybridized products, on the other hand, are largely unknown.

Since the last decade, there has been a surge of interest in acute toxicity research based on the biological and ecological effects of ENs in the short term.

However, research into the effects of ENs in living conditions is still lacking (Hansen *et al*., 2008). There is also a knowledge gap in the theory of estimating environmental concentrations using the releasing rate as a metric (Moudgil *et al*., 2006).

It has been stated that the current theory of chemical and particulate behavior in the atmosphere does not match the properties of nanomaterials. Recently, the hypothesis has been focused solely on direct measurement and evaluation of existing nanomaterials in living systems, with a greater emphasis on the parameters involved in the release process (for example, acidity, pH, charged ions, and organic matter level).

Two major conclusions were reported by the theories; First, rather than using real measurements, the quantity estimation of nanomaterials in water surfaces is based on predictions.

Second, nanomaterials could be dissolved, latched onto chemical molecules/ions, clamped, converted into other chemicals by microorganisms, or mineralized until being fully destroyed by the dissolution of organic carbon or its generation or the decomposition of organic carbon-based materials (Savage *et al*., 2007). According to some sources, whether or not the dissolved material is degraded, the dissolution process causes nanoparticles to vanish and become less persistent. In theory, manufacturing measurement methods necessitate a greater quantity of test materials (Golimowski *et al*., 2009).

More comprehensive studies must concentrate on the possibility of possible locations where ENs is concentrated, agglomerated, or interact with organic matter (Monteiro *et al*., 2010). This is critical, particularly in the case of wastewater treatment, where it is possible that some ENs will accumulate in the sewage. Bioaccumulation is also a possibility due to the concentration of ENs in specific organs (Walker *et al*., 2002). The aggregation of ENs will result in sedimentation as a result of the bioaccumulation process, and species will be able to pick up ENs by inhalation or ingestion. Some microorganisms can also be transferred through epithelial surfaces (such as the lining of the lungs, gills, skin, or intestines) (Sanchis *et al*., 2012).

In the meantime, ENs can be picked up by microorganisms by simple diffusion across cell membranes, or even after membrane damage (Sanchis *et al*., 2012). In this case, the transfer mechanism relies on the dispersion, concentration, and dissolution of ENs prior to ingestion.

Furthermore, the waters could concentrate some semiconductor-engineered nanomaterials, which could then be directly transferred to the soil or the ecosystem's food chain (Sohaebuddin *et al*., 2010). A recent analysis of quantum dot transfer in a simple aquatic food chain found that nanomaterials could be transferred to rotifers through ciliated protozoan dietary uptake (Elliot, 2011).

According to other research, depending on the material type and food chain, there is some scope for transferring nanomaterials across layers of the food chain (Potera *et al*., 2010).

Aquatic microorganisms are faced with a challenge because nanomaterials, particularly silver nanoparticles, have an antibacterial or virucidal effect on them (Liden, 2011). Studies on microorganisms, invertebrates, and fish, for example, have shown a broad variety of effects on the presence of various ENs on microorganisms, invertebrates, and fish (Kreider *et al*., 2010). The findings so far have pointed to the potential for dangerous effects at lethal and sublethal levels (for example, behavior, reproduction, growth, and development) on the output of reactive O2 species, inflammatory responses, and cytostatic effects at lethal and sublethal levels (for example, behavior, reproduction, growth, and development) (Stamm *et al*., 2012). Some findings on the possible effects on the movement of ENs to embryos, aggregation, and food chain transition back this up (Kreider et al, 2010). As compared to other colloidal particles, small particles tend to agglomerate or aggregate, which explains why it is found in the atmosphere (Bagheri *et al.,* 2013).

ENs may be present in the atmosphere and are unlikely to be disassociated by dissolution or agglomeration (Hansen *et al*., 2008).There are no peer-reviewed publications on the concentration of ENs in environmental compartments, such as surface water or soil, in terms of peer-review.

Indeed, rather than actual values, EN quantity calculation is based on expected values (Holsapple *et al*., 2005).

Indeed, the quantity estimate of ENs is focused on expected rather than real values, which may be considered appropriate indicators for the accurate calculation of ENs in living system risk assessment, which is still being debated (Aitken *et al*., 2006). When assessing the impact of nanomaterials in living systems, several factors should be taken into account, including practical exposure concentrations and doses.

When assessing the impact of nanomaterials in living systems, several factors should be taken into account, including practical exposure concentrations and doses.

This would have influenced ENs bioavailability, which will in turn determine the biological uptakes.

2.2 Gold (Au) nanoparticles

Gold (Au) is classified as a hazardous material, and the toxicity of Au in ionic or dissolved form has been identified in a variety of species (Karamushka *et al*., 1999).

The toxicity of Au has been harnessed in the form of Au nanoparticles to serve as antibacterial agents in biocide coatings, soap, toothpaste, and shampoo, and it is the most commonly used nanoparticle in over 25 consumer items (Catherine *et al*., 2008). On the long run, the development and use of Au nanoparticles in the environment, as well as their possible discharge into the environment, can trigger severe toxicity issues (Hauck *et al*., 2008).

Brown mustard (Brassica juncea) and alfalfa (Medicago sativa), for example, showed a rise in Au uptake with a corresponding change in Au concentration in the substrate and exposure time (Bogdan *et al*., 2012). Both species are considered hyper accumulators of Au

nanoparticles, according to the Au nanoparticles found in the nucleus and the defamation applications (Arora *et al*., 2011). Au nanoparticles are also transported within cells through plasmodesmata, according to research conducted by the researchers.

Images taken with a transmission electron microscope of rice roots showed that different sizes of Au particles are deposited in the form of vacuoles (Pereault *et al*., 2012). The cell damage was caused by large Au nanoparticles penetrating through small pores (Katherine et al., 2014). In onion (*Allium cepa*) root tip cells, chromatin bridges, cell disintegration, and stickiness have been reported, causing cell division to be disrupted (Feretti *et al*., 2007).

2.3 Silver (Ag) nanoparticles

Rizzello *et al*. 2014 investigated the potential applications of silver (Ag) nanoparticles in biomedicine, including imaging and chemical sensing. Ag nanoparticles are made using chemical, electrochemical, photochemical, laser ablations, and other processes.

While bulk Ag is considered "clean," if Ag nanoparticles are to be mass-produced for in-vivo use on a large scale, they must be tested for environmental impact and biocompatibility (Fernando and Chris, 1997). Furthermore, exposure data revealed that Ag nanoparticles were present in the atmosphere at low but rising concentrations, with estimates ranging between 0.1 and 2.9 mgl-l in sludge and surface water, respectively (Elizabeth and Christer, 1998).

According to some research, Ag nanoparticles may have a biological effect at concentrations up to 1000 times lower than dissolved Ag+ (Lee *et al*., 2005)

Furthermore, some findings revealed that Ag nanoparticles have minor toxicity at doses as low as 5 mgl-1,with greater growth inhibitions (Hogstrand *et al*., 1996).

Ag nanoparticles in the atmosphere clearly endanger larger plants and, as a result, ecosystem function (Adalto *et al*., 2003). At concentrations of 4500 gmgl-1, 6000 gml-1, and 3000 gml-1, Ag nanoparticles have negative effects on seed germination, root, and shoot growth in rice

(*Oryza sativa*), Mung bean (*Vigna radiata*), and Chinese cabbage (*Brassica campestris*), respectively (Cakmak *et al*.,1991).

In addition, Ag nanoparticles with a size of around 40 nm have the potential to be toxic to *Chlamydomonas reinhardtii* algae and Cucurbita pepo (Hans et al., 1999).

Ag nanoparticles, rather than bulk sizes, caused 4.4 to 10 times more reductions in biomass and transpiration rates in *Cucurbita pepo* (Sahar, 2014; Chen *et al*., 2012; Howe and Merchant, 1992). Meanwhile, for *Medicago sativa* and *Brassica juncea* species, the limits of absorption and distribution of Ag nanoparticles have been investigated (Inokuchi *et al*., 1997).

The results of a study on zucchini plant seed germination and root growth in a hydroponic solution containing Ag nanoparticles revealed no negative effects, but there were decreases in plant biomass and transpiration rates when the plants were grown longer in the presence of Ag nanoparticles (Colman *et al*. (2012). Using onion root tips, researchers investigated the genotoxic and cytotoxic effects of Ag nanoparticles.

In onions, Ag nanoparticles inhibited cell division and induced cell disintegration (Yin *et al*., 2011; there are some records of more toxic effects in *Chlamydomonas reinhardtii* algae exposed to Ag nanoparticles as $AgNO_3$, at a particle size of 40 nm) (Cheng *et al*., 2011)

Some research has focused on the impact of Ag nanoparticles on aquatic plants (Wuncheng et al., 1986). The studies used Lemna minor L. clone to investigate the phytotoxicity of Ag nanoparticles.

The final results showed that even at low concentrations (5 mgl-1), plant growth was inhibited after exposure to a large range of Ag nanoparticles (20 to 100 nm). (Hans *et al*., 1999).

Many different studies involving plant media have looked at the effects of Ag nanoparticles (Lee *et al*., 2012). The research looked at soil nematodes, the microbial population in the soil, and other related issues.

While Ag nanoparticles with sizes as small as 29 nm have been shown to reduce the germination of lettuce and cucumber seeds (Hans *et al*., 1999), there has been no evidence of a toxic effect on the germination of barley and ryegrass exposed to Ag nanoparticles. Ag nanoparticles with sizes less than 100 nm have also been shown to minimize pumpkin biomass and transpiration (Cucurbita pepo) (Hans *et al*., 1999).

As the concentration of Ag nanoparticles increased, more Ag nanoparticles were found in the popular grass Lolium multiflorum (Slade *et al*., 1993).

In addition, onion (Allium cepa) has been shown to disrupt metaphase, stickiness, the Chromatin Bridge, and have other cytological effects (Slade *et al*., 1993). Alternative approaches, rather than soil media, have been used in the majority of nanotoxicological studies on plants so far. The majority of these studies were carried out in aqueous solutions like basal medium, deionized water, or Hoagland medium. (Avishai *et al*., 2018; Nwaichi *et al*., 2016).

2.4 Cadmium (Cd) nanoparticles

Mitchell *et al*. (1999) studied using standard toxicity research methods, the short-term effects of Cadmium (Cd) nanoparticles on the root growth of carrot, cucumber, tomato, and lettuce species.

Seedling growth was found to be inversely related to Cd exposure, with tomato, carrot, lettuce, and cucumber serving as the sensitive end points among the test plants. Except for tomatoes, root growth has not been significantly inhibited by the existence of Cd nanomaterials, but has been surprisingly promoted (Clarke *et al*.1989).

Microscopic photographs of the roots of Cd-exposed plants revealed a decrease in root wilt and diameter, as well as the disintegration of the root epidermis; the clutter root surface showed obvious stress in Cd solution. (Wang, 1996; Groppa *et al*., 2008 ; Somashekaraiah *et al*.,1992) After the addition of Cd nanoparticles, many root hairs were seen growing and there was lack of disintegration on the surface of the root system were observed, and Cd nanoparticles crystals were also detected on the plants' root surface.

2.5 Titanium oxide (TiO_2) nanoparticles

Although, titanium oxide nanoparticles (TiO_2) are extensively utilized in daily life products, the research of their uptake and translocation in the plant is restricted, particularly on food crops (Eva *et al*., 2008). Due to its small size (<5 nm), TiO_2 nanoparticles tend to form a covalent bond with most of the no-conjugate natural organic matter, translocate, and following the tissue and cells' specific distribution (Feizi *et al*., 2012). The overall toxic effects of TiO_2 nanoparticles are found in the algal species, such as *Desmodesmus subspicatus* (Simon *et al*., 1997). Furthermore, TiO_2 nanoparticles produce reactive oxygen species upon interaction with organisms or ultraviolet radiation (Kamali, *et al.,* 2013). For example, with the presence of TiO_2, the root of *Arabidopsis thaliana* releases mucilage and forms a pectin hydrogel capsule in neighboring root (Smalle *et al.*, 2011).

TiO_2 nanoparticles show an increase in nitrate reducates in Soybean (Glycine max), enhanced (Minfang *et al*., 2013) the ability to absorb/use water, and stimulate the antioxidant system. For example, TiO_2 nanoparticles treated seeds produced plants that had 73% more dry weight,

three times higher photosynthetic rates, and 45% rise in chlorophyll a formation compared to the control over the germination period of 30 days (Mingfang *et al*., 2013). The growth rate of spinach seeds, on the contrary, was proportional to the size of the materials, indicating that the smaller the nanomaterials, the better the germination (Zheng *et al*., 2005; Yang *et al*., 2006). Some studies claimed that the TiO_2 nanoparticles might have elevated the absorption of inorganic nutrients, accelerated the breakdown of organic substances, and caused quenching by oxygen free radicals formed during the photosynthetic process, consequently improving the photosynthetic rate (You *et al*., 2006). To increase seed germination rate, the key is the penetration of nanomaterials into the seed. Meanwhile, TiO_2, increased plant growth in spinach by improving nitrogen metabolism that promotes the adsorption of nitrate (Sooyen *et al.*, 2013; Yang *et al*., 2006). The same study indicated the negative effects of TiO_2 nanoparticles towards the seed germination percentage and the number of roots for the species *Oryza sativa* L. This, in turn, accelerates the conversion of inorganic nitrogen into organic nitrogen, thus increasing the fresh and dry weight (Masfaraud *et al*., 2011). Using bulk and nanosized TiO_2 at $60\ mgl^{-1}$ promoted sage and seed germination percentages (Castiglione *et al*., 2004). Exposure of sage seeds to $60\ mgl^{-1}$ bulk and TiO_2 nanoparticles gained the lowest mean germination time, but higher concentrations did not increase the mean germination time (Kamali *et al*., 2013). Application of TiO_2 Nanoparticles to seeds increased the vigour index of sage compared to the control and bulk TiO_2 treatments. However, the presence of TiO_2 also positively impacted the plants' growth. For example, TiO_2 nanoparticles were observed to promote the growth of spinach through an improvement in nitrogen metabolism and photosynthetic rate

2.6 Zinc/zinc oxide (Zn/ZnO) nanoparticles

Zinc (Zn) and Zinc oxide (ZnO) are categorized as commonly used metal/metal oxide engineered nanomaterials. Zn is an essential micronutrient for humans, animals, and plants

(Bertsch *et al*., 2009). ZnO is mostly utilized in a range of applications such as sunscreens and other personal care products, solar cells, and photo catalysis, biosensors, and electrodes (Ma *et al*., 2009). According to the analysis of 289 soil samples collected from different countries in the world, Zn/ZnO deficiency was found to be the most widespread micronutrient deficiency and the fourth most important yield-limiting nutrient after nitrogen, phosphorus, and potassium (Adamson *et al*., 2000).

Due to its increasing utilization in consumer products, it is quite possible that through both accidental release and deliberate application, Zn/ZnO might find their way into atmospheric environments, whether terrestrial or aquatic. It induces noticeable effect on many organisms, especially on plants, which are an essential base component to all ecosystems (Hussein *et al*., 2002).

A number of researchers described the key role of Zn/ZnO nanomaterials in plant growths and yield (Hussein *et al*., 2002). For example, higher plant mostly absorbs Zn as a divalent cation (Zn^{2+}), which acts either as a functional, structural, or as the metal component of enzymes or a regulatory cofactor of numerous enzymes. Zn nanomaterials are needed for chlorophyll production, fertilization, pollen function, and germination (Sharma *et al*., 2009) among the micronutrients, Zn affects the susceptibility of plants via drought stress (Sharma *et al*., 2009). The germination rate of the plant may be affected in the presence of Zn and ZnO. ZnO nanomaterials are hazardous and affect both the chromosomal and the cellular facets (Sooyen *et al*., 2013). Furthermore, the presence of the ZnO nanoparticles also promoted the permeation of onion *(Allium cepa*) roots and effected the roots' elongation, genetic materials, and metabolisms (Reddy *et al*., 2016; Bai *et al*., 2010; Stella *et al*., 2010). The ZnO suspension meaningfully inhibited root growth of corn, with the termination of root development (Ma *et al*., 2009; Huang *et al*., 2002)

Growth of roots was halted with seed soaking and incubation in the suspension of Zn/ZnO nanoparticles. It also indicates that Zn^{2+} is more toxic in ryegrass species compared to ZnO nanoparticles (Sharma *et al*., 2009; Adamson *et al*., 2000; Hussein *et al*., 2002). The root growths are found in seedling of ryegrass, radish, and rape exposed to less than 10 mgl^{-1} of ZnO/Zn nanoparticles. The toxicity of ZnO nanoparticle could not mostly come from its dissolution at the root surface, but also inside the tissue (Sooyen *et al.*, 2013).

The toxicity of ZnO nanoparticle and Zn^{2+} could be derived by two theories; a chemical toxicity based on chemical composition and the stress or stimuli caused by the size, shape, and surface of the ZnO nanoparticles (Wang *et al*., 2004) Both theories significantly affected the cell culture response of the plants. A number of mechanisms underlined the efficiency of Zn/ZnO. Depending on the plant species and the experimental conditions, the most important mechanism may be Zn/ZnO utilization in tissues, called the internal efficiency, or Zn/ZnO uptake, called the external efficiency (Fiskesjo *et al*., 1993). This, in turn, helped ZnO nanoparticle enter the root cells and inhibit seedling growth.

2.7 Copper and copper oxide (Cu/CuO) nanoparticles

Copper/Copper oxide (Cu/CuO) nanoparticles could block water channels through adsorption and increase the possibility for radical penetration into onion roots (Fiskesjo *et al*., 1993; Arambasic *et al*., 1995; Geremias *et al*., 2010). This, in turn, spoils the complete stages of cell division and cellular metabolism (Arambasic et *al*., 1995). The bioavailability and toxicity of Cu nanoparticles to the Mung bean (*Phaseolus radiates*) and wheat (*Triticum aestivum*) species employed plant agar test as a growth substrate for the homogenous exposure of nanoparticles (Munzuroglu *et al*., 2002). Wheat crop showed a greater accumulation of Cu nanoparticles in its roots due to the roots' morphology. The bioavailability was estimated by calculating the bioaccumulation factor defined as the Cu

nanoparticles concentration in the plants, divided by the concentration of Cu nanomaterials in the growth media (Keltjens *et al.*, 1998). Growth inhibition of a seedling exposed to different concentrations of Cu nanomaterials on Mung bean (*Phaseolus radiates*) was more sensitive compared to wheat (*Triticum aestivum*) (Keltjens *et al.*, 1998). A cupric ion released from Cu nanoparticles had negligible effects on the concentration ranges, and the apparent toxicity was clearly the result of Cu nanomaterials (Ogunkunle *et al*., 2018). With increasing concentration of Cu nanoparticles and agglomeration of particles, the rates of bioaccumulation increased (Tani *et al*., 2005). Bioaccumulation of Cu nanoparticles increased with its concentration in the growth media. Some studies demonstrated the plant agar test as a good protocol to test phytotoxicity of Cu nanoparticles, which is hardly water-soluble. Moreover, studies on the effects of Cu nanoparticles on the growth of zucchini plants showed reduced length of emerging roots, although the germination of lettuce seeds in the presence of Cu nanomaterials showed an increase in the shoot-to-root ratio compared to the control plants (Lagriffoul *et al*., 1998).

2.8 Tomatoes (*Solanium Lycopersicum* L.)

Tomato (*Solanium Lycopersicum* L.) varies in nutritional value, colour, sugars, and their ratios in the fruits differ as well. The two most important carotenoids in tomato fruits are lycopene, which determines the fruit's red colour, and β-carotene, which accounts for approximately 7% of tomato carotenoids (Nguyen *et al*., 2015). Therefore, tomato products and their quality can be characterized by the contents of these elements. Humans gets 85% of their lycopene from tomatoes and tomato products (leyva *et al*., 2014) which is the reason why tomatoes are used in functional food products (Shi *et al*., 2012) and sometimes as functional foods. Epidemiological studies and other studies associated with the consumption of tomato products for the prevention of chronic diseases, such as cancer and cardiovascular disease, confirm that tomato products are functional foods and show that lycopene and β-

carotene act as an antioxidant (Tonucci *et al*., 1995). Currently preference for natural antioxidants, some of which are added intentionally during processing in the food industry advocated increasingly in synthetic antioxidants changes by the 'safer natural mixtures'. This option has been made available through the worldwide consumer and some exist inherently in foods. Carotenoids comprise the group of the most abundant micronutrients in fruits and vegetable; also, their dietary consumption is related to a lower frequency of some cancer types of as well as reinforces prevention against the cardiovascular diseases (Chen *et al*., 2013). Flower and fruit colour is caused by different types of pigments belonging to the terpenoid and phenylpropanoid classes (Lenore and Susan, 2000). Carotenoids, chlorophylls, and anthocyanins are the three main groups of pigments. Colour characteristics, in some plants, can be determined by domestication of agronomic traits, while in others, the increase of these pigments in tissues can occur naturally. This could be applied to tomato (*Lycopersicum esculentum* L.), which has several carotenoids, such as lycopene and β-carotene, among others. The amount of these carotenoids is principally determined by the tomato cultivar and genotype (Viskelis *et al*., 2015). It has been established that carotene, nitrates, and sugar amounts in fruits and root crop vegetables depend on plant genotype, meteorological conditions, fertilization, and soil composition (Karkleliene, 2014; Levy, 2004). The levels of the essential antioxidant vitamins, in contrast with other antioxidative defenses, are determined mainly by the plant's dietary supply. One major vitamin for enriching human diets is the antioxidant vitamin C (ascorbic acid). This vitamin can counteract the oxidizing effects of lipids by scavenging free radicals that have been found to be major promoters of certain diseases (Omenn *et al*., 1996; Albanes , 1999). Recently, it has been demonstrated that carotenoids react cooperatively and synergistically with vitamin C, serving to regenerate a pro-oxidant radical carotenoid following the antioxidant reduction

of a radical species (Kritchevski *et al*., 1999). Vitamin C usually found in vegetables and fruits, and it is a natural antioxidant. Ascorbic acid plays an important role in biochemical processes such as the formation of collagen, absorption of iron, and its involvement in the immune response and the synapses. However, a high amount of this antioxidant for human could be painful and cause adverse effects.

2.9 Beans (*Phaseolus vulgaris* L.)

Beans *(Phaseolus vulgaris* L.*)* is also known as the common bean, green bean or kidney bean which is an herbaceous annual plant that originated in central and south America but is now cultivated in many parts of the world (Peltry *et al*., 2012) widely cultivated for its delicious seeds which add flavour and protein to the diets of millions of people throughout the world. This ancient crop belongs to the family Leguminosame or Fabaceae and like many other legumes it has the ability to fix nitrogen from the air through a symbiotic relationship with bacteria housed in root nodules (Wagner, 2011; Wang and Yang, 2017). As a result, common bean is high in protein and in many parts of the world it is considered the 'meat of the poor' (Maphosa and Jideani, 2017). The impressive diversity of colours, textures and tastes of the common bean make it a popular choice for people everywhere. In 2010, total world production of dry beans was 23 million metric tons, harvested from over 30 million hectares. World production of green beans in 2010 was 17.7 million ton, harvested from 15.1 million hectares (UNFAO, 2010). Bean leaves have been used to trap bedbugs in houses (Szyndler *et al.,* 2013). Microscopic hairs trichomes on the bean leave entrap the insects (Szyndler *et al.,* 2013). From ancient times, beans were used as device in various methods of divination. Fortune-telling using beans are called favomancy.

The three commonly known types of green beans are: string or snap beans, which may be round or have a flat pod; stringless or French beans, which lack a tough, fibrous "string"

running along the length of the pod; and runner beans, which belong to a separate species, *Phaseolus coccineus.* Green beans may have a purple rather than green pod, which changes to green when cooked. Wax beans are *P. vulgaris* beans that have a yellow or white pod. Wax bean cultivars are commonly grown. The plants are often of the bush form (Philips *et al*., 2003). Compared to dry beans, green and wax beans provide less starch and protein and more vitamin A and vitamin C. Green beans and wax beans are often steamed, boiled, stir-fried or baked in casseroles. The possible profit and accidental dangers of NPs to the surroundings and individual health are crucial to appraise and likely to produce a reduced amount of poisonous and more degradable NPs to reduce the ecological hazard in the later years. It has been postulated that hundreds of different kinds of products are present in the market place and a lot of it might materialize in the coming years with different description and new applications (Rajput *et al*., 2017).

Furthermore, the era of nanotechnology began in the late 1990s, and the claim of nanomaterials to the surroundings reached $ 23.4 billion in 2014 while the global market for nanocomposites totaled $ 2.0 billion in 2017 and is estimated to reach $ 7.3 billion by 2022, growing at a compound annual growth rate of 29.5% for the period of 2017-2022 (BBC, 2018).

The real form of the worldwide discovery of NPs is still relatively unavailable. A current Inference indicated that more than 200 metric tons of nano-sized Cu and CuO synthesized or Produced in 2010 and yearly 5500 tons of Zn NPs are produced in the form of a wide range of products (Conolly *et al.,* 2016; Zuverza-Mena *et al*., 2015). Moreover, applications of NPs are gaining grounds and this increase the number of issues such as ethical, health and safety, technological, policy and regulatory, and issues linked to decisively release of NPs into the surroundings (Bundschuh *et al*., 2018; Tiede *et al*., 2008). Even in the absence of acute

toxicity, bioaccumulation and long-term exposure of NPs to plants may have an impact on the food chain, which is unrequited or unaccounted for (Tiede *et al*., 2008).

Metal oxide NPs of ZnO and CuO; the most important NPs, possess a mixture of characteristics of metal materials and nanoparticles. These two nanoparticles are among the essential materials needed by plant for metabolic and physiological processes and it has been employed for a wide range of useful materials for human use like in cosmetics, as semiconductors, in plastic making, glass industry, ceramics, cement, rubber materials, food supplements batteries, agricultural industries, environmental remediation, fuel additives, textile industries and waste water treatments (Azizi *et al*., 2017; Rajput *et al*., 2017; Sturikova *et al*., 2018).

The use of engineered NPs in agricultural practices and medical sectors has been established and this has solved countless challenges as compared to the conservative methods or ways (Rai *et al*., 2018; Raliya *et al*., 2 017). The moment NPs gets into the soil, it may impact soil physical and chemical composition or characteristics, work together with other pollutants, form a new novel type of poisonous compounds and distrupt soil microbial functionality, plant growth and performance (Loureiro *et al*., 2018; Rajput *et al*., 2017; Soni *et a*l., 2015).

2.10 Bulk Copper and Zinc/Zinc-Oxide on Plant Growth and Developments.

There are different reports available on the effects of copper and zinc-oxide on plants especially beans and tomato. Cherif *et al*. (2011) reported dose dependent effects of bulk Zn on *Solanium lycopersicum* plant. This research revealed that when about 10, and 50 μmol/L of Zn was used to grow tomatoes, growth was stimulated, photosynthetic pigments was also enhanced. Enzyme activities were also improved at this low concentration. Enzyme activities such as guaiacol peroxidases (GPOD), catalase (CAT), ascorbate peroxidase (APX) and

glutathione reductase (GR) but these parameters studied were reduced at elevated concentration of 100, and 150 μmol/L of Zn (Cherif *et al*., 2011).

Furthermore, Sivasanker *et al*. (2012) reported that leaf area of tomato decreased with increase in the zinc content of the soil. However, it increased at 50 and 100 mg kg^{-1} soil level. It was also reported by John *et al*. (2013) that there was a decline in chlorophyll content in plants exposed to heavy metals stress such as copper. Kumar *et al*. (2011) also reported the tolerance responses of bulk copper and zinc on wheat by examining its biochemicals (chlorophyll, protein and proline) contents. It was noticed that increased doses of up to 100 g ha-1 copper enhanced / improved the content of chlorophyll, leaf area and yield in *Zea mays* plants as reported by Barbosa *et al*. (2014). However, there was a decrease in the results obtained in the studied parameters at higher doses. Asli *et al*. (2009) reported several studies showing that the concentrations of Zn in seeds are positively correlated with germination. Furthermore, Zn supplementation significantly increased percentage of seed germination, germination index, and vigour index (Cakmak *et al*., 2009). Zn is the most critical micronutrient affecting protein synthesis and required at the early stage of seed development.

Patel *et al*. (2013) reported the growth inhibitory effect of cadmium and arsenic on *Phaseolus aureus* Roxb which was reduced significantly by the application of lower level of zinc (25 ppm), the researchers further revealed that the application of zinc could not overcome the toxicity of cadmium and arsenic beyond levels of 50 ppm. Gurmani *et al.* (2012) suggested that soil application of Zn may increase both quantitative and qualitative yield of tomato. Their study also revealed that the concentration of Zn increased in leaves, fruit and root of tomato with increasing level of Zn application this was observed when Zn treatments of 5, 10 and 15 mg kg^{-1} was used. Sivasankar *et al.* (2012) reported improvement in growth and yield of four different plants due to zinc application. The plants were chilli (*Capsicum annuum),*

marigold *(Tagetes erecta),* mustard *(Brassica juncea)* and pigeon pea *(Cajanus cajan). The* observation was made with zinc sulphate treatment of 50, 100,150, 200 and 250 mg/kg

Luisa and Miguel (2006) observed that dry mass, root length, and foliar area of tomato decreased with time when Cu solution ranging from 0.05, 0.15, 0.20, and 0.35 mM Cu concentration was applied. Their findings further revealed that copper accumulated more heavily in roots than in leaves. Mineral uptake was affected by increasing Cu concentrations in solution with calcium (Ca), iron (Fe), and zinc (Zn) contents in leaves. It was further observed that the activities of three enzymes studied in leaves (guaiacol peroxidases (GPOD), catalase (CAT), and polyphenol oxidase (PPO) increased transiently, probably as an early response mechanism against Cu induced oxidative stress. At higher Cu concentrations, this defense mechanism broke down and the activities of the enzymes decreased accordingly. Copper (Cu) supplementary concentration in sand of, respectively 0 (control) and 10 μg g−1 (Cu stress) was used to cultivate *Cucumis sativus* Seedlings and the following observations were made by Vinit Dunand *et al*. (2002). It was shown that the responses of cucumber leaves to copper addition depended on their growth stage i.e whether young or matured leaves. Furthermore it was revealed that there was reduction in the leaf area of young expanding leaves while matured leaves showed a sharp decline in photosynthesis**.**

CHAPTER THREE

MATERIALS AND METHODS

3.1 Source of Materials and Description of the Varieties

Zinc oxide nanoparticles (nZnO) and Copper nanoparticles (nCu) were purchased from Wacker and Company in Germany in South-East Bavaria. Bulk copper and zinc oxide were purchased from Lab trade Nigeria Limited, Ilorin, Kwara State, Nigeria. The seeds for the experiment were obtained from Institute of Agricultural Research (IAR), in Ahmadu Bello University, Samaru, Zaria, and Kaduna State. The variety of beans that was used is Sam pea 11 and is a small- sized white bean. The variety of tomato that was used was Roman VF which is circular with very small cream seeds.

3.2 Characterization of Nanoparticles

Preparation of the nanoparticles was according to the method described by Oh *et al*. (2007). nZnO and nCu in the ratio 1:1 was weighed and was dispersed in double distilled water (DDW) to form slurries. This was stirred and evaporated to dryness in an oven at 70^0C. The nanoparticles was further washed with double distilled water, filtered and further dried in an oven at 100^0C for 24 hrs. This was grinded to fine powder with the aid of mortar and pestle.

3.2.1 Field Scanning Electron Microscopy

Field Scanning Electron Microscopy (FESEM) was done according to the method described by Fatoki *et al*. (2012). The Field Scanning Electron Microscopy (FESEM) of the nanomaterials was viewed separately with the use of a Nova Nano SEM 230 Scanning electron microscope at the centre for Nanoscience and Nanotechnology, Sathyabama Institute of Science and Technology, Chennai, India.

3.2.2 Analysis of Carbon, nitrogen and oxygen

Carbon, Nitrogen and oxygen analyses were done according to the method of Fatoki *et al*. (2012). Three milligrams (3mg) of the nanoparticle was weighed into a tin capsule which was sealed and loaded on Euro Ea analyzer where samples w combusted and analyzed for percentage carbon, nitrogen and oxygen content with the aid of Energy Dispersive X-ray Spectroscopy (EDX).

3.3 Determination of the size of Nanoparticles

Particle size was determined according to the method described by Hong *et al*. (2014). Three milligrams (3mg) of nZnO and nCu was separately weighed and dispersed into 5mls of water to form slurries which were poured into a digestion flask where particles were examined using a Field Scanning Electron Microscope (FESEM) and this was used to determine the particle size.

3.4 Determination of the physico-chemical parameters of the soil

The soil that was used for the experiment was obtained from the University of Ilorin Botanical Garden, Ilorin, Nigeria. The soil was characterized for selected physico-chemical parameters according to the standard methods for soil analysis as described by page *et al*. (1982). About one gramme of the soil was weighed and sieved through 1mm sieve to remove soil debris and particles. The sieved soil was digested with 1 ml HNO_3 and 3 mls HCl; this was heated on a hot plate until brownish fumes were expelled. Analysis for cations was done using the atomic absorption spectrophotometer (Bulk scientific ACUSSYS 211). pH metre was used for the determination of the soil pH while the soil thermometer was used for the determination of the temperature of the soil.

3.5 Experimental design

The experiment was carried out in a screen house at the Botanical Garden of the University of Ilorin, Ilorin, and Kwara State, Nigeria. This study area falls within the coordinates of Longitude 4˚38.920᾽ E to 4˚39.971᾽ E and Latitude 8˚28 .230’ N to 8˚28.230᾽N.

Seeds of tomato and bean were sterilized in sodium hypochlorite solution for ten minutes in accordance with the method described by USEPA (1996). The seeds used were rinsed with double distilled water three times. Viability test was done on the seeds and subsequently, the sprouted seeds were used for further experiments. Healthy seeds (at least, four) were grown in pots containing 1.7 kg of sandy loamy soil spiked with different quantities nanoparticles and bulk particles. It is worthy to note that planting commenced on 1st April and was terminated after 12 weeks in June (90 days) for both cropping years (2017 and 2018). The treatments consisted of four different concentrations (0, 300, 600 and 1000 mg/kg) each of ZnO and Cu bulk and nanoparticles; each was replicated thrice to make a total of 48 pots of nanoparticles treated plants and 48 pots of bulk treated plants. A total of 96 pots were used for the experiment; 24 pots each for tomato and bean, all laid out in a randomized block design (RBD). The growth performances of bean and tomato plants were separately determined according to the method of Olayinka *et al*. (2015). Determination of growth performances of the seed of beans and tomatoes commenced 2 weeks after planting and continued fortnightly till the emergence of flower and fruits. Measurement of growth parameters such as leaf length, leaf breadth, leaf area, stem girth, number of leaves, and chlorophyll content also commenced 2 weeks after planting and fortnightly till plants were harvested.

3.6 Measurement of growth parameters

3.6.1 Leaf length

Leaf length was determined by using the metre rule. Three plants were tagged per treatment from the experimental pot, three leaves were selected randomly and measurements were taken from the base of the leaf to the tip of the leaf. This was done at two weeks interval for the three leaves.

3.6.2 Leaf breadth

Leaf breadth measurement was done at two weeks interval. Three plants were tagged per treatment from the experimental pot, three leaves were selected randomly and measurements were taken from the widest part of the leaf with the aid of the aid of thread and extrapolated on the metre rule.

3.6.3 Leaf area

Leaf area was determined by using the meter rule to take measurements and substituting values obtained in to the following formula: $A = 0.75 \times L \times B$ (where A means the area, L means the length of the plant, B means the breadth of the plant and 0.75 is a constant used on the field to get accurate values on the field). Three leaves were selected per treatment, the values obtained were then substituted into the above formula and leaf area was obtained.

3.6.4 Number of leaves

For the number of leaves, three plants were tagged from the experimental pot and the number of leaves was determined by counting the total number of leaves of each treatment. All the number of leaves for the three replicates was summed up and this was computed to be the number of leaves.

3.6.5 Stem girth

Stem girth was determined from the tagged plants with the use of thread and the thread was later placed on the metre rule to take readings or measurements of the thickness of the plants.

3.6.6 Chlorophyll content determination

Available chlorophyll content was determined according to the method described by Makeen *et al.* (2007). This was by acetone incubation method. Fifty milligram (50 mg) of the leaf tissue was weighed, placed in a sample bottle with 5 mls of 80 % acetone. The sample bottle was shaken from time to time; it was then placed in refrigerator for 48 hrs. The extracted liquid was filtered through glass wool to remove leaf pieces and transferred to another graduated tube. A clean cuvette for the Spectrophotometer was obtained and filled with two-thirds of acetone. The cuvette chamber was wiped with a tissue paper and put into the V-3000PC Spectrophotometer and the wave length was set at 663nm. The cuvette chamber was covered and the Spectrophotometer was set to zero (0) absorbance with the blank in place. The blank was removed and saved for the next measurement. The extract was gently swirled in the test-tube and a second cuvette was filled with two- thirds full. The cuvette was wiped clean, inserted into the Spectrophotometer and the hatch was closed. The wavelength at 663 was used and results were obtained. These procedures were repeated at wavelength 645nm. The chlorophyll contents were determined by using Arnon's formula.

Chl a (mg g^{-1}) = [(12.7 $\times A_{663}$) - (2.6 $\times A_{645}$] /mg leaf tissue ×ml acetone ----------1

Chl b (mg g^{-1}) = [(22.9 $\times A_{645}$) - (4.68$\times A_{663}$)] / mg leaf tissue) × ml acetone --------2

Chl total = [(20.2 $\times A_{645}$) + (8.02$\times A_{663}$)] / mg leaf tissue) × ml acetone ----------3

3.7 Determination of productivity parameters of beans and tomatoes

Productivity of beans and tomatoes were investigated and recorded as soon as there is emergence of flowers and fruits on a weekly basis. Productivity of beans and tomatoes seeds was done according to the methods described by Olayinka *et al*. (2015) with little modifications. The following parameters were measured.

3.7.1 Day to flowering

This is the number of days it takes for the first flower to emerge from each experimental pot after sowing in the pot

3.7.2 Day to fruiting

This means days from transplant to the emergence of the first fruit (s).

3.7.3 Number of fruits or pods per plant

This parameter was taken at harvest time for beans and periodically at fruit maturity for tomato. It was done manually by separating the pods or fruits from the tagged plant. This was done for at least three plants per treatment. The total number was taken, and then the mean was calculated as the number of fruits or matured pods.

3.7.4 Number of seeds per pod

Number of seeds per pod was determined manually by counting the number of seeds in a matured pod. This was done for at least three pods per treatment.

3.7.5 Number of seeds per plant

Number of seeds per plant was determined manually by adding the number of seeds on a plant, three plants were selected and mean of the total number of seeds were taken.

3.7.6 Fresh weight

Fresh weight was determined after harvest. The plants were uprooted, washed thoroughly with water, separated into different parts, the stems, the roots and the leaves. These were weighed with a weighing balance and the values obtained were recorded.

3.7.7 Dry matter

Dry matter was determined after harvest (12 weeks). The plants were uprooted, washed thoroughly with double distilled water, separated into different parts: the stems; the roots; and the leaves. Only the leaves and the stem were used because productivity deals with the above ground plants parts. This was then dried in an oven for 72 hrs, finally the samples were weighed with a weighing balance then the values obtained were recorded.

3.8 Non enzymatic and enzymatic antioxidants of bean and tomato

3.8.1 Non enzymatic antioxidant

3.8.2 Determination of ascorbic acid content

Determination of ascorbic acid content was performed by the method of Klein and Perry (1982). The sample (0.1g) of ripe tomato and that of mature beans after harvest were weighed separately and mixed with metaphosphoric acid of about 0.1 g L^{-1} and left to stand for 45 min at 4˚C under constant stirring. It was centrifuged at 15,000× g. About 1 ML of the sample was taken from the supernatant and mixed with 2, 6-dichlorophenol-indolphenol acid. The absorbance was read at 515 nm. The results were expressed as milligrams of ascorbic acid per 100 g fresh weight (mg AA 100 g^{-1} FW). Beckman Coulter Du 730, U-V visible spectrophotometer was used.

3.8.2.1 Determination of total carotenoids: lycopene and beta-carotene

Lycopene and beta carotene were determine according to the method of Nagata and Yamashita (1992). Sample of about 0.1g of either beans or tomato was measured separately

and mixed with 20 Ml of hexane: acetone solution (3:2). An aliquot was taken from the supernatant and measured at 453, 505 and 663 nm in a spectrophotometer (Beckman Coulter Du 730, U-V visible spectrophotometer) and the content of lycopene and beta-carotene was estimated using the following equations:

Lycopene = - 0.0458 A_{663} + 0.204 A_{645} + 0.372 A_{505} - 0.0806 A_{453} ----------4

Beta-carotene = 0.216 A_{663} - 1.220 A_{645} - 0.304 A_{505} + 0.452 A_{453} ----------5

The quantitative analysis of carotenoids was performed using the method described by Oniga *et al*. (2004) and the results were expressed in carotenoids (mg/g dried weight). The carotenoids were extracted in hexane, at room temperature. The content in total carotenoids was calculated using the formula: mg carotenoids/g = A× V × 10/ (A1cm1% × G) -------6

Where A = is the absorbance of solution at 450 nm, V = is the volume (= 50 ml),

The results were expressed in milligrams per 100 g fresh weight (mg 100 g^{-1} FW)

3.8.3 Determination of enzymatic antioxidant activities

3.8.3.1 Determination of ascorbate peroxidase (APX)

The method of Nakano and Asada (1981) was used. In this method 1 g of fresh leaf and root were separately ground and homogenized with 4 µl 0.5 Mm ascorbate, 10 µl 0.2 mM H_2O_2, plus 886 µl 50 mm potassium phosphate buffer (pH 7.4) and absorbance readings from the Spectrophotometer (U-V visible spectrophotometer 725 N), were taken at 290 nm for about 3 min.

3.8.3.2 Determination of Catalase activities (CAT)

Catalase activity in the plant was determined according to the method described by Aebi (1974). Plant parts (roots and leaf) were harvested and homogenized with liquid nitrogen.

One ml (1ml) of phosphate buffer was added per 100mg plant (fresh weight). The homogenates were centrifuged at 4000 × g at 4° C for 10 min to remove gross particles plant debris. The supernatant was diluted two-fold in phosphate buffer (this was kept aside for enzyme activities analysis). To about 666 µl of the initial supernatant, 334 µl of 73 mM H_2O_2 was added and absorbance was read at 240 nm for 3 mins. One unit of enzyme activity is defined as a decrease in absorbance of 0.001/min at 240nm (U-V visible spectrophotometer 725 N was used).

3.8.3.3 Determination of Superoxide dismutase (SOD)

Superoxide dismutase was determined according to the method of Beyer and Fidovich (1987). 1 g of fresh leaf and root samples were homogenized under ice cold conditions in 3ml extraction buffer, containing 50 mM phosphate buffer (pH 7.4). A one gram (1 g) of Polyvinylpyrrolidone (PVP) and 0.5 % (v/v) Triton X- 100 at 4°C was centrifuged at 10,000 × g for 20 min to obtain a supernatant fraction used for the assay. To about 50-150 µl extract, 3.5 ml of O_2 generating solution containing 14.3 mM methionine, 82.5 µM nitroblue tetrazolium (NBT) and 2.2 µM riboflavin were added. The extract was adjusted to a final volume of 0.3 ml with 50mM K-phosphate (pH 7.8 and 0.1 mM Na_2 EDTA). The reaction was allowed to run for 10 min and ended by switching off the light. The change in nitroblue tetrazolium (NBT) was determined by reading absorbance at 560 nm (U-V visible spectrophotometer 725 N). One unit of SOD is defined as the amount of enzyme that produced a 50 % inhibition of nitroblue tetrazolium (NBT) reduction under assay conditions.

3.9 Stress attributes determination

3.9.1 Determination of malondialdehyde (MDA)

Lipid peroxidation of the formed MDA in the sample was determined according to the method of Li. (2000). The plant material (0.5 g of the leaf or root) was homogenized using

pestle and mortar with 3 ml of 0.5 % thiobarbituric acid in 20 % thiochloroacetic acid (w/v).The reacting mixture was incubated at 100˚c for about 30 min and the reaction was terminated in cool water. It was centrifuged at 10,000 x g for 10 mins. Absorbance was measured spectrophotometrically (U-V visible spectrophotometer 725 N) at three different wave lengths of 532, 450 and 600nm. MDA concentration was by the following formula: MDA (µmol/L) = 6.45 (A_{532}-A_{600})-0.56A_{450} ----------7

3.9.2 Determination of hydrogen peroxide

Hydrogen peroxide determination was by the method of Nakano and Asada, (1984). The root or leaf part of about 0.5 g was harvested and homogenized with liquid nitrogen; about 1 ml of phosphate buffer was added per 100 mg. It was centrifuged at 4000 x g at 4˚C for 10 mins to remove gross particles plant debris, and then the supernatant was diluted in two-folds in phosphate buffer. To 100 µl of the supernatant, 450 µl of 17 m M H_2O_2 and 450 µl of 25mM ascorbate were added. Absorbance was read at 290 nm for 3 mins. One unit of enzyme activity is defined as a decrease in absorbance of 0.001/min at 290 nm (U-V visible spectrophotometer 725 N).

3.9.3 Determination of Proline

Proline determination was done according to the method described by Carillo *et al.* (2008)**.** This was carried out after three months of germination with 0.5 g of the sample weighed and 5 milliliters (5 mls) of 80 % ethanol was added to the sample, and was gently shaken to ensure homogeneity of the sample. A 100µl of the reaction mixture was pippetted and another 50µl of ethanol was added into the screwed cap tubes, this was sealed and heated at 95^0 C in water bath for 20 minutes. This was centrifuged at 10,000 rpm for 1 min. The tube contents were transferred into a 1.5 ml cuvette and a Spectrophotometer was used to read the result at 500 nm wavelength (Beckman Coulter Du 730, U-V visible spectrophotometer).

3.10 Biochemical constituents of tomatoes and beans

3.10.1 Determination of protein

Determination of protein was done at three months after germination and this was done according to the method described by Milka *et al*. (2006). The nanoparticles treated bean seed were immediately homogenized with 2mL each of water, 0.5mol/L NaCl, 70% ethanol, and 0.05M acetic acid for 2 hr which had been previously ice-cold with potassium phosphate buffer (0.1 M, pH 7.4). The homogenates were centrifuged for 5 min at 4500 rpm and the supernatants were saved and used to determine the protein content and this was determined by using Bradford assay with the microplate assay and bovine serum albumin as standard (0–0.75 mg/ml).

3.10.2 Seed starch

Seed starch was determined at three months (12 weeks) after germination. The method of Verma and Dubey (2001) with little modifications was adopted. A sample of 100mg of dried plant sample was grinded in 2mL of 80% ethanol and then heated (80^0C) in a water bath for 30min. After cooling to room temperature, the extract was centrifuged at 14000 rpm for 30min; a process that was repeated twice. The precipitate was dried at 70˚C for 24 hrs. Two milliliter (2 mls) of double distilled water was added and the mixture was heated in a water bath at 90˚C for 15 mins. After cooling to ambient temperature, 1 ml of concentrated tetraoxosulphate VI acid was added. The suspension was stirred for 15 mins and the final volume was adjusted to 5 mls using doubled distilled water. The supernatant starch content was quantified following the method of AOAC (1990) and expressed in mg/100 g dry weight. Seed starch were determined spectrophotometrically at λ= 490 nm using Beckman Coulter DU 730 (UV-Visible spectrophotometer).

3.10.3 Determination of copper and zinc contents

Root were dried in an oven at 70 ˚ C for 24 hrs and one gram (1g) was measured, it was grinded with pestle and mortar then weighed into a clean digestion flask. About 9 ml of Conc. HNO_3 and 3 ml of Conc. HCl was added (3:1). The sample was heated on a hot plate until all brownish fumes were expelled and solution filtered. The filtrate was diluted to 25 ml-mark with a deionised water and analysed for Cu and Zn content with the Atomic Absorption Spectrophotometer at 350 nm (Beckman Coulter Du 730, U-V visible spectrophotometer).

3.10.4 Statistical analysis

Data were subjected to two ways Analysis of Variance (ANOVA) and this was to analyse the results of the effects of the nano and bulk particles to check if there were significant interactions in the results obtained. Duncan multiple range test (DMRT) was used to separate the means in the concentrations and the metal salt of the bulk and nano particles used at 0.05 level of significance using SPSS version 23 Software.

CHAPTER FOUR

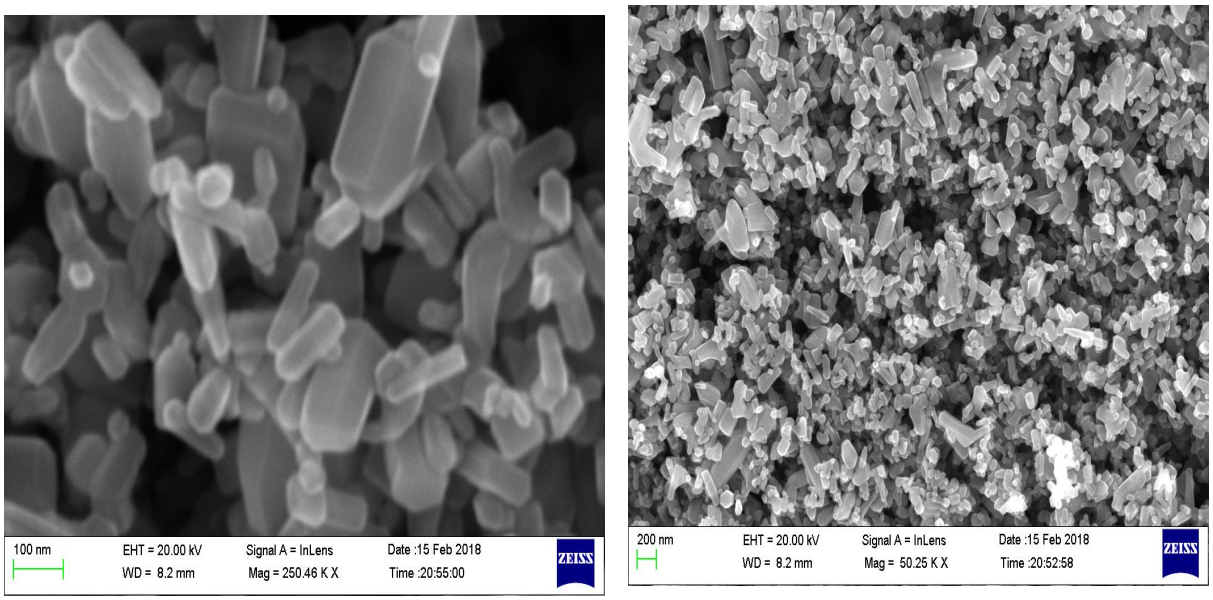
RESULTS

4.1 Characterization of the nanoparticles used

Figure 1 shows the nCu as shown by Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDX). The width of nCu was 8.2nm. X-ray diffraction peaks of copper nanoparticles (nCu) at low and high magnifications are presented in Fig. 2. There are some sharp peaks of light intensity and this sharp diffraction peaks are an indication of the good crystalline nature of copper nanoparticles which is inevitably responsible for its relative purity.

The EDX technique is a non-destructive analysis which is of particular interest to this research because it ensures quality control assurance and product maximization. The relevance is to detect elements present in the copper and zinc oxide nanoparticles. The EDX structure of the copper nano revealed the presence of oxygen, while carbon and nitrogen compounds were absent (Fig.1).

Figure 3 shows Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDX) structure of Zinc oxide nanoparticles (nZnO). There are some strong X-ray diffraction peaks of nZnO as in the case of nCu. The presence of oxygen was also observed while carbon and nitrogen were absent in the zinc oxide nanoparticles as shown in Fig. 4



a b

Figure 1: FESEM micrograph of nCu particles used for the experiment at (a) high and (b) low

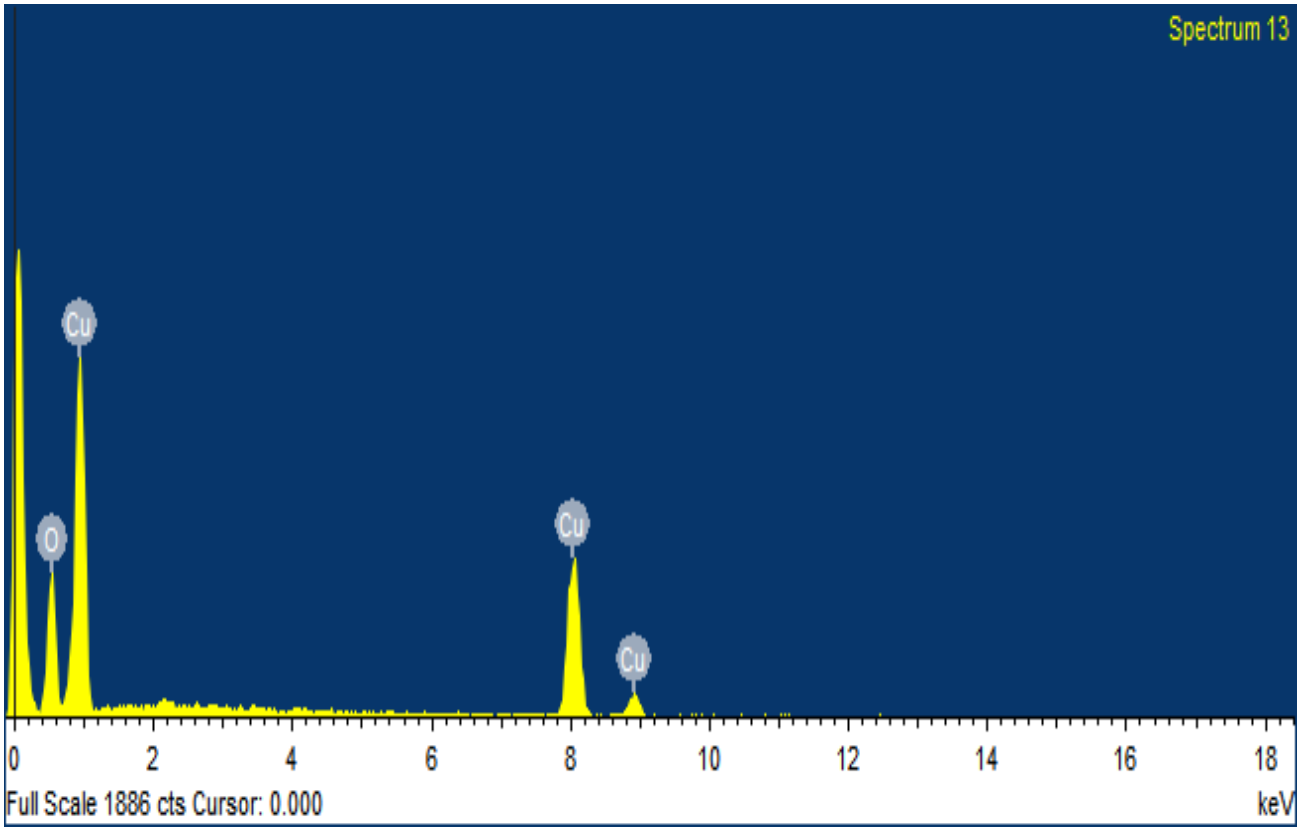
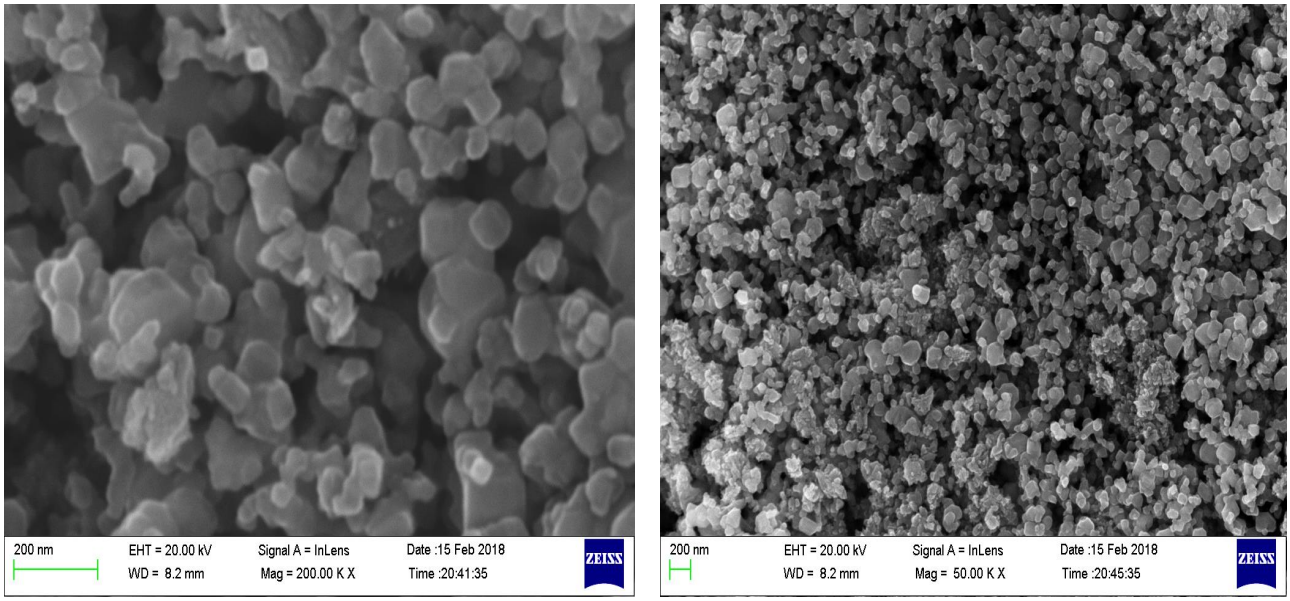


Figure 2: Energy-dispersive X-ray spectroscopy (EDX) of nCu nanoparticles



a **b**

Figure 3: FESEM micrograph of nZnO nanoparticles used for the experiment at (a) high and (b) low magnifications.

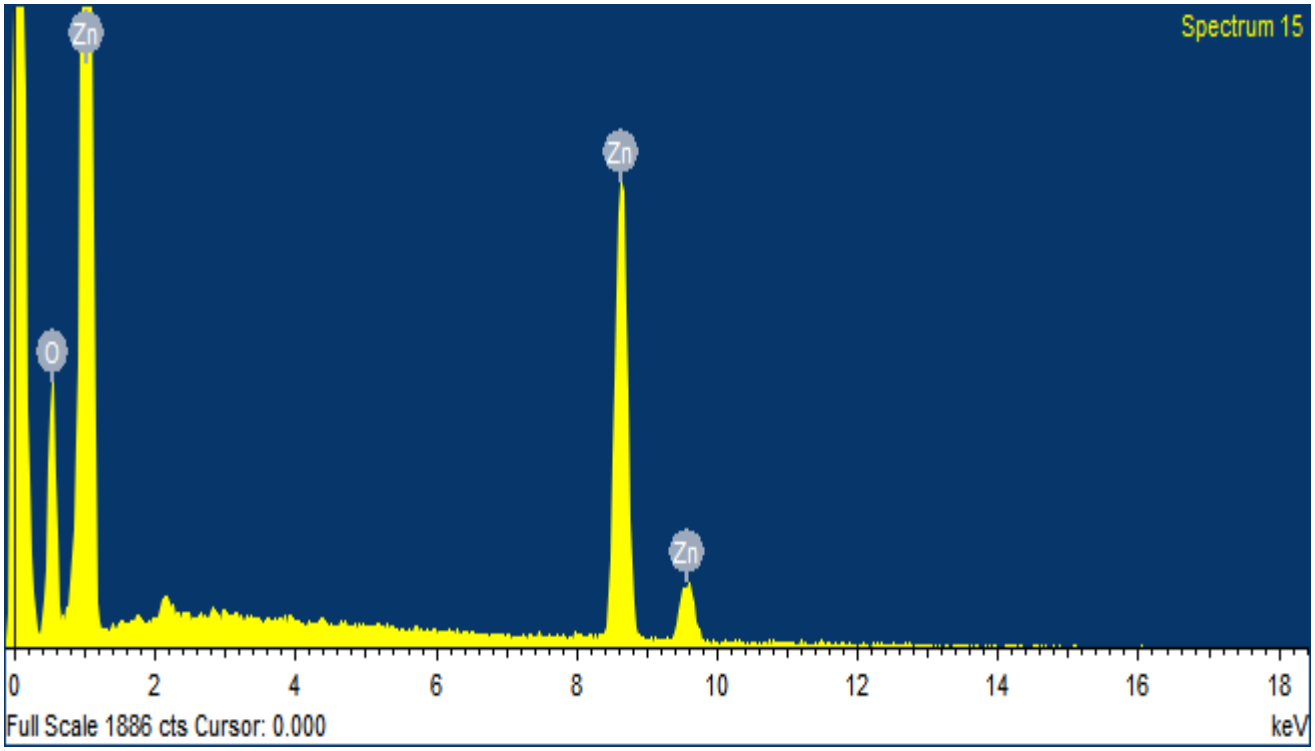


Figure 4: Energy-dispersive X-ray spectroscopy (EDS) of nZnO particles

Table 1 presents the physicochemical properties of copper nanoparticles (nCu). The molecular weight of nCu as revealed by Energy Dispersive X-ray spectroscopy (EDX) was 90.29 g/ml and its density was 70.07g/cm^3. Copper nanoparticles are black brown in appearance with an average particle size of 25nm. It is spherical or rod-like in shape. The nCu contained about 9.7 g/ml of oxygen while carbon and nitrogen were absent.

Table 2 shows the physicochemical properties of zinc oxide nanoparticles (nZnO). The molecular weight of nZnO as revealed by Energy Dispersive X-ray spectroscopy (EDX) was 68.29 g/ml and the density was 34.51g/cm^3. Zinc oxide nanoparticles are crystalline (white) in nature with an average size of less than 100 nm. It is irregularly shaped with diverse sizes. The oxygen content of nZnO was 31.71 g/ml while carbon and hydrogen were absent.

4.2 Physico-chemical parameters of the soil used for the experiment

Table 3 shows the physico-chemical parameters of the soil used for the experiment. The metals investigated in the soil were magnesium (Mg) which was 1.01 ppm, calcium (Ca) was 8.62ppm, Sodium (Na) was 93.21 ppm, Potassium (K) was 10.56 ppm, Phosphorous (P) was 54.3ppm, pH was 6.40, Electrical Conductivity (E.C) was 30.00 S/m and insitu temperature was 30.36◦C.

4.3 Leaf lengths of beans

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on leaf length of bean plants during 2017 and 2018 cropping seasons are presented in Tables 4-7.

There was a significant interaction ($p \leq 0.05$) between the metal salts and concentration on the leaf length of beans of 2017 cropping season at 2-8 WAP while significant highest leaf length was recorded with the use of copper nanoparticles (nCu) at 2-8 WAP and significant lowest value was however recorded in the control plants (Table 4). The control produced the

shortest leaves. However, 300 and 600 mg/kg of the metal salts were found to be statistically the same ($p \leq 0.05$). At 2, 6, and 8 WAP all treatments produced same sized leaves statistically ($P \leq 0.05$). Table 4 shows that treatment had significant interactive effective effects. In addition, the shortest leaves were obtained in the control plants. The nanoparticles enhanced the leaf lengths of beans with nCu producing the longest leaves. In addition, the nanoparticles produced longer leaves than the respective bulk metal/compound. The nanoparticles produced the longest leaves at 4 WAP which reduced at 6 WAP. On the other hand, the bulk metal increased the leaf lengths throughout the experiment while n ZnO produced the values that were close to that of nCu.

Table 5 shows the interactive effects among metal salts and the different concentrations on the leaf length of bean in 2017 cropping season. The data generated showed that all treatments produced beans with longer leaves than the control.

Table 6 shows the effects of nanoparticles and bulk particles on leaf length of beans in 2018 cropping season. The nanoparticles better enhanced the leaf lengths of beans than the bulk. The leaf length increased throughout the period of the experiment. Copper nanoparticles treated beans produced beans statistically longer leaves than the nZnO. All treatments have significantly ($p \leq 0.05$) longer leaves than the control. The 300 and 600 mg/kg treatments had same leaf lengths statistically. The treatments had significant interactions ($p \leq 0.05$) on leaf lengths of beans in 4-8 WAP (Table 6). Furthermore, significant largest leaf lengths were recorded in the nano zinc oxide 300 mg/kg treated plants at 4 WAP (Table 7). Similar trends were observed at 6 and 8 WAP. Leaves of nanoparticles treated plants were longer than the bulk-treated plants statistically at ($p \leq 0.05$) but at 8 WAP, n ZnO -treated plants produced statistically the same ($p \leq 0.05$) leaf lengths.

Table 1: Physico-chemical parameters of copper nanoparticles

Physico-chemical parameters	Description
Molecular weight (g/ml)	90.29 g/ml
Appearance	Black-brown
Morphology	Spherical/rod shaped
Particle size	25 nm
Density	70.07 g/cm^3
Oxygen content	9.71 g/ml
Carbon content	Absent
Nitrogen	Absent

Table 2: Physico-chemical parameters of zinc oxide nanoparticles

Physico-chemical parameters	Description
Molecular weight (g/ml)	62.29 g/ml
Appearance	Crystalline white
Morphology	irregular
Particle size	< 100 nm
Density	34.51g/cm^3
Oxygen content	31.71 g/ml
Carbon content	Absent
Nitrogen	Absent

Table 3: Physicochemical parameters of the soil used

Studied parameters	Values
Magnesium (Mg) (ppm)	1.01
Calcium (Ca) (ppm)	8.62
Sodium (Na) (ppm)	93.21
Potassium (K) (ppm)	10.56
Phosphorus (P) (ppm)	54.30
pH	6.40
Electrical conductivity (S/m)	30.00
Temperature (T˚)	30.36
Copper (mg/kg)	Not detected
Zinc (mg/kg)	Not detected

Table 4: Effects of nanoparticles and bulk particles (nCu and ZnO) on leaf length (cm) of beans for 2017 cropping season.

	Leaf length (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	4.73[a]	5.02[a]	4.73[a]	4.82[a]
nZnO	3.51[b]	4.16[b]	3.93[b]	3.88[b]
bCu	1.99[d]	2.27[c]	3.18[b]	3.05[b]
bZnO	2.49[c]	2.68[c]	3.93[b]	3.75[b]
Concentrations				
Control	1.85[c]	1.92[c]	2.02[c]	2.25[c]
300 mg/kg	4.06[a]	4.68[a]	4.81[a]	4.78[a]
600 mg/kg	3.72[b]	4.12[a]	3.93[b]	3.96[b]
1000 mg/kg	3.08[b]	3.40[b]	3.73[b]	4.51[a]
Interaction	0.000[*]	0.008[*]	0.028[*]	0.011[*]

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$. nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 5: Interactive effect between metal salts and various concentrations on the leaf length of beans for 2017 cropping season

Metal salt	2 WAP	4 WAP	6 WAP	8 WAP
Control	2.17 ± 0.15^{ef}	2.03 ± 0.58^{ef}	1.8 ± 0.82^{f}	2.00 ± 1.00^{ef}
nCu 300 mg/kg	5.37 ± 0.57^{ab}	6.00 ± 1.00^{a}	6.17 ± 0.29^{a}	5.17 ± 0.90^{ab}
nCu 600 mg/kg	5.50 ± 0.44^{ab}	$6.70\pm0.0.75^{a}$	5.33 ± 2.10^{ab}	5.80 ± 1.15^{ab}
nCu 1000 mg/kg	5.87 ± 0.90^{ab}	5.33 ± 1.26^{ab}	5.63 ± 0.64^{ab}	6.30 ± 0.60^{a}
nZnO 300 mg/kg	5.33 ± 0.42^{ab}	6.33 ± 1.15^{a}	6.00 ± 1.00^{a}	6.23 ± 1.70^{a}
nZnO 600 mg/kg	4.10 ± 0.79^{cd}	4.73 ± 1.17^{cd}	4.50 ± 1.32^{cd}	3.70 ± 0.52^{de}
nZnO 1000mg/kg	2.43 ± 1.53^{ef}	3.53 ± 2.34^{de}	3.40 ± 2.60^{de}	3.53 ± 2.45^{de}
bCu 300 mg/kg	2.43 ± 0.57^{ef}	2.73 ± 0.11^{ef}	3.00 ± 0.00^{de}	3.27 ± 0.21^{de}
bCu 600 mg/kg	1.97 ± 0.57^{ef}	2.03 ± 0.15^{ef}	2.24 ± 0.25^{ef}	2.67 ± 0.58^{de}
bCu 1000 mg/kg	2.00 ± 0.00^{ef}	2.50 ± 0.00^{ef}	3.07 ± 0.12^{de}	3.77 ± 0.25^{de}
bZnO 300 mg/kg	3.10 ± 0.10^{de}	3.67 ± 0.29^{de}	4.81 ± 1.46^{cd}	4.40 ± 0.44^{cd}
bZnO 600 mg/kg	3.30 ± 0.17^{de}	3.00 ± 0.00^{de}	3.93 ± 1.59^{de}	3.67 ± 0.58^{de}
bZnO 1000mg/kg	2.03 ± 0.58^{ef}	2.23 ± 0.25^{ef}	3.73 ± 1.64^{de}	4.43 ± 0.60^{cd}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide.

Table 6: Effects of nanoparticles and bulk particles (nCu and ZnO) on leaf length of beans (cm) during 2018 cropping season.

	Leaf length (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	4.59[a]	4.62[a]	4.71[a]	5.09[a]
nZnO	3.55[b]	4.13[a]	4.53[a]	4.55[a]
bCu	1.8[d]	2.38[c]	2.31[c]	2.26[c]
bZnO	2.32[c]	2.59[c]	2.48[c]	2.40[c]
Concentrations				
Control	1.84[d]	1.83[d]	2.08[c]	2.25[c]
300 mg/kg	3.78[b]	4.38[a]	4.48[a]	4.36[a]
600 mg/kg	3.74[b]	4.22[a]	4.02[a]	4.09[a]
1000 mg/kg	3.11[b]	3.36[b]	3.51[b]	3.61[b]
Interaction	0.135 N.S	0.000*	0.028[*]	0.011[*]

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 7: Interactive effect between metal salts and various concentrations on the leaf length (cm) of beans during 2018 cropping season

	Leaf length (cm)		
Metal salt	4 WAP	6 WAP	8 WAP
Control	1.87 ± 0.29^{ef}	1.85 ± 0.82^{ef}	2.60 ± 0.56^{cd}
nCu 300 mg/kg	5.33 ± 1.19^{ab}	6.17 ± 0.29^{a}	5.43 ± 0.90^{ab}
nCu 600 mg/kg	6.40 ± 0.69^{a}	5.40 ± 2.12^{ab}	6.40 ± 0.44^{a}
nCu 1000 mg/kg	4.67 ± 0.76^{bc}	4.73 ± 0.46^{bc}	5.77 ± 0.89^{ab}
nZnO 300 mg/kg	6.00 ± 1.00^{a}	6.00 ± 1.00^{a}	6.27 ± 1.70^{a}
nZnO 600 mg/kg	4.50 ± 1.32^{bc}	5.00 ± 0.50^{ab}	4.77 ± 0.67^{bc}
nZnO 1000 mg/kg	4.17 ± 1.26^{bc}	5.33 ± 0.58^{ab}	4.57 ± 1.40^{bc}
bCu 300 mg/kg	2.86 ± 0.12^{cd}	2.77 ± 0.25^{cd}	2.80 ± 0.00^{cd}
bCu 600 mg/kg	2.43 ± 0.15^{de}	2.17 ± 0.15^{de}	2.00 ± 0.00^{de}
bCu 1000 mg/kg	2.50 ± 0.00^{de}	2.07 ± 0.11^{de}	2.20 ± 0.10^{de}
bZnO 300 mg/kg	1.80 ± 0.10^{ef}	3.00 ± 0.00^{c}	2.93 ± 0.57^{c}
bZnO 600 mg/kg	3.53 ± 0.45^{c}	3.50 ± 0.00^{c}	3.20 ± 0.00^{c}
bZnO 1000 mg/kg	2.10 ± 0.10^{de}	1.90 ± 0.10^{de}	1.90 ± 0.10^{ef}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide.

4.4 Leaf breadth in beans

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on leaf breadth of bean plants during 2017 and 2018 cropping seasons are presented in Tables 8-11.

Table 8 shows the effects of nanoparticles and bulk particles on leaf breadth of beans for 2017 cropping season. The nanoparticles better enhanced the leaf breadth of beans than the bulk particles and the control. The leaf breadth continued to increase throughout the period of the experiment in copper nanoparticles treated plants but in zinc oxide nanoparticles treated plant, a decrease in leaf breadth was observed at 6-8 WAP. All treatments were significantly higher than the control ($p \leq 0.05$). There was a significant interactive effect ($p \leq 0.05$) between the metal salts and concentration on the leaf breadth of beans in 2017 cropping season at 2-8 WAP. Significant thickest leaf breadth was recorded in nCu and nZnO from 2-6 WAP while there were no significant differences in the metal salts at 8 WAP (Table 8).

Table 9 shows the interactive effects among metal salts and the different concentrations on the leaf breadth of bean in 2017 cropping season. The data generated showed that all the treatments produced beans with wider leaf breadth than the control, copper and zinc oxide nanoparticles had the same effects of increasing the leaf breadth more than the bulk copper and zinc compounds. Meanwhile bulk compounds increased the leaf breadth linearly throughout the period of the experiment but nanoparticles compounds decreased the leaf breadths between 6-8 WAP.

Furthermore, nCu 300 and 600 mg/kg recorded the most significant leaf breadths at 2 WAP and the shortest value of leaf breadth was found in the control plants (Table 9). At 4WAP, the most significant ($p \leq 0.05$) metal was nZnO 300 mg/kg and similar trend was found in 6 WAP. Meanwhile, bZnO 300 and 600 mg/kg had the widest leaf breadth at 8 WAP for 2017 cropping season.

Table 10 shows the interactive effects among metal salts and the different concentrations on leaf breadth of beans in 2018 cropping season. The data obtained revealed that nanoparticles compounds treated beans had wider leaf breadth in comparison with the bulk treated plants and that nanoparticles copper produced pronounced leaf breadth than the zinc oxide nanoparticles. Moreover, the effect of 300 and 600 mg/kg treatments is greater than that of 1000 mg/kg treatment. In addition, there were also significant interaction ($p \leq 0.05$) between the metal salts and concentration on leaf breadth of beans at 2-6 WAP of 2018 cropping season.

Significant widest leaf breadth was recorded in nCu and nZnO treatments from 2-6 WAP while significantly narrow leaf breadth was recorded in bulk Cu and ZnO (Table 10). Irrespective of the metal salt, the control recorded significantly lowest ($p \leq 0.05$) leaf breadth from 2-6 WAP. However, the control, 300, 600 and 1000 mg/kg of the metal salts produced statistically the same leaf breadth at 8 WAP (Table 10). It should be noted as well that there was no significant interactive effects between the metal salts and concentrations on leaf breadth at 8 WAP.

Table 11 shows the interactive effects among metal salts and different concentrations on the leaf breadth of beans in 2017 cropping season. All nanoparticles treatments had values that were greater than the control; this means that the treatment had significant effects on the leaf breadth in beans. Meanwhile, copper nanoparticles had values that were greater than zinc oxide nanoparticles treated plants but nanoparticles treated plants produced significantly widest leaf length than their corresponding bulk counterparts. Furthermore, at 2 WAP, nCu 300 mg/kg recorded the most significantly ($p \leq 0.05$) widest leaf breadth in beans in 2018 cropping season. The most narrow leaf breadth was recorded in the control. At 4-6 WAP, similar trend were observed with the highest significant leaf breadth found in nCu

Table 8: Effects of nanoparticles and bulk particles (Cu and ZnO) on leaf breadth (cm) of beans during 2017 copping season.

	Leaf breadth (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	2.11[b]	2.45[a]	2.49[a]	2.56[a]
nZnO	2.69[a]	2.72[a]	2.22[ab]	2.39[a]
bCu	1.53[c]	1.53[c]	1.79[c]	2.51[a]
bZnO	1.91[c]	1.90[c]	2.20[bc]	2.78[a]
Concentrations				
Control	0.75[c]	1.43[c]	1.82[c]	2.33[a]
300 mg/kg	2.39[b]	2.71[a]	2.55[a]	2.43[a]
600 mg/kg	2.84[a]	2.15[b]	2.22[b]	2.67[a]
1000 mg/kg	2.24[b]	2.30[b]	2.00[b]	2.82[a]
Interaction	0.000*	0.000*	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 9: Interactive effect between metal salts and various concentrations on the leaf breadth (cm) of beans during 2017 cropping season

	Leaf breadth (cm)			
Metal salt	2 WAP	4 WAP	6 WAP	8 WAP
Control	0.40 ± 0.26^{g}	1.63 ± 0.29^{cde}	1.98 ± 0.51^{cde}	2.67 ± 0.58^{bcd}
nCu 300 mg/kg	3.20 ± 0.20^{a}	3.13 ± 0.12^{a}	2.63 ± 0.15^{bcd}	2.10 ± 0.10^{bcd}
nCu 600 mg/kg	3.17 ± 0.15^{a}	2.47 ± 0.23^{bcd}	2.47 ± 0.58^{bcd}	1.92 ± 0.10^{de}
nCu 1000 mg/kg	2.60 ± 0.10^{bcd}	2.57 ± 0.50^{bcd}	2.90 ± 0.57^{ab}	1.50 ± 0.00^{de}
nZnO 300 mg/kg	2.77 ± 0.59^{bcd}	3.50 ± 0.87^{a}	3.30 ± 0.26^{a}	2.17 ± 0.06^{bcd}
nZnO 600 mg/kg	2.63 ± 0.51^{bcd}	2.53 ± 0.84^{bcd}	2.20 ± 0.35^{bcd}	2.30 ± 0.30^{bcd}
nZnO 1000 mg/kg	1.57 ± 1.24^{de}	3.20 ± 0.50^{a}	1.40 ± 1.00^{ef}	2.20 ± 0.35^{bcd}
bCu 300 mg/kg	2.00 ± 0.00^{cde}	1.73 ± 0.21^{ef}	2.10 ± 0.10^{bcd}	2.47 ± 0.11^{bcd}
bCu 600 mg/kg	1.37 ± 0.41^{ef}	1.78 ± 0.13^{ef}	1.92 ± 0.10^{ef}	2.50 ± 0.50^{bcd}
bCu 1000 mg/kg	1.50 ± 0.00^{ef}	1.53 ± 0.15^{ef}	1.50 ± 0.00^{ef}	3.10 ± 0.44^{a}
bZnO 300 mg/kg	2.20 ± 0.10^{bcd}	1.90 ± 0.10^{cde}	2.17 ± 0.06^{bcd}	3.37 ± 1.44^{a}
bZnO 600 mg/kg	2.23 ± 0.23^{bcd}	1.97 ± 0.06^{cde}	$2.30\pm1.0.30^{bcd}$	3.43 ± 0.21^{a}
bZnO 1000 mg/kg	1.94 ± 0.03^{cde}	1.97 ± 0.21^{cde}	2.20 ± 0.35^{bcd}	2.33 ± 0.58^{bcd}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide.

Table 10: Effects of nanoparticles and bulk particles (Cu and ZnO) on leaf breadth (cm) of beans during 2018 cropping season.

Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	2.70[a]	2.48[a]	2.49[a]	2.40[a]
nZnO	2.72[a]	2.70[a]	2.45[a]	3.11[a]
bCu	1.46[c]	1.69[c]	1.60[c]	1.73[c]
bZnO	1.93[b]	1.61[c]	1.52[c]	1.60[c]
Concentrations				
Control	1.78[b]	1.28[b]	1.72[b]	2.28[a]
300 mg/kg	2.50[a]	2.48[a]	2.31[a]	2.24[a]
600 mg/kg	2.48[a]	2.43[a]	2.25[a]	2.20[a]
1000 mg/kg	2.21[a]	2.24[a]	1.75[b]	2.07[a]
Interaction	0.000*	0.001*	0.005*	0.65 N.S

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 11: Interactive effect between metal salts and various concentrations on the leaf breadth (cm) of beans during 2018 cropping season

	Leaf breadth (cm)		
Metal salt	2 WAP	4 WAP	6 WAP
Control	1.17 ±0.76 ^{hi}	1.23±0.29^{hi}	1.28±0.51^{hi}
nCu 300 mg/kg	3.53±0.41^{a}	3.33±0.15^{a}	3.07±0.46^{ab}
nCu 600 mg/kg	3.17±0.42^{ab}	3.07±0.12^{ab}	2.50±0.44^{cde}
nCu 1000 mg/kg	2.93 ±0.12^{cde}	2.47±0.38^{cde}	2.40±0.53^{cde}
nZnO 300 mg/kg	2.80±0.50^{cde}	3.00±0.50^{ab}	3.30±0.26^{a}
nZnO 600 mg/kg	3.00±0.20 ^{ab}	3.17 ±0.76^{ab}	2.77±0.38^{cde}
nZnO 1000 mg/kg	2.57±0.76^{cde}	3.30±0.17^{a}	1.77±0.46^{efg}
bCu 300 mg/kg	1.83±0.06^{efg}	2.10±0.10^{cde}	1.57±0.599^{efg}
bCu 600 mg/kg	1.33±0.31^{gh}	1.70±0.10^{efg}	1.87±0.58^{efg}
bCu 1000 mg/kg	1.43±0.06^{gh}	1.40±0.10^{gh}	1.29±0.00^{gh}
bZnO 300 mg/kg	1.83±0.06^{efg}	2.48±0.61^{cde}	1.30±0.10^{gh}
bZnO 600 mg/kg	2.40±0.10^{cde}	2.43±0.79^{cde}	1.87±0.11^{efg}
bZnO 1000 mg/kg	1.90±0.10^{ef}	2.24±0.78^{cde}	1.63±0.23^{efg}

Values are mean± S. D, n= 96, values with the same superscript along treatments are not significant at p≤ 0.05, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.5 Leaf Area in Beans

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on leaf area of bean plants for 2017 and 2018 cropping seasons are presented in Tables 12-15.

Table 12 shows the effects of nanoparticles and bulk particles on the leaf area of beans in 2017 cropping season. Copper and zinc oxide nanoparticles enhanced the leaf area of beans in 2017 cropping season. Copper and zinc oxide nanoparticles enhanced the leaf area of beans with nCu producing the largest leaf area. However, the nanoparticles generally produced larger leaf areas than the respective bulk metals/compounds the nanoparticles produced larger leaf areas at 4 WAP which reduced at 6 WAP and increases at 8 WAP. On the other hand the bulk treated plants increased at 2 WAP but decreased between the periods of 4-6 WAP and later peaked at 8 WAP during the course of the experiment. In the same vein bulk copper showed improvement over bulk zinc oxide but generally, bulk effects on the leaf area of beans is less compared with the nanomaterials/ compounds. It should be noted that there was no significant ($p \leq 0.05$) interactive effects of the metal salts with the concentration on the leaf area of beans at 8 WAP and that 300 and 600 mg/kg produced better results by enhancing the leaf area while 1000 mg/kg treatment decreased the leaf area.

There were significant interactive effects between the metal salts and concentration on leaf area of beans during 2-6 WAP in 2017 cropping season ($p \leq 0.05$) (Table 12).

Table 13 shows the interactive effects among metal salts and their different concentrations on the leaf area of beans in 2017 cropping season. All treatments produced leaf areas that were better enhanced than the control. Copper treated plants also produce leaves with wider leaf area across the weeks. It should however be noted that bulk zinc oxide showed tremendous improvements over bulk copper in terms of enhancing the leaf area of beans in 2017 cropping season. Nanoparticles treated plants produced the most significant ($p \leq 0.05$) leaf areas and

the data obtained was high from young age and continued to fluctuate through out the period of the experimentation except with nCu that deviated from this pattern while bulk treated plants produced data that were low in young age but later increased along the line.

At 2-6 WAP, nCu 300, 600 and 100 mg/kg treatments were particularly wider than all other leaf areas (Table 13). Furthermore, there were significant interactive rffects between the metal salts and concentration at 2-6 WAP in 2018 cropping season ($p \leq 0.05$). Irrespective of the metal salt used, the control produced the lowest significant leaf areas ($p \leq 0.05$) (Tables 12 and 14).

Table 14 further shows the effect of nanoparticles on leaf area of beans in 2018 cropping season. All treatments produced leaf areas that were better enhanced than the control plants. Nanoparticles treated plants produced data that were higher than bulk treated plants and this was particularly so with copper nanoparticles at 2-8 WAP. In the same vein, bulk zinc oxide had an edge or improvement over the bulk copper interms of leaf area enhancement. Furthermore, leaf area of the nanoparticles treated plants continued to decrease over the period of exposure of the plant meanwhile bulk particles treated plants fluctuates progressively over the period of experimentation. There were no significant interactive effects of the metal salt with the concentration ($p \leq 0.05$) on the leaf area of beans in 8WAP of 2018 cropping season.

Table 15 shows the interactive effects among metal salts and their different concentration on the leaf area of beans in 2018 cropping season. A ll treatments produced better leaf area than the control; nanoparticles treatment better enhanced the leaf area better than their corresponding bulk compounds during 2 WAP while zinc oxide nanoparticles better enhanced it during 4-6 WAP. There was no particular pattern of growth for the data of the leaf area of beans from nanoparticles treated plants. Bulk copper treated plants increased the

leaf area at age of 2-6 WAP while bulk zinc oxide treated plants showed fluctuations or no particular trend in the growth pattern of the leaf area in 2018 cropping season of beans.

Table 15 further shows that leaf areas were significant ($p \leq 0.05$) at 2-6 WAP 300, 600, and 1000 mg/kg treatments while bulk particles (bCu 1000, and bZnO 1000 mg/kg) treatmetns produced very low leaf areas though they were not the most significantly lowest values recorded.

4.6 Number of leaves in beans

Descriptive statistics of the Cu and ZnO effects of bulk and nanoparticles on number of leaves in bean plants in 2017 and 2018 cropping season are presented in tables 16-19.

In table 16, copper nanoparticles produced the highest number of leaves in beans in 2017 cropping season; this was followed by zinc oxide. Furthermore, bulk copper produced number of leaves that were lower than the control. Efficacy of treatments 600 and 1000 mg/kg reduced progressively during 2-6 WAP of the period of experimentation.

There were significant interactive effects among the metal salt and concentration on number of leaves of beans in 2017 and 2018 cropping seasons during 2-8 WAP. The metallic salts that produced significantly highest number of leaves were nCu and nZnO (Table 16).

In table 17, copper nanoparticles produced number of leaves that were higher than zinc oxide nanoparticles during 2-4 WAP while the highest was produced during 6-8 WAP in nZnO. It is worthy to note that during 2 WAP, bulk zinc oxide 300 and 600 mg/kg treatments produced number of leaves that were higher than that produced by the control.

In all the weeks except during 2-4 WAP, the control produced the lowest significant ($p \leq 0.05$) number of leaves. During 2-4 WAP of 2017 and 2018 cropping season, the most significant

number of leaves was with nCu 300, 600 and 1000 mg/kg (Table 17) while the least significant number of leaves was produced by the control.

In table 18, copper nanoparticles produced number of leaves that were higher than all other treatments and the number of leaves fluctuates throughout the period of experimentation. There was no particular pattern in the number of leaves produced with zinc oxide nanoparticle and bulk copper while bulk zinc oxide produced number of leaves produced that increased throughout the period of the experiment. Furthermore, all treatments produced higher number of leaves than the control plants. There were significant interactive effects in all the weeks.

Table 19 shows the interactive effects among metal salts and various concentrations on number of leaves in beans in 2018 cropping season. The lowest number of leaves was produced from the control plants while the highest number of leaves was produced in nCu 600 mg/kg treatment in the second week of planting except nCu 600 mg/kg treatment. During 4 WAP, higher values were produced in all metallic salts.

Bulk copper produced number of leaves that were concentration dependent based on the values obtained from the use of various concentrations (300, 600 and 1000) which decreases from high values to low ones at 2 WAP. Meanwhile the opposite was the case with the use of nZnO, though concentration dependent increase in the number of leaves in beans was observed: these increased from low values to high values during 2 WAP

Table 12: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf area (cm^2) of beans during 2017 cropping season.

	Leaf area(cm^2)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	12.30^{a}	17.20^{a}	10.46^{b}	11.22^{a}
nZnO	9.86^{b}	12.94^{a}	8.29^{b}	10.15^{b}
bCu	7.86^{c}	6.43^{c}	4.21^{d}	7.12^{c}
bZnO	5.25^{d}	5.24^{d}	4.00^{d}	6.24^{c}
Concentrations				
Control	1.11^{f}	2.28^{e}	2.68^{e}	4.38^{d}
300 mg/kg	8.12^{b}	9.96^{a}	9.64^{a}	10.5^{a}
600 mg/kg	7.22^{b}	7.26^{b}	6.89^{c}	7.29^{b}
1000 mg/kg	5.11^{d}	6.43^{c}	6.32^{c}	8.35^{b}
Interaction	0.002*	0.000*	0.000*	0.15 N.S

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 13: Interactive effect between metal salts and various concentrations on the leaf area (cm^2) of beans during 2017 cropping season

	Leaf area(cm^2)		
Metal salt	2 WAP	4 WAP	6 WAP
Control	0.68 ± 0.47^{i}	2.51 ± 0.49^{gh}	2.47 ± 0.68^{gh}
nCu 300 mg/kg	12.94 ± 2.17^{ab}	14.20 ± 4.66^{a}	12.20 ± 1.28^{ab}
nCu 600 mg/kg	13.07 ± 0.15^{a}	12.47 ± 2.39^{ab}	10.38 ± 5.77^{bc}
nCu 1000 mg/kg	11.42 ± 1.64^{ab}	10.58 ± 4.41^{bc}	12.39 ± 3.47^{ab}
nZnO 300 mg/kg	10.96 ± 1.69^{bc}	16.88 ± 6.26^{a}	14.98 ± 3.57^{a}
nZnO 600 mg/kg	8.30 ± 3.27^{cd}	9.44 ± 5.48^{bc}	7.65 ± 3.53^{cd}
nZnO 1000 mg/kg	3.81 ± 4.89^{ef}	8.68 ± 6.59^{cd}	4.87 ± 5.39^{ef}
bCu 300 mg/kg	3.65 ± 0.09^{ef}	3.57 ± 0.56^{ef}	2.88 ± 1.39^{fg}
bCu 600 mg/kg	2.01 ± 0.58^{gh}	2.72 ± 0.33^{fg}	3.24 ± 0.53^{ef}
bCu 1000 mg/kg	2.25 ± 0.00^{gh}	3.17 ± 0.71^{ef}	3.45 ± 0.13^{ef}
bZnO 300 mg/kg	4.95 ± 0.20^{ef}	5.19 ± 0.21^{de}	6.67 ± 0.24^{de}
bZnO 600 mg/kg	5.52 ± 0.48^{de}	4.43 ± 0.13^{ef}	6.29 ± 1.08^{de}
bZnO 1000 mg/kg	2.95 ± 0.11^{fg}	3.32 ± 0.71^{ef}	4.56 ± 0.76^{ef}

Values are mean$\pm$ S. D, n= 96, values with the same superscript across treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 14: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf area (cm^2) of beans during 2018 cropping season

	Leaf area (cm^2)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	10.19^{a}	9.06^{a}	8.49^{b}	9.75^{a}
nZnO	7.40^{b}	9.52^{a}	8.99^{b}	10.70^{a}
bCu	2.08^{d}	3.12^{c}	2.75^{c}	2.96^{c}
bZnO	3.34^{c}	3.19^{c}	2.87^{c}	2.79^{c}
Concentrations				
Control	2.19^{e}	1.77^{e}	2.66^{e}	4.15^{d}
300 mg/kg	7.91^{a}	8.74^{a}	8.77^{a}	7.86^{a}
600 mg/kg	7.66^{a}	8.29^{a}	7.00^{a}	7.15^{a}
1000 mg/kg	5.67^{c}	6.11^{b}	4.71^{c}	6.99^{b}
Interaction	0.002*	0.000*	0.000*	0.12 N.S

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 15: Interactive effect between metal salts and various concentrations on the leaf area (cm^2) of beans during 2018 cropping season

	Leaf area (cm^2)		
Metal salt	2 WAP	4 WAP	6 WAP
Control	2.04 ± 1.34^{gh}	1.87 ± 0.38^{hi}	2.47 ± 0.68^{gh}
nCu 300 mg/kg	14.02 ± 1.9^{a}	12.67 ± 3.27^{c}	14.15 ± 1.85^{a}
nCu 600 mg/kg	13.61 ± 3.37^{a}	14.76 ± 2.18^{a}	9.69 ± 2.70^{c}
nCu 1000 mg/kg	11.10 ± 4.89^{ab}	8.76 ± 2.78^{cd}	7.66 ± 1.18^{cd}
nZnO 300 mg/kg	9.55 ± 3.15^{c}	13.63 ± 3.67^{ab}	14.67 ± 4.51^{a}
nZnO 600 mg/kg	9.41 ± 2.18^{c}	10.50 ± 3.0^{bc}	14.83 ± 2.62^{a}
nZnO 1000 mg/kg	6.49 ± 2.33^{de}	10.23 ± 2.71^{bc}	10.38 ± 1.42^{bc}
bCu 300 mg/kg	2.98 ± 0.13^{fgh}	3.57 ± 0.56^{fg}	7.00 ± 1.52^{de}
bCu 600 mg/kg	1.97 ± 0.28^{hi}	2.72 ± 0.33^{fgh}	3.19 ± 1.00^{fg}
bCu 1000 mg/kg	2.15 ± 0.09^{ghi}	3.17 ± 0.35^{fg}	3.03 ± 0.22^{fg}
bZnO 300 mg/kg	5.08 ± 0.12^{de}	5.19 ± 0.21^{de}	3.00 ± 0.00^{fg}
bZnO 600 mg/kg	5.64 ± 0.15^{de}	4.43 ± 0.13^{ef}	4.90 ± 0.30^{ef}
bZnO 1000 mg/kg	2.95 ± 0.23^{gh}	3.32 ± 0.70^{fg}	2.32 ± 0.22^{gh}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 16: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of leaves of beans during 2017 cropping season

	Number of leaves			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	4.62^{b}	3.04^{c}	6.26^{a}	4.50^{b}
nZnO	3.23^{c}	3.01^{c}	5.83^{b}	3.96^{c}
bCu	1.47^{d}	1.14^{d}	3.11^{c}	2.01^{c}
bZnO	1.98^{d}	0.18^{e}	3.00^{c}	1.75^{d}
Concentrations				
Control	5.00^{c}	4.00^{c}	3.33^{d}	3.58^{d}
300 mg/kg	9.17^{a}	9.75^{a}	9.17^{a}	9.89^{a}
600 mg/kg	9.58^{a}	8.83^{a}	6.17^{b}	6.66^{b}
1000 mg/kg	8.82^{a}	8.18^{a}	6.27^{b}	8.21^{a}
Interaction	0.000*	0.002 *	0.002*	0.004*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 17: Interactive effect between metal salts and various concentrations on the number of leaves of beans during 2017 cropping season

Metal salt	2 WAP	4 WAP	6 WAP	8 WAP
Control	6.33 ± 3.06^{gh}	4.33 ± 0.58^{hij}	3.67 ± 1.15^{ijk}	3.67 ± 1.15^{ijk}
nCu 300 mg/kg	12.67 ± 2.52^{ab}	14.33 ± 2.08^{a}	10.33 ± 4.16^{cd}	9.67 ± 4.04^{de}
nCu 600 mg/kg	15.33 ± 0.58^{a}	13.33 ± 2.08^{ab}	5.67 ± 2.52^{ghi}	6.00 ± 1.73^{gh}
nCu 1000 mg/kg	13.00 ± 1.64^{ab}	11.00 ± 2.65^{cd}	8.67 ± 0.58^{ef}	10.00 ± 1.73^{cd}
nZnO 300 mg/kg	11.67 ± 1.53^{cd}	11.00 ± 4.58^{cd}	14.67 ± 4.51^{a}	12.67 ± 1.15^{ab}
nZnO 600 mg/kg	10.00 ± 1.00^{cd}	8.33 ± 4.51^{ef}	$6.33\pm1.15d^{gh}$	5.67 ± 4.04^{ghi}
nZnO 1000mg/kg	9.33 ± 1.15^{de}	10.33 ± 2.89^{cd}	5.00 ± 0.00^{ghi}	5.33 ± 4.04^{ghi}
bCu 300 mg/kg	4.67 ± 0.58^{fgh}	5.33 ± 0.58^{ghi}	6.00 ± 0.00^{gh}	7.34 ± 2.43^{fg}
bCu 600 mg/kg	5.67 ± 0.58^{ghi}	5.67 ± 0.58^{ghi}	5.00 ± 0.00^{ghi}	5.46 ± 1.38^{ghi}
bCu 1000 mg/kg	6.00 ± 0.00^{gh}	5.00 ± 0.00^{ghi}	6.67 ± 4.16^{gh}	8.76 ± 1.39^{ef}
bZnO 300 mg/kg	7.67 ± 0.58^{fg}	8.33 ± 0.58^{ef}	6.67 ± 0.57^{gh}	9.88 ± 1.63^{de}
bZnO 600 mg/kg	7.33 ± 1.53^{fg}	8.00 ± 2.00^{ef}	6.29 ± 1.08^{gh}	9.50 ± 1.99^{de}
bZnO 1000 mg/kg	6.00 ± 0.00^{gh}	5.50 ± 0.71^{ghi}	6.00 ± 0.00^{gh}	9.00 ± 3.18^{de}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 18: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of leaves of beans during 2018 cropping season

	Number of leaves			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	10.17^{a}	10.58^{a}	7.83^{b}	7.67^{b}
nZnO	5.66^{c}	8.17^{b}	6.42^{c}	6.42^{c}
bCu	6.25^{c}	5.50^{cd}	4.88^{d}	5.13^{cd}
bZnO	5.66^{cd}	6.75^{c}	7.00^{b}	7.00^{b}
Concentrations				
Control	4.17^{c}	4.17^{c}	4.25^{c}	3.83^{c}
300 mg/kg	6.77^{b}	9.42^{a}	9.17^{a}	6.75^{b}
600 mg/kg	8.86^{a}	9.08^{a}	6.75^{b}	6.66^{b}
1000 mg/kg	7.13^{b}	8.75^{a}	6.67^{b}	8.21^{a}
Interaction	0.000*	0.004*	0.002*	0.003*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 19: Interactive effect between metal salts and various concentrations on number of leaves in beans during 2018 cropping season

	Number of leaves			
Metal salt	2 WAP	4 WAP	6 WAP	8 WAP
Control	4.67 ± 1.53^{fgh}	4.33 ± 0.57^{fgh}	3.67 ± 1.15^{ghi}	3.67 ± 1.15^{ghi}
nCu 300 mg/kg	11.00 ± 1.00^{b}	14.00 ± 1.00^{a}	10.33 ± 4.16^{cd}	10.33 ± 4.16^{cd}
nCu 600 mg/kg	14.00 ± 1.00^{a}	12.67 ± 0.58^{a}	7.67 ± 1.53^{cde}	7.67 ± 1.5^{cde}
nCu 1000 mg/kg	11.00 ± 1.00^{b}	12.33 ± 3.50^{a}	9.67 ± 0.58^{cd}	9.67 ± 0.58^{cd}
nZnO 300 mg/kg	3.73 ± 0.55^{ghi}	10.67 ± 4.1^{cd}	13.00 ± 5.29^{a}	13.00 ± 5.29^{a}
nZnO 600 mg/kg	8.44 ± 0.86^{de}	$8.0\ \pm4.00^{de}$	$4.67\pm1.15d^{fgh}$	4.67 ± 1.15^{fgh}
nZnO 1000 mg/kg	5.79 ± 0.83^{efg}	9.67 ± 2.50^{bcd}	4.33 ± 2.3^{fgh}	4.33 ± 2.31^{fgh}
bCu 300 mg/kg	7.67 ± 0.57^{de}	5.67 ± 0.57^{efg}	5.33 ± 0.58^{efg}	$5.67\ \pm0.50^{efg}$
bCu 600 mg/kg	7.33 ± 1.53^{de}	7.33 ± 0.58^{de}	6.00 ± 0.00^{ef}	6.33 ± 0.58^{ef}
bCu 1000 mg/kg	5.67 ± 0.57^{efg}	6.00 ± 0.00^{ef}	6.00 ± 00^{ef}	7.00 ± 0.00^{de}
bZnO 300 mg/kg	4.67 ± 0.57^{fgh}	8.33 ± 0.58^{de}	8.00 ± 1.00^{de}	8.87 ± 0.58^{de}
bZnO 600 mg/kg	5.67 ± 0.58^{efg}	8.33 ± 0.58^{de}	8.67 ± 0.58^{de}	8.33 ± 0.58^{de}
bZnO 1000 mg/kg	6.00 ± 0.00^{ef}	7.00 ± 0.00^{de}	6.67 ± 1.15^{ef}	7.00 ± 1.00^{de}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.7 Stem girth in beans

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on stem girth of bean plants for 2017 and 2018 cropping seasons are presented in Tables 20-23.

Table 20 shows the interactive effects of nanoparticles and bulk particles on stem girth (cm) of beans in 2017 cropping season. Zinc oxide nanoparticles produced thickest stem throughout the period of the experiment but this was closely followed by copper nanoparticles. All treatments produced stems that are thicker than the control. There were no significant interactive effects between the metal salts and various concentrations on the stem girth during 6 WAP.

There were significant interactive effects ($p \leq 0.05$) among the metal salts and concentrations on the stem girth at 2, 4, and 8 WAP (Table 20). The greatest and significant stem girth was produced by treatment of zinc oxide for most of the weeks (Tables 20 and 22). It should be noted that there was no significant interactive effects between the metal salts and concentration on stem girth at 6 WAP for 2017 and 2018 cropping season.

In Table 23, zinc oxide 300,600 and 1000 mg/kg produced the thickest stem girths and this is closely followed by copper nanoparticles. It is worthy to note however that higher dosage of the metal salts increased the thickness of the stem even with bulk copper 1000 mg/kg treatment at 2 WAP.

Table 20: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stem girth (cm) of beans during 2017 cropping season

	Stem girth (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	1.87^{c}	2.03^{b}	1.97^{c}	2.87^{a}
nZnO	7.49^{a}	2.08^{b}	1.86^{c}	2.99^{a}
bCu	1.40^{c}	1.95^{c}	1.88^{c}	1.40^{c}
bZnO	1.66^{c}	1.96^{c}	1.93^{c}	1.54^{c}
Concentrations				
Control	1.11^{c}	1.55^{c}	1.67^{c}	1.17^{c}
300 mg/kg	3.89^{a}	2.43^{b}	2.05^{b}	3.89^{a}
600 mg/kg	3.84^{a}	2.06^{b}	1.85^{c}	3.84^{a}
1000 mg/kg	3.65^{a}	1.98^{c}	2.08^{b}	3.65^{a}
Interaction	0.000*	0.000*	0.679 N.S	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 21: Interactive effect between metal salts and various concentrations on stem girth (cm) of beans during 2017 cropping season

	Stem girth (cm)		
Metal salt	2 WAP	4 WAP	8 WAP
Control	1.38 ± 0.57^{cd}	1.47 ± 0.25^{cd}	1.33 ± 0.58^{cd}
nCu 300 mg/kg	2.20 ± 0.14^{ab}	3.10 ± 0.17^{a}	2.67 ± 0.43^{a}
nCu 600 mg/kg	2.55 ± 0.16^{a}	2.53 ± 0.21^{a}	2.32 ± 0.38^{ab}
nCu 1000 mg/kg	2.64 ± 0.48^{a}	1.78 ± 0.39^{c}	2.96 ± 0.20^{a}
nZnO 300 mg/kg	2.56 ± 0.19^{a}	2.68 ± 0.16^{a}	2.75 ± 0.76^{a}
nZnO 600 mg/kg	2.53 ± 0.22^{a}	2.64 ± 0.09^{a}	2.05 ± 0.42^{bc}
nZnO 1000 mg/kg	2.64 ± 0.46^{a}	2.15 ± 0.99^{bc}	2.86 ± 0.10^{a}
bCu 300 mg/kg	1.86 ± 0.79^{bc}	1.57 ± 0.12^{cd}	1.70 ± 0.10^{cd}
bCu 600 mg/kg	2.11 ± 0.11^{bc}	1.93 ± 0.06^{bc}	2.20 ± 0.10^{bc}
bCu 1000 mg/kg	2.20 ± 0.19^{bc}	1.20 ± 0.12^{cd}	1.13 ± 0.21^{d}
bZnO 300 mg/kg	1.22 ± 0.00^{cd}	1.93 ± 0.06^{bc}	1.50 ± 0.10^{cd}
bZnO 600 mg/kg	2.16 ± 0.58^{bc}	2.13 ± 0.12^{bc}	2.17 ± 0.29^{bc}
bZnO 1000 mg/kg	2.12 ± 1.15^{bc}	1.67 ± 0.23^{cd}	2.13 ± 0.29^{bc}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 22: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stem girth (cm) of beans during 2018 cropping season

	Stem girth (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	1.27^{c}	1.95^{b}	1.86^{b}	2.39^{b}
nZnO	7.99^{a}	1.96^{b}	1.06^{c}	2.46^{b}
bCu	1.20^{c}	2.02^{b}	1.08^{c}	1.01^{c}
bZnO	1.05^{c}	2.08^{c}	1.03^{c}	1.23^{c}
Concentrations				
Control	1.00^{b}	1.98^{c}	1.70^{c}	1.72^{c}
300 mg/kg	3.00^{a}	2.45^{b}	2.00^{b}	2.62^{b}
600 mg/kg	3.80^{a}	2.40^{b}	1.00^{c}	2.25^{b}
1000 mg/kg	3.00^{a}	2.28^{b}	2.00^{b}	2.26^{b}
Interaction	0.000*	0.040*	0.779 N.S	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 23: Interactive effect between metal salts and various concentrations on stem girth (cm) of beans during 2018 cropping season

	Stem girth (cm)		
Metal salt	2 WAP	4 WAP	8 WAP
Control	1.96 ± 0.38^{de}	1.30 ± 0.26^{fg}	2.167 ± 0.29^{de}
nCu 300 mg/kg	1.86 ± 0.79^{de}	2.9 ± 0.10^{de}	3.36 ± 0.25^{cde}
nCu 600 mg/kg	2.41 ± 0.11^{de}	2.10 ± 0.10^{de}	3.01 ± 0.28^{cde}
nCu 1000 mg/kg	2.26 ± 0.19^{de}	1.82 ± 0.50^{ef}	2.92 ± 0.32^{cde}
nZnO 300 mg/kg	11.00 ± 1.0^{a}	2.63 ± 0.15^{de}	4.33 ± 0.56^{cd}
nZnO 600 mg/kg	9.33 ± 0.58^{b}	2.40 ± 0.10^{de}	2.59 ± 1.15^{de}
nZnO 1000 mg/kg	8.67 ± 1.15^{b}	1.90 ± 0.46^{de}	2.90 ± 0.10^{de}
bCu 300 mg/kg	1.37 ± 0.06^{ef}	2.10 ± 0.10^{de}	1.40 ± 0.00^{fg}
bCu 600 mg/kg	1.67 ± 0.06^{de}	1.93 ± 0.06^{cd}	1.60 ± 0.17^{ef}
bCu 1000 mg/kg	2.17 ± 0.57^{de}	2.23 ± 0.25^{de}	1.80 ± 0.17^{ef}
bZnO 300 mg/kg	1.37 ± 0.11^{fg}	2.07 ± 0.15^{de}	1.37 ± 0.11^{fg}
bZnO 600 mg/kg	1.97 ± 0.06^{de}	1.80 ± 0.10^{ef}	1.80 ± 0.26^{ef}
bZnO 1000 mg/kg	1.50 ± 0.00^{ef}	1.90 ± 0.10^{ef}	1.43 ± 0.06^{fg}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.8 Leaf lengths in Tomato

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on leaf length (cm) of tomato plants for 2017 and 2018 cropping seasons are presented in Tables 24-27.

Table 24 shows the effects of Cu and ZnO nanoparticles and bulk particles on the leaf length of tomato (cm) in 2017 cropping season.

There were no significant interactive effects ($p \leq 0.05$) among the metal salts and concentration on leaf length of tomato during 2017 cropping season at 4-6 WAP but there was significant interactive effects ($p \leq 0.05$) among the metal salts and concentration on leaf lengths of tomato during 2017 cropping season at 2 and 8 WAP (Table 24). The most significant metal salts were nCu and nZnO. It should be noted that there was no significant difference in the lengths of beans plants produced from copper, zinc oxide nanoparticles, and bulk zinc oxide during 2 WAP. However, all treatments produced leaf lengths that were longer than the control.

Table 25 shows the interactive effects among the metal salts and various concentrations on leaf length (cm) of tomato in 2017 croppping season. All treatments produced longer leaf lengths than those that were produced in bCu 300 and 1000 mg/kg treatments. Copper nanoparticles treatment produced longer leaf lengths than zinc oxide nanoparticles and bulk zinc oxide treatments produced longer leaf lengths than bulk copper numerically. The most significant metal salts were nCu and nZnO in 2017 cropping season.

In table 26, zinc oxide nanoparticles produced leaves that were longer than that produced by copper nanoparticles during 4-8 WAP. Meanwhile, bulk copper produced longer leaves than bulk zinc oxide during 2 WAP. It should be noted that all nanoparticles treatments produced longer leaves than the control plants and that there were significant ($p \leq 0.05$) interactive

effects between metal salts and concentrations on the leaf lengths of tomato plants throughout the period of experimentation.

In table 27, control plants produced leaves that were longer than bulk copper and bulk zinc oxide 300 mg/kg treatments during 2 WAP. The most significant result of leaf length was recorded with the use of 300 and 600 mg/kg zinc oxide treatments in all the weeks in tomato.

Table 24: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf length (cm) of tomato during 2017 cropping season

	Leaf length (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	1.58^{c}	2.83^{b}	3.00^{a}	2.88^{b}
nZnO	1.63^{c}	3.04^{a}	3.03^{a}	2.81^{b}
bCu	1.19^{c}	1.48^{c}	3.10^{a}	2.30^{b}
bZnO	1.56^{c}	1.91^{c}	2.91^{b}	2.42^{b}
Concentrations				
Control	1.18^{c}	1.98^{c}	2.68^{a}	2.74^{b}
300 mg/kg	1.38^{c}	2.33^{b}	3.44^{a}	2.37^{b}
600 mg/kg	1.62^{c}	2.32^{b}	2.93^{a}	2.35^{b}
1000 mg/kg	1.91^{c}	2.79^{a}	2.92^{a}	2.98^{a}
Interaction	0.006*	0.135 N.S	0.820 N.S	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 25: Interactive effect between metal salts and various concentrations on leaf length of tomato during 2017 cropping season

Metal salt	2 WAP	8 WAP
Control	1.47 ± 0.45^{de}	2.83 ± 0.76^{bc}
nCu 300 mg/kg	1.8 ± 1.36^{de}	2.67 ± 1.16^{bc}
nCu 600 mg/kg	1.43 ± 0.60^{de}	2.27 ± 0.68^{bc}
nCu 1000 mg/kg	1.60 ± 0.10^{de}	4.33 ± 0.38^{a}
nZnO 300 mg/kg	2.57 ± 0.40^{bc}	3.93 ± 0.38^{a}
nZnO 600 mg/kg	1.57 ± 0.40^{de}	3.93 ± 0.90^{a}
nZnO 1000 mg/kg	1.93 ± 0.15^{de}	2.27 ± 1.08^{bc}
bCu 300 mg/kg	0.93 ± 0.06^{ef}	2.87 ± 0.25^{bc}
bCu 600 mg/kg	2.00 ± 0.00^{cd}	3.30 ± 0.42^{bc}
bCu 1000 mg/kg	0.10 ± 0.05^{ef}	3.00 ± 0.40^{bc}
bZnO 300 mg/kg	1.20 ± 0.10^{de}	1.73 ± 0.25^{de}
bZnO 600 mg/kg	1.60 ± 0.48^{de}	2.00 ± 0.16^{cd}
bZnO 1000 mg/kg	2.05 ± 0.08^{cd}	2.70 ± 0.24^{bc}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 26: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf length (cm) of tomato during 2018 cropping season

Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	2.02[b]	2.83[a]	3.00[a]	2.88[a]
nZnO	2.53[a]	2.41[b]	3.03[a]	2.81[a]
bCu	1.05[c]	1.48[c]	3.10[a]	2.30[b]
bZnO	1.28[c]	1.91[c]	2.91[a]	2.42[b]
Concentrations				
Control	1.24[c]	1.57[c]	2.02[b]	2.28[b]
300 mg/kg	1.90[b]	2.33[b]	3.98[a]	3.23[a]
600 mg/kg	2.08[b]	2.47[b]	2.86[b]	3·31[a]
1000 mg/kg	1.73[c]	2.41[b]	2.88[b]	3.23[a]
Interaction	0.000*	0.000 *	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 27: Interactive effect between metal salts and various concentrations on leaf length (cm) of tomato during 2018 cropping season

	Leaf breadth (cm)			
Metal salt	2 WAP	4 WAP	6 WAP	8 WAP
Control	1.67 ± 0.15^{de}	2.10 ± 0.17^{cd}	2.20 ± 0.10^{cd}	2.77 ± 0.15^{cd}
nCu 300 mg/kg	2.43 ± 0.06^{cd}	3.17 ± 0.17^{ab}	3.67 ± 0.15^{ab}	4.10 ± 0.10^{ab}
nCu 600 mg/kg	1.97 ± 0.58^{cd}	2.77 ± 0.37^{cd}	3.33 ± 0.29^{ab}	5.27 ± 0.21^{a}
nCu 1000 mg/kg	2.00 ± 0.00^{cd}	2.02 ± 0.04^{cd}	3.20 ± 0.10^{ab}	2.90 ± 0.10^{cd}
nZnO 300 mg/kg	3.10 ± 0.10^{ab}	3.17 ± 0.58^{ab}	3.70 ± 0.10^{ab}	2.77 ± 0.65^{cd}
nZnO 600 mg/kg	3.30 ± 0.17^{ab}	2.37 ± 0.47^{cd}	2.80 ± 0.30^{cd}	2.25 ± 0.07^{cd}
nZnO 1000 mg/kg	2.03 ± 0.06^{cd}	2.00 ± 0.00^{cd}	2.20 ± 0.10^{cd}	2.90 ± 0.10^{cd}
bCu 300 mg/kg	1.00 ± 0.00^{ef}	1.48 ± 0.39^{de}	1.57 ± 0.58^{de}	2.77 ± 0.65^{cd}
bCu 600 mg/kg	1.50 ± 0.31^{de}	2.15 ± 0.07^{cd}	2.35 ± 0.07^{cd}	2.25 ± 0.71^{cd}
bCu 1000 mg/kg	1.50 ± 0.00^{de}	2.00 ± 0.00^{cd}	2.00 ± 0.00^{cd}	2.00 ± 0.70^{cd}
bZnO 300 mg/kg	1.07 ± 0.06^{ef}	1.50 ± 0.10^{de}	2.97 ± 0.21^{cd}	1.93 ± 0.15^{de}
bZnO 600 mg/kg	1.53 ± 0.56^{de}	2.25 ± 0.50^{cd}	2.80 ± 0.4^{cd}	2.58 ± 0.09^{cd}
bZnO 1000 mg/kg	1.45 ± 0.72^{de}	2.32 ± 0.12^{cd}	3.07 ± 0.49^{ab}	3.18 ± 0.17^{ab}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.9 Leaf Breadths in tomato

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on leaf breadth of tomato plants during 2017 and 2018 cropping seasons are presented in Tables 28-31.

In table 28, there was no significant difference in the data produced in leaf breadth from the use of copper and zinc oxide nanoparticles during 2, 4 and 8 WAP. The thickest leaf breadths numerically were produced during 8 WAP in copper nanoparticles treatments.

There was no significant ($P \leq 0.05$) interactive effects among the metal salts and concentration on leaf breadth of tomato at 2 and 6 WAP for 2017 cropping season. However, there were significant interactive effects during 4 and 8 WAP.

In table 29, control produced leaf breadths that were thicker than bulk treatments during 4 and 8 WAP during 2017 cropping season. The most significant leaf breadth was produced with nZnO 1000 mg/kg treatment.

In table 30, copper nanoparticles produced leaf breadth that was thicker than bulk copper during 2 and 8 WAP. In addition, bulk zinc oxide produced leaf breadths that were thicker than bulk copper throughout the period of the experimentation. All treatments produced improved leaf bredth of tomato throughout the period of experiment.

Table 31 shows the interactive effects among the metal salts and various concentrations on leaf breadth of tomato in 2018 cropping season. Control plants produced leaf breadths that were thicker than bulk compounds during 2 WAP but generally, zinc oxide produced the thickest leaf breadths.

Table 28: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf breadth (cm) of tomato during 2017 cropping season.

	Leaf area (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	0.95^{d}	1.77^{c}	1.48^{c}	3.01^{a}
nZnO	0.76^{d}	1.97^{c}	0.94^{d}	2.78^{b}
bCu	0.38^{d}	0.49^{d}	0.93^{d}	0.69^{d}
bZnO	0.76^{d}	0.89^{d}	0.94^{d}	0.93^{d}
Concentrations				
Control	1.53^{b}	1.57^{b}	1.07^{b}	1.22^{b}
300 mg/kg	0.72^{c}	1.83^{b}	1.13^{b}	2.44^{a}
600 mg/kg	0.35^{c}	0.49^{c}	1.36^{b}	2.18^{a}
1000 mg/kg	0.72^{c}	0.89^{c}	1.48^{b}	1.63^{b}
Interaction	0.355 N.S	0.041*	0.391 N.S	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 29: Interactive effect between metal salts and various concentrations on leaf breadth (cm) of tomato for 2017 cropping season

	Leaf breadth (cm)	
Metal salt	4 WAP	8 WAP
Control	1.33 ± 0.61^{bc}	1.13 ± 0.71^{cd}
nCu 300 mg/kg	1.93 ± 0.32^{ab}	2.7 ± 0.75^{a}
nCu 600 mg/kg	1.67 ± 0.99^{bc}	1.1 ± 0.17^{cd}
nCu 1000 mg/kg	2.13 ± 0.61^{a}	2.13 ± 0.40^{a}
nZnO 300 mg/kg	2.20 ± 0.26^{a}	1.90 ± 0.50^{bc}
nZnO 600 mg/kg	1.47 ± 0.58^{bc}	1.43 ± 0.40^{bc}
nZnO 1000 mg/kg	2.27 ± 0.59^{a}	0.40 ± 0.10^{def}
bCu 300 mg/kg	$0.60\ \pm0.10^{def}$	$0.87\ \pm1.53^{def}$
bCu 600 mg/kg	1.03 ± 1.00^{cd}	1.20 ± 0.00^{cd}
bCu 1000 mg/kg	$0.80\pm0.0.10^{def}$	1.20 ± 0.02^{cd}
bZnO 300 mg/kg	0.73 ± 0.21^{def}	1.33 ± 0.15^{bc}
bZnO 600 mg/kg	1.13 ± 0.12^{cd}	1.10 ± 0.10^{cd}
bZnO 1000 mg/kg	1.03 ± 0.05^{cd}	0.20 ± 0.10^{def}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 30: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf breadth (cm) of tomato during 2018 cropping season.

	Leaf breadth (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	1.53^{c}	1.57^{c}	1.73^{c}	3.01^{a}
nZnO	0.72^{b}	1.83^{c}	2.10^{b}	2.78 ^{b}
bCu	0.35^{d}	0.49^{d}	0.89^{d}	0.60^{d}
bZnO	0.72^{d}	0.89^{d}	1.04^{c}	1.49^{c}
Concentrations				
Control	0.76^{c}	0.73^{c}	0.94^{c}	1.20^{c}
300 mg/kg	1.35^{b}	1.48^{b}	1.88^{b}	2.61^{a}
600 mg/kg	1.33^{b}	1.64^{b}	1.75^{b}	2.56^{a}
1000 mg/kg	1.16^{b}	1.06^{b}	1.24^{b}	1.81^{b}
Interaction	0.003 *	0.000 *	0.033 *	0.000*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 31: Interactive effect between metal salts and various concentrations on leaf breadth (cm) of tomato for 2018 cropping season.

	Leaf breadth (cm)			
Metal salt	2 WAP	4 WAP	6 WAP	8 WAP
Control	1.23 ± 0.57^{cd}	1.10 ± 0.10^{cd}	1.23 ± 0.20^{cd}	1.63 ± 0.15^{cd}
nCu 300 mg/kg	2.0 ± 0.00^{bc}	2.13 ± 0.06^{bc}	2.43 ± 0.21^{bc}	3.90 ± 0.10^{a}
nCu 600 mg/kg	1.37 ± 0.42^{cd}	1.77 ± 0.21^{cd}	1.90 ± 0.10^{cd}	3.37 ± 0.38^{a}
nCu 1000 mg/kg	1.50 ± 0.00^{cd}	1.27 ± 0.25^{cd}	1.33 ± 0.29^{cd}	3.13 ± 0.15^{a}
nZnO 300 mg/kg	2.13 ± 0.15^{bc}	2.47 ± 0.15^{bc}	2.90 ± 0.10^{bc}	4.13 ± 0.15^{a}
nZnO 600 mg/kg	2.23 ± 0.23^{bc}	2.63 ± 0.31^{bc}	2.93 ± 0.10^{bc}	3.40 ± 0.40^{a}
nZnO 1000mg/kg	1.94 ± 0.03^{cd}	1.13 ± 0.15^{cd}	1.33 ± 0.15^{cd}	1.97 ± 0.15^{cd}
bCu 300 mg/kg	0.30 ± 0.00^{de}	0.50 ± 0.00^{de}	0.96 ± 0.31^{de}	0.50 ± 0.00^{de}
bCu 600 mg/kg	0.53 ± 0.05^{de}	0.70 ± 0.10^{de}	1.13 ± 0.12^{cd}	0.73 ± 0.45^{de}
bCu 1000 mg/kg	0.30 ± 0.10^{de}	0.53 ± 0.00^{de}	1.17 ± 0.58^{cd}	1.20 ± 0.00^{ef}
bZnO 300 mg/kg	0.97 ± 0.06^{de}	0.57 ± 0.15^{de}	1.20 ± 0.10^{cd}	1.90 ± 0.36^{cd}
bZnO 600 mg/kg	1.20 ± 0.10^{cd}	1.07 ± 0.12^{cd}	1.03 ± 0.84^{cd}	2.56 ± 1.18^{bc}
bZnO 1000 mg/kg	0.90 ± 0.36^{de}	1.00 ± 0.00^{cd}	2.13 ± 0.15^{bc}	0.93 ± 0.35^{de}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.10 Leaf area (cm^2) in tomato

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on leaf area (cm^2) of tomato plants for 2017 and 2018 cropping seasons are presented in Tables 32-35.

Table 32 shows that there was no significant ($P \leq 0.05$) difference between the leaf areas produced in tomato with the use of nanoparticles while bulk zinc oxide produced better leaf areas than bulk copper in tomato plants.There were no significant ($P \leq 0.05$) interective effects among the metal salts and the concentration on the leaf area of tomato at 2-6 WAP in 2017 cropping season (Table 32) but there was a significant interactive effects at 8 WAP.

The most significant values of leaf areas were produced in nCu 1000 mg/kg and nZnO 300 mg/kg treatments (Table 33).

Table 34 shows the effects of Cu and ZnO nanoparticles and bulk particles on leaf area of tomato during 2018 cropping season. There was a significant interactive effect at 2-8 WAP. All treatments produced leaf areas that were higher than the control and the most significant metals were n Cu and nZnO.

Table 35 shows the interactive effect among the metal salts and various concentrations on leaf area of tomato in 2018 cropping season, bulk zinc oxide produced leaves with wider leaf area than the bulk copper treated plants. Furthermore, the control plants produced leaves that were wider than the bulk copper treated plants. It is worthy to note that significant values were produced during 8 WAP. The most significant metal salts for all the weeks were nCu and nZnO while the shortest values of leaf area were produced from the bulk treated plants.

Table 32: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf area (cm^2) of tomato during 2017 cropping season.

	Leaf area (cm^2)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	1.17^{c}	3.94^{a}	1.28^{c}	3.48^{a}
nZnO	0.96^{d}	4.86^{a}	4.24^{a}	3.29^{a}
bCu	0.39^{d}	0.57^{d}	1.28^{c}	0.69^{d}
bZnO	1.05^{c}	1.39^{c}	2.04^{bc}	0.91^{d}
Concentrations				
Control	0.54^{d}	2.37^{b}	2.41^{b}	1.79^{c}
300 mg/kg	0.91^{d}	2.77^{b}	3.32^{a}	2.43^{b}
600 mg/kg	1.01^{c}	2.30^{b}	2.43^{b}	1.63^{c}
1000 mg/kg	1.33^{c}	3.59^{a}	3.43^{a}	2.59^{a}
Interaction	0.085 N.S	0.305 N.S	0.216 N.S	0.002*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 33: Interactive effect between metal salts and various concentrations on leaf area (cm^2) of tomato during 2017 cropping season.

	Leaf area (cm^2)
Metal salt	8 WAP
Control	2.78 ± 0.18^{cd}
nCu 300 mg/kg	2.17 ± 0.26^{cd}
nCu 600 mg/kg	1.93 ± 0.80^{de}
nCu 1000 mg/kg	7.05 ± 2.56^{a}
nZnO 300 mg/kg	5.83 ± 2.74^{ab}
nZnO 600 mg/kg	2.63 ± 1.87^{cd}
nZnO 1000mg/kg	1.92 ± 1.45^{de}
bCu 300 mg/kg	1.34 ± 0.39^{de}
bCu 600 mg/kg	1.85 ± 0.33^{de}
bCu 1000 mg/kg	0.35 ± 0.12^{ef}
bZnO 300 mg/kg	2.64 ± 0.05^{cd}
bZnO 600 mg/kg	1.18 ± 0.24^{de}
bZnO 1000mg/kg	5.24 ± 0.28^{ab}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 34: Effects of Nanoparticles and bulk particles (Cu and ZnO) on leaf area of tomato during 2018 cropping season.

	Leaf area (cm^2)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	2.36^{c}	3.56^{b}	1.28^{c}	8.99^{a}
nZnO	3.74^{b}	3.46^{b}	4.24^{b}	7.34^{b}
bCu	0.29^{d}	0.57^{d}	1.28^{c}	1.00^{d}
bZnO	0.84^{d}	1.39^{c}	2.04^{c}	2.77^{c}
Concentrations				
Control	0.92^{e}	1.01^{d}	1.52^{d}	2.22^{c}
300 mg/kg	2.39^{c}	3.11^{a}	4.66^{b}	7.24^{a}
600 mg/kg	2.41^{c}	3.29^{bc}	3.79^{bc}	6.79^{a}
1000 mg/kg	1.70^{d}	1.86^{d}	2.84^{c}	4.43^{b}
Interaction	0.0000*	0.000*	0.001*	0.000*

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at P$\leq$ 0.05, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 35: Interactive effect between metal salts and various concentrations on leaf area (cm^2) of tomato for 2018 cropping season.

	Leaf area (cm^2)			
Metal salt	2 WAP	4 WAP	6 WAP	8 WAP
Control	1.55 ± 0.21^{fg}	1.73 ± 0.20^{fg}	2.26 ± 0.34^{ef}	3.38 ± 0.10^{ef}
nCu 300 mg/kg	3.65 ± 0.09^{ef}	5.07 ± 0.05^{cd}	6.68 ± 0.49^{cd}	11.99 ± 0.60^{a}
nCu 600 mg/kg	2.01 ± 0.58^{ef}	4.57 ± 0.75^{de}	4.73 ± 0.25^{de}	12.57 ± 1.19^{a}
nCu 1000 mg/kg	2.25 ± 0.00^{ef}	2.87 ± 0.66^{ef}	3.2 ± 0.76^{ef}	8.00 ± 0.61^{b}
nZnO 300 mg/kg	4.93 ± 0.22^{de}	5.86 ± 0.46^{cd}	8.05 ± 0.43^{b}	12.71 ± 0.64^{a}
nZnO 600 mg/kg	2.23 ± 0.23^{ef}	4.74 ± 1.45^{de}	6.17 ± 0.77^{cd}	8.68 ± 1.38^{b}
nZnO 1000mg/kg	5.52 ± 0.48^{cd}	1.50 ± 0.08^{fg}	2.20 ± 0.245^{ef}	4.59 ± 0.95^{de}
bCu 300 mg/kg	0.23 ± 0.00^{gh}	0.68 ± 0.28^{gh}	1.14 ± 0.38^{fg}	1.04 ± 0.25^{fg}
bCu 600 mg/kg	0.48 ± 0.14^{gh}	2.13 ± 0.27^{ef}	1.93 ± 0.22^{fg}	0.68 ± 0.47^{gh}
bCu 1000 mg/kg	0.19 ± 0.98^{gh}	1.41 ± 0.27^{fg}	0.33 ± 0.12^{gh}	2.15 ± 0.59^{ef}
bZnO 300 mg/kg	0.73 ± 0.05^{gh}	0.82 ± 0.23^{gh}	2.78 ± 0.12^{ef}	2.97 ± 0.16^{ef}
bZnO 600 mg/kg	1.62 ± 0.05^{fg}	1.70 ± 0.17^{fg}	2.34 ± 1.88^{ef}	5.26 ± 0.21^{cd}
bZnO 1000mg/kg	1.42 ± 0.57^{fg}	1.64 ± 0.15^{fg}	5.61 ± 0.53^{cd}	2.15 ± 0.59^{ef}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.11 Number of leaves in tomato

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on number of leaves in tomato plants for 2017 and 2018 cropping seasons are presented in Tables 36-39.

Table 36 shows the effects of Cu and ZnO nanoparticles and bulk particles on number of leaves of tomato in 2017 cropping season. Bulk particles produced number of leaves that were statistically the same as nanoparticles. Furthermore, bulk zinc oxide treated plants produced better leaf numbers than bulk copper counterpart. All treatments produced increased number of leaves in comparison with the control.

Table 37 shows that the highest numbers of leaves were produced in zinc oxide treated tomato plants throughout the period of experimentation. In addition, all nanoparticles treatments produced leaves that were higher than the control. In the same vein, bulk zinc produced leaves that were higher than bulk copper treated tomato plants. Table 37 further shows the interactive effect between metal salts and various concentrations on number of leaves in tomato in 2017 cropping season and the most significant ($P \leq 0.05$) number of leaves was recorded in 300 mg/kg in nZnO treatments during 2 WAP.

Table 38 shows the effects of Cu and ZnO nanoparticles and bulk particles on number of leaves in tomato in 2018 cropping season. Zinc oxide nanoparticles produced number of leaves that were higher than that produced by copper nanoparticles. All treatments produced leaves that were higher in number than the control plants throughout the period of the experimentation. There is significant ($P \leq 0.05$) interactive effects between the metal salts and concentration on the number of leaves in tomato at 2-8 WAP in 2017 cropping season. Significant highest number of leaves was produced wit nCu metal salts at 2-8 WAP. It is worthy to note that at 2 WAP, nano particles recorded significantly highest values (Tables 38 and 39). In addition, all nano particles treatments were higher in terms of numberas of leaves than the control.

Table 36: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of leaves of tomato during 2017 cropping season

	Number of leaves			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	14.13[a]	11.31[a]	7.00[b]	14.17[a]
nZnO	15.25[a]	11.50[a]	7.83[b]	13.75[a]
bCu	13.33[a]	8.00[b]	4.88[c]	12.33[a]
bZnO	13.83[a]	10.58[b]	6.42[c]	11.25[a]
Concentrations				
Control	13.50[a]	8.30[c]	4.25[d]	10.33[c]
300 mg/kg	16.08[a]	12.75[a]	9.17[c]	15.33[a]
600 mg/kg	14.33[a]	11.42[b]	6.75[d]	14.08[a]
1000 mg/kg	7.25[c]	9.83[c]	6.67[d]	11.83[b]
Interaction	0.005*	0.045*	0.002*	0.003*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 37: Interactive effect between metal salts and various concentrations on number of leaves in tomato during 2017 cropping season

	Number of leaves		
Metal salt	2 WAP	4 WAP	6 WAP
Control	0.80 ± 0.30^{de}	1.93 ± 0.32^{cd}	1.43 ± 1.18^{cd}
nCu 300 mg/kg	1.13 ± 1.06^{cd}	1.67 ± 0.99^{cd}	2.30 ± 0.26^{bc}
nCu 600 mg/kg	0.87 ± 0.49^{de}	1.33 ± 0.61^{cd}	1.10 ± 0.44^{cd}
nCu 1000 mg/kg	1.0 ± 0.36^{cd}	2.13 ± 0.35^{bc}	1.43 ± 0.18^{cd}
nZnO 300 mg/kg	3.73 ± 0.55^{a}	2.20 ± 0.26^{bc}	1.80 ± 0.80^{cd}
nZnO 600 mg/kg	0.80 ± 0.30^{de}	1.47 ± 0.58^{cd}	2.10 ± 0.17^{bc}
nZnO 1000 mg/kg	0.70 ± 0.20^{de}	2.67 ± 0.58^{bc}	1.67 ± 0.06^{cd}
bCu 300 mg/kg	0.40 ± 0.00^{ef}	0.60 ± 0.10^{de}	1.20 ± 0.00^{cd}
bCu 600 mg/kg	0.53 ± 0.06^{de}	0.33 ± 1.0^{ef}	0.50 ± 0.10^{de}
bCu 1000 mg/kg	0.80 ± 0.17^{de}	0.80 ± 1.00^{de}	2.10 ± 0.10^{bc}
bZnO 300 mg/kg	0.93 ± 0.06^{de}	0.73 ± 0.21^{de}	1.20 ± 0.00^{cd}
bZnO 600 mg/kg	1.00 ± 0.0^{cd}	1.13 ± 0.12^{cd}	0.50 ± 0.10^{de}
bZnO 1000 mg/kg	0.90 ± 0.61^{de}	1.03 ± 0.06^{cd}	2.17 ± 0.10^{bc}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 38: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of leaves in tomato during 2018 cropping season

	Number of leaves			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	13.06^{a}	9.75^{b}	13.06^{a}	12.17^{bc}
nZnO	15.25^{a}	11.31^{bc}	15.88^{a}	14.17^{a}
bCu	5.00^{e}	8.00^{d}	11.25^{bc}	10.75^{c}
bZnO	6.08^{e}	9.58^{d}	11.92^{bc}	11.38^{bc}
Concentrations				
Control	10.00^{c}	6.00^{e}	9.08^{c}	8.67^{d}
300 mg/kg	14.33^{a}	11.17^{b}	15.83^{a}	15.08^{a}
600 mg/kg	16.08^{a}	11.08^{b}	14.75^{a}	13.58^{a}
1000 mg/kg	12.25^{b}	11.50^{b}	11.50^{b}	13.33^{a}
Interaction	0.000*	0.000*	0.001*	0.001*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 39: Interactive effect between metal salts and various concentrations on number of leaves of tomato during 2018 cropping season

	Number of leaves			
Metal salt	2 WAP	4 WAP	6 WAP	8 WAP
Control	2.67 ± 0.58^{ef}	2.80 ± 0.00^{ef}	2.98 ± 0.58^{ef}	2.99 ± 0.58^{ef}
nCu 300 mg/kg	10.67 ± 1.53^{bc}	13.00 ± 1.00^{a}	14.83 ± 1.53^{a}	14.00 ± 1.00^{a}
nCu 600 mg/kg	10.00 ± 0.58^{bc}	13.33 ± 0.58^{a}	11.00 ± 1.00^{b}	13.33 ± 1.52^{a}
nCu 1000 mg/kg	10.00 ± 0.00^{bc}	9.67 ± 0.58^{bc}	11.00 ± 1.00^{b}	12.33 ± 0.58^{ab}
nZnO 300 mg/kg	7.67 ± 0.58^{cd}	13.00 ± 1.73^{a}	11.0 ± 1.00^{b}	10.33 ± 0.58^{bc}
nZnO 600 mg/kg	7.33 ± 1.53^{cd}	11.00 ± 1.00^{b}	10.00 ± 1.00^{bc}	10.00 ± 1.00^{bc}
nZnO 1000mg/kg	9.67 ± 0.58^{cd}	9.33 ± 1.15^{cd}	9.00 ± 1.00^{cd}	10.33 ± 1.53^{bc}
bCu 300 mg/kg	4.67 ± 0.57^{de}	5.67 ± 0.57^{de}	8.30 ± 0.58^{d}	7.00 ± 1.00^{cd}
bCu 600 mg/kg	5.67 ± 0.58^{de}	6.00 ± 0.00^{de}	8.67 ± 0.58^{d}	8.33 ± 0.58^{d}
bCu 1000 mg/kg	6.00 ± 0.58^{de}	6.70 ± 1.00^{de}	6.70 ± 1.15^{de}	3.10 ± 0.00^{ef}
bZnO 300 mg/kg	3.00 ± 1.73^{ef}	4.00 ± 0.00^{ef}	5.67 ± 1.15^{de}	3.00 ± 2.65^{ef}
bZnO 600 mg/kg	3.50 ± 0.00^{ef}	3.00 ± 1.00^{ef}	4.33 ± 0.58^{ef}	3.00 ± 2.65^{ef}
bZnO 1000mg/kg	3.67 ± 0.58^{ef}	7.00 ± 0.00^{cd}	5.33 ± 1.15^{de}	3.67 ± 2.08^{ef}

Values are mean$\pm$ S. D, n=96, values with the same superscript across treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.12 Stem girth in Tomato

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on stem girth of tomato plants for 2017 and 2018 cropping seasons are presented in Tables 40-43.

Table 40 shows that 300 mg/kg treated plants produced stems that were thicker than 600 and 1000 mg/kg treatments during 2 WAP. In the same vein zinc oxide nanoparticles produced stems in tomato that were higher than that produced in copper nanoparticles treated tomato.

There was a significant interactive effect among the metal salt and concentration on stem girth of tomato during 2-6 WAP in 2017 cropping season. Zinc oxide nanoparticles recorded the most significant ($p \leq 0.05$) stem girth.

Table 41 shows the interactive effect among metal salts and various concentrations on stem girth of tomato in 2017 cropping season. Copper nanoparticles of 1000 mg/kg and zinc oxide nanoparticles 300 mg/kg produced the thickest stems during 2 and 4 WAP.

Table 42 further shows that there was a significant interactive effect among the metal salt and concentration on stem girth during 2 and 6 WAP. The most significant metal was also zinc oxide nanoparticles throughout the period of the experiment but bulk zinc oxide recorded the least significant ($p \leq 0.05$) stem girth during 2 WAP of 2018.

Table 43 shows the interactive effect among metal salt and concentration on stem girth of tomato in 2018 cropping season. The thickest stem dirth during 2 WAP was from copper nanoparticles 1000 mg/kg while the least significant ($p \leq 0.05$) values were produced in the bulk treated plants. Furthermore, the highest values from the data produced showed that the thickest stem girth at 4 WAP was from copper nanoparticles 300 mg/kg treatments which were higher than that produced in the control.

Table 40: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stem girth (cm) of tomato during 2017 cropping season

	Stem girth (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	1.02[c]	1.32[c]	1.82[b]	2.12[b]
nZnO	1.34[c]	1.65[b]	2.19[b]	3.96[a]
bCu	0.98[c]	1.46[c]	2.13[b]	2.15[b]
bZnO	0.79[c]	1.53[b]	1.54[b]	2.01[b]
Concentrations				
Control	1.01[d]	1.29[d]	1.62[c]	1.56[c]
300 mg/kg	1.23[d]	1.78[c]	7.72[a]	3.79[c]
600 mg/kg	0.73[d]	1.28[d]	7.69[a]	2.38[c]
1000 mg/kg	0.16[d]	1.64[c]	5.13[b]	2.46[c]
Interaction	0.000*	0.000*	0.000*	0.012*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 41: Interactive effect between metal salts and various concentrations on stem girth (cm) of tomato during 2017 cropping season

	Stem girth (cm)			
Metal salt	2 WAP	4 WAP	6 WAP	8 WAP
Control	0.47 ± 0.57^{de}	0.50 ± 0.14^{de}	2.18 ± 0.57^{bc}	2.01 ± 0.93^{bc}
nCu 300 mg/kg	1.20 ± 0.14^{cd}	1.68 ± 0.57^{cd}	1.00 ± 0.14^{cd}	1.91 ± 0.55^{cd}
nCu 600 mg/kg	1.38 ± 0.57^{cd}	0.83 ± 0.14^{de}	1.33 ± 0.14^{cd}	1.95 ± 0.55^{cd}
nCu 1000 mg/kg	1.97 ± 0.95^{cd}	2.27 ± 0.96^{bc}	2.77 ± 0.96^{b}	2.59 ± 0.75^{b}
nZnO 300 mg/kg	2.23 ± 0.38^{bc}	2.53 ± 0.38^{bc}	3.03 ± 0.38^{a}	3.78 ± 0.66^{a}
nZnO 600 mg/kg	1.01 ± 0.38^{cd}	$1.\ 31\pm0.38^{cd}$	$1.81\ \pm0.38^{cd}$	3.50 ± 0.49^{a}
nZnO 1000mg/kg	0.97 ± 0.16^{de}	1.07 ± 0.24^{cd}	1.77 ± 0.16^{cd}	2.56 ± 1.93^{b}
bCu 300 mg/kg	1.60 ± 0.10^{cd}	2.07 ± 0.12^{bc}	2.83 ± 0.06^{b}	2.87 ± 0.06^{b}
bCu 600 mg/kg	0.67 ± 0.40^{de}	1.23 ± 0.95^{cd}	2.83 ± 0.06^{b}	2.57 ± 0.21^{b}
bCu 1000 mg/kg	1.23 ± 0.06^{cd}	1.20 ± 0.00^{cd}	$2.63\ \pm0.06^{b}$	2.10 ± 0.10^{bc}
bZnO 300 mg/kg	0.90 ± 0.10^{de}	2.00 ± 0.00^{bc}	1.50 ± 1.15^{cd}	1.60 ± 0.10^{cd}
bZnO 600 mg/kg	0.70 ± 0.10^{de}	1.73 ± 0.21^{bc}	1.50 ± 0.0^{cd}	1.50 ± 0.50^{cd}
bZnO 1000mg/kg	0.53 ± 0.14^{de}	2.00 ± 1.00^{bc}	1.80 ± 1.15^{cd}	1.60 ± 0.20^{cd}

n= 96, values with the same superscript across treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 42: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stem girth (cm) of tomato during 2018 cropping season

	Stem girth (cm)			
Metal salts	2 WAP	4 WAP	6 WAP	8 WAP
nCu	1.60[b]	1.92[b]	2.12[a]	2.41[a]
nZnO	1.53[b]	2.09[a]	2.41[a]	1.70[b]
bCu	0.96[c]	1.46[b]	2.01[a]	2.11[a]
bZnO	0.66[c]	1.52[b]	2.08[a]	1.98[a]
Concentrations				
Control	0.78[c]	1.25[c]	1.41[c]	1.13[c]
300 mg/kg	1.38[c]	2.30[a]	2.63[a]	2.67[a]
600 mg/kg	1.25[c]	1.79[b]	2.48[a]	2.09[a]
1000 mg/kg	1.20[c]	1.68[b]	2.13[a]	2.26[a]
Interaction	0.000*	0.826 N.S	0.000*	0.063 N.S

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 43: Interactive effect between metal salts and various concentrations on stem girth (cm) of tomato during 2018 cropping season

	Stem girth (cm)	
Metal salt	2 WAP	6 WAP
Control	0.93 ± 0.12^{ef}	1.67 ± 0.15^{de}
nCu 300 mg/kg	1.43 ± 0.06^{de}	2.73 ± 0.21^{bc}
nCu 600 mg/kg	1.70 ± 0.10^{de}	2.17 ± 0.21^{c}
nCu 1000 mg/kg	2.33 ± 0.58^{bc}	1.90 ± 0.10^{de}
nZnO 300 mg/kg	1.70 ± 0.20^{de}	1.77 ± 0.15^{de}
nZnO 600 mg/kg	1.97 ± 0.06^{de}	3.10 ± 0.10^{a}
nZnO 1000mg/kg	1.50 ± 0.00^{de}	2.77 ± 0.15^{bc}
bCu 300 mg/kg	1.30 ± 0.10^{de}	2.10 ± 0.10^{c}
bCu 600 mg/kg	0.60 ± 0.35^{ef}	2.77 ± 0.15^{bc}
bCu 1000 mg/kg	0.63 ± 0.06^{ef}	2.10 ± 0.10^{c}
bZnO 300 mg/kg	0.80 ± 0.10^{ef}	2.43 ± 0.15^{c}
bZnO 600 mg/kg	0.73 ± 0.23^{ef}	2.60 ± 0.10^{bc}
bZnO 1000mg/kg	0.43 ± 0.06^{ef}	2.10 ± 0.17^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.13 Chlorophyll content in Beans during 2 and 4 WAP 2017

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on chlorophyll Contents of beans plants during 2 and 4 WAP of 2017 cropping seasons are presented in Tables 44-47.

Table 44 shows the chlorophyll content of beans exposed to copper and zinc oxide nanoparticles and bulk particles after 2 weeks of planting in 2017 cropping season.

Chlorophyll a was highest in copper nanoparticles treated plants followed by zinc oxide nanoparticles treated plants and the lowest was produced in bulk zinc oxide treated plants as well as bulk treated plants. Treatments concentration of 1000 mg/kg enhanced the production of chlorophyll more than 300 mg/kg concentration. The control plants produced more chlorophyll than the 600 mg/kg treatments.

Furthermore, chlorophyll b was high in bulk copper treated plants than in copper nanoparticles treated plants. In the same vein, bulk zinc oxide produced increased content of chlorophyll than its zinc oxide counterparts numerically. The content of chlorophyll b increased progressively from control to 1000 mg/kg

Total chlorophyll content was highest in copper treated plants followed by zinc oxide treated plants and followed by the bulk treated plants. The control plants produced chlorophyll b and total chlorophyll that were higher than all other plants. There were significant ($p \leq 0.05$) interactive effects among the metal salts and concentration on chlorophyll content of beans at 2-4 WAP in 2017 cropping season. All treatments reduced chlorophyll content.

Table 44 shows that all treatments during the period of exposure of bean plants to nano and bulk particles reduced the contents of chlorophyll a, b and total.

Table 45 shows the effect of Cu and ZnO nanoparticles and bulk particles on chlorophyll content of beans during 2 WAP in 2017 cropping season. Copper and zinc oxide produced statistically ($p \leq 0.05$) the same chlorophyll a, b and total chlorophyll during 2 WAP.

Table 46 shows the interactive effects among metal salts and various concentrations on the chlorophyll content of beans during 4 WAP in 2017 copping season. All treatments reduced chlorophyll a, b and total chlorophyll.

Table 47 shows the effects of Cu and ZnO bulk and nanoparticles on chlorophyll content of beans during 4 WAP in 2017 cropping season. The control plants produced the most significant ($p \leq 0.05$) chlorophyll of all the treatments during 4 WAP in 2017 cropping season. There was a significant interactive effect of the metal salt and concentration on chlorophyll a, b and total during 4 WAP and the most significant ($p \leq 0.05$) was with the control.

4.14 Chlorophyll content in Beans during 2 and 4 WAP 2018

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on chlorophyll Contents of beans plants during 2018 cropping seasons are presented in Tables 48-51.

Table 48 shows that the most significant result of chlorophyll a was with the control and nano copper treated plants produced improved quantity of chlorophyll.

In table 49, there were significant effects of the metal salt on chlorophyll a, b and total at 2 WAP of 2018 cropping season. Zinc oxide nanoparticles and bulk copper treated beans produced higher chlorophyll numerically than the copper nanoparticles and bulk zinc oxide treated plants.

In table 50, all treatments reduced the chlorophyll content in relation to the control. Furthermore, zinc oxide treated plants showed a significant increase in the chlorophyll contents numerically during 4 WAP in 2018 cropping season. The control plants produced the most significant ($p \leq 0.05$) chlorophyll a which is not different significantly from the chlorophyll produced from zinc oxide nanoparticles 1000 mg/kg treatments. The least significant values were from the bulk treated plants. In addition, the control still produced the highest content of chlorophyll b during 4 WAP in 2018 cropping season. The same trend was followed in the content of total chlorophyll.

In table 51, all treatments produced reduced chlorophyll content making the most significant treatment to be the control. Zinc oxide nanoparticles treatment produced enhanced chlorophyll a, b and total especially with treatment 1000 mg/kg.

Table 44: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of beans 2 WAP during 2017 cropping season

Metal salts	Chlorophyll a	Chlorophyll Chlorophyll b	(mg/g fw) Total Chlorophyll
nCu	0.82[b]	0.66[b]	1.48[a]
nZnO	0.66[b]	0.63[b]	1.28[a]
bCu	0.51[b]	0.82[b]	1.08[a]
bZnO	0.59[b]	0.66[b]	0.99[b]
Concentrations			
Control	0.59[b]	1.00[a]	1.34[a]
300 mg/kg	0.64[b]	0.72[b]	1.27[a]
600 mg/kg	0.53[b]	0.54[b]	0.83[b]
1000 mg/kg	0.83[b]	0.44[b]	0.93[b]
Interaction	0.000*	0.001*	0.002*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 45: Interactive effect between metal salts and various concentrations on the chlorophyll (mg/g fw) content of beans at 2 WAP during 2017 cropping season

Metal salt	Chlorophyll (mg/g fw) Chlorophyll a	Chlorophyll b	Total Chlorophyll
Control	0.87 ± 0.53^{b}	1.90 ± 0.50^{a}	1.96 ± 0.23^{a}
nCu 300 mg/kg	0.77 ± 0.47^{b}	0.97 ± 0.40^{b}	1.73 ± 0.11^{a}
nCu 600 mg/kg	0.77 ± 0.11^{b}	0.57 ± 0.12^{b}	1.40 ± 0.12^{b}
nCu 1000 mg/kg	0.93 ± 0.41^{b}	0.43 ± 0.21^{c}	1.37 ± 0.21^{b}
nZnO 300 mg/kg	0.73 ± 0.25^{b}	0.40 ± 0.10^{c}	1.13 ± 0.40^{b}
nZnO 600 mg/kg	0.40 ± 0.11^{c}	0.73 ± 0.45^{b}	1.13 ± 0.23^{b}
nZnO 1000mg/kg	0.87 ± 0.47^{b}	0.47 ± 0.25^{c}	1.33 ± 0.23^{b}
bCu 300 mg/kg	0.57 ± 0.47^{b}	0.53 ± 0.81^{b}	0.88 ± 0.19^{c}
bCu 600 mg/kg	0.53 ± 0.20^{b}	0.40 ± 0.10^{c}	0.41 ± 0.24^{c}
bCu 1000 mg/kg	0.63 ± 0.35^{b}	0.31 ± 0.35^{c}	0.71 ± 0.10^{c}
bZnO 300 mg/kg	0.53 ± 0.20^{b}	0.10 ± 0.75^{c}	0.35 ± 0.05^{c}
bZnO 600 mg/kg	0.40 ± 0.10^{c}	0.47 ± 0.15^{c}	0.44 ± 0.30^{c}
bZnO 1000mg/kg	0.43 ± 0.06^{c}	0.50 ± 0.25^{b}	0.31 ± 0.20^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 46: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of beans 4 WAP during 2017 cropping season

Metal salts	Chlorophyll a	Chlorophyll Chlorophyll b	(mg/g fw) Total Chlorophyll
nCu	0.11[b]	0.78[a]	0.94[a]
nZnO	0.24[b]	0.43[b]	0.67[a]
bCu	1.53[a]	0.82[a]	1.13[a]
bZnO	0.24[b]	0.66[a]	0.92[a]
Concentrations			
Control	0.34[b]	1.27[a]	1.27[a]
300 mg/kg	0.12[b]	1.06[a]	1.08[a]
600 mg/kg	0.19[b]	0.56[a]	0.56[a]
1000 mg/kg	0.23[b]	0.70[a]	0.70[a]
Interaction	0.000*	0.002*	0.001*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant, N.S = not significant

Table 47: Interactive effect between metal salts and various concentrations on the chlorophyll (mg/g fw) content of beans at 4 WAP during 2017 cropping season

Metal salt	Chlorophyll (mg/g fw) Chlorophyll a	Chlorophyll b	Total Chlorophyll
Control	1.12±0.14^{c}	1.57±0.15^{b}	2.74±0.15^{a}
nCu 300 mg/kg	0.11±0.08^{d}	1.77±0.19^{b}	1.88±1.19^{b}
nCu 600 mg/kg	0.47±0.14^{d}	0.27±0.15^{d}	0.41±0.24^{d}
nCu 1000 mg/kg	0.18±0.14^{d}	0.53±0.15^{c}	0.71±0.10^{c}
nZnO 300 mg/kg	0.53±0.40^{c}	0.23±0.06^{d}	0.35±0.05^{d}
nZnO 600 mg/kg	0.11±0.08^{d}	0.27±0.21^{d}	0.44±0.30^{d}
nZnO 1000mg/kg	0.18±0.14^{d}	0.17 ±0.06^{d}	0.31 ±0.20^{d}
bCu 300 mg/kg	0.12±0.77^{d}	0.39±0.01^{d}	0.75±0.91^{c}
bCu 600 mg/kg	0.06±0.00^{e}	0.45±0.07^{d}	0.61±0.13^{c}
bCu 1000 mg/kg	0.14±0.10^{d}	0.40±0.09^{d}	0.61±0.13^{c}
bZnO 300 mg/kg	0.12±0.00^{d}	0.10±0.75^{d}	0.29±0.76^{d}
bZnO 600 mg/kg	0.29±0.18^{d}	0.43±0.15^{d}	0.74±0.06^{c}
bZnO 1000mg/kg	0.29±0.18^{d}	0.44±0.31^{d}	0.89±0.33^{c}

Values are mean± S. D, n= 96, values with the same superscript along treatments are not significant at p≤ 0.05, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 48: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of beans 2 WAP during 2018 cropping season

Metal salts	Chlorophyll a	Chlorophyll Chlorophyll b	(mg/g fw) Total Chlorophyll
nCu	1.03[b]	0.77[b]	1.79[a]
nZnO	0.81[b]	0.56[b]	1.37[b]
bCu	0.72[b]	0.69[b]	1.42[b]
bZnO	0.50[b]	0.64[b]	1.14[b]
Concentrations			
Control	0.96[b]	0.95[b]	1.78[a]
300 mg/kg	0.83[b]	0.47[c]	1.12[b]
600 mg/kg	0.55[b]	0.48[c]	1.03[b]
1000 mg/kg	0.65[b]	0.75[b]	1.48[b]
Interaction	0.000*	0.002*	0.001*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 49: Interactive effect between metal salts and various concentrations on the chlorophyll (mg g fw) content of beans at 2 WAP during 2018 cropping season

Metal salt	Chlorophyll a	Chlorophyll (mg/g fw) Chlorophyll b	Total chlorophyll
Control	1.70 ± 0.10^{b}	0.65 ± 0.38^{c}	2.70 ± 0.10^{a}
nCu 300 mg/kg	1.23 ± 0.11^{c}	1.00 ± 0.21^{c}	1.97 ± 0.11^{b}
nCu 600 mg/kg	0.80 ± 0.00^{c}	0.70 ± 0.04^{c}	1.80 ± 0.00^{b}
nCu 1000 mg/kg	1.00 ± 0.58^{c}	0.59 ± 0.06^{c}	1.89 ± 0.43^{b}
nZnO 300 mg/kg	0.73 ± 0.42^{c}	0.90 ± 0.09^{c}	1.16 ± 0.32^{c}
nZnO 600 mg/kg	0.50 ± 0.10^{c}	0.67 ± 0.07^{c}	1.24 ± 0.12^{c}
nZnO 1000mg/kg	1.30 ± 0.10^{c}	0.75 ± 0.12^{c}	1.30 ± 0.10^{c}
bCu 300 mg/kg	0.80 ± 0.40^{c}	0.17 ± 0.15^{d}	0.80 ± 0.40^{c}
bCu 600 mg/kg	0.60 ± 0.14^{c}	0.62 ± 0.13^{c}	1.00 ± 1.15^{c}
bCu 1000 mg/kg	0.60 ± 0.14^{c}	0.27 ± 0.28^{d}	0.79 ± 0.18^{c}
bZnO 300 mg/kg	0.53 ± 0.06^{c}	0.27 ± 0.28^{d}	0.17 ± 0.01^{d}
bZnO 600 mg/kg	0.38 ± 0.15^{d}	0.34 ± 0.25^{d}	0.98 ± 0.00^{c}
bZnO 1000mg/kg	0.40 ± 0.10^{d}	0.67 ± 0.10^{c}	1.06 ± 0.10^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 50: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/ g fw) content of tomato 4 WAP during 2018 cropping season

Metal salts	Chlorophyll a	Chlorophyll Chlorophyll b	(mg g fw) Total Chlorophyll
nCu	0.41[c]	0.56[b]	1.79[a]
nZnO	0.98[b]	0.47[c]	1.37[b]
bCu	0.58[b]	0.96[b]	1.05[b]
bZnO	0.22[c]	0.47[c]	0.69[b]
Concentrations			
Control	0.60[a]	0.69[a]	1.08[a]
300 mg/kg	0.44[b]	0.41[b]	1.24[a]
600 mg/kg	0.12[b]	0.51[a]	0.87[a]
1000 mg/kg	0.58[a]	0.68[a]	0.87[a]
Interaction	0.002*	0.003*	0.001*

Values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 51: Interactive effect between metal salts and various concentrations on the chlorophyll content of beans at 4 WAP for 2018 cropping season

Metal salt	Chlorophyll (mg/g fw) Chlorophyll a	Chlorophyll b	Total Chlorophyll
Control	2.04 ± 0.00^{b}	2.73 ± 0.42^{a}	3.20 ± 0.17^{a}
nCu 300 mg/kg	0.10 ± 0.00^{d}	0.50 ± 0.00^{c}	2.20 ± 0.17^{b}
nCu 600 mg/kg	0.73 ± 0.15^{c}	0.53 ± 0.15^{c}	1.40 ± 0.10^{c}
nCu 1000 mg/kg	0.73 ± 0.06^{c}	0.47 ± 0.12^{d}	2.37 ± 0.66^{b}
nZnO 300 mg/kg	1.20 ± 0.00^{c}	0.10 ± 0.00^{d}	1.23 ± 0.76^{c}
nZnO 600 mg/kg	1.50 ± 0.00^{b}	0.31 ± 0.00^{d}	0.73 ± 0.15^{c}
nZnO 1000mg/kg	1.20 ± 0.00^{c}	1.00 ± 0.00^{c}	2.37 ± 0.21^{b}
bCu 300 mg/kg	0.17 ± 0.06^{d}	0.73 ± 0.06^{c}	1.03 ± 0.91^{c}
bCu 600 mg/kg	0.04 ± 0.01^{e}	0.97 ± 0.89^{c}	1.00 ± 0.91^{c}
bCu 1000 mg/kg	0.33 ± 0.21^{d}	0.77 ± 0.40^{c}	1.10 ± 0.61^{c}
bZnO 300 mg/kg	0.31 ± 0.25^{d}	0.31 ± 0.24^{d}	0.62 ± 0.48^{c}
bZnO 600 mg/kg	0.14 ± 0.16^{d}	0.22 ± 0.18^{d}	0.35 ± 0.30^{d}
bZnO 1000mg/kg	0.06 ± 0.01^{e}	0.47 ± 0.06^{d}	0.53 ± 0.05^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.15 Chlorophyll content in Tomato during 2 and 4 WAP of 2017 cropping season

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on chlorophyll contents of tomato plants during 2018 cropping seasons are presented in Tables 52-55

Table 52 shows the effects of Cu and ZnO nanoparticles and bulk particles on chlorophyll content of tomato during 2 WAP in 2017 cropping season. Zinc oxide nanoparticles and bulk Cu enhanced the production of chlorophyll a while nano Cu and ZnO enhanced the production of chlorophyll b during 2 WAP of 2017. The control plants produced the highest content of chlorophyll a, b and total. Furthermore, there were significant interactive effects between the metal salts and chlorophyll a, b and total in tomato during 2 WAP in 2017 cropping season.

Table 53 shows the interactive effects among metal salts and various concentrations on the chlorophyll contents of tomato during 2 WAP in 2017. All treatments reduced the contents of chlorophyll a and total chlorophyll contents and the most significant chlorophyll a was produced in the control plants while the least significant chlorophyll a content was produced in bulk treated plants. In the same vein, total chlorophyll was highest in the control plants and the least significant total chlorophyll was produced in the bulk treated tomato plants.

Table 54 shows the effects of Cu and ZnO nanoparticles and bulk particles on chlorophyll content of tomato during 4WAP in 2017 cropping season. There were significant ($p \leq 0.05$) interactive effects of the metal salts and concentration on chlorophyll a, b and total. Chlorophyll a was produced in high quantity in plants treated with n nZnO numerically while the least significant ($p \leq 0.05$) content of chlorophyll a was produced in bulk zinc oxide treated plants. In addition, chlorophyll b was highest in plants treated with copper nanoparticles while the least was also produced in bulk zinc oxide numerically. Nanoparticles treated plants produced the highest quantity of total chlorophyll and the least were from bulk

treated plants. There were no significant difference in the quantity of chlorophyll a, b and total in control and 300 mg/kg treatments.

Table 55 shows the interactive effects between metal salts and various concentrations on the chlorophyll content of tomato during 4 WAP in 2017cropping season. All treatments reduced the content of chlorophyll a, b and total.

4.16 Chlorophyll content in tomato during 2 and 4 WAP of 2018 cropping season

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on chlorophyll contents of tomato plants during 2018 cropping seasons are presented in Tables 56-59.

Table 56 shows the effects of Cu and ZnO nanoparticles and bulk particles on chlorophyll content of tomato during 2 WAP in 2018 cropping season. There were significant interactive effects in the metal salts and concentrations on the content of chlorophyll a, b, and total in tomato plants during 2 WAP in 2018 cropping season.

Table 57 shows that there was a significant effect of all the metal salts on tomato plants during 2 WAP in 2018. Treatments reduced the content of chlorophyll a, b and total chlorophyll. Table 58 shows the interactive effects among metal salts and various concentrations on the chlorophyll content of tomato during 2 WAP in 2018 cropping season. Chlorophyll a was highest in plants treated with zinc oxide nanoparticles and there were significant difference between those treated with copper nanoparticles, bulk copper and bulk zinc oxide. All treatments reduced the contents of chlorophyll throughout the period of the experimentation. There were significant interactive effect among the metal salts and concentrations onchlorophyll b and total chlorophyll in tomato during 4 WAP in 2018 croppping. season.Table 59 shows that chlorophyll a, b and total were produced in high quantity in the control plants

Table 52: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of tomato 2 WAP during 2017 cropping season

Metal salts	Chlorophyll (mg/g fw) Chlorophyll a	Chlorophyll b	Total Chlorophyll
nCu	0.13^{b}	0.35^{b}	0.48^{ab}
nZnO	0.24^{b}	0.34^{b}	0.59^{a}
bCu	0.22^{b}	0.08^{c}	0.29^{b}
bZnO	0.10^{b}	0.08^{c}	0.18^{b}
Concentrations			
Control	0.29^{b}	0.23^{b}	0.52^{a}
300 mg/kg	0.17^{b}	0.17^{b}	0.34^{b}
600 mg/kg	0.11^{b}	0.19^{b}	0.29^{b}
1000 mg/kg	0.08^{c}	0.26^{b}	0.34^{b}
Interaction	0.018*	0.000*	0.005*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 53: Interactive effect between metal salts and various concentrations on the chlorophyll (mg g fw) content of tomato at 2 WAP for 2017 cropping season

Metal salt	Chlorophyll (mg/g fw) Chlorophyll a	Chlorophyll b	Total chlorophyll
Control	1.15 ± 0.90^{b}	1.54 ± 0.18^{a}	2.02 ± 0.08^{a}
nCu 300 mg/kg	0.13 ± 0.06^{c}	0.43 ± 0.23^{c}	1.22 ± 0.72^{b}
nCu 600 mg/kg	0.11 ± 0.08^{c}	0.35 ± 0.50^{c}	1.34 ± 0.15^{b}
nCu 1000 mg/kg	0.15 ± 0.13^{c}	0.92 ± 0.95^{b}	1.67 ± 0.18^{a}
nZnO 300 mg/kg	0.17 ± 0.06^{c}	0.37 ± 0.12^{c}	1.22 ± 0.18^{b}
nZnO 600 mg/kg	0.17 ± 0.14^{c}	0.51 ± 0.10^{b}	1.55 ± 0.18^{a}
nZnO 1000mg/kg	0.10 ± 0.00^{c}	0.33 ± 0.06^{c}	0.94 ± 0.18^{b}
bCu 300 mg/kg	0.27 ± 0.15^{c}	0.31 ± 0.11^{c}	1.03 ± 0.00^{b}
bCu 600 mg/kg	0.11 ± 0.08^{c}	0.19 ± 0.06^{c}	1.00 ± 0.21^{b}
bCu 1000 mg/kg	0.03 ± 0.10^{c}	0.05 ± 0.01^{d}	0.09 ± 0.30^{d}
bZnO 300 mg/kg	0.12 ± 0.16^{c}	0.25 ± 0.21^{c}	0.82 ± 0.10^{b}
bZnO 600 mg/kg	0.02 ± 0.10^{d}	0.13 ± 0.17^{c}	0.61 ± 0.18^{b}
bZnO 1000mg/kg	0.04 ± 0.05^{d}	0.06 ± 0.05^{d}	0.42 ± 0.18^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 54: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of tomato 4 WAP during 2017 cropping season

Metal salts	Chlorophyll (mg/g fw) Chlorophyll a	Chlorophyll b	Total Chlorophyll
nCu	0.10^{b}	0.45^{b}	0.61^{a}
nZnO	0.25^{b}	0.29^{b}	0.52^{a}
bCu	0.13^{b}	0.18^{b}	0.31^{b}
bZnO	0.09^{c}	0.17^{b}	0.27^{b}
Concentrations			
Control	0.18^{b}	0.34^{b}	0.52^{a}
300 mg/kg	0.16^{b}	0.32^{b}	0.47^{b}
600 mg/kg	0.11^{b}	0.27^{b}	0.38^{b}
1000 mg/kg	0.15^{b}	0.16^{b}	0.31^{b}
Interaction	0.017*	0.116*	0.000*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 55: Interactive effect between metal salts and various concentrations on the chlorophyll content of tomato at 4 WAP during 2017 cropping season

		Chlorophyll	**(mg/g fw)**
Metal salt	Chlorophyll a	Chlorophyll b	Total Chlorophyll
Control	1.13 ± 0.06^{b}	1.50 ± 0.17^{b}	2.52 ± 0.10^{a}
nCu 300 mg/kg	0.11 ± 0.09^{d}	0.60 ± 0.17^{c}	1.50 ± 0.10^{b}
nCu 600 mg/kg	0.20 ± 0.10^{d}	0.40 ± 0.10^{d}	1.20 ± 0.10^{c}
nCu 1000 mg/kg	0.20 ± 0.10^{d}	0.30 ± 0.17^{d}	0.64 ± 0.00^{c}
nZnO 300 mg/kg	0.30 ± 0.17^{d}	0.45 ± 0.10^{d}	1.00 ± 0.00^{c}
nZnO 600 mg/kg	0.17 ± 0.14^{d}	0.30 ± 0.20^{d}	1.20 ± 0.10^{c}
nZnO 1000mg/kg	0.10 ± 0.00^{d}	0.20 ± 0.10^{d}	0.50 ± 0.10^{c}
bCu 300 mg/kg	0.05 ± 0.04^{e}	0.27 ± 0.06^{d}	0.53 ± 0.10^{c}
bCu 600 mg/kg	0.03 ± 0.00^{e}	0.20 ± 0.10^{d}	0.25 ± 0.10^{d}
bCu 1000 mg/kg	0.10 ± 0.16^{d}	0.13 ± 0.16^{d}	0.40 ± 0.10^{d}
bZnO 300 mg/kg	0.02 ± 0.01^{e}	0.08 ± 0.00^{e}	0.23 ± 0.10^{d}
bZnO 600 mg/kg	0.02 ± 0.05^{e}	0.04 ± 0.10^{e}	0.09 ± 0.10^{e}
bZnO 1000mg/kg	0.07 ± 0.05^{e}	0.01 ± 0.05^{e}	0.16 ± 0.10^{d}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 56: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of tomato 2 WAP during 2018 cropping season

Metal salts	Chlorophyll a	Chlorophyll Chlorophyll b	(mg/g fw) Total Chlorophyll
nCu	0.22[b]	0.24[b]	0.46[b]
nZnO	0.28[b]	0.24[b]	0.52[a]
bCu	0.17[b]	0.12[b]	0.28[b]
bZnO	0.14[b]	0.15[b]	0.29[b]
Concentrations			
Control	0.23[b]	0.24[b]	0.48[a]
300 mg/kg	0.25[b]	0.21[b]	0.46[a]
600 mg/kg	0.19[b]	0.13[b]	0.32[b]
1000 mg/kg	0.12[b]	0.18[b]	0.30[b]
Interaction	0.001*	0.00*	0.003*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 57: Interactive effect between metal salts and various concentrations on the chlorophyll (mg/g fw) content of tomato at 2 WAP during 2018 cropping season

	Chlorophyll (mg/g fw)		
Metal salts	Chlorophyll a	Chlorophyll b	Total chlorophyll
Control	1.08 ± 0.01^{a}	1.39 ± 0.10^{a}	1.43 ± 0.00^{a}
nCu 300 mg/kg	0.03 ± 0.03^{d}	0.20 ± 0.23^{c}	0.62 ± 0.00^{b}
nCu 600 mg/kg	0.05 ± 0.04^{d}	0.15 ± 0.02^{c}	0.40 ± 0.10^{b}
nCu 1000 mg/kg	0.07 ± 0.14^{d}	0.28 ± 0.23^{c}	0.70 ± 0.29^{b}
nZnO 300 mg/kg	0.37 ± 0.21^{b}	0.47 ± 0.06^{b}	0.96 ± 0.00^{a}
nZnO 600 mg/kg	0.10 ± 0.10^{c}	0.15 ± 0.26^{c}	0.78 ± 0.10^{a}
nZnO 1000mg/kg	0.30 ± 0.00^{b}	0.13 ± 0.16^{c}	0.46 ± 0.00^{b}
bCu 300 mg/kg	0.01 ± 0.00^{d}	0.80 ± 0.05^{b}	0.99 ± 0.04^{a}
bCu 600 mg/kg	0.05 ± 0.04^{d}	0.13 ± 0.01^{c}	0.16 ± 0.00^{b}
bCu 1000 mg/kg	0.24 ± 0.04^{b}	0.03 ± 0.02^{d}	0.29 ± 0.01^{b}
bZnO 300 mg/kg	0.12 ± 0.09^{c}	0.40 ± 0.00^{c}	0.91 ± 0.00^{a}
bZnO 600 mg/kg	0.03 ± 0.01^{d}	0.08 ± 0.01^{d}	0.09 ± 0.01^{d}
bZnO 1000mg/kg	0.04 ± 0.10^{d}	0.07 ± 0.09^{d}	0.31 ± 0.00^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 58: Effects of Nanoparticles and bulk particles (Cu and ZnO) on chlorophyll (mg/g fw) content of tomato 4 WAP during 2018 cropping season

Metal salts	Chlorophyll a	Chlorophyll Chlorophyll b	(mg/g fw) Total Chlorophyll
nCu	0.09[a]	0.26[b]	0.36[a]
nZnO	0.15[b]	0.27[b]	0.41[a]
bCu	0.09[d]	0.04[d]	0.14[b]
bZnO	0.09[d]	0.17[b]	0.26[b]
Concentrations			
Control	0.17[b]	0.28[b]	0.45[a]
300 mg/kg	0.12[b]	0.18[b]	0.29[b]
600 mg/kg	0.07[c]	0.11[b]	0.17[b]
1000 mg/kg	0.07[c]	0.21[b]	0.28[b]
Interaction	0.000*	0.036*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 59: Interactive effect between metal salts and various concentrations on the chlorophyll (mg/g fw) content of tomato at 4 WAP during 2018 cropping season

	Chlorophyll (mg/g fw)		
Metal salts	Chlorophyll a	Chlorophyll b	Total chlorophyll
Control	1.10 ± 0.00^{a}	1.40 ± 0.10^{a}	1.45 ± 0.00^{a}
nCu 300 mg/kg	0.02 ± 0.01^{d}	0.18 ± 0.27^{c}	0.51 ± 0.10^{b}
nCu 600 mg/kg	0.02 ± 0.01^{d}	0.13 ± 0.06^{c}	0.46 ± 0.10^{b}
nCu 1000 mg/kg	0.05 ± 0.04^{d}	0.33 ± 0.06^{b}	0.90 ± 0.09^{b}
nZnO 300 mg/kg	0.27 ± 0.21^{c}	0.37 ± 0.06^{b}	0.56 ± 0.00^{b}
nZnO 600 mg/kg	0.20 ± 0.10^{c}	0.13 ± 0.06^{c}	0.73 ± 0.20^{b}
nZnO 1000mg/kg	0.10 ± 0.00^{c}	0.10 ± 0.00^{c}	0.35 ± 0.00^{c}
bCu 300 mg/kg	0.10 ± 0.00^{c}	0.70 ± 0.50^{b}	0.90 ± 0.04^{b}
bCu 600 mg/kg	0.05 ± 0.04^{d}	0.12 ± 0.16^{c}	0.18 ± 0.00^{c}
bCu 1000 mg/kg	0.22 ± 0.04^{c}	0.05 ± 0.06^{d}	0.29 ± 0.00^{c}
bZnO 300 mg/kg	0.10 ± 0.09^{c}	0.20 ± 0.00^{c}	0.50 ± 0.00^{b}
bZnO 600 mg/kg	0.02 ± 0.01^{d}	0.04 ± 0.02^{d}	0.09 ± 0.00^{d}
bZnO 1000mg/kg	0.20 ± 0.10^{d}	0.09 ± 0.09^{d}	0.31 ± 0.00^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.17 Flowering and fruiting in Bean plants during 2017 and 2018 cropping season

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on flowering and fruiting of bean plants for 2017 and 2018 cropping seasons are presented in Tables 60-63.

Table 60 shows the effects of Cu and ZnO nanoparticles and bulk particles on flowering and fruiting in beans in 2017 cropping season. Bulk zinc oxide delayed flowering in beans and the same trend was observed in fruiting.

Table 60 further revealed that there were significant interactive effects among the metal salts and concentration on flowering and fruiting in beans in the year 2017 cropping season. The bulk zinc oxide metal salts recorded the most significantly longest number of days to flowering and fruiting.

Table 61 shows that copper and zinc oxide nanoparticles and bulk copper treated beans flowered earlier than the control suggesting that their treatments enhanced flowering in beans. The copper nanoparticles treated beans flowered about twenty one days earlier than the control. The same trend was also observed for the days to fruiting and that copper nanoparticle treated beans fruited after forty six to forty eight (46-48) days. Bulk copper flowered after sixty three to sixty four days (63-64). The results showed that copper and zinc oxide nanoparticles and bulk copper enhanced flowering and fruiting in beans.

Table 62 shows the effects of Cu and ZnO nanoparticles and bulk particles on flowering and fruiting in bean during 2017 cropping season. Copper nanoparticles treated beans flowered and fruited earlier than the control. Twelve to thirteen days earlier for flowering and fruiting. It is worthy to note that concentrations delayed flowering by seven (7) days and seven to ten (7-10) days for fruiting earlier than other treatments. About thirteen (13) days earlier than the

control plants. This suggests that copper nanoparticles enhanced flowering and fruting in bean plants.

Futhermore, in 2018 cropping season, flowering started after 55 days of planting in the control plants while in copper nanoparticles 300 mg/kg treatments, flowers emerged after 42 days of planting. The longest number of days for flowering and fruiting was with bulk zinc oxide 300, 600 and 1000 mg/kg treatments (Table 63).

Table 64 shows that there were significant interactive effect among the metal salt and concentration on flowering and fruiting in tomato during 2017 cropping season. Nanoparticles treated plants flowered earlier than the control (4-5) days. Zinc oxide and copper banoparticles fruited earlier than the control (7-9) days.

Table 65 revealed that all treatments flowered earlier than the control (< 70) days while the control flowered on the 75^{th} day. Furthermore, nanoparticles of copper and zinc oxide 300 mg/kg flowered after 53 days each respectively. The bulk copper 600 and 1000 mg/kg and bulk zinc oxide treatments delayed flowering by 1-6 days respectively. Nano zinc oxide 1000 mg/kg matured by day 65, copper nanoparticles 300 and 600 mg/ kg treatments matured by day 66 and 67 respectively. It is worthy to note that all treatments especially nanoparticles enhanced better fruiting and flowering than bulk materials and the control.

Table 66 shows that copper nanoparticles 300 and 600 mg/kg and zinc oxide nanoparticles 300 and 600 mg/kg flowered and fruited earlier while other treatments delayed flowering and fruiting in tomato plants. Similar trends were also observed in table 67.

Table 60: Effects of Nanoparticles and bulk particles (Cu and ZnO) on flowering and fruiting (days) of bean for 2017 cropping season.

Flowering and Metal salts	Fruiting (days) Flowering	Fruiting
nCu	43.08[c]	45.75[c]
nZnO	50.00[c]	60.00[b]
bCu	58.75[b]	62.92[b]
bZnO	64.63[b]	71.88[a]
Concentrations		
Control	56.92[a]	62.75[a]
300 mg/kg	50.92[b]	54.00[b]
600 mg/kg	52.75[b]	60.92[a]
1000 mg/kg	56.75[a]	61.83[a]
Interaction	0.001*	0.004*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 61: Interactive effect between metal salts and various concentrations on flowering and fruiting of bean for 2017 cropping season

Metal salt	**Flowering and** Flowering	**Fruiting (days)** Fruiting
Control	63.00 ± 1.00^{b}	73.30 ± 0.00^{a}
nCu 300 mg/kg	42.67 ± 0.58^{d}	46.67 ± 0.58^{c}
nCu 600 mg/kg	42.67 ± 1.15^{d}	46.67 ± 1.15^{c}
nCu 1000 mg/kg	44.00 ± 0.00^{d}	48.00 ± 0.00^{c}
nZnO 300 mg/kg	55.00 ± 0.00^{c}	60.33 ± 0.58^{b}
nZnO 600 mg/kg	54.00 ± 0.00^{c}	60.00 ± 0.00^{b}
nZnO 1000mg/kg	55.00 ± 0.00^{c}	60.00 ± 0.00^{b}
bCu 300 mg/kg	60.00 ± 0.58^{b}	65.00 ± 0.00^{b}
bCu 600 mg/kg	60.00 ± 0.00^{b}	64.33 ± 0.58^{b}
bCu 1000 mg/kg	63.00 ± 0.00^{b}	63.33 ± 0.58^{b}
bZnO 300 mg/kg	70.00 ± 0.04^{a}	75.00 ± 0.00^{a}
bZnO 600 mg/kg	70.00 ± 0.04^{a}	76.70 ± 0.58^{a}
bZnO 1000mg/kg	70.00 ± 0.04^{a}	75.00 ± 0.00^{a}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 62: Effects of Nanoparticles and bulk particles (Cu and ZnO) on flowering and fruiting (days) of bean during 2018 cropping season.

Flowering and Metal salts	Fruiting (days) Flowering	Fruiting
nCu	43.08[d]	48.75[d]
nZnO	50.75[c]	55.00[c]
bCu	58.63[b]	62.92[b]
bZnO	63.38[a]	70.19[a]
Concentrations		
Control	56.67[b]	69.83[b]
300 mg/kg	49.83[c]	59.92[c]
600 mg/kg	56.42[b]	62.25[b]
1000 mg/kg	60.50[a]	70.33[a]
Interaction	0.019*	0.040*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 63: Interactive effect between metal salts and various concentrations on flowering and fruiting (days) of bean for 2018 cropping season

Metal salt	**Flowering and** Flowering	**Fruiting (days)** Fruiting
Control	55.00 ± 0.00^{c}	56.67 ± 5.77^{cd}
nCu 300 mg/kg	42.67 ± 0.58^{d}	46.67 ± 1.15^{ef}
nCu 600 mg/kg	42.67 ± 1.15^{d}	46.67 ± 1.15^{ef}
nCu 1000 mg/kg	44.00 ± 0.00^{d}	48.00 ± 0.00^{ef}
nZnO 300 mg/kg	55.67 ± 1.00^{c}	63.33 ± 0.58^{b}
nZnO 600 mg/kg	54.00 ± 1.00^{c}	52.67 ± 2.52^{cd}
nZnO 1000mg/kg	55.00 ± 0.00^{c}	63.33 ± 0.58^{b}
bCu 300 mg/kg	60.00 ± 0.00^{b}	65.00 ± 0.00^{b}
bCu 600 mg/kg	60.00 ± 0.00^{b}	65.00 ± 0.00^{b}
bCu 1000 mg/kg	53.00 ± 0.00^{c}	65.00 ± 0.00^{b}
bZnO 300 mg/kg	68.33 ± 1.15^{a}	74.00 ± 0.00^{a}
bZnO 600 mg/kg	69.00 ± 0.00^{a}	75.33 ± 0.58^{a}
bZnO 1000mg/kg	69.00 ± 1.00^{a}	73.00 ± 1.00^{a}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 64: Effects of Nanoparticles and bulk particles (Cu and ZnO) on flowering and fruiting (days) of tomato for 2017 cropping season.

Metal salts	Flowering and Flowering	Fruiting (days) Fruiting
nCu	58.82[b]	67.58[b]
nZnO	56.92[b]	63.42[b]
bCu	67.38[a]	77.50[a]
bZnO	68.31[a]	78.63[a]
Concentrations		
Control	65.92[a]	70.25[a]
300 mg/kg	59.67[b]	68.83[b]
600 mg/kg	64.00[a]	69.50[b]
1000 mg/kg	61.17[a]	79.92[a]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 65: Interactive effect between metal salts and various concentrations on flowering and fruiting (days) of tomato for 2017 cropping season

Metal salt	**Flowering and** Flowering	**Fruiting (days)** Fruiting
Control	75.00±0.00[a]	79.00±0.00[a]
nCu 300 mg/kg	53.33±1.53[c]	66.33±0.00[b]
nCu 600 mg/kg	61.33±2.31[b]	66.33±0.00[b]
nCu 1000 mg/kg	63.33±0.58[b]	67.00±0.00[b]
nZnO 300 mg/kg	53.00±1.00[c]	60.00±0.00[b]
nZnO 600 mg/kg	60.67±4.04[b]	68.33±2.89[b]
nZnO 1000mg/kg	56.67±2.89[c]	65.00±0.00[b]
bCu 300 mg/kg	69.00±1.73[b]	72.33±2.89[a]
bCu 600 mg/kg	73.00±2.00[a]	77.00±5.77[a]
bCu 1000 mg/kg	71.00±1.73[a]	74.00±0.00[a]
bZnO 300 mg/kg	63.00±2.64[b]	73.33±5.77[a]
bZnO 600 mg/kg	63.00±2.65[b]	73.00±2.65[a]
bZnO 1000mg/kg	72.67±7.51[a]	75.00±7.51[a]

Values are mean± S. D, n= 96, values with the same superscript along treatments are not significant at p≤ 0.05, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 66: Effects of Nanoparticles and bulk particles (Cu and ZnO) on flowering and fruiting of tomato during 2018 cropping season.

Flowering and Metal salts	Fruiting (days) Flowering	Fruiting
nCu	58.75[b]	66.92[c]
nZnO	58.58[b]	70.92[b]
bCu	69.38[a]	80.25[a]
bZnO	70.81[a]	83.88[a]
Concentrations		
Control	67.83[a]	76.42[a]
300 mg/kg	62.33[a]	73.75[a]
600 mg/kg	64.75[a]	75.67[a]
1000 mg/kg	65.83[a]	77.33[a]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 67: Interactive effect between metal salts and various concentrations on flowering and fruiting (days) of tomato during 2018 cropping season

Flowering and Metal salt	Fruiting (days) Flowering	Fruiting
Control	76.67±1.53[a]	85.00±2.00[a]
nCu 300 mg/kg	53.33±2.89[c]	60.00±0.00[c]
nCu 600 mg/kg	58.00±0.00[c]	62.67±2.31[c]
nCu 1000 mg/kg	63.67±3.20[b]	70.00±0.00[b]
nZnO 300 mg/kg	53.33±0.58[c]	70.67±1.15[b]
nZnO 600 mg/kg	57.33±6.68[c]	70.00±0.00[b]
nZnO 1000mg/kg	60.00±0.00[b]	71.67±1.53[b]
bCu 300 mg/kg	74.33±4.04[a]	81.67 ±2.89[a]
bCu 600 mg/kg	76.67±1.53[a]	85.00 ±2.00[a]
bCu 1000 mg/kg	76.00±1.00[e]	83.00 ±3.00[a]
bZnO 300 mg/kg	68.33±5.77[b]	82.64±0.62[a]
bZnO 600 mg/kg	67.00±1.73[b]	82.00±0.00[a]
bZnO 1000mg/kg	66.00±1.73[b]	83.67±5.13[a]

Values are mean± S. D, n= 96, values with the same superscript along treatments are not significant at p≤ 0.05, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.18 Seed morphology in Beans during 2017 and 2018 cropping season

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO)) on number of pod per plant, number of seed per pod, number of seed per plant and pod length of bean for 2017 and 2018 cropping seasons are presented in Tables 68-75.

Table 68 shows the effects of Cu and ZnO nanoparticles and bulk particles on the number of pods per plant, number of seeds per pod, number of seed per plant and pod length in bean plant during 2017 and 2018 cropping seasons. Highest number of pods per plants was found in 600 mg/kg of the metal salt applications. Copper and zinc oxide nanoparticles treated beans produced significantly ($p \leq 0.05$) highest number of pods than the control as well in 2017 and 2018 cropping season. The nanoparticles treated beans produced higher number of pods than the bulk treated plants.

Table 69 shows the interactive effects among metal salts and various concentrations on number of pod per bean plant during 2017 and 2018 cropping seasons. The 300, 600 and 1000 mg/kg copper and zinc oxide nanoparticles and bulk copper as well as bulk zinc oxide produced more pods than the control in 2017 and 2018 cropping seasons. This shows that zinc or copper (nano or bulk) enhanced the productivity of beans.

Table 70 shows the eff ects of copper and zinc oxide on number of seeds per bean pod during 2017 and 2018 cropping season. All the bean treatments in both years had significant interactive effects on the number of seeds per pod.

Table 71 shows the interactive effects among metal salts and various concentrations on number of seeds per pod during 2017 and 2018 cropping seasons. Copper nanoparticles treated bean had higher number of seeds per pod in both years than bulk treated bean. The

highest number of pod was however produced from copper nanoparticles treatments of 300, 600 and 1000 mg/kg and zinc oxide nanoparticles 600 mg/kg.

Table 72 shows the effects of copper and zinc oxide on number of seeds per bean plant during 2017 and 2018 cropping seasons. All treatments except bulk zinc oxide in 2018 produced number of seeds per bean plant (greater than six) (> 6) than the control.

Table 73 shows the interactive effects among metal salts and various concentrations on number of seed per bean plant during 2017 and 2018 cropping seasons. Copper and zinc oxide nanoparticles treated bean plants produced more seeds per plant in both years than the control. It is worthy to note that copper nanoparticles produced the highest number of seeds (12.33 and 11.33) in both years.

Table 73 shows the effects of copper and zinc oxide on pod length during 2017 and 2018 cropping seasons. Copper and zinc oxide, bulk copper and zinc oxide all increased pod length in 2017 while all the treatments reduced the pod length in 2018 cropping season.

Table 74 shows the interactive effects among metal salts and various concentrations on number of seed per pod during 2017 and 2018 cropping seasons. All concentrations of copper nanoparticles and 300 mg/kg of zinc oxide nanoparticles produced longer pods than the control plants. In the same vein, all treatments enhanced the length of beans except bulk zinc oxide in both cropping seasons.

There was a significant interactive effect of the metal salts and concentration on number of pod per plant, number of seed per plant and pod length of beans in 2017 and 2018 cropping seasons (Tables 68-75).

Table 68: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of pod per plant during 2017 and 2018 cropping season.

Metal salts	Number of pod per plant (2017)	Number of pod per plant (2018)
nCu	3.33[a]	4.00[a]
nZnO	3.33[a]	3.83[a]
bCu	1.88[b]	1.88[b]
bZnO	2.38[b]	1.81[b]
Concentrations		
Control	2.17[c]	2.42[b]
300 mg/kg	2.83[b]	2.83[b]
600 mg/kg	3.50[a]	3.33[a]
1000 mg/kg	2.58[b]	2.92[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 69: Interactive effect between metal salts and various concentrations on number of pod per plant during 2017 and 2018 cropping season.

Metal salt	Number of pod per plant (2017)	Number of pod per plant (2018)
Control	1.25 ± 0.58^{e}	1.22 ± 0.00^{e}
nCu 300 mg/kg	4.33 ± 0.58^{a}	5.00 ± 0.00^{a}
nCu 600 mg/kg	5.00 ± 1.73^{a}	5.33 ± 0.58^{a}
nCu 1000 mg/kg	2.67 ± 0.58^{c}	4.33 ± 0.58^{a}
nZnO 300 mg/kg	4.00 ± 0.00^{a}	4.00 ± 0.00^{a}
nZnO 600 mg/kg	5.00 ± 0.00^{a}	4.33 ± 0.58^{a}
nZnO 1000mg/kg	2.00 ± 0.00^{c}	3.00 ± 0.00^{b}
bCu 300 mg/kg	1.43 ± 0.58^{de}	1.33 ± 0.20^{de}
bCu 600 mg/kg	2.33 ± 0.58^{c}	2.33 ± 0.58^{c}
bCu 1000 mg/kg	3.00 ± 0.00^{b}	3.00 ± 0.00^{b}
bZnO 300 mg/kg	1.67 ± 0.58^{de}	1.00 ± 0.00^{ef}
bZnO 600 mg/kg	1.67 ± 0.58^{de}	1.53 ± 0.18^{de}
bZnO 1000mg/kg	2.67 ± 0.58^{c}	1.30 ± 0.53^{de}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 70: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of seed per pod during 2017 and 2018 cropping season.

Metal salts	Number of seed per pod (2017)	Number of seed per pod (2018)
nCu	4.08[a]	4.25[a]
nZnO	3.92[a]	4.17[a]
bCu	3.25[b]	2.88[b]
bZnO	3.25[b]	3.06[b]
Concentrations		
Control	3.00[b]	3.00[b]
300 mg/kg	3.92[a]	3.67[a]
600 mg/kg	4.42[a]	4.25[a]
1000 mg/kg	3.17[b]	3.00[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 71: Interactive effect between metal salts and various concentrations on number of seed per pod during 2017 and 2018 cropping season.

Metal salt	Number of seed per pod (2017)	Number of seed per pod (2018)
Control	3.00 ± 0.00^{d}	3.00 ± 0.00^{d}
nCu 300 mg/kg	6.00 ± 0.00^{a}	6.00 ± 0.00^{a}
nCu 600 mg/kg	5.00 ± 0.00^{b}	5.00 ± 0.00^{b}
nCu 1000 mg/kg	3.93 ± 0.58^{c}	3.70 ± 0.00^{c}
nZnO 300 mg/kg	3.67 ± 1.15^{c}	3.67 ± 0.58^{c}
nZnO 600 mg/kg	5.00 ± 0.00^{b}	5.00 ± 1.00^{b}
nZnO 1000mg/kg	4.00 ± 0.00^{c}	5.00 ± 0.00^{b}
bCu 300 mg/kg	3.00 ± 0.00^{d}	2.00 ± 0.00^{e}
bCu 600 mg/kg	3.67 ± 0.58^{c}	3.20 ± 1.00^{c}
bCu 1000 mg/kg	3.00 ± 0.00^{d}	3.00 ± 0.00^{d}
bZnO 300 mg/kg	3.00 ± 0.00^{d}	3.00 ± 0.00^{d}
bZnO 600 mg/kg	3.67 ± 0.58^{c}	3.00 ± 0.00^{d}
bZnO 1000mg/kg	3.33 ± 0.58^{d}	3.00 ± 0.00^{d}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 72: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of seed per plant during 2017 and 2018 cropping season.

Metal salts	Number of seed per plant (2017)	Number of seed per plant (2018)
nCu	9.08[a]	8.75[a]
nZnO	7.00[b]	6.92[b]
bCu	7.13[b]	6.50[b]
bZnO	5.25[c]	4.69[c]
Concentrations		
Control	6.08[b]	6.00[b]
300 mg/kg	7.92[a]	7.42[a]
600 mg/kg	7.42[a]	6.58[a]
1000 mg/kg	6.42[b]	6.25[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 73: Interactive effect between metal salts and various concentrations on number of seed per plant bean during 2017 and 2018 cropping season.

Metal salt	Number of seed per plant (2017)	Number of seed per plant (2018)
Control	6.33 ± 0.58^{c}	6.00 ± 0.00^{c}
nCu 300 mg/kg	12.33 ± 2.52^{a}	11.33 ± 2.5^{a}
nCu 600 mg/kg	9.00 ± 1.00^{b}	8.67 ± 0.58^{b}
nCu 1000 mg/kg	8.67 ± 2.31^{b}	9.00 ± 1.73^{b}
nZnO 300 mg/kg	9.33 ± 0.58^{b}	9.00 ± 0.00^{b}
nZnO 600 mg/kg	9.00 ± 1.73^{b}	8.00 ± 1.00^{b}
nZnO 1000mg/kg	6.67 ± 0.58^{c}	6.67 ± 0.58^{c}
bCu 300 mg/kg	6.00 ± 0.00^{cd}	8.00 ± 0.00^{b}
bCu 600 mg/kg	6.67 ± 0.58^{c}	5.67 ± 0.58^{c}
bCu 1000 mg/kg	6.00 ± 1.00^{cd}	5.00 ± 0.00^{de}
bZnO 300 mg/kg	4.00 ± 0.00^{de}	3.67 ± 0.58^{de}
bZnO 600 mg/kg	5.00 ± 0.00^{de}	4.00 ± 0.00^{de}
bZnO 1000mg/kg	4.33 ± 0.58^{de}	4.33 ± 0.58^{de}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 74: Effects of Nanoparticles and bulk particles (Cu and ZnO) on pod length of beans during 2017 and 2018 cropping season.

Metal salts	Pod length (2017)	Pod length (2018)
nCu	3.59[a]	3.85[a]
nZnO	2.63[b]	3.11[b]
bCu	3.32[b]	3.05[b]
bZnO	3.09[b]	3.03[b]
Concentrations		
Control	6.08[a]	3.67[b]
300 mg/kg	7.92[a]	3.02[b]
600 mg/kg	7.42[a]	3.32[b]
1000 mg/kg	6.42[b]	3.03[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 75: Interactive effect between metal salts and various concentrations on number of seed per plant of bean during 2017 and 2018 cropping season

Metal salt	Pod length (2017)	Pod length (2018)
Control	3.00 ± 0.00^{b}	3.2 ± 0.27^{b}
nCu 300 mg/kg	4.55 ± 0.48^{a}	4.80 ± 0.00^{a}
nCu 600 mg/kg	3.39 ± 0.79^{b}	3.94 ± 0.63^{a}
nCu 1000 mg/kg	3.42 ± 0.46^{b}	3.37 ± 0.45^{b}
nZnO 300 mg/kg	3.74 ± 0.15^{a}	3.70 ± 0.00^{a}
nZnO 600 mg/kg	2.58 ± 0.11^{c}	2.90 ± 0.53^{c}
nZnO 1000mg/kg	2.17 ± 0.09^{c}	2.85 ± 0.00^{c}
bCu 300 mg/kg	3.23 ± 0.06^{b}	3.23 ± 0.00^{b}
bCu 600 mg/kg	3.50 ± 0.00^{b}	3.43 ± 0.06^{b}
bCu 1000 mg/kg	3.55 ± 0.00^{b}	3.51 ± 0.09^{b}
bZnO 300 mg/kg	2.97 ± 0.06^{c}	2.93 ± 0.12^{c}
bZnO 600 mg/kg	3.30 ± 0.10^{b}	3.00 ± 0.10^{b}
bZnO 1000mg/kg	2.33 ± 0.29^{c}	2.40 ± 0.26^{c}

Values are mean$\pm$ S. D, n=96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.19 Fruit morphology in tomato fruit

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO)) on number of fruit per plant, number of seed per fruit, number of seed per plant and fruit length of tomato for 2017 and 2018 cropping seasons are presented in Tables 76-84.

Table 76 shows the effects of Cu and ZnO of bulk and nanoparticles on number of fruits per tomato plants in 2017 and 2018 cropping season. All the treatments except bulk copper produced more fruits per tomato plants than the control. The copper nanoparticles treatment produced the highest number of fruits in both years. The interactive effects were significant in both years.

The interactive effects among metal salts and various concentrations on number of fruits per tomato plants during 2017 and 2018 cropping season are shown in table 77. All treatments produced more fruits than the control in 2017 and 2018. The most significant result for number of fruits per tomato plant was recorded in nCu treatments in both years while the least significant number of fruits per tomato plant was observed in the control plants. Therefore the nCu increased the number of fruits per plant.

Table 78 shows the effects Cu and ZnO of bulk and nanoparticles on number of seeds per tomato fruit in 2017 and 2018 cropping seasons. The nano zinc oxide treatment had more seeds per fruit of tomato. In addition, all treatments other than bulk zinc oxide produced more seeds than the control in both years. There were significant interactive effects among the metal salt and concentration on number of seed per fruit of tomato for the two cropping seasons (Table 78). In addition the most significant concentration was recorded in the nanoparticles (nCu and nZnO) treatments.

In table 79, the nano copper and nano zinc oxide produced more seeds per fruit than the control. The 300 mg/kg nano copper produced more than the control as well.

In table 80, all treatments except the bulk zinc oxide treatment produced more seeds per plant than the control in 2017 and 2018 cropping seasons. The interactive effects of the treatments were significant at $p \leq 0.05$.

In table 81, copper and zinc oxide nanoparticles together with all the concentrations of copper and zinc oxide treatments produced more number of seeds per tomato plants in 2017 and in 2018; copper nanoparticles treatments produced the highest number of seeds. The most significant concentration was from copper and zinc oxide nanoparticles. Furthermore, the control plants had results that were very close to that of bulk treated plants (Table 81).

Table 82 shows the effects of Cu and ZnO of bulk and nanoparticles on length of tomato fruit in both years. All treatments except bulk zinc oxide produced longer tomato fruits during 2017 and 2018 cropping seasons with copper nanoparticles producing the longest (2.89 cm and 2.95 cm) during 2017 and 2018 respectively.

Table 83 shows that all treatments produced longer tomato length than the control in both years.

Table 76: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of fruit per plant tomato during 2017 and 2018 cropping season.

Metal salts	Number of fruit per plant (2017)	Number of fruit per plant (2018)
nCu	2.33[a]	2.17[a]
nZnO	2.08[a]	2.08[a]
bCu	1.63[b]	1.63[b]
bZnO	2.00[b]	1.88[b]
Concentrations		
Control	1.75[b]	1.67[b]
300 mg/kg	2.08[a]	2.00[a]
600 mg/kg	2.25[a]	2.08[a]
1000 mg/kg	2.08[a]	2.08[a]
Interaction	0.000*	0.000*

n= 96, values with the same superscript across treatments are not significant at $P \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 77: Interactive effect between metal salts and various concentrations on number of fruit per plant of tomato during 2017 and 2018 cropping season.

Metal salt	Number of fruit per plant (2017)	Number of fruit per plant (2018)
Control	1.76 ± 0.58^{d}	1.0 ± 0.00^{d}
nCu 300 mg/kg	2.67 ± 0.58^{b}	3.0 ± 0.00^{a}
nCu 600 mg/kg	3.00 ± 0.00^{a}	2.33 ± 0.58^{b}
nCu 1000 mg/kg	2.33 ± 1.15^{b}	2.33 ± 0.58^{b}
nZnO 300 mg/kg	2.67 ± 0.58^{b}	2.67 ± 0.58^{b}
nZnO 600 mg/kg	2.00 ± 0.00^{c}	2.00 ± 0.00^{c}
nZnO 1000mg/kg	2.00 ± 0.00^{c}	2.00 ± 0.00^{c}
bCu 300 mg/kg	2.00 ± 0.00^{c}	1.00 ± 0.00^{e}
bCu 600 mg/kg	2.00 ± 0.00^{c}	2.00 ± 0.00^{c}
bCu 1000 mg/kg	2.00 ± 0.00^{c}	2.00 ± 0.00^{c}
bZnO 300 mg/kg	2.00 ± 0.00^{c}	1.33 ± 0.58^{d}
bZnO 600 mg/kg	2.00 ± 0.00^{c}	2.00 ± 0.00^{c}
bZnO 1000mg/kg	2.08 ± 0.52^{c}	2.00 ± 0.00^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 78: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of seed per fruit of tomato during 2017 and 2018 cropping season.

Metal salts	Number of seed per fruit of tomato (2017)	Number of seed per fruit of tomato (2018)
nCu	8.93[a]	9.17[a]
nZnO	10.00[a]	10.08[a]
bCu	8.38[b]	8.13[b]
bZnO	7.38[C]	7.25[c]
Concentrations		
Control	7.83[b]	8.08[b]
300 mg/kg	9.00[a]	8.17[b]
600 mg/kg	9.25[a]	9.67[a]
1000 mg/kg	8.25[b]	8.42[b]
Interaction	0.000*	0.001*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 79: Interactive effect between metal salts and various concentrations on number of seed per fruit of tomato for 2017 and 2018 cropping season.

Metal salt	Number of seed per fruit of tomato (2017)	Number of seed per fruit of tomato (2017)
Control	7.67 ± 0.58^{c}	8.33 ± 0.58^{c}
nCu 300 mg/kg	11.33 ± 1.15^{a}	9.00 ± 6.08^{b}
nCu 600 mg/kg	9.00 ± 0.00^{b}	11.33 ± 2.08^{a}
nCu 1000 mg/kg	7.67 ± 0.58^{c}	8.00 ± 1.00^{c}
nZnO 300 mg/kg	10.00 ± 0.00^{a}	9.67 ± 1.15^{b}
nZnO 600 mg/kg	11.33 ± 1.15^{a}	11.67 ± 1.53^{a}
nZnO 1000mg/kg	11.33 ± 1.15^{a}	11.33 ± 0.58^{a}
bCu 300 mg/kg	7.33 ± 0.58^{c}	7.00 ± 0.00^{c}
bCu 600 mg/kg	9.00 ± 0.00^{b}	8.67 ± 0.58^{c}
bCu 1000 mg/kg	7.00 ± 0.00^{c}	6.67 ± 0.58^{d}
bZnO 300 mg/kg	7.33 ± 0.58^{c}	7.00 ± 0.00^{c}
bZnO 600 mg/kg	7.67 ± 0.58^{c}	7.00 ± 0.00^{c}
bZnO 1000mg/kg	7.00 ± 0.00^{c}	7.67 ± 0.58^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 80: Effects of Nanoparticles and bulk particles (Cu and ZnO) on number of seed per plant of tomato during 2017 and 2018 cropping season.

Metal salts	Number of seed per plant of tomato (2017)	Number of seed per plant of tomato (2018)
nCu	11.75[a]	11.42[a]
nZnO	11.75[a]	11.17[a]
bCu	10.63[b]	10.13[b]
bZnO	9.94[b]	7.25[c]
Concentrations		
Control	10.00[c]	9.75[b]
300 mg/kg	11.67[a]	11.25[a]
600 mg/kg	11.42[a]	11.50[a]
1000 mg/kg	10.50[b]	10.08[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 81: Interactive effect between metal salts and various concentrations on number of seed per plant of tomato during 2017 and 2018 cropping seasons.

Metal salt	Number of seed per plant of tomato (2017)	Number of seed per plant of tomato (2017)
Control	10.00 ± 0.00^{b}	9.67 ± 0.58^{c}
nCu 300 mg/kg	14.00 ± 1.73^{a}	14.67 ± 1.15^{a}
nCu 600 mg/kg	12.00 ± 0.00^{a}	12.33 ± 1.15^{a}
nCu 1000 mg/kg	10.00 ± 0.00^{b}	9.00 ± 0.00^{c}
nZnO 300 mg/kg	13.00 ± 0.00^{a}	12.00 ± 0.00^{a}
nZnO 600 mg/kg	12.00 ± 0.00^{a}	11.33 ± 0.58^{b}
nZnO 1000mg/kg	12.00 ± 0.00^{a}	11.33 ± 0.58^{b}
bCu 300 mg/kg	10.00 ± 0.00^{b}	9.33 ± 0.57^{c}
bCu 600 mg/kg	11.00 ± 0.00^{b}	11.00 ± 0.00^{b}
bCu 1000 mg/kg	10.00 ± 0.00^{b}	10.00 ± 0.00^{b}
bZnO 300 mg/kg	9.67 ± 0.58^{c}	9.00 ± 0.00^{c}
bZnO 600 mg/kg	10.67 ± 0.58^{b}	11.33 ± 0.58^{b}
bZnO 1000mg/kg	10.00 ± 0.00^{b}	10.00 ± 0.00^{b}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 82: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fruit length of tomato during 2017 and 2018 cropping season.

Metal salts	Fruit length of tomato (2017)	Fruit length of tomato (2018)
nCu	2.89[a]	2.95[a]
nZnO	2.63[a]	2.51[a]
bCu	2.82[a]	2.58[a]
bZnO	2.36[b]	2.18[b]
Concentrations		
Control	2.52[b]	2.34[c]
300 mg/kg	2.91[a]	2.65[a]
600 mg/kg	2.58[b]	2.57[b]
1000 mg/kg	2.54[b]	2.52[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 83: Interactive effect between metal salts and various concentrations on fruit length of tomato during 2017 and 2018 cropping season.

Metal salt	Fruit length of tomato (2017)	Fruit length of tomato (2018)
Control	2.00 ± 0.00^{c}	2.00 ± 0.00^{c}
nCu 300 mg/kg	3.00 ± 0.00^{a}	3.17 ± 0.34^{a}
nCu 600 mg/kg	3.02 ± 0.19^{a}	3.12 ± 0.09^{a}
nCu 1000 mg/kg	3.04 ± 0.06^{a}	3.00 ± 0.00^{a}
nZnO 300 mg/kg	3.74 ± 0.15^{a}	2.80 ± 0.10^{b}
nZnO 600 mg/kg	2.58 ± 0.11^{b}	2.63 ± 0.06^{b}
nZnO 1000mg/kg	2.17 ± 0.00^{c}	2.63 ± 0.06^{b}
bCu 300 mg/kg	2.50 ± 0.00^{b}	2.50 ± 0.00^{b}
bCu 600 mg/kg	2.6 ± 0.00^{b}	2.50 ± 0.17^{b}
bCu 1000 mg/kg	2.70 ± 0.00^{b}	2.40 ± 0.00^{c}
bZnO 300 mg/kg	2.40 ± 0.35^{c}	2.13 ± 0.12^{c}
bZnO 600 mg/kg	2.10 ± 0.17^{c}	2.03 ± 0.06^{c}
bZnO 1000mg/kg	2.23 ± 0.06^{c}	2.07 ± 0.06^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.20 Fresh and dry weights of beans

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO) on fresh and dry weights of bean and tomato for 2017 and 2018 cropping seasons are presented in Tables 84-91.

In table 84, the nanoparticles (Cu and ZnO) treated beans produced higher fresh and dry weights than the beans in control. Concentrations of 300 and 600 mg/kg also had higher fresh and dry weights than the control in both cropping years. Both copper and zinc oxide nanoparticles including bulk copper and zinc oxide increase the fresh and dry weights of beans in 2018.

There was a significant interactive effect among the metal salt and concentration on fresh and dry weights of bean in 2017 and 2018 cropping season. The most Significant ($p \leq 0.05$) concentrations were 300 mg/kg.

In table 85, all treatments except zinc oxide nanoparticles 600 and 1000 mg/kg and bulk zinc oxide 1000 mg/kg treatments produced higher fresh and dry weights in 2017. In 2018, copper 300 mg/kg produced less weight. It is worthy to note that the bulk zinc oxide (1000 mg/kg) particles treated plants were statistically the same with that of the control.

In table 86, only copper nanoparticles and bulk copper 300 mg/kg and 1000 mg/kg treatments produced higher fresh and dry weights in 2017 cropping season. However, in 2018, all treatments had more fresh and dry weights than the control.

Table 87 shows the interactive effects among the metal salts and various concentrations on fresh and dry weights of beans during 2018 cropping seasons. All treatments produced fresh weight that was greater than the control in 2018. Furthermore, copper and zinc oxide nanoparticles and bulk copper treatments produced more dry weights of beans in 2018. It

should be noted however, that the control plants produced dry weights which are statistically the same with bulk zinc oxide treated plants.

Table 88 shows the effects of Cu and ZnO nanoparticles and bulk particles on fresh and dry weights of tomato during 2017 cropping season. Copper and zinc oxide nanoparticles and concentrations of 300 mg/kg produced higher fresh weights in 2017. In addition, copper and zinc oxide nanoparticles and concentrations of 300 and 600 mg/kg produced higher dry weights than the control treatment. The effects on dry weight matter in 2017 were significant at $p \leq 0.05$.

Table 89 shows the interactive effects among the metal salts and various concentrations on fresh and dry weights of tomato during 2017 cropping season. All treatments had higher fresh weights than the control while all others except copper nanoparticles 1000 mg/kg and bulk copper 600 and 1000 mg/kg had higher dry weights than the control in 2017.

In table 90, copper and zinc oxide nanoparticles 300 and 600 mg/kg treatments produced higher fresh weights than the control. All treatments other than bulk copper and zinc oxide produced more dry weights than the control. Therefore, copper and zinc oxide nanoparticles enhanced fresh and dry weights of tomato.

In table 91, all treatments produced greater fresh and dry weights of tomato in 2018.

Table 84: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fresh and dry weights (g) of beans during 2017 cropping season.

	Weights (g)	
Metal salts	Fresh weight (2017)	Dry weight (2017)
nCu	1.86[a]	0.89[a]
nZnO	1.55[a]	0.78[a]
bCu	1.40[b]	1.05[a]
bZnO	1.33[b]	0.99[a]
Concentrations		
Control	1.45[b]	0.79[c]
300 mg/kg	1.88[a]	1.11[a]
600 mg/kg	1.57[a]	0.98[b]
1000 mg/kg	1.24[c]	0.79[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 85: Interactive effect between metal salts and various concentrations on fresh and dry weights (g) of beans during 2017 cropping season.

Metal salt	Weights (g) Fresh weight (2017)	Dry weight (2017)
Control	1.03 ± 0.13^{c}	0.85 ± 0.60^{b}
nCu 300 mg/kg	1.53 ± 0.25^{bc}	0.51 ± 0.17^{c}
nCu 600 mg/kg	2.43 ± 0.15^{a}	1.33 ± 0.16^{a}
nCu 1000 mg/kg	1.78 ± 0.06^{b}	0.85 ± 0.06^{b}
nZnO 300 mg/kg	2.72 ± 0.23^{a}	1.38 ± 0.15^{a}
nZnO 600 mg/kg	0.80 ± 0.97^{d}	0.40 ± 0.48^{d}
nZnO 1000mg/kg	0.96 ± 0.36^{cd}	0.48 ± 0.18^{d}
bCu 300 mg/kg	1.50 ± 0.00^{bc}	1.23 ± 0.21^{a}
bCu 600 mg/kg	1.50 ± 0.00^{bc}	1.10 ± 0.17^{b}
bCu 1000 mg/kg	1.43 ± 0.06^{c}	1.27 ± 0.06^{a}
bZnO 300 mg/kg	1.77 ± 0.58^{b}	1.30 ± 0.10^{a}
bZnO 600 mg/kg	1.53 ± 0.47^{bc}	1.10 ± 0.10^{b}
bZnO 1000mg/kg	0.80 ± 0.10^{d}	0.57 ± 0.12^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 86: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fresh and dry weights (g) of beans during 2018 cropping season.

	Weights (g)	
Metal salts	Fresh weight (2018)	Dry weight (2018)
nCu	1.72[a]	1.45[a]
nZnO	1.31[b]	0.90[b]
bCu	1.46[a]	1.08[c]
bZnO	1.33[b]	0.91[b]
Concentrations		
Control	1.38[b]	0.82[b]
300 mg/kg	1.67[a]	1.12[a]
600 mg/kg	1.31[b]	1.21[a]
1000 mg/kg	1.41[b]	1.13[a]
Interaction	0.000*	0.000*

n=96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 87: Interactive effect between metal salts and various concentrations on fresh and dry weights (g) of beans during 2018 cropping season

Metal salt	Weights (g) Fresh weight (2018)	Dry weight (2018)
Control	0.78 ± 0.13^{f}	0.85 ± 0.60^{f}
nCu 300 mg/kg	1.56 ± 0.11^{bcd}	1.20 ± 0.35^{c}
nCu 600 mg/kg	1.71 ± 0.25^{bc}	2.07 ± 0.12^{a}
nCu 1000 mg/kg	1.90 ± 0.00^{b}	1.67 ± 0.12^{b}
nZnO 300 mg/kg	2.50 ± 0.00^{a}	1.23 ± 0.06^{cde}
nZnO 600 mg/kg	0.78 ± 0.97^{f}	0.73 ± 0.40^{d}
nZnO 1000mg/kg	1.02 ± 0.51^{def}	0.80 ± 0.17^{d}
bCu 300 mg/kg	1.50 ± 0.00^{bcd}	1.23 ± 0.06^{cde}
bCu 600 mg/kg	1.53 ± 0.00^{bcd}	1.23 ± 0.06^{cde}
bCu 1000 mg/kg	1.53 ± 0.06^{bcd}	1.23 ± 0.06^{cde}
bZnO 300 mg/kg	1.13 ± 0.15^{cde}	0.80 ± 0.00^{f}
bZnO 600 mg/kg	1.20 ± 0.00^{cde}	0.80 ± 0.00^{f}
bZnO 1000mg/kg	1.20 ± 0.00^{cde}	0.80 ± 0.00^{f}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 88: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fresh and dry weights (g) of tomato during 2017 cropping season.

	Weights (g)	
Metal salts	Fresh weight (2017)	Dry weight (2017)
nCu	1.50[a]	0.79[b]
nZnO	1.72[a]	1.04[a]
bCu	1.19[b]	0.67[b]
bZnO	1.13[b]	0.69[b]
Concentrations		
Control	1.39[a]	0.81[a]
300 mg/kg	1.45[a]	0.89[a]
600 mg/kg	1.36[a]	0.84[a]
1000 mg/kg	1.31[a]	0.65[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 89: Interactive effect between metal salts and various concentrations on fresh and dry weights (g) of tomato for 2017 cropping season.

Metal salt	Weights (g) Fresh weight (2017)	Fresh weight (2017)
Control	1.00 ± 0.00^{c}	0.60 ± 0.10^{b}
nCu 300 mg/kg	1.67 ± 0.15^{a}	1.10 ± 0.26^{a}
nCu 600 mg/kg	1.48 ± 0.19^{a}	0.90 ± 0.16^{b}
nCu 1000 mg/kg	1.29 ± 0.42^{b}	0.27 ± 0.06^{c}
nZnO 300 mg/kg	1.80 ± 0.00^{a}	0.97 ± 0.06^{b}
nZnO 600 mg/kg	1.90 ± 0.97^{a}	1.23 ± 0.06^{a}
nZnO 1000mg/kg	1.63 ± 0.06^{a}	1.07 ± 0.06^{a}
bCu 300 mg/kg	1.03 ± 0.06^{c}	0.60 ± 0.00^{b}
bCu 600 mg/kg	1.00 ± 0.00^{c}	0.43 ± 0.06^{c}
bCu 1000 mg/kg	1.13 ± 0.12^{b}	0.50 ± 0.10^{b}
bZnO 300 mg/kg	1.30 ± 0.26^{b}	0.90 ± 0.00^{b}
bZnO 600 mg/kg	1.07 ± 0.12^{c}	0.80 ± 0.10^{b}
bZnO 1000mg/kg	1.17 ± 0.06^{b}	0.77 ± 0.06^{b}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 90: Effects of Nanoparticles and bulk particles (Cu and ZnO) on fresh and dry weights (g) of tomato during 2018 cropping season.

	Weights (g)	
Metal salts	Fresh weight (2018)	Dry weight (2018)
nCu	1.67[a]	1.10[a]
nZnO	1.69[a]	0.89[b]
bCu	1.20[b]	0.67[c]
bZnO	1.09[b]	0.77[c]
Concentrations		
Control	1.39[a]	0.80[b]
300 mg/kg	1.45[a]	0.86[b]
600 mg/kg	1.46[a]	0.85[b]
1000 mg/kg	1.30[b]	0.96[a]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 91: Interactive effect between metal salts and various concentrations on fresh and dry weights (g) of tomato during 2018 cropping season.

Metal salt	Weights (g) Fresh weight (2018)	Dry weight (2018)
Control	1.00 ± 0.00^{b}	0.53 ± 0.13^{c}
nCu 300 mg/kg	1.93 ± 0.06^{a}	1.13 ± 0.06^{b}
nCu 600 mg/kg	1.90 ± 0.00^{a}	1.20 ± 0.00^{b}
nCu 1000 mg/kg	1.27 ± 0.06^{b}	1.20 ± 0.06^{b}
nZnO 300 mg/kg	1.87 ± 0.06^{a}	0.96 ± 0.08^{b}
nZnO 600 mg/kg	1.67 ± 0.60^{a}	0.67 ± 0.23^{b}
nZnO 1000mg/kg	1.13 ± 0.06^{b}	1.07 ± 0.06^{b}
bCu 300 mg/kg	1.00 ± 0.00^{c}	0.53 ± 0.06^{c}
bCu 600 mg/kg	1.13 ± 0.06^{b}	0.53 ± 0.06^{c}
bCu 1000 mg/kg	1.13 ± 0.12^{b}	0.57 ± 0.06^{c}
bZnO 300 mg/kg	1.00 ± 0.00^{c}	0.80 ± 0.10^{b}
bZnO 600 mg/kg	1.13 ± 0.06^{b}	1.00 ± 0.00^{b}
bZnO 1000mg/kg	1.13 ± 0.06^{b}	1.00 ± 0.00^{b}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.21 Non enzymatic antioxidant of bean during 2017 and 2018 cropping season

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO)) on non enzymatic antioxidant of bean during 2017 and 2018 cropping seasons are presented in Tables 92-107.

Table 92 shows the effects of Cu and ZnO nanoparticles and bulk particles on ascorbic acid content (mg/100 g fw) of bean during 2017 and 2018 cropping seasons. All treatments other than bulk copper produced more ascorbic acid than the control in 2017. In 2018, all treatments except bulk copper and zinc oxide produced more ascorbic acid than the control. The effects of the treatments were significant at $p \leq 0.05$.

Table 93 shows that copper nanoparticles and zinc oxide nanoparticles 600 mg/kg had more ascorbic acid than the control in 2017. In the same vein, nano copper 300, 600 and 1000 mg/kg and 600 mg/kg nano zinc oxide produced more ascorbic acid than the control in 2018.

Table 94 shows that all treatments produced higher total carotenoids in beans in both cropping years.

In table 95 all treatments produced significantly higher total carotenoids than the control. Nanoparticles increased total carotenoids significantly at $p \leq 0.05$.

Table 96 shows that copper and zinc oxide nanoparticles of 300 mg/kg concentration produced significantly greater lycopene than the control in 2017 while in 2018 copper nanoparticles of 300 mg/kg treatments produced more lycopene in beans.

In table 97, copper and zinc oxide nanoparticles of 300, 600 and 1000 mg/kg treatments produced more lycopene than other treatments and the control plants.

Table 98 shows the effects of Cu and ZnO nanoparticles and bulk particles on beta-carotene content (mg/100 g fw) of beans during 2017 and 2018 cropping seasons. Copper and zinc oxide nanoparticles of 300 and 600 mg/kg produced higher quantity of lycopene in both years. Nanoparticles enhanced the lycopene content of beans.

In table 99, beta carotene was better enhanced by copper and zinc oxide nanoparticles of 300 and 600 mg/kg respectively. The least significant beta carotene was produced from the control plants and the bulk treated plants during the two cropping seasons.

Table 100 shows the effects of Cu and ZnO nanoparticles and bulk particles on the ascorbic acid content (mg 100 g fw) of tomato. All treatments produced tomato with higher ascorbic acid content than tomato in 2017 and 2018 cropping seasons. The interactive effects were also significant at $p \leq 0.05$.

Table 101 shows that all treatments enhanced the ascorbic acid content of tomato in both cropping years. This was particularly so especially with the nanoparticles treated tomato plants.

In table 102, all except bulk copper and zinc oxide produced higher quantity of ascorbic acid than the control plants in 2017 cropping season while all treatments produced ascorbic acids that were higher than the control in 2018 cropping seasons. There were significant interactive effects among the metal salts and concentration on the ascorbic acid content of tomato in both cropping years.

Table 103 shows the interactive effects among metal salts amd various concentrations on total carotenoids content of tomato during 2017 and 2018 cropping seasons. All except bulk zinc oxide 600 and 1000 mg/kg and bulk copper 600 mg/kg produced total carotenoid that are

higher than the control in 2017 cropping season. All treatment produced higher total carotenoids than the control in 2018.

Table 104, shows that zinc oxide nanoparticles produced higher content of lycopene in both years and this was closely followed by copper nanoparticles. Concentration of 600 mg/kg was the most significant treatment producing the highest lycopene content in both years.

Table 105 shows the interactive effect among metal salts and various concentrations on lycopene content of tomato during 2017 and 2018 cropping seasons. All treatments produced higher lycopene content in tomato fruits in 2017 and 2018.

In table 106, all treatments produced more beta-carotene than the control in both cropping years. There were significant interactive effects among metal salts and various concentrations on the beta-carotene content of tomato fruit.

Table 107 shows that all treatments produced higher quantity of beta-carotene than the control plants. It is worthy to note that nanoparticles treated tomato plants enhanced the production of beta-carotene in tomato

Table 92: Effects of Nanoparticles and bulk particles (Cu and ZnO) on ascorbic acid (mg/100 g fw) content of bean during 2017 and 2018 cropping season.

Metal salts	Ascorbic acid content (mg/100 g fw) (2017)	Ascorbic acid content (mg/100 g fw) (2018)
nCu	2.32[a]	2.45[a]
nZnO	2.56[a]	2.62[a]
bCu	2.01[b]	2.00[b]
bZnO	2.11[b]	1.98[b]
Concentrations		
Control	2.08[b]	2.11[b]
300 mg/kg	2.29[a]	2.34[a]
600 mg/kg	2.31[a]	2.33[a]
1000 mg/kg	2.35[a]	2.28[a]
Interaction	0.000*	0.000*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 93: Interactive effect between metal salts and various concentrations on ascorbic acid content of bean for 2017 and 2018 cropping season.

Metal salt	Ascorbic acid content (mg/100 g fw) (2017)	Ascorbic acid content (mg/100 g fw) (2018)
Control	1.10 ± 0.00^{b}	1.10 ± 0.00^{b}
nCu 300 mg/kg	1.24 ± 0.08^{a}	1.26 ± 0.02^{a}
nCu 600 mg/kg	1.19 ± 0.07^{a}	1.23 ± 0.06^{a}
nCu 1000 mg/kg	1.20 ± 0.08^{a}	1.08 ± 0.01^{b}
nZnO 300 mg/kg	1.14 ± 0.015^{b}	1.16 ± 0.14^{a}
nZnO 600 mg/kg	1.31 ± 0.41^{a}	1.31 ± 0.39^{a}
nZnO 1000mg/kg	1.07 ± 0.01^{b}	1.06 ± 0.01^{b}
bCu 300 mg/kg	1.06 ± 0.53^{b}	1.02 ± 0.00^{b}
bCu 600 mg/kg	1.03 ± 0.01^{b}	1.02 ± 0.00^{b}
bCu 1000 mg/kg	1.03 ± 0.00^{b}	1.02 ± 0.00^{b}
bZnO 300 mg/kg	1.04 ± 0.05^{b}	1.01 ± 0.01^{b}
bZnO 600 mg/kg	1.04 ± 0.05^{b}	1.02 ± 0.01^{b}
bZnO 1000mg/kg	1.01 ± 0.01^{b}	1.01 ± 0.00^{b}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 94: Effects of Nanoparticles and bulk particles (Cu and ZnO) on total carotenoid content of bean during 2017 and 2018 cropping season.

Metal salts	Total carotenoid content (mg/100 g fw) (2017)	Total carotenoid content (mg/100 g fw) (2018)
nCu	2.53[a]	2.49[a]
nZnO	2.69[a]	2.52[a]
bCu	2.45[b]	2.29[b]
bZnO	2.35[b]	2.30[b]
Concentrations		
Control	2.43[c]	2.14[c]
300 mg/kg	2.73[a]	2.79[a]
600 mg/kg	2.69[a]	2.68[a]
1000 mg/kg	2.58[a]	2.46[b]
Interaction	0.002*	0.001*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 95: Interactive effect between metal salts and various concentrations on total carotenoid content (mg/100 g fw) of bean during 2017 and 2018 cropping season.

Metal salt	Total carotenoid content (mg/100 g fw)	Total carotenoid content (mg/100 g fw)
Control	1.97 ± 0.12^{c}	1.50 ± 0.20^{c}
nCu 300 mg/kg	2.77 ± 0.02^{a}	2.90 ± 0.01^{a}
nCu 600 mg/kg	2.71 ± 0.01^{a}	2.89 ± 0.16^{a}
nCu 1000 mg/kg	2.66 ± 0.01^{a}	2.69 ± 0.06^{a}
nZnO 300 mg/kg	2.70 ± 0.01^{a}	2.72 ± 0.07^{a}
nZnO 600 mg/kg	2.61 ± 0.01^{a}	2.52 ± 0.13^{a}
nZnO 1000mg/kg	2.52 ± 0.02^{a}	2.96 ± 0.05^{a}
bCu 300 mg/kg	2.05 ± 0.04^{b}	2.04 ± 0.12^{b}
bCu 600 mg/kg	2.09 ± 0.04^{b}	2.08 ± 0.03^{b}
bCu 1000 mg/kg	2.02 ± 0.03^{b}	2.00 ± 0.09^{b}
bZnO 300 mg/kg	2.07 ± 0.01^{b}	2.01 ± 0.08^{b}
bZnO 600 mg/kg	2.12 ± 0.16^{b}	2.04 ± 0.11^{b}
bZnO 1000mg/kg	2.01 ± 0.02^{b}	2.09 ± 0.32^{b}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 96: Effects of Nanoparticles and bulk particles (Cu and ZnO) on lycopene (mg/100 g fw) content of bean during 2017 and 2018 cropping season.

Metal salts	Lycopene (mg/100 g fw) (2017)	Lycopene (mg/100 g fw) (2018)
nCu	1.46^{a}	0.16^{b}
nZnO	0.39^{b}	0.14^{b}
bCu	0.04^{c}	0.04^{c}
bZnO	0.04^{c}	0.03^{c}
Concentrations		
Control	0.02^{b}	0.01^{b}
300 mg/kg	0.12^{a}	0.14^{a}
600 mg/kg	0.04^{b}	0.04^{b}
1000 mg/kg	0.04^{b}	0.04^{b}
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 97: Interactive effect between metal salts and various concentrations on lycopene content (mg/100 g fw) of bean during 2017 and 2018 cropping season.

Metal salt	lycopene content (mg/100 g fw) (2017)	lycopene content (mg/100 g fw) (2018)
Control	0.05 ± 0.01^{c}	0.05 ± 0.01^{c}
nCu 300 mg/kg	2.73 ± 0.02^{a}	2.74 ± 0.15^{a}
nCu 600 mg/kg	2.71 ± 0.01^{a}	2.08 ± 0.01^{b}
nCu 1000 mg/kg	2.66 ± 0.01^{a}	2.06 ± 0.01^{b}
nZnO 300 mg/kg	2.70 ± 0.01^{a}	2.15 ± 0.01^{b}
nZnO 600 mg/kg	2.61 ± 0.01^{a}	2.13 ± 0.01^{b}
nZnO 1000mg/kg	2.52 ± 0.02^{a}	2.15 ± 0.00^{b}
bCu 300 mg/kg	2.05 ± 0.04^{b}	2.03 ± 0.00^{b}
bCu 600 mg/kg	2.05 ± 0.04^{b}	2.03 ± 0.01^{b}
bCu 1000 mg/kg	2.02 ± 0.03^{b}	2.03 ± 0.00^{b}
bZnO 300 mg/kg	2.09 ± 0.01^{b}	2.03 ± 0.00^{b}
bZnO 600 mg/kg	2.02 ± 0.16^{b}	2.03 ± 0.01^{b}
bZnO 1000mg/kg	2.01 ± 0.02^{b}	2.02 ± 0.00^{b}

Values are mean $\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 98: Effects of Nanoparticles and bulk particles (Cu and ZnO) on Beta-carotene content (mg/100 g fw) of bean during 2017 and 2018 cropping season.

Metal salts	Beta- carotene (mg/100 g fw) (2017)	Beta- carotene (2018) (mg/100 g fw)
nCu	1.13^{a}	1.17^{a}
nZnO	1.14^{a}	1.16^{a}
bCu	1.07^{b}	1.05^{b}
bZnO	1.03^{b}	1.02^{b}
Concentrations		
Control	1.09^{b}	1.08^{b}
300 mg/kg	1.09^{b}	1.13^{a}
600 mg/kg	1.14^{a}	1.15^{a}
1000 mg/kg	1.05^{b}	1.04^{b}
Interaction	0.001*	0.000*

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p\leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 99: Interactive effect between metal salts and various concentrations on Beta-carotene content (mg/100 g fw) of bean for 2017 and 2018 cropping season.

Metal salt	Beta- carotene content (mg/100 g fw) (2017)	Beta- carotene content (mg/100 g fw) (2018)
Control	1.10 ± 0.00^{b}	1.10 ± 0.00^{b}
nCu 300 mg/kg	1.16 ± 0.08^{a}	1.26 ± 0.02^{a}
nCu 600 mg/kg	1.19 ± 0.08^{a}	1.23 ± 0.06^{a}
nCu 1000 mg/kg	1.17 ± 0.01^{a}	1.18 ± 0.001^{a}
nZnO 300 mg/kg	1.09 ± 0.01^{b}	1.16 ± 0.14^{a}
nZnO 600 mg/kg	1.31 ± 0.41^{a}	1.31 ± 0.39^{a}
nZnO 1000mg/kg	1.07 ± 0.01^{b}	1.06 ± 0.01^{b}
bCu 300 mg/kg	1.06 ± 0.05^{b}	1.02 ± 0.00^{b}
bCu 600 mg/kg	1.03 ± 0.01^{b}	1.02 ± 0.00^{b}
bCu 1000 mg/kg	1.03 ± 0.01^{b}	1.01 ± 0.01^{b}
bZnO 300 mg/kg	1.04 ± 0.05^{b}	1.01 ± 0.01^{b}
bZnO 600 mg/kg	1.02 ± 0.00^{b}	1.02 ± 0.01^{b}
bZnO 1000mg/kg	1.01 ± 0.01^{b}	1.01 ± 0.00^{b}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 100: Effects of Nanoparticles and bulk particles (Cu and ZnO) on content of ascorbic acid (mg/100 g fw) of tomato during 2017 and 2018 cropping season.

Metal salts	Ascorbic acid (2017) (mg/100 g fw)	Ascorbic acid (mg/100 g fw) (2018)
nCu	7.17[a]	7.06[a]
nZnO	7.13[a]	7.09[a]
bCu	4.16[b]	4.21[b]
bZnO	4.27[b]	4.32[b]
Concentrations		
Control	4.12[b]	4.16[b]
300 mg/kg	6.25[a]	6.31[a]
600 mg/kg	6.20[a]	6.07[a]
1000 mg/kg	6.18[a]	6.18[a]
Interaction	0.000*	0.000*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 101: Interactive effect between metal salts and various concentrations on ascorbic acid content (mg/100 g fw) of tomato during 2017 and 2018 cropping season.

Metal salt	Ascorbic acid (2017) (mg/100 g fw)	Ascorbic acid (mg/100 g fw) (2018)
Control	4.00 ± 0.00^{d}	4.10 ± 0.00^{d}
nCu 300 mg/kg	9.10 ± 0.00^{a}	9.00 ± 0.06^{a}
nCu 600 mg/kg	8.03 ± 0.15^{b}	7.64 ± 0.61^{c}
nCu 1000 mg/kg	7.53 ± 0.06^{c}	7.47 ± 0.23^{c}
nZnO 300 mg/kg	7.61 ± 0.14^{c}	7.61 ± 0.13^{c}
nZnO 600 mg/kg	8.17 ± 0.15^{b}	8.13 ± 0.12^{b}
nZnO 1000mg/kg	8.60 ± 0.10^{b}	8.47 ± 0.06^{b}
bCu 300 mg/kg	4.25 ± 0.00^{d}	4.25 ± 0.01^{d}
bCu 600 mg/kg	4.10 ± 0.02^{d}	4.20 ± 0.01^{d}
bCu 1000 mg/kg	4.09 ± 0.01^{d}	4.43 ± 0.15^{d}
bZ nO 300 mg/kg	4.06 ± 0.01^{d}	4.37 ± 0.32^{d}
bZnO 600 mg/kg	4.51 ± 0.44^{d}	4.26 ± 0.38^{d}
bZnO 1000mg/kg	4.51 ± 0.44^{d}	4.35 ± 0.35^{d}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 102: Effects of Nanoparticles and bulk particles (Cu and ZnO) on total carotenoid (mg/100 g fw) content of tomato during 2017 and 2018 cropping season.

Metal salts	Total carotenoid (mg/100 g fw) (2017)	Total carotenoid (2018) (mg/100 g fw)
nCu	6.63[a]	6.54[a]
nZnO	6.76[a]	6.45[a]
bCu	3.69[b]	3.68[b]
bZnO	3.71[b]	3.62[b]
Concentrations		
Control	5.00[a]	3.47[b]
300 mg/kg	5.74[a]	5.75[a]
600 mg/kg	5.85[a]	5.80[a]
1000 mg/kg	5.86[a]	5.70[a]
Interaction	0.000*	0.000*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 103: Interactive effect between metal salts and various concentrations on total carotenoid (mg/100 g fw) content of tomato during 2017 and 2018 cropping season.

Metal salt	Total carotenoid (2017) (mg/100 g fw)	Total carotenoid (2018) (mg/100 g fw)
Control	3.60 ± 0.18^{c}	3.33 ± 0.11^{c}
nCu 300 mg/kg	7.53 ± 0.12^{b}	7.56 ± 0.10^{b}
nCu 600 mg/kg	7.72 ± 0.24^{b}	7.61 ± 0.18^{b}
nCu 1000 mg/kg	7.70 ± 0.17^{b}	7.66 ± 0.15^{b}
nZnO 300 mg/kg	8.00 ± 0.00^{a}	7.77 ± 0.26^{b}
nZnO 600 mg/kg	8.60 ± 0.66^{a}	8.30 ± 0.26^{a}
nZnO 1000mg/kg	6.83 ± 2.89^{b}	6.67 ± 2.83^{b}
bCu 300 mg/kg	3.74 ± 0.06^{c}	3.86 ± 0.22^{c}
bCu 600 mg/kg	3.59 ± 0.09^{c}	3.61 ± 0.08^{c}
bCu 1000 mg/kg	3.82 ± 0.27^{c}	3.50 ± 0.00^{c}
bZnO 300 mg/kg	3.68 ± 0.26^{c}	3.86 ± 0.19^{c}
bZnO 600 mg/kg	3.49 ± 0.04^{c}	3.67 ± 0.00^{c}
bZnO 1000mg/kg	3.50 ± 0.00^{c}	3.50 ± 0.00^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 104: Effects of Nanoparticles and bulk particles (Cu and ZnO) on lycopene content of tomato during 2017 and 2018 cropping season.

Metal salts	Lycopene (mg/100 g fw) (2017)	Lycopene (mg/100 g fw) (2018)
nCu	5.46^{b}	4.96^{b}
nZnO	6.76^{a}	7.02^{a}
bCu	2.21^{c}	2.49^{c}
bZnO	3.31^{c}	2.34^{c}
Concentrations		
Control	3.28^{c}	3.27^{c}
300 mg/kg	4.38^{b}	4.48^{ab}
600 mg/kg	4.55^{b}	4.72^{a}
1000 mg/kg	4.95^{a}	4.28^{b}
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 105: Interactive effect between metal salts and various concentrations on lycopene content of tomato during 2017 and 2018 cropping season.

Metal salt	Lycopene (mg/100 g fw) (2017)	Lycopene (mg/100 g fw) (2018)
Control	2.00 ± 0.00^{f}	2.00 ± 0.00^{f}
nCu 300 mg/kg	5.83 ± 0.06^{c}	5.83 ± 0.00^{c}
nCu 600 mg/kg	5.87 ± 0.15^{c}	5.86 ± 0.15^{c}
nCu 1000 mg/kg	5.76 ± 0.15^{c}	5.77 ± 0.15^{c}
nZnO 300 mg/kg	6.73 ± 0.06^{b}	6.73 ± 0.06^{b}
nZnO 600 mg/kg	7.87 ± 1.67^{a}	7.87 ± 1.67^{b}
nZnO 1000mg/kg	9.67 ± 0.58^{a}	9.67 ± 0.06^{a}
bCu 300 mg/kg	2.73 ± 0.24^{d}	2.39 ± 0.01^{e}
bCu 600 mg/kg	2.60 ± 0.35^{d}	2.27 ± 0.03^{e}
bCu 1000 mg/kg	2.23 ± 0.27^{e}	2.21 ± 0.01^{e}
bZnO 300 mg/kg	2.40 ± 0.00^{d}	2.34 ± 0.01^{e}
bZnO 600 mg/kg	2.23 ± 0.01^{e}	2.21 ± 0.01^{e}
bZnO 1000mg/kg	2.30 ± 0.00^{e}	2.17 ± 0.01^{e}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 106: Effects of Nanoparticles and bulk particles (Cu and ZnO) on Beta-carotene (mg/100 g fw) content of tomato during 2017 and 2018 cropping season.

Metal salts	Beta-carotene (mg/100 g fw) (2017)	Beta-carotene (mg/100 g fw) (2018)
nCu	6.04[a]	5.98[a]
nZnO	6.15[a]	6.03[a]
bCu	2.31[b]	2.30[b]
bZnO	2.49[b]	2.38[b]
Concentrations		
Control	2.08[c]	2.06[c]
300 mg/kg	4.75[b]	4.61[b]
600 mg/kg	5.18[a]	5.09[a]
1000 mg/kg	5.05[a]	4.95[a]
Interaction	0.000*	0.000*

n=96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 107: Interactive effect between metal salts and various concentrations on Beta-carotene content of tomato during 2017 and 2018 cropping season.

Metal salt	Beta-carotene (mg/100 g fw) (2017)	Beta-carotene (mg/100 g fw) (2018)
Control	2.07 ± 0.12^{e}	2.07 ± 0.12^{e}
nCu 300 mg/kg	7.50 ± 0.17^{a}	7.37 ± 0.06^{a}
nCu 600 mg/kg	8.13 ± 0.23^{a}	8.20 ± 0.06^{a}
nCu 1000 mg/kg	6.47 ± 0.06^{b}	6.30 ± 026^{b}
nZnO 300 mg/kg	6.80 ± 0.10^{b}	6.37 ± 0.06^{b}
nZnO 600 mg/kg	7.70 ± 0.10^{a}	7.43 ± 0.06^{a}
nZnO 1000mg/kg	8.00 ± 0.00^{a}	8.20 ± 0.10^{a}
bCu 300 mg/kg	2.32 ± 0.02^{d}	2.37 ± 0.06^{d}
bCu 600 mg/kg	2.67 ± 0.12^{d}	2.60 ± 0.10^{d}
bCu 1000 mg/kg	3.07 ± 0.06^{c}	2.97 ± 0.15^{c}
bZnO 300 mg/kg	2.37 ± 0.11^{d}	2.33 ± 0.06^{d}
bZnO 600 mg/kg	2.21 ± 0.08^{d}	2.13 ± 0.06^{d}
bZnO 1000mg/kg	2.67 ± 0.15^{d}	2.37 ± 0.12^{d}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

4.22 Enzymatic antioxidants in Bean and Tomato during 2017 and 2018 cropping seasons

Descriptive statistics of the effects of bulk and nanoparticles (Cu and ZnO)) on enzymatic antioxidant of bean and tomato for 2017 and 2018 cropping seasons are presented in Tables 108-119

Table 108 shows the effects of Cu and ZnO bulk and nanoparticles on enzyme activities of ascorbate peroxidase (APX) (µml/mg) in bean and tomato during 2017 and 2018 cropping seasons. In 2017, only copper bulk and copper nanoparticles produced more APX than the control. It was copper nanoparticles and bulk copper treatments that produced more APX. There were significant ($p \leq 0.05$) interactive effects among the metal salts and various concentrations on the productions on the production of ascorbate peroxidase during the two cropping seasons.

Table 109 shows that all treatments produced less APX than the control during the two cropping seasons. There was a significant ($p \leq 0.05$) interactive effects in the metal salts and concentrations of the nanoparticles used on the antioxidant enzyme activities on the APX for the two growing seasons. The most significant salts ($p \leq 0.05$) were with copper nanoparticles and the control plants while the least significant ($p \leq 0.05$) data were from the bulk treated plants.

Table 110 shows APX of tomato during 2017 and 2018 cropping seasons. All treatments produced lesser APX than the control. Copper nanoparticles enhanced the production of more APX. The same trend was also observed in table 111.

Table 112 shows the effects of Cu and ZnO bulk and nanoparticles on enzyme activities of catalase (CAT) (µml/mg). All treatments produced more CAT than the control in beans.

Concentrations increased significantly the antioxidant enzyme activities of catalase (CAT) in bean during 2017 and 2018 cropping seasons.

Table 113 shows that all treatments significantly ($p \leq 0.05$) increased the antioxidant enzyme activities of CAT in beans. Enhanced production of more CAT than the control in 2017 and 2018 was observed.

Table 114 shows that there were significant interactive effects among the metal salts and concentration on the production of CAT in tomato during 2017 and 2018 cropping seasons from the control.

Table 115 shows that all treatments significantly ($p \leq 0.05$) increased the antioxidants enzyme activities of CAT in tomato.

Table 116 shows that all treatments produced less superoxide dismutase (SOD) than the control. This shows that the treatment reduced the activities of SOD significantly ($p \leq 0.05$).

The interactive effects among the metal salts and various concentrations on antioxidants enzymes activities of SOD in beans during 2017 and 2018 cropping years is presented in table 117. Only copper nanoparticles 300 mg/kg statistically had same SOD activities with the control in 2017 cropping season. However, the control activities were numerically greater than other treatments. In 2018, zinc oxide nanoparticles 300 and 1000 mg/kg increased the SOD activities numerically.

In table 118, the nanoparticles and bulk particles produced more SOD activities than various concentrations; all treatments had higher SOD activities than the control. Simmilar trend was however observed in table 119.

Table 120 shows the effects of Cu and ZnO nanoparticles and bulk particles on stress attributes or activities of malondialdehyde (MDA) in beans during 2017 and 2018 cropping seasons. All the nanoparticles and bulk particles treated beans had significantly higher ($p \leq 0.05$) MDA in bean during 2017 and 2018 cropping seasons.

In table 121, all treatments the treated bean had significantly ($p \leq 0.05$) higher activities than the control in 2017 and 2018 cropping seasons. There were significant ($p \leq 0.05$) interactive effects among the nanoparticles and bulk copper and zinc oxide in bean plants.

In table 122, all treatments produced more MDA than the control in both years and there was an increased enzyme activity with increased concentrations.

In table 123, nanoparticles treated bean produced higher content of hydrogen peroxide than the bulk treated plants. In addition, zinc oxide treated plants produced a higher content of hydrogen peroxide than the copper treated plants.

An increased activity with increased concentrations was also observed during the period of experimentation. All treatments had significantly ($p \leq 0.05$) higher hydrogen peroxide activities in beans than the control in both cropping years. The interactive effects were also highly significant.

Table 124 shows that hydrogen peroxide activities was significantly ($p \leq 0.05$) higher in all treatments in 2017 and 2018 cropping seasons. Copper and zinc oxide nanoparticles and bulk particles seem to increase the activities of hydrogen peroxide in beans. Furthermore, increased activities were enhanced with increased concentrations.

Table 125 shows the effects of Cu and ZnO nanoparticles and bulk particles on stress attributes hydrogen peroxide in tomato during 2017 and 2018 cropping seasons.

Nanoparticles treated plants produced higher contents of hydrogen peroxide in tomato plants than bulk treated tomato plants. All treatments increased hydrogen peroxide activities in tomato and there were also significant interactive effects amond the metal salts and various concentrations on the stress activities of hydrogen peroxide in tomato plants.

In table 126, all treatments were higher than the control with respect to hydrogen peroxide activities in both cropping years.

Table 127 shows that all treatments reduced the induction of stress enzymes of proline in beans than the control plants. In addition, treatments concentration dependent increase was also observed; which means that concentrations reduced proline activities in bean plant during 2017 and 2018 cropping years. Significant interactive effects were also observed throughout the period of the experimentation. Similar trends were observed in table 128.

In table 129, copper and zinc oxide nanoparticles treated tomato plants produced more proline than what was produced in the control plants.

In table 130, various concentrations reduced the activities of proline than the control. Significant interactive effects were observed as well in tomato planted in 2017 and 2018 cropping years.

Table 131 shows that all treatments statistically produced same starch with the control but these were numerically different in both cropping years.

Table 132 shows that all treatments reduced the starch contents in beans. This means that all the treatments do not enhance the production of starch in beans in both years.

Table 133 shows that nanoparticles treated plants produced same starch as the control in both years. All the concentrations produced lesser starch content with respect to the control in both years.

Table 134 shows the interactive effect among metal salts and various concentrations on starch content of tomato during 2017 and 2018 cropping seasons. Copper nanoparticles treated plants produced starch which is statistically the same with the control plants in both cropping seasons.

Table 135 shows that copper nanoparticles treated beans produced protein that is equal to the control statistically but the control numerically contained /has more protein content. All concentrations reduced protein content in beans.

Table 136 shows that various concentrations decrease the content of protein in beans in 2017 and 2018 cropping years. Concentrations produced reduced protein contents statistically in bean. The same trends were also observed in tables 137 and 138.

Tables 140-143 shows the effects of Cu and ZnO nanoparticles and bulk particles on copper and zinc uptake in bean plant during 2017 and 2018 cropping seasons. Accumulation of either the copper or zinc salts was highest in the root of both bean and tomato plants.

Table 108: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of ascorbate peroxidise (APX) (µml/mg) of bean during 2017 and 2018 cropping seasons.

Metal salts	APX (µml/mg) (2017)	APX (µml/mg) (2018)
nCu	27.32[a]	26.16[a]
nZnO	21.43[b]	20.51[b]
bCu	29.98[a]	25.76[a]
bZnO	11.07[c]	11.06[c]
Concentrations		
Control	23.33[a]	17.02[b]
300 mg/kg	18.86[a]	18.93[a]
600 mg/kg	19.28[a]	18.07[a]
1000 mg/kg	18.00[a]	17.85[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 109: Interactive effect between metal salts and various concentrations antioxidant enzyme activities of ascorbate peroxidise (APX) (µml/mg) of bean 2017 and 2018 cropping seasons

Metal salt	APX (µml/mg) (2017)	APX (µml/mg) (2018)
Control	39.00 ± 1.00^{a}	39.00 ± 1.00^{a}
nCu 300 mg/kg	29.83 ± 0.76^{bc}	29.77 ± 0.64^{bc}
nCu 600 mg/kg	24.67 ± 2.89^{cd}	20.64 ± 0.35^{de}
nCu 1000 mg/kg	15.79 ± 1.06^{efgh}	15.23 ± 0.20^{efgh}
nZnO 300 mg/kg	36.33 ± 1.52^{b}	26.67 ± 1.53^{cd}
nZnO 600 mg/kg	24.67 ± 0.58^{cd}	25.00 ± 1.00^{cd}
nZnO 1000mg/kg	17.33 ± 2.08^{ef}	23.00 ± 2.65^{cd}
bCu 300 mg/kg	20.17 ± 1.18^{ef}	20.40 ± 16.97^{ef}
bCu 600 mg/kg	11.12 ± 0.73^{gh}	11.30 ± 0.52^{gh}
bCu 1000 mg/kg	10.33 ± 2.08^{gh}	11.15 ± 0.26^{gh}
bZnO 300 mg/kg	9.10 ± 1.59^{gh}	8.90 ± 1.39^{ij}
bZnO 600 mg/kg	16.67 ± 1.53^{fg}	15.33 ± 0.58^{fg}
bZnO 1000mg/kg	11.33 ± 1.15^{gh}	12.00 ± 0.00^{gh}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 110: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of ascorbate peroxidise (APX) (µml/mg) of tomato during 2017 and 2018 cropping seasons.

Metal salts	APX (µml/mg) (2017)	APX (µml/mg) (2018)
nCu	38.39[a]	37.64[a]
nZnO	32.33[a]	28.23[b]
bCu	37.25[a]	26.63[b]
bZnO	26.19[b]	26.63[b]
Concentrations		
Control	64.67[a]	63.58[a]
300 mg/kg	32.69[b]	29.12[b]
600 mg/kg	19.14[c]	20.04[c]
1000 mg/kg	13.98[d]	15.62[c]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 111: Interactive effect between metal salts and various concentrations antioxidant enzyme activities of ascorbate peroxidise (APX) (µml/mg) of tomato during 2017 and 2018 cropping seasons.

Metal salt	APX (µml/mg) (2017)	APX (µml/mg) (2018)
Control	64.67 ±8.96^{a}	63.67±10.97^{a}
nCu 300 mg/kg	36.08±4.63^{b}	39.67±3.06^{b}
nCu 600 mg/kg	27.88±11.93^{cd}	24.83±12.34^{cd}
nCu 1000 mg/kg	17.95±1.71^{ef}	22.38±4.72^{cd}
nZnO 300 mg/kg	38.00±2.00^{b}	27.49±7.33^{cd}
nZnO 600 mg/kg	24.00±1.70^{cd}	17.67±3.2^{ef}
nZnO 1000mg/kg	9.67±0.58^{gh}	14.08±0.93^{ef}
bCu 300 mg/kg	25.00±5.00^{cd}	28.67±1.15^{cd}
bCu 600 mg/kg	14.00±0.73^{ef}	23.33±3.51^{cd}
bCu 1000 mg/kg	10.00±0.00^{gh}	16.00 ±2.65^{ef}
bZnO 300 mg/kg	31.67±1.53^{b}	30.67 ±3.79^{b}
bZnO 600 mg/kg	17.67±2.52^{ef}	14.3±2.81^{ef}
bZnO 1000mg/kg	11.33±3.21^{gh}	10.00±2.00^{gh}

Values are mean± S. D, n= 96, values with the same superscript along treatments are not significant at p≤ 0.05, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 112: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of catalase (CAT) (µml/mg) in bean during 2017 and 2018 cropping seasons.

Metal salts	CAT (µml/mg) (2017)	CAT (µml/mg) (2018)
nCu	47.63^{a}	46.67^{a}
nZnO	45.26^{a}	44.38^{a}
bCu	27.24^{c}	27.88^{c}
bZnO	38.87^{b}	39.56^{b}
Concentrations		
Control	25.30^{d}	26.58^{d}
300 mg/kg	39.45^{c}	28.62^{c}
600 mg/kg	46.54^{b}	45.58^{b}
1000 mg/kg	52.91^{a}	51.61^{a}
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 113: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of catalase (CAT) (µml/mg) in bean during 2017 and 2018 cropping seasons.

Metal salt	CAT (µml/mg) (2017)	CAT (µml/mg) (2018)
Control	25.30 ± 0.30^{gh}	27.00 ± 1.73^{gh}
nCu 300 mg/kg	46.10 ± 0.26^{d}	42.68 ± 2.40^{d}
nCu 600 mg/kg	51.80 ± 0.89^{c}	50.89 ± 1.17^{c}
nCu 1000 mg/kg	67.30 ± 2.01^{a}	66.11 ± 2.01^{a}
nZnO 300 mg/kg	45.37 ± 0.38^{d}	43.13 ± 1.51^{d}
nZnO 600 mg/kg	49.37 ± 0.55^{d}	50.13 ± 0.12^{c}
nZnO 1000mg/kg	61.00 ± 1.00^{b}	59.00 ± 2.65^{b}
bCu 300 mg/kg	27.33 ± 3.06^{gh}	27.00 ± 1.73^{gh}
bCu 600 mg/kg	30.00 ± 0.00^{ef}	28.00 ± 1.00^{ef}
bCu 1000 mg/kg	35.00 ± 1.73^{ef}	31.67 ± 0.58^{ef}
bZnO 300 mg/kg	39.00 ± 1.73^{d}	40.67 ± 3.21^{d}
bZnO 600 mg/kg	55.00 ± 0.00^{c}	52.33 ± 0.58^{c}
bZnO 1000mg/kg	48.33 ± 2.08^{d}	49.67 ± 2.31^{d}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 114: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of catalase (CAT) (µml/mg) in tomato during 2017 and 2018 cropping seasons.

Metal salts	CAT (µml/mg) (2017)	CAT (µml/mg) (2018)
nCu	23.06[a]	20.95[a]
nZnO	21.45[a]	24.22[a]
bCu	13.24[c]	13.13[c]
bZnO	23.72[a]	21.81[a]
Concentrations		
Control	11.45[c]	10.31[c]
300 mg/kg	16.99[b]	16.76[b]
600 mg/kg	18.48[b]	19.64[b]
1000 mg/kg	38.03[a]	36.29[a]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 115: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of catalase (CAT) (µml/mg) in tomato during 2017 and 2018 cropping seasons.

Metal salt	CAT (µml/mg) (2017)	CAT (µml/mg) (2018)
Control	11.48 ± 1.35^{fg}	10.34 ± 0.06^{fg}
nCu 300 mg/kg	15.83 ± 1.27^{fg}	15.33 ± 0.11^{fg}
nCu 600 mg/kg	19.42 ± 0.12^{de}	17.89 ± 1.15^{de}
nCu 1000 mg/kg	45.51 ± 0.53^{a}	40.22 ± 0.04^{ab}
nZnO 300 mg/kg	20.83 ± 1.99^{de}	22.70 ± 3.06^{de}
nZnO 600 mg/kg	18.33 ± 1.53^{de}	19.33 ± 0.58^{de}
nZnO 1000mg/kg	35.25 ± 16.10^{bc}	44.63 ± 3.84^{a}
bCu 300 mg/kg	13.97 ± 1.70^{fg}	13.00 ± 1.00^{fg}
bCu 600 mg/kg	14.51 ± 1.42^{fg}	18.33 ± 1.53^{de}
bCu 1000 mg/kg	41.37 ± 4.23^{ab}	30.33 ± 8.08^{cd}
bZnO 300 mg/kg	17.33 ± 0.53^{de}	16.00 ± 0.00^{fg}
bZnO 600 mg/kg	21.67 ± 1.53^{de}	23.00 ± 2.65^{de}
bZnO 1000mg/kg	30.00 ± 0.00^{cd}	30.00 ± 0.00^{cd}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 116: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of superoxide dismutase (SOD) (µml/mg) in bean during 2017 and 2018 cropping seasons.

Metal salts	SOD (µml/mg) (2017)	SOD (µml/mg) (2018)
nCu	1660.50[a]	1524.67[b]
nZnO	1491.59[b]	1979.19[a]
bCu	1178.05[c]	1178.63[c]
bZnO	782.95[d]	786.43[d]
Concentrations		
Control	2033.12[a]	2013.03[a]
300 mg/kg	1193.92[b]	1277.08[b]
600 mg/kg	927.94[c]	1036.39[c]
1000 mg/kg	826.40[d]	1011.67[c]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 117: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of superoxide dismutase (SOD) (µml/mg) in bean during 2017 and 2018 cropping seasons.

Metal salt	SOD (µml/mg) (2017)	SOD (µml/mg) (2018)
Control	2033.12 ±41.05^{a}	2006.33±30.99^{a}
nCu 300 mg/kg	1916.23±74.99^{a}	1545.67±39.58^{c}
nCu 600 mg/kg	1350.00±259.81^{bc}	1380.00±10.00^{bc}
nCu 1000 mg/kg	1342.67±39.51^{bc}	1166.67±57.74^{d}
nZnO 300 mg/kg	1444. 46 ±441.00^{bc}	2197.67±64.79^{a}
nZnO 600 mg/kg	1374.85±335.69^{bc}	1673.10±84.00^{bc}
nZnO1000mg/kg	1113.94±285.01^{c}	2039.66±33.87^{a}
bCu 300 mg/kg	748.33±28.90^{d}	706.67±11.55^{d}
bCu 600 mg/kg	539.48±0.89^{de}	645.00±5.00^{de}
bCu 1000 mg/kg	454.33±14.19^{de}	436.67 ±5.77^{de}
bZnO 300 mg/kg	666.67±104.08^{de}	658.33 ±90.04^{de}
bZnO 600 mg/kg	447.44±2.88^{de}	447.48±7.00^{de}
bZnO 1000mg/kg	394.67±6.81^{ef}	403.67±2.50^{ef}

Values are mean± S. D, n= 96, values with the same superscript along treatments are not significant at p≤ 0.05, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 118: Effects of Nanoparticles and bulk particles (Cu and ZnO) on antioxidant enzyme activities of superoxide dismutase (SOD) (µml/mg) in tomato during 2017 and 2018 cropping seasons.

Metal salts	SOD (µml/mg) (2017)	SOD (µml/mg) (2018)
nCu	469.47[a]	491.11[a]
nZnO	494.64[a]	463.86[a]
bCu	364.75[b]	370.38[b]
bZnO	223.07[c]	221.63[c]
Concentrations		
Control	656.68[a]	653.33[a]
300 mg/kg	391.12[b]	385.36[b]
600 mg/kg	245.98[c]	248.92[c]
1000 mg/kg	210.94[d]	209.77[d]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 119: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of superoxide dismutase (SOD) (µml/mg) in tomato during 2017 and 2018 cropping seasons.

Metal salt	SOD (µml/mg) (2017)	SOD (µml/mg) (2018)
Control	660.68 ±10.00^{a}	653.33±5.77^{a}
nCu 300 mg/kg	613.80±34.30^{b}	600.10±13.83^{b}
nCu 600 mg/kg	321.74±29.42^{e}	323.67±13.83^{e}
nCu 1000 mg/kg	282.33±2.51^{f}	278.33±10.26^{f}
nZnO 300 mg/kg	560.00±10.00^{b}	553.33±5.77^{b}
nZnO 600 mg/kg	409.47±0.50^{c}	409.67±0.58^{c}
nZnO1000mg/kg	349.09±56.58^{d}	348.09±55.23^{d}
bCu 300 mg/kg	239.33±9.24^{e}	245.33 ±3.21^{e}
bCu 600 mg/kg	120.00±0.00^{fg}	133.67 ±9.50^{fg}
bCu 1000 mg/kg	100.00±0.00^{hi}	102.00 ±3.00^{hi}
bZnO 300 mg/kg	151.33±2.31^{fg}	142.67 ±0.58^{fg}
bZnO 600 mg/kg	132.71±5.56^{fg}	128.67±3.51^{fg}
bZnO1000mg/kg	112.33±1.53^{hi}	110.67±4.73^{hi}

Values are mean± S. D, n= 96, values with the same superscript along treatments are not significant at p≤ 0.05, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 120: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attribute or activities of malondialdehyde (MDA (µml/mg) in bean during 2017 and 2018 cropping seasons.

Metal salts	MDA (µml/mg) (2017)	MDA (µml/mg) (2018)
nCu	20.80[a]	21.19[a]
nZnO	18.40[b]	19.43[b]
bCu	13.09[d]	12.89[d]
bZnO	16.18[c]	15.11[c]
Concentrations		
Control	12.27[c]	12.27[c]
300 mg/kg	18.02[b]	18.02[b]
600 mg/kg	21.23[a]	21.23[a]
1000 mg/kg	17.85[b]	17.85[b]
Interaction	0.003*	0.001*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 121: Interactive effect between metal salts and various concentrations on stress attributes or activities of Malondialdehyde (MDA) (µml/mg) in beans during 2017 and 2018 cropping seasons.

Metal salt	MDA(µml/mg) (2017)	MDA (µml/mg) (2018)
Control	12.17 ± 0.15^{gh}	12.17 ± 0.15^{gh}
nCu 300 mg/kg	20.00 ± 2.00^{bc}	23.00 ± 1.00^{bc}
nCu 600 mg/kg	34.33 ± 4.04^{a}	$32.673.06^{a}$
nCu 1000 mg/kg	16.70 ± 0.65^{de}	16.92 ± 0.15^{de}
nZnO 300 mg/kg	15.49 ± 4.04^{de}	18.31 ± 4.17^{de}
nZnO 600 mg/kg	23.00 ± 2.65^{bc}	24.37 ± 1.58^{bc}
nZnO1000mg/kg	26.02 ± 1.75^{b}	25.96 ± 1.73^{b}
bCu 300 mg/kg	13.23 ± 1.02^{ef}	13.03 ± 0.96^{ef}
bCu 600 mg/kg	14.17 ± 0.2^{ef}	13.55 ± 0.37^{ef}
bCu 1000 mg/kg	12.17 ± 0.15^{gh}	12.17 ± 0.15^{gh}
bZnO 300 mg/kg	17.83 ± 1.89^{de}	17.73 ± 0.23^{de}
bZnO 600 mg/kg	17.00 ± 1.00^{de}	14.33 ± 1.53^{ef}
bZnO1000mg/kg	19.00 ± 1.00^{de}	16.33 ± 1.15^{de}

Values are mean $\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 122: Effects of Nanoparticles and bulk particles (Cu and ZnO) on enzyme activities or attributes of malondialdehyde (MDA) (µml/mg) in tomato during 2017 and 2018 cropping seasons.

Metal salts	MDA (µml/mg) (2017)	MDA (µml/mg) (2018)
nCu	21.51[a]	22.62[a]
nZnO	22.02[a]	22.55[a]
bCu	11.83[c]	11.09[c]
bZnO	14.57[b]	13.62[b]
Concentrations		
Control	8.97[d]	9.11[d]
300 mg/kg	13.54[c]	12.81[c]
600 mg/kg	20.82[b]	20.62[b]
1000 mg/kg	27.51[a]	28.19[a]
Interaction	0.001*	0.001*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 123: Interactive effect between metal salts and various concentrations stress attributes or activities of Malondialdehyde (MDA) (µml/mg) in tomato during 2017 and 2018 cropping seasons.

Metal salt	MDA (µml/mg) (2017)	MDA (µml/mg) (2018)
Control	8.73 ± 0.43^{d}	9.20 ± 0.17^{d}
nCu 300 mg/kg	15.33 ± 0.58^{c}	15.61 ± 0.77^{c}
nCu 600 mg/kg	27.93 ± 1.49^{b}	28.80 ± 0.52^{b}
nCu 1000 mg/kg	34.03 ± 4.71^{a}	36.80 ± 1.85^{a}
nZnO 300 mg/kg	16.67 ± 2.08^{c}	15.00 ± 1.00^{c}
nZnO 600 mg/kg	25.67 ± 1.15^{b}	26.67 ± 3.20^{b}
nZnO1000mg/kg	37.00 ± 0.00^{a}	39.33 ± 4.04^{a}
bCu 300 mg/kg	12.00 ± 0.00^{c}	10.99 ± 0.89^{d}
bCu 600 mg/kg	15.67 ± 0.58^{c}	14.67 ± 0.58^{c}
bCu 1000 mg/kg	20.00 ± 0.00^{b}	18.00 ± 1.0^{c}
bZnO 300 mg/kg	10.15 ± 0.09^{d}	9.63 ± 0.27^{d}
bZnO 600 mg/kg	14.00 ± 0.00^{c}	12.33 ± 0.58^{c}
bZnO1000mg/kg	19.00 ± 0.00^{c}	18.57 ± 0.31^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 124: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attribute or activities of hydrogen peroxide (H_2O_2) (µml/mg) in bean during 2017 and 2018 cropping seasons.

Metal salts	H_2O_2 (µml/mg) (2017)	H_2O_2 (µml/mg) (2018)
nCu	25.64^{b}	26.18^{b}
nZnO	41.16^{a}	28.14^{b}
bCu	19.82^{c}	20.14^{c}
bZnO	28.12^{b}	28.13^{b}
Concentrations		
Control	16.15^{d}	14.76^{d}
300 mg/kg	30.44^{c}	30.29^{c}
600 mg/kg	34.25^{b}	34.08^{b}
1000 mg/kg	36.66^{a}	37.76^{a}
Interaction	0.004*	0.002*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 125: Interactive effect between metal salts and various concentrations on stress attribute or activities of hydrogen peroxide (H_2O_2) in bean during 2017 and 2018 cropping seasons.

Metal salt	H_2O_2 (µml/mg) (2017)	H_2O_2 (µml/mg) (2018)
Control	16.15 ± 2.66^{fg}	16.15 ± 2.66^{fg}
nCu 300 mg/kg	24.92 ± 1.07^{de}	25.75 ± 0.47^{c}
nCu 600 mg/kg	29.00 ± 0.99^{d}	28.59 ± 1.18^{c}
nCu 1000 mg/kg	32.50 ± 0.72^{b}	34.22 ± 0.29^{b}
nZnO 300 mg/kg	49.42 ± 0.39^{a}	46.55 ± 3.64^{a}
nZnO 600 mg/kg	48.53 ± 0.13^{a}	48.29 ± 0.87^{a}
nZnO1000mg/kg	50.54 ± 0.72^{a}	53.62 ± 4.45^{a}
bCu 300 mg/kg	20.53 ± 0.77^{de}	21.31 ± 1.47^{de}
bCu 600 mg/kg	23.98 ± 0.53^{de}	48.29 ± 0.87^{a}
bCu 1000 mg/kg	25.28 ± 0.39^{c}	25.76 ± 1.45^{c}
bZnO 300 mg/kg	26.90 ± 0.82^{c}	27.55 ± 1.17^{c}
bZnO 600 mg/kg	35.50 ± 0.87^{b}	35.27 ± 0.60^{b}
bZnO1000mg/kg	38.33 ± 0.58^{b}	37.42 ± 0.99^{b}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 126: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attribute or activities of hydrogen peroxide (H_2O_2) (µml/mg) in tomato during 2017 and 2018 cropping season.

Metal salts	H_2O_2 (µml/mg) (2017)	H_2O_2 (µml/mg) (2018)
nCu	21.87[a]	24.86[a]
nZnO	20.05[a]	24.06[a]
bCu	14.81[b]	14.76[b]
bZnO	19.08[b]	19.87[b]
Concentrations		
Control	10.69[d]	12.73[c]
300 mg/kg	18.23[c]	24.28[a]
600 mg/kg	22.10[b]	25.52[a]
1000 mg/kg	26.21[a]	22.71[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 127: Interactive effect between metal salts and various concentrations on stress attributes or activities of hydrogen peroxide (H_2O_2) (µml/mg) in tomato during 2017 and 2018 cropping seasons.

Metal salt	H_2O_2 (µml/mg) (2017)	H_2O_2 (µml/mg) (2018)
Control	10.69 ± 0.48^{h}	10.60 ± 0.00^{h}
nCu 300 mg/kg	18.38 ± 0.15^{f}	22.37 ± 0.05^{bc}
nCu 600 mg/kg	26.89 ± 1.30^{b}	28.45 ± 2.89^{a}
nCu 1000 mg/kg	31.53 ± 2.32^{a}	15.33 ± 0.34^{fg}
nZnO 300 mg/kg	19.36 ± 0.57^{ef}	33.30 ± 5.10^{a}
nZnO 600 mg/kg	21.15 ± 3.56^{bc}	25.51 ± 0.63^{b}
nZnO1000mg/kg	29.00 ± 1.47^{a}	30.02 ± 0.38^{a}
bCu 300 mg/kg	15.57 ± 0.37^{fg}	15.86 ± 0.94^{fg}
bCu 600 mg/kg	23.98 ± 0.53^{bc}	19.97 ± 1.08^{de}
bCu 1000 mg/kg	19.73 ± 0.49^{de}	23.69 ± 0.98^{bc}
bZnO 300 mg/kg	19.62 ± 0.54^{de}	19.52 ± 0.47^{de}
bZnO 600 mg/kg	20.64 ± 1.23^{de}	23.29 ± 1.64^{bc}
bZnO1000mg/kg	22.23 ± 1.57^{bc}	21.80 ± 0.57^{bc}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 128: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attributes or activities of proline (µml/mg) in bean during 2017 and 2019 cropping seasons.

Metal salts	Proline (µml/mg) (2017)	Proline (µml/mg) (2018)
nCu	0.55^{a}	0.55^{a}
nZnO	0.52^{a}	0.55^{a}
bCu	0.46^{b}	0.42^{b}
bZnO	0.35^{c}	0.36^{c}
Concentrations		
Control	0.66^{a}	0.66^{a}
300 mg/kg	0.42^{b}	0.41^{b}
600 mg/kg	0.39^{b}	0.40^{b}
1000 mg/kg	0.38^{b}	0.39^{b}
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 129: Interactive effect between metal salts and various concentrations on antioxidant enzyme activities of proline (µml/mg) in bean during 2017 and 2018 cropping seasons.

Metal salt	Proline (µml/mg) (2017)	Proline (µml/mg) (2018)
Control	0.66 ± 0.01^{a}	0.66 ± 0.01^{a}
nCu 300 mg/kg	0.54 ± 0.04^{b}	0.54 ± 0.03^{b}
nCu 600 mg/kg	0.50 ± 0.01^{b}	0.53 ± 0.02^{b}
nCu 1000 mg/kg	0.49 ± 0.01^{bc}	0.48 ± 0.02^{bc}
nZnO 300 mg/kg	0.48 ± 0.01^{bc}	0.46 ± 0.03^{bc}
nZnO 600 mg/kg	0.49 ± 0.01^{bc}	0.50 ± 0.00^{bc}
nZnO1000mg/kg	0.45 ± 0.01^{bc}	0.57 ± 0.01^{b}
bCu 300 mg/kg	0.33 ± 0.06^{de}	0.30 ± 0.00^{de}
bCu 600 mg/kg	0.30 ± 0.10^{de}	0.23 ± 0.01^{f}
bCu 1000 mg/kg	0.37 ± 0.06^{de}	0.30 ± 0.00^{de}
bZnO 300 mg/kg	0.33 ± 0.01^{de}	0.33 ± 0.02^{de}
bZnO 600 mg/kg	0.27 ± 0.06^{f}	0.35 ± 0.01^{de}
bZnO1000mg/kg	0.20 ± 0.00^{g}	0.20 ± 0.00^{g}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 130: Effects of Nanoparticles and bulk particles (Cu and ZnO) on stress attributes or activities of proline in tomato during 2017 and 2018 cropping season

Metal salts	Proline (µml/mg) (2017)	Proline (µml/mg) (2018)
nCu	2.06[a]	2.06[a]
nZnO	2.06[a]	2.06[a]
bCu	1.07[b]	1.06[b]
bZnO	1.05[c]	1.06[b]
Concentrations		
Control	1.59[a]	1.59[a]
300 mg/kg	1.56[b]	1.56[b]
600 mg/kg	1.56[b]	1.55[b]
1000 mg/kg	1.54[b]	1.54[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 131: Interactive effect between metal salts and various concentrations on stress attributes or activities of proline (µml/mg) in tomato during 2017 and 2018 cropping season

Metal salt	Proline (µml/mg) (2017)	Proline (µml/mg) (2018)
Control	2.09 ± 0.09^{a}	2.09 ± 0.01^{a}
nCu 300 mg/kg	2.04 ± 0.003^{ab}	2.06 ± 0.05^{ab}
nCu 600 mg/kg	2.06 ± 0.01^{ab}	2.07 ± 0.02^{ab}
nCu 1000 mg/kg	2.04 ± 0.00^{ab}	2.04 ± 0.02^{ab}
nZnO 300 mg/kg	2.06 ± 0.02^{ab}	2.05 ± 0.01^{ab}
nZnO 600 mg/kg	2.06 ± 0.10^{ab}	2.06 ± 0.01^{ab}
nZnO1000mg/kg	2.05 ± 0.00^{b}	2.04 ± 0.01^{b}
bCu 300 mg/kg	1.07 ± 0.00^{cd}	1.06 ± 0.01^{cd}
bCu 600 mg/kg	1.06 ± 0.01^{cd}	1.04 ± 0.04^{cd}
bCu 1000 mg/kg	1.04 ± 0.00^{cd}	1.04 ± 0.01^{cd}
bZnO 300 mg/kg	1.05 ± 0.00^{cd}	1.06 ± 0.01^{cd}
bZnO 600 mg/kg	1.05 ± 0.06^{cd}	1.05 ± 0.01^{cd}
bZnO1000mg/kg	1.03 ± 0.01^{cd}	1.04 ± 0.01^{cd}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 132: Effects of Nanoparticles and bulk particles (Cu and ZnO) on starch (mg/100 g fw) content in bean during 2017 and 2018 cropping seasons.

Metal salts	Starch (mg/100 g fw) (2017)	Starch (mg/100 g fw) (2018)
nCu	5.38[a]	5.45[a]
nZnO	5.37[a]	5.23[b]
bCu	5.37[a]	5.23[b]
bZnO	5.29[b]	5.17[b]
Concentrations		
Control	5.45[a]	5.41[a]
300 mg/kg	5.23[b]	5.21[b]
600 mg/kg	5.29[b]	5.17[b]
1000 mg/kg	5.24[b]	5.16[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 133: Interactive effect between metal salts and various concentrations on starch (mg/100 g fw) content in bean during 2017 and 2018 cropping seasons.

Metal salt	Starch (mg/100 g fw) (2017)	Starch (mg/100 g fw) (2018)
Control	5.49 ± 0.01^{a}	5.49 ± 0.01^{a}
nCu 300 mg/kg	5.29 ± 0.01^{bc}	5.25 ± 0.22^{bc}
nCu 600 mg/kg	5.15 ± 0.01^{cd}	5.14 ± 0.01^{cd}
nCu 1000 mg/kg	5.15 ± 0.01^{cd}	5.17 ± 0.01^{bc}
nZnO 300 mg/kg	5.12 ± 0.02^{cd}	5.14 ± 0.05^{cd}
nZnO 600 mg/kg	5.04 ± 0.00^{ef}	5.04 ± 0.00^{ef}
nZnO1000mg/kg	5.01 ± 0.00^{ef}	5.0 ± 0.00^{ef}
bCu 300 mg/kg	5.27 ± 0.12^{bc}	5.17 ± 0.06^{bc}
bCu 600 mg/kg	5.37 ± 0.06^{b}	5.23 ± 0.06^{bc}
bCu 1000 mg/kg	5.23 ± 0.06^{bc}	5.17 ± 0.26^{bc}
bZnO 300 mg/kg	5.27 ± 0.12^{bc}	5.27 ± 0.06^{bc}
bZnO 600 mg/kg	5.35 ± 0.13^{bc}	5.27 ± 0.06^{bc}
bZnO1000mg/kg	5.27 ± 0.14^{bc}	5.30 ± 0.11^{b}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 134: Effects of Nanoparticles and bulk particles (Cu and ZnO) on starch (mg/100 g fw) content in tomato during 2017 and 2018 cropping season

Metal salts	Starch (mg/100 g fw) (2017)	Starch (mg/100 g fw) (2018)
nCu	3.59^{a}	3.56^{a}
nZnO	3.52^{a}	3.52^{a}
bCu	3.38^{b}	3.43^{a}
bZnO	2.83^{c}	2.80^{c}
Concentrations		
Control	3.52^{a}	3.49^{a}
300 mg/kg	3.28^{b}	3.25^{b}
600 mg/kg	3.22^{b}	3.22^{b}
1000 mg/kg	3.28^{b}	3.16^{b}
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 135: Interactive effect between metal salts and various concentrations on starch (mg/100 g fw) content in tomato during 2017 and 2018 cropping season

Metal salt	Starch (mg/100 g fw) (2017)	Starch (mg/100 g fw) (2018)
Control	3.77 ± 0.01^{a}	3.77 ± 0.01^{a}
nCu 300 mg/kg	3.55 ± 0.01^{ab}	3.46 ± 0.01^{b}
nCu 600 mg/kg	3.53 ± 0.01^{ab}	3.49 ± 0.04^{bc}
nCu 1000 mg/kg	3.51 ± 0.01^{ab}	3.53 ± 0.06^{ab}
nZnO 300 mg/kg	3.45 ± 0.01^{bc}	3.45 ± 0.01^{bc}
nZnO 600 mg/kg	3.42 ± 0.01^{bc}	3.48 ± 0.18^{bc}
nZnO1000mg/kg	3.42 ± 0.01^{bc}	3.40 ± 0.00^{bc}
bCu 300 mg/kg	3.26 ± 0.45^{de}	3.39 ± 0.33^{bc}
bCu 600 mg/kg	3.17 ± 0.15^{de}	3.13 ± 0.06^{de}
bCu 1000 mg/kg	3.03 ± 0.12^{ef}	2.90 ± 0.13^{ef}
bZnO 300 mg/kg	2.86 ± 0.06^{ef}	2.69 ± 0.02^{ef}
bZnO 600 mg/kg	2.75 ± 0.17^{ef}	2.78 ± 0.11^{ef}
bZnO1000mg/kg	2.50 ± 0.10^{ef}	2.79 ± 0.26^{ef}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 136: Effects of Nanoparticles and bulk particles (Cu and ZnO) on protein (mg/100 g fw) content in bean during 2017 and 2018 cropping season

Metal salts	Protein (mg/100 g fw) (2017)	Protein (mg/100 g fw) (2018)
nCu	11.13[a]	11.79[a]
nZnO	11.04[b]	11.00[b]
bCu	11.07[b]	11.02[b]
bZnO	9.67[b]	9.69[b]
Concentrations		
Control	12.87[a]	12.87[a]
300 mg/kg	9.93[b]	10.09[b]
600 mg/kg	9.88[b]	10.14[b]
1000 mg/kg	9.77[b]	10.03[b]
Interaction	0.020*	0.030*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 137: Interactive effect between metal salts and various concentrations on protein (mg/100 g fw) content in bean during 2017 and 2018 cropping seasons.

Metal salt	protein (mg/100 g fw) (2017)	Protein (mg/100 g fw) (2018)
Control	12.87 ± 0.01^{a}	12.87 ± 0.01^{a}
nCu 300 mg/kg	10.65 ± 0.00^{bc}	11.25 ± 0.06^{b}
nCu 600 mg/kg	10.53 ± 0.01^{bc}	11.45 ± 0.16^{b}
nCu 1000 mg/kg	10.47 ± 0.01^{bc}	11.58 ± 0.01^{b}
nZnO 300 mg/kg	10.47 ± 0.01^{bc}	10.49 ± 0.02^{bc}
nZnO 600 mg/kg	10.43 ± 0.01^{bc}	10.46 ± 0.01^{bc}
nZnO1000mg/kg	10.40 ± 0.00^{bc}	10.44 ± 0.04^{bc}
bCu 300 mg/kg	10.00 ± 0.00^{cd}	9.89 ± 0.09^{cd}
bCu 600 mg/kg	9.94 ± 0.07^{cd}	9.96 ± 0.09^{cd}
bCu 1000 mg/kg	9.33 ± 0.57^{de}	9.20 ± 0.39^{de}
bZnO 300 mg/kg	8.59 ± 0.10^{de}	8.71 ± 0.20^{de}
bZnO 600 mg/kg	8.60 ± 0.08^{de}	8.68 ± 0.19^{de}
bZnO1000mg/kg	8.88 ± 0.13^{de}	8.88 ± 0.11^{de}

Values are mean$\pm$ S. D, n= 96, values with the same superscript across treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 138: Effects of Nanoparticles and bulk particles (Cu and ZnO) on protein (mg/100 g fw) content in tomato during 2017 and 2018 cropping seasons.

Metal salts	Protein (mg/100 g fw) (2017)	Protein (mg/100 g fw) (2018)
nCu	6.38[a]	6.11[b]
nZnO	6.25[a]	6.13[b]
bCu	6.05[b]	5.90[b]
bZnO	4.72[c]	4.62[c]
Concentrations		
Control	6.98[a]	7.00[a]
300 mg/kg	5.39[b]	5.16[b]
600 mg/kg	5.37[b]	5.11[b]
1000 mg/kg	5.23[b]	5.07[b]
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 139: Interactive effect between metal salts and various concentrations on protein (mg/100 g fw) content in tomato during 2017 and 2018 cropping season

Metal salt	Protein (mg/100 g fw) (2017)	Protein (mg/100 g fw) (2018)
Control	7.81 ± 0.01^{a}	7.81 ± 0.01^{a}
nCu 300 mg/kg	5.95 ± 0.01^{b}	5.59 ± 0.12^{b}
nCu 600 mg/kg	5.89 ± 0.01^{b}	5.68 ± 0.21^{b}
nCu 1000 mg/kg	5.88 ± 0.01^{b}	5.37 ± 0.71^{b}
nZnO 300 mg/kg	5.86 ± 0.03^{b}	5.59 ± 0.12^{b}
nZnO 600 mg/kg	5.77 ± 0.01^{b}	5.61 ± 0.14^{b}
nZnO1000mg/kg	5.56 ± 0.31^{b}	5.52 ± 0.25^{b}
bCu 300 mg/kg	5.00 ± 0.00^{b}	4.88 ± 0.49^{c}
bCu 600 mg/kg	5.00 ± 0.00^{b}	4.57 ± 0.01^{c}
bCu 1000 mg/kg	4.67 ± 0.20^{c}	4.68 ± 0.05^{c}
bZnO 300 mg/kg	4.75 ± 0.17^{c}	4.57 ± 0.01^{c}
bZnO 600 mg/kg	4.82 ± 0.06^{c}	4.59 ± 0.05^{c}
bZnO1000mg/kg	4.79 ± 0.17^{c}	4.70 ± 0.12^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 140: Effects of Nanoparticles and bulk particles (Cu and ZnO) on copper and zinc content (mg/kg) in bean during 2017 and 2018 cropping seasons.

Metal salts	Copper and zinc (mg/kg) content (2017)	Copper and zinc (mg/kg) content (2018)
nCu	35.69^{c}	108.13^{b}
nZnO	51.50^{c}	154.50^{a}
bCu	16.82^{d}	50.47^{c}
bZnO	24.77^{d}	73.01^{c}
Concentrations		
Control	6.67^{e}	20.00^{d}
300 mg/kg	22.49^{d}	67.48^{c}
600 mg/kg	41.95^{c}	125.85^{b}
1000 mg/kg	60.32^{c}	180.29^{a}
Interaction	0.000*	0.000*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 141: Interactive effect between metal salts and various concentrations on copper and zinc content (mg/kg) in bean during 2017 and 2018 cropping seasons.

Metal salt	Copper and zinc content (mg/kg) (mg/kg) (2017)	Copper and zinc content (mg/kg) (2018)
Control	6.67 ± 1.91^{gh}	20.00 ± 5.73^{gh}
nCu 300 mg/kg	28.75 ± 2.50^{ef}	86.25 ± 7.50^{de}
nCu 600 mg/kg	40.00 ± 6.49^{de}	120.00 ± 19.59^{c}
nCu 1000 mg/kg	67.33 ± 8.74^{de}	206.25 ± 33.33^{b}
nZnO 300 mg/kg	27.08 ± 15.73^{ef}	81.25 ± 47.19^{de}
nZnO 600 mg/kg	70.58 ± 23.65^{de}	211.75 ± 70.98^{b}
nZnO1000mg/kg	101.67 ± 30.68^{c}	305.00 ± 92.03^{a}
bCu 300 mg/kg	20.61 ± 2.08^{ef}	61.82 ± 8.02^{de}
bCu 600 mg/kg	26.37 ± 1.08^{ef}	79.10 ± 3.23^{de}
bCu 1000 mg/kg	30.90 ± 0.57^{ef}	92.70 ± 1.72^{cd}
bZnO 300 mg/kg	13.53 ± 2.80^{gh}	40.60 ± 8.41^{de}
bZnO 600 mg/kg	30.08 ± 12.54^{ef}	92.53 ± 37.62^{cd}
bZnO1000mg/kg	41.36 ± 0.06^{de}	117.19 ± 11.88^{c}

Values are mean$\pm$ S. D, n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

Table 142: Effects of Nanoparticles and bulk particles (Cu and ZnO) on copper and zinc content (mg/kg) in tomato during 2017 and 2018 cropping season

Metal salts	Copper and zinc content (2017)	Copper and zinc content (2018)
nCu	25.08[d]	75.35[c]
nZnO	59.63[c]	184.92[a]
bCu	20.27[d]	51.17[c]
bZnO	27.05[d]	104.47[b]
Concentrations		
Control	9.58[c]	29.06[b]
300 mg/kg	39.03[b]	158.24[a]
600 mg/kg	37.77[b]	108.52[a]
1000 mg/kg	47.89[b]	137.85[a]
Interaction	0.000*	0.002*

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide, * = significant

Table 143: Interactive effect between metal salts and various concentrations on copper and zinc (mg/kg) content in tomato during 2017 and 2018 cropping seasons.

Metal salt	Copper and zinc content (2017)	Copper and zinc content (2018)
Control	9.58 ± 1.91^{ij}	29.17 ± 5.91^{gh}
nCu 300 mg/kg	35.42 ± 10.63^{gh}	106.25 ± 31.89^{cd}
nCu 600 mg/kg	23.33 ± 4.39^{gh}	70.00 ± 13.17^{ef}
nCu 1000 mg/kg	32.00 ± 27.42^{gh}	96.00 ± 8.25^{cd}
nZnO 300 mg/kg	56.25 ± 11.11^{gh}	171.77 ± 35.17^{cd}
nZnO 600 mg/kg	68.75 ± 11.12^{ef}	226.25 ± 27.13^{ab}
nZnO1000mg/kg	103.92 ± 15.38^{cd}	$312.5.0 \pm 47.19^{a}$
bCu 300 mg/kg	34.47 ± 3.33^{gh}	79.78 ± 2.83^{ef}
bCu 600 mg/kg	15.00 ± 0.00^{ij}	42.50 ± 4.33^{ef}
bCu 1000 mg/kg	11.00 ± 0.50^{ij}	23.75 ± 2.22^{hi}
bZnO 300 mg/kg	30.00 ± 1.00^{gh}	275.17 ± 34.60^{ab}
bZnO 600 mg/kg	44.00 ± 1.00^{gh}	95.33 ± 12.89^{ef}
bZnO1000mg/kg	44.67 ± 0.58^{gh}	119.17 ± 13.77^{cd}

n= 96, values with the same superscript along treatments are not significant at $p \leq 0.05$, nCu = copper nanoparticles, nZnO =zinc oxide nanoparticles, bCu = bulk copper, bZnO = bulk zinc oxide

CHAPTER FIVE

DISCUSSION, CONCLUSION AND RECOMMENDATION

5.1 Discussion

Characterization of the nanoparticles used for this research revealed the presence of large amount of oxygen in nZnO; this is possibly due to higher reactivity of the nanoparticles (Akanbi gada *et al*., 2019) which may lead to slight oxidation during synthesis and/or storage of the nanoparticles. Furthermore this could also possibly come from a surfactant that was used by the manufacturer to stabilize the NPs during production as this is in tandem with the report of Ogunkunle *et al*. (2018) who studied the effects of manufactured nano-copper on copper uptake, bioaccumulation and enzyme activities in cowpea grown on soil substrate.

Zinc oxide nanoparticles (nZnO) has particle size of between 10-100 nm with irregularly shaped rod like structures which are larger and more diverse and this is similar to the report of Jahan *et al.* (2018) who evaluated the toxicity of ZnO and TiO_2 nanomaterials in hydroponic red bean (*Vigna angularis*). It also has large amount of oxygen of about 31.71 % and highly crystalline in nature. The presence of higher oxygen could be as a result of impurities or presence of oxides which could be during synthesis or storage.

Soil pH is an important factor that influences several processes in the growth and development of plant. Some of the processes are soil bacteria activities, nutrient availability, and nutrient leaching and soil structure. It has been reported that soil bacteria activities are highest at pH range of between 5.5 -7.0 and plant nutrients leach out of soils more rapidly in a soil with pH of less than 5.0 (Rousk *et al*., 2009). Generally, optimum pH range for tomato plant is 5.5-7.7 and for legumes is 6.0-7.5 (Rousk *et al*., 2009). The observed pH in this study was 6.4 which mean the soil has good prospects for planting.

Significant leaf length, leaf breadth, leaf area, number of leaves and stem girth were observed in both bean and tomato plants with the use of nCu and nZnO and this is particularly so especially at low dosage of 300 and 600 mg/kg but there was reduction in the growth attributes at high dosage. This result is in tandem with the findings of Rayhaneh *et al*. (2016) and Ramesh *et al.* (2015). Their researches revealed that there were reduction of the growth attributes of tomato and wheat at elevated or high dosage of nZnO. This observation was further suggested to be due to metal oxide induced toxicity as Cu and ZnO are metals that are organ and size specific (Ogunkunle *et al*., 2017). This study showed that plants that were treated with nanoparticles have an edge or improvement over bulk –treated and the control plants. The reason for this could be that mineral nutrients encapsulated in nano forms promoted plant nutrition as reported elsewhere (Fedoreneko *et al*., 2015; Naeem *et al*., 2017).

In addition, a number of mechanisms underlined the efficiency of nZnO and nCu uptake depending on the plant species, size of the nanoparticles and the environmental conditions as reported by Fiskesjo *et al*. (1993). The results of this research slightly disagree with that of Olga *et al*. (2016) who reported simultaneous stimulating and inhibitory actions of the effect of Cu and Zn nanoparticles at their individual and combined application on growth paramaters of *Pistia stratiotes.* It is worthy to note that the size of Cu nanoparticles is < 25nm and that of Zn is 10-100nm. It has been reported that the size of nanoparticles can influence the surface reactivity of the plant under study, the smaller the size the higher the reactivity (Asli *et al*., 2009; Barrena *et al*., 2009; Ogunkunle *et al*., 2018).

Chlorophyll a, b and total was significantly reduced and affected in bean and tomato throughout the period of experimentation (2017and 2018) by either the nanoparticles or bulk particles compared to control plants. This result agrees with the findings of Mukherjee *et al*., 2013; Wang *et al*., 2016 a, b; Jahan *et al*., 2018; Akanbi-Gada *et al*., 2019 a, b). Mukherjee *et*

al. 2013 reported a decreased chlorophyll content which was significant at early growing stage of tomato and green pea exposed to nanoparticulate ZnO. Furthermore similar trends was also observed and reported by Wang *et al*. (2016) who reported chlorophyll a reduction in 300 mg/L ZnO nanoparticles treated *Arabidopsis thaliana.*

The significant reduction in contents of chlorophyll a, b and total could be an indication of the possibility of oxidative stress due to the treatments in leaves. It has been suggested by Falco *et al*. 2011 that chlorophyll a is one of the major photosynthetic pigments which are highly sensitive to photo-degradation than other pigments and this could be a good pointer of nanoparticles toxicity. However, there are some reports that are contrary to the findings of this research like that of Raliya *et al*. (2017; 2015) who posited that there were increase in chlorophyll content of several plants with the application of biologically synthesised nZnO. This result further disagree with that of Song *et al*., 2013 who reported that there was no significant difference in chlorophyll content of tomato upon exposure to 1000 and 500 mg TiO_2 per litre. In addition, the fundamental mechanism that is responsible for the differences in the effects of nanoparticles on photosynthetic pigments could be related to the concentrations of the nanoparticles used, types of plants and the prevailing environmental conditions. Disturbance in photosynthetic activity can result in oxidative stress in plants.

The number of days to fruiting and flower emergence was more in the bulk-treated and control plants in both beans and tomato plants. Flowers and fruits emerged earlier in the nanoparticles-treated plants during the two cropping seasons. The phytotoxic tendencies of Cu and ZnO nanoparticles were shown at higher concentrations or dosage especially in tomato plants. This means that Cu and ZnO nanoparticles delayed or inhibited flowering and fruiting because of less bioavailability of these metals to plants due to its large particle size and also less solubility (10- 100 nm zinc oxide and >25 nm copper nanoparticles was used for

this research). Furthermore, dose dependent response was observed with the lowest number of days for flower emergence occurring in the nanoparticles-treated plants. Similar dose dependent responses were recorded by authors like Lin and Xing (2007); He *et al*., (2011).

Productivity parameters of bean and tomato were examined by considering yield based on the data obtained in number of pods or fruits per plant, number of seed per pod or fruit, number of seed per plant or fruit and pod or fruit length . Significant yield parameters were from nCu and nZnO especially at low dosage of 300 and 600 mg/kg. This is in line with the findings of Sanghamitra *et al*., 2015 where subtle positive response in kidney bean yield parameters at certain nano- CeO_2 concentration were observed. Furthermore, Mukherjee *et al*., 2015 posited that the exposure of green pea to nZnO regardless of type generally had little effect on the green pea pod characteristics. Their research further revealed that pod length, pod weight and number of seed per pod did not change as a function of treatments except with the use of doped 250 mg/kg nanoparticles. The use of Cu and ZnO as fertilizer is an emerging field of environmental biology but the mechanism underlying this enhancement to boost agricultural productivity is poorly understood. However, plant productivity depends on a number of factors including mineral assimilation, cell differentiation and synthesis of stored reserve in the endosperm which could be an advantage for growth and developmental progress of the test plants (Taiz and Zeiger, 1998).

Fresh and dry weights recorded significant highest values with the use of nCu and nZnO. This result contradict that of Mukherjee *et al.* (2015) which revealed that regardless of the particle type, the fresh and dry weights of green pea were unaffected by nZnO treatments. The reason for the difference in results could be due to the size of the nanoparticles used, the prevailing environmental conditions, exposure period and type of plant used.

Significant values were obtained for all the non-enzymatic antioxidants examined in this research with the use of nCu and nZnO. These findings agree with the work of Hernandez-Fuentes *et al*. (2017) who reported stimulatory effects of copper nanoparticles on total phenols, beta-carotene and ascorbic acid in tomato plant. The results of this research are also in tandem with the findings of Akanbi-Gada *et al*. (2019b). The results of the non – antioxidant enzyme activities further suggests that nCu and nZnO do not have negative effects especially at low dosage on the non-enzymatic antioxidants in bean and especially tomato. Tomato had about three times fold increase of ascorbic acid, lycopene and beta-carotene over bean plants. This means that nCu and nZnO treatment does not have an inhibitory effect on the induction of the antioxidant compounds in the tomato fruit.

Reactive oxygen species (ROS) are normal by-products of plant that are undergoing natural cell functions but increased production of ROS may result from both biotic and abiotic stress in plants (Foyer and Shigeoka, 2011). There was concentration dependent increase in hydrogen peroxide and malondialdehyde (MDA) in this study and this could be a potential stressor in plants. The high hydrogen peroxide generation in the root of bean and tomato plants could be as a result of aging duration on nCu and nZnO in the soil as aging can greatly affect toxicity of nanomaterials in soil due to process of adsorption and dissolution speed (Reedy *et al*., 2016). The result of this study agrees with that of Akanbi-Gada *et al*., but contrasted with the result of Mukherjee *et al*., 2013 in green pea where it was reported that there was no significant over production of hydrogen peroxide by the roots exposed to 0-500 mg/kg nZnO.

The result of MDA also agrees with that of Rao and Shekhawat 2016 where it was reported that MDA content in Brassica increased significantly in CuO-treated roots at concentrations up to 1500 mg/L. Superoxide dismutase (SOD) ascorbate peroxidase (APX) were down

regulated with respect to control and this may be attributed to the simultaneous increase in the generation of hydrogen peroxide and lipid peroxidation in the form of malondialdehyde (MDA) production because SOD is known to mop or scavenge the activities of superoxide free radicals. CAT activities were up regulated when compared with the control as observed in this study. CAT is involved in the defence system of plants against accumulation of ROS by breaking down hydrogen peroxide to water and oxygen. This result aligns with that of Hernandez-Viezcas *et al*. (2013) who reported an increase in CAT activity in roots of Velvet mesquite (*Prosopis juliflora-velutina*) that was grown in soil exposed to nZnO at 400 mg/kg.

The exposure of the seed to nZnO and nCu generally had little effects on the quality of the seeds when compared with the control. The quality of the seeds was determined by determining the protein and starch contents. There were significant differences at all evaluation time with respect to control in the content of starch and protein. This could be due to differential responses of seeds to carbohydrate and protein metabolism at varying levels of copper and zinc oxide nanoparticles treatments. This result agrees with that of Sanghamitra *et al*., 2015. This aspect of food science in nanotechnology is still open to debate. It become imperative therefore, to further re-examine the safety of the nanoparticles-exposed plants so as to ascertain its safety before consumption as there are varied opinions of researchers on this aspect of Ecotoxicological studies.

Cu and Zn accumulation in the root of bean and tomato were dose dependent and plants treated with high doses of 600 and 1000 mg/kg respectively had higher accumulation than the control and 300 mg/kg treatments. There was about three times fold increase of the metal salts in the root. The roots as the first point of contact of plants with the soil have a significant role in the nutrient uptake. This result is in tandem with that of Ogunkunle *et al*., 2017 where it was posited that there was significant accumulation especially at 500 and 1000 mg/kg of

nano Cu in German round pea exposed to nano Cu (< 25 nm) through soil substrate. The result of this research further corroborates that of Akanbi-Gada *et al*. 2019 where a dose dependent increase was reported in tomato plants with the use of nZnO.

5.2 Conclusion

The findings of this research suggested that nZnO and nCu toxicity varies with nanoparticles properties, size, and type of plant used as well as the type of soil used for planting or cultivation. This study has been able to show that nZnO and nCu has a tendency to promote growth and productivity responses in beans and tomatoes especially at low dosages. This will eventually translate to higher yield or bumper harvest. This makes nZnO and nCu an emerging tool in agriculture for improved agricultural practices. People consume beans basically because it provides man with protein among other nutrients and it is a major building block of the body tissues. People also consume tomato because of the antioxidant properties it possesses and the result of this research revealed that all the antioxidant enzymes were not impacted upon negatively. The result on seed quality revealed that accumulation of Zn and Cu was up regulated in comparison with the control. These findings could only mean that nZnO and nCu can enter the food chain through edible plants tissues like leaf, stem and seeds which may affect the food quality of beans and tomatoes.

5.3 Contributions to Knowledge

The findings of the study have contributed to knowledge in the following ways;

i. Copper and zinc oxide nanoparticles enhanced growth attributes of both bean and tomato plants
ii. Copper and zinc oxide nanoparticles portends serious toxicity to root tissues, due to the significant uptake of Cu and Zn by promoting accumulation of hydrogen peroxide

(H_2O_2) and increased the lipid peroxidation inform of malondialdehyde (MDA) content at high dosage

iii. Copper and zinc oxide nanoparticles poses no/mild effect on the leaf tissues as no significant accumulation of H_2O_2 was observed. Also, only CAT activity in the leaves was enhanced significantly at all Copper and zinc oxide nanoparticles concentrations.

iv. Furthermore, non-enzymatic antioxidants in the mature ripe fruits of tomato were significantly increased at high Copper and zinc oxide nanoparticles doses.

v. The study provides information on the toxic effect of Copper and zinc oxide nanoparticles applied to tomato and bean at high dosage via soil route (as particulates), as the numerous researches on Cu and ZnO nanoparticles are carried out only via medium which are not naturally environmental realistic in agriculture such as Hoagland and hydroponic mediums

vi. It also shows that nutrients in fruits of tomato and beans may be impacted/ affected by nano Cu and ZnO despite the fact that the two salts are micronutrients.

5.4 Recommendations

i. It is recommended that the seeds and fruits from this research should be further subjected to in-vivo testing so as to ascertain their safety for human and animal consumption

ii. Synergistic use of both copper and zinc oxide nanoparticles should be encouraged

iii. Researches should be done using field testing of copper and zinc oxide nanoparticles

iv. Reduced dosage of the nanoparticles of copper and zinc oxide should be encouraged to be administered on the plants since both metals are required in small quantities by plants

REFERENCES

Abdolmaleki, A., Mallakpour, S., and Borandeh, S. (2012). Effect of silane-modified ZnO on morphology and properties of bionoacomposites based on poly (ester amide) containing tyrosine linkages. *Poly.Bull*, 10 (69):15-28.

Adalto, B. and Chris, M. W. (2003). Mechanism of acute silver toxicity in *Daphnia magna*, *Environmental Toxicology and Chemistry*, 22 (6): 1361–1367.

Adamson, I. Y. R. Prieditis, H. Hedgecock, C. and Vincent, R. (2000). "Zinc is the toxic factor in the lung response to an atmospheric particulate sample," *Toxicology and Applied Pharmacology*, 166(2): 111–119.

Aebi, H. (1974). Catalases. In: Bergmeyer, H.U. (Ed.), *Methods of Enzymatic Analysis*. Academic Press, 502 New York, pages 673-684.

Ahmed, M. A. A. (2019). Nanofertilizer application to increase growth and yield of sweet Pepper under potassium levels. *Journal of Agric Research and Technology*, 19 (4):55-60.

Aitken, R.J. Chaudhry, M.Q. Boxall, A.B. and Hull, M. (2006). Manufacture and use of Nanomaterials: effects of annealing temperature on density quantum dots solid state nanoparticle in *Allium cepa*. *Science Total Environment*, 407(19):5243–5246.

Akanbi-Gada, M. A., Ogunkunle, C. O., Abiola, O. Ilesanmi, Abiola, G., Femi-Adepoju, Latifat, O., Sidiq and Paul, O.Fatoba. (2019b). Effects of Zinc Oxide Nanoparticles on Chlorophyll content, Growth attributes, Antioxidant Enzyme activities and Bioaccumulation of common Bean (*Phaseolus vulgaris* L.) Grown in soil medium. *Journal of Environmental Science, Toxicology and Food Technology* (IOSR-JESTFT) 13(10):9-15.

Akanbi-Gada, M. A., Ogunkunle, C. O., Vishwakarma, V, Viswanathan K. and Fatoba, P. O. (2019a). Phytotoxicity of nano-zinc oxide to tomato plant (*Solanum lycopersicum* L.): Zn uptake, stress enzymes response and influence on non-enzymatic antioxidants in fruits. Journal of *Environmental Innovation and Technology*, 14(100325).

Albanes, D. (1999).''Beta carotene and lung cancer: a case study. *The American Journal of Clinical Nutrition*, 69 (6):1345-1350.

Amini, F. and Ehsanpour, A. A. (2005). Soluble proteins, proline, carbohydrates and Na^+/K^+ Changes in two tomatoes (*Lycopersicon esculentum* Mill.) cultivars invitro salt stress. *A.M .Journal of Biochemistry Biotechnology* 7(4):212-214.

AOAC (1990). *Official Methods of Analysis of the Association of Official Analytical Chemists 15th* Ed.Washington. Helrich,K.(Ed.) Arlington

Arambašić, M. B., Bjelić, S. and Subakov, G. (1995.). "Acute toxicity of heavy metals (copper, lead, zinc), phenol and sodium on *Allium cepa* L., *Lepidium sativum*. L. and *Daphnia magna* St.: comparative investigations and the practical applications," *Water Research*, 29(2): 497–503.

Arora, S. Sharma ,P. S. Kumar, R. Nayan, P. K. Khanna, and Zaidi ,M. G. H. (2011). Gold nanoparticle induced enhancement in growth and seed yield of *Brassica juncea*. *Plant Growth Regulation*, 3: 303–310.

Asli, S., Aydinalp, C. and Marinova, S. (2009): The effect of heavy metals on seed germination and plant growth on Alfalfa Plant (*Medicago Sativa*). *Bulgaria Journal of Agricultural Science*, 15: 347-350.

Avishai, K., Assaf, Z., Ashimal, K. and Avi,.S. (2018). Therapeautic nanoparticles penetrate Leaves and deliver nutrients to Agricultural crops. Scientific Reports 8(1):3-6.

Azizi, M., Ghourchian, H., Yazdian, F., Dashtestani, F.and AlizadehZeinabas, H. (2017). Cytotoxic effect of albumin coated copper nanoparticle on human breast cancer cells of MDA-MB 231. Plos One, 12:0188639-0188639.

Bagheri, S. Chekin, .F.and Abd Hamid,S.B (2013). Synthesis of Pt doped TiO2 nanoparticles: characterization and application for electrocatalytic oxidation of 1-methionine, Sensors and Actuators. *Journal of Biochemistry*, 177: 898–903.

Bai, W., Zhang, Z., Tian, W. (2010). "Toxicity of zinc oxide nanoparticles to zebrafish embryo: a physicochemical study of toxicity mechanism." *Journal of Nanoparticle Research*, 12, (5): 1645–1654.

Bandyopadhyay, S., Peralta-Videa, J.A., Plascencia-Villa G.M., Jose´-Yacama, N.and Gardea-Torresdey, J.L. (2013). Hazard Matter. *Journal of Environment*, 30(5):379-380.

Barbosa, D.P., Moritz, N. and Nicolai, D.J. (2014). Biogas-digestate as nutrient source for biomass production of Sida hermaphrodita, Zea mays.L and Medicago sativa L. *Energy Procedia*, 59:120-126.

Barenna, R., Casals, E., Colan, J., Font, X., Sanchez, A.and Puntes, V. (2009). Evaluation of the ecotoxicology of model nanoparticles. *Chemosphere*, 850-785.

Batista, A., Carlos, A., Silvera, L., Ronald, G. K. and Nicholas, A. (2015). Nonadditive of nanoparticle interactions. *Science*, 12 (42):477-478.

BBC (2018). Nanocomposites, Nanoparticles, Nanoclays and Nanotubes: Global Markets to 2022. Accessed 20th December, 2018.

Bertsch, P. M. Glenn, T. C., Kabengi, N. J., and Williams P.M. (2009) "Toxicity of manufactured zinc oxide nanoparticles in the nematode *Caenorhabditis elegans. Environmental Toxicology and Chemistry*, 5 (6): 1324–1330.

Beyer, W. F. and Fridovich, I. (1987). Assaying for superoxide dismutase activity: some large consequences of minor changes in conditions. *Analytical Biochemistry* 161: 559-566.

Blade, S. F., Shetty, .S. V. R., Terao, .T. and Singh, B. B.(2005). Recent developments In cowpea cropping systems research. In Singh, B.B., Mohan Raj, D. R., Dashiell, K. E., & Jackai, L. E. N. (Eds.) *Advances in Cowpea Research*, International Institute of Tropical Agriculture and Japan International Research Center for Agricultural Sciences.

Bogdan, N., Perreault, F. N., Morin, M., Claverie, J. and Popovic, R.(2012). Interaction of gold nanoglycodendrimers with algal cells (*Chlamydomonas reinhardtii*) and their effect on physiological processes. *Nanotoxicology* 2: 109–120.

Bundschuh, M., Filser, J., Luderwald, S., Mckee, M.S., Metreveli, G. and Schaumann, G.E. (2018). Nanoparticles in the environment: where do we come from, where do we go to? *Environmental Sciences Europe,* 1(12):30-36.

Buzea, C., Pacheco, I. I. and Robbie, K.(2007). Nanomaterials and nanoparticles: Sources and toxicity. *Biointerphases*, 2 (4): 17–71.

Cakmak, I. and Horst, W.J. (1991) Effect of aluminium on lipid peroxidation, superoxide dismutase, catalase, and peroxidase activities in root tips of soybean (*Glycine max*). *Physiology of Plants*, 83:463-468.

Cakmak, I., Marschner, H., Bangerth, F. (2009). Effect of zinc nutritional status on growth, Protein metabolism and levels of indole-3-acetic acid and other phytohormones in bean (*Phaseolus vulgaris* L.). *Journal of Experimental Botany*, 40: 405–412.

Carillo, P., Gibon, Y. and Wiki, P. (2008). Protocol: Extraction and determination of proline. *Journal of Biological Chemistry*, 215:655-660.

Carmen, I.U., Chithra, P., Huang, Q., Takhistov, P., Liu, S., and Kokini, J.L. (2003). Nanotechnology: a new frontier in food science. *Food Technology*, 13 (57):24–29.

Castiglione, M.R., Giorgetti, L., Geri, C. and Cremonini, R.(2004).The effects of nano-TiO_2 on seedgermination, development and mitosis of root tip cells of *Vicia narbonensis* L. and *Zea mays* L. *Journal of Nanoparticle Research,* 13(6):2443–2449.

Catherine, J.M., Anand, M.G., and John, W.S. (2008). Gold nanoparticles in biology: beyond toxicity to cellular imaging, *Accounts of Chemical Research*, 5 (12): 1721–1730.

Chen, .L. Zhou, L. Liu, .Y. Deng, S. Wu, H. and Wang, G. (2012). Toxicological effects of nanometer titanium dioxide (nano-TiO_2) on *Chlamydomonas reinhardtii*. *Ecotoxicology of Environ*ment, 9(84):155−162.

Chen, J., Song, Y., Zhang, L. (2013). Lycopene/Tomato consumption and the risk of prostrate cancer: a systematic review and meta-analysis of prospecticve studies. *Nutrition Science Vitaminol*, 59(3):213-223.

Cheng, Y., Yin, L., Lin, S., Wiesner, M., Bernhardt, E., and Liu, J. (2011). "Toxicity reduction of polymer-stabilized silver nanoparticles by sunlight," *Journal of Physical Chemistry*, 115: (11) 4425–4432.

Cherif, J., Mediouni, C., Ammar, W. B. and Jemal, F. (2011). Interactions of zinc and cadmium toxicity in their effects on growth and in antioxidative systems in tomato plants (*Solanum lycopersicum* L.). *Journal of Environmental Sciences*, 23: 837–844

Chinnamuthu, C.R., and Boopathi, P.M. (2009). Nanotechnology and Agroecosystem. *Madras Agric Journal*, 96:17-31.

Christensen, L.P, Christensen, K.J., Thybo, A.K (2006). Effect of organic growing systems on sensory quality and chemical composition of tomatoes. *Food Science and Technology*, 39 (8): 835-843.

Clarke, B.B and Brennan, E. (1989). Differential cadmium accumulation and phytotoxicity in sixteen tobacco cultivars. Journal of the Air and waste Management Association, 39(10):1319-1322.

Colman, A. J., Unrine, J.M., Colman, B. P., Bone, A. J., Gondikas, A. P. and Matson C. W. (2012). Biotic and abiotic interactions in aquatic microcosms determine fate and toxicity of Ag nanoparticles. Aggregation and dissolution, *Environmental Science and Technology*, 13:6915–6924.

Connolly, M., Fernandez, M., Conde, E., Torrent, F., Navas, J.M., and Fernandez-Cruz, M. L. (2016). Tissue distribution of zinc and subtle oxidative stress effects after dietary administration of ZnO nanoparticles to rainbow trout. Science of the total Environment, 555(552):334-343.

Cossins, D. (2014). Next generation: nanoparticles augment plant functions. The incorporation of synthetic nanoparticles into plants can enhance photosynthesis and transform leaves into biochemical sensors. *The Scientist, News & Opinion*, 1: 525-528

DeRosa, M.C., Monreal, C., Schnitzer, M., Walsh, R. and Sultan, Y. (2010) Nanotechnology in fertilizers. *National Nanotechnology,* 5:91.

Devalapally, H. A., Chakilam, M. M., and Amiji, A. (2007). Biogenic production of zinc oxide nanoparticles from aqueous extracts of *Duranta erecta* L. *Journal of Pharmaceutical Sciences,* 96 (10): 2547-2565.

Dhiman, P., Batoo, K. M., Kotnala, R. K. and Singh, M. (2012). Fe-doped ZnO delivery to plants. *Plant Science,* 11 (179):154–163.

Elizabeth, A.F. and Christer, H. (1998). Acute silver toxicity to seawater-acclimated rainbow trout: influence of salinity on toxicity and silver speciation, *Environmental Toxicology and Chemistry,* 17(4):589–593.

Elliot, K.C. (2011). Nanomaterials and the precautionary principle. Environmental Toxicology and Environmental Health perspectives, 119(6):240-245.

EPA (2007).Nanotechnology white Paper. U.*S Environmental Protection agency Report*, EPA 100/B-07/001, Washinton D.C 20460, USA.

Eva, M.S., Anders, B., Matthias, K. and Stefan, T. (2008). Insignificant acute toxicity of TiO_2 nanoparticles to willow trees, *Journal of Soils and Sediments*, 9(1):46–53.

Fatoki, S.O., Ayanda, S., Folahan, A, Bhekumusa, J. and Beatrice, O.(2012). Preparation and characterization of activated carbon – nFe3O4, activated carbon – nSiO_2 and activated carbon – nZnO Hybrid. *Materials*, 29:178-191.

Falco, W.F., Queiroza, Fernandesa, J. and Boteroa, E.R. (2011). Interaction between chlorophyll and silver nanoparticles: Aclose analysis of chlorophyll fluorescence quenching. *Journal of Photochemistry and PhotoBiology A Chemistry*, 299:203-209.

Feizi, H. Rezvani, P., Moghaddam, N. and Fotovat, A. (2012). Impact of bulk and nanosized titanium dioxide TiO_2 on wheat seed germination and seedling growth. Biological Trace Element Research, 146 (1): 101-106.

Feretti, D. I., Zerbini, C., Zani, E., Ceretti, M., Moretti, M., and Monarca. S.(2007). *Allium cepa* chromosome aberration and micronucleus tests applied to study genotoxicity of extracts from pesticide-treated vegetables and grapes. *Food Additives* and *Contaminants*, 3(5): 6561–572.

Fernando, G., and Chris, M.W. (1997). The relative importance of water hardness and chloride levels in modifying the acute toxicity of silver to rainbow trout (*Oncorhynchus mykiss*), *Environmental Toxicology and Chemistry*, 16 (11): 2363–2368.

Fiskesjo, G. (1993). Allium Test I: A 2-3 day plant test for toxicity assessment by measuring. The mean root growth of onions *(Allium cepa* L.), *Environmental Toxicology and Water Quality*, 8 (4): 461–470.

Foss, H.S. and Baun, A. Michelson, E.S., Kamper, A. Borling, P. and Stuer-Lauridsen, F. (2009) Nanomaterials in consumer products, Nanomaterials: Risks and Benefits frontier in food science. *Food Technology*, 20 (57):24–29.

Foyer, H.C and Shigeoka, S. (2011). Understanding oxidative stress and antioxidant functions to enhance photosynthesis. Plant physiology, 155 (1) 93-100.

Gardea-Torresdey, J.L., Rico, C. M. and White, J. C. (2014). Trophic transfer, transformation, and impact of engineered nanomaterials in terrestrial environments. *Environmental Science and Technology*, 48(20): 5-8

Geremias, R. D., Fattorini, V., Fávere, T. D., and Pedrosa, R. C. (2010). "Bioaccumulation and toxic effects of copper in common onion *Allium cepa* .L." *Chemistry and Ecology*, 26(1): 19–26.

Ghormade, M. Deshpande, V. and Paknikar, K.M. (2011). Perspectives for nano biotechnology enabled protection and nutrition of plants. *Biotechnology Advances*, 29 (6): 792–803.

Golimowski, J., Bystrzejewska-Piotrowska, G., and Urban, P.L. (2009).Nanoparticles: their potential toxicity, waste and environmental management. *Waste Management*, 29(9): 2587–2593.

Granqvist, C., Buhrman, R., Wyns, J., and Sievers, A. (1976). Far-Infrared Absorption in Ultrafine Particles. *Physical Review Letters,* 37 (10): 625–629.

Groppa, M. D., Rosales, E. P., Iannone, M. F. and Benavides, M. P. (2008). "Nitric oxide, polyamines and Cd-induced phytotoxicity in wheat roots," *Phytochemistry,* 69(14): 2609–2615.

Gurmani, A.R., Din, J.U., Khan, S.U., Andaleep, R., Waseem, K. A., Khan K, and Hadyat, U. (2012). Soil Application of zinc improves growth and yield of tomato. *International Journal of Agricultural Biology*, 14: 91–96.

Hans T.R. (1999). Bioaccumulation and toxicity of silver compounds: a review, *Environmental Toxicology and Chemistry*, 18(1):89–108.

Hansen, S.F., Michelson, E.S., Kamper, A. P., Borling, F., Stuer-Lauridsen, and Baun, A. (2008). Categorization framework to aid exposure assessment of nanomaterials in consumer products, *Ecotoxicology*, 17(5): 438–447.

Hauck, T.S. Ghazani, A.A. and Chan, W.C. (2008). Assessing the effect of surface chemistry on gold nanorod uptake, toxicity, and gene expression in mammalian cells, *Small*, 4(1):153–159.

Hayashi, C. Uyeda, R. and Tasaki, A. (1997). Ultra-fine particles: exploratory science and technology. Translation of the Japan report of the related ERATO Project (1981–86). Noyes Publications.

He, L., Liu, A. Mustapha, A. and Lin, M. (2011). Antifungal activity of zinc nanoparticles against *Botrytis anerea* and *Penicillium expansium*. *Microbiology Resource*, 166:207-215.

Hernandez-Fuentes, A.D., Lopez-Vargas, E.R., Pinedo Espinoza, J.M., Campos-Montiel, R.G., Valedes-Reyna, J. and Juarez-Maldonado, A. (2017). Postharvest behaviour of bioactive compounds in tomato fruits treated with Cu nanoparticles and NaCl stress. *Journal of Applied Science*, 7(10), 980.

Hernandez-Viezcas, J.A., Castillo-Michel, H., Andrews, J.C., Cotte, M., Rico, C., Peralta Videa, J.R., Ge, Y., Priester, J.H., Holden, P.A., Gardea-Torresday, J.L. (2013). Insitu synchrotron X-ray fluorescence mapping and speciation of CeO_2 and ZnO nanoparticles in soil cultivated soybean (*Glycin max*). ACS Nano 7 (2):1415-1423.

Himanshu, A. (2013). In Kind Food Transfers-II: Impact on Nutrition and Implications for Food Security and Its Costs. *Economic and Political Weekly*, 48 (47): 60-73.

Hogstrand, C., Galvez, F. and Wood, C.M. (1996). Toxicity, silver accumulation and methallothionein induction in fresh water rainbow trout during exposure to different silver salts, Environmental Toxicology and Chemistry, 15(7):1102-1108.

Holsapple, M.P, Farland, H. Landry T.D. (2005). Research strategies for safety evaluation of nanomaterials, part II: toxicological and safety evaluation of nanomaterials, current challenges and data needs, *Toxicological Sciences*, 88(1): 12–17.

Hong, F. You,. Liu, C., Gao, F., Wu, C., and Yang, P., (2014). Influence of nano-anatase TiO_2 on the nitrogen metabolism of growing spinach and tomato as a function of varietal and technological factors. *Journal of Agriculture and Nutrition*, 10(129): 5 -8

Howe, G. and Merchant, S. (1992).“Heavy metal-activated synthesis of peptides in *Chlamydomonas reinhardtii*,” Plant Physiology, 98 (1): 127–136.

Huang, F., Tai, M., Chou, K.W., and Chang, Y.C. (2002). "Cytotoxicity of resin-, zinc oxide eugenol and calcium hydroxide-based root canal sealers on human periodontal ligament cells and permanent V79 cells," *International Endodontic Journal*, 35(2): 153–158.

Hussein, M. Z,. Bin, Z., Zainal, A., Yahaya, H. and. Foo, D. W. V.(2002)."Controlled release of a plant growth regulator, α-naphthaleneacetate from the lamella of Zn-Al-layered double hydroxide nanocomposite. *Journal of Controlled Release*, 82(23):417–427.

Inokuchi, R., Itagaki, T., wiskich, J.T Nakayama, K. and Okada, M. (1997). An NADP glutamate dehydrogenase from the green alga Bryopsis maxima. Purification and properties. Plant and Cell Physiology, 38(3):327-335.

Jahan, S., Alias, Y.B., Abubakar, A.F. and Yussof, I. (2008). Toxicity evaluation of ZnO and TiO_2 nanomaterials in hydroponic red bean (*Vigna angularis*) plants: Physiology, biochemistry andkinetic transport. Journal of Environmental Science, 1,http//dx.doi.org/10.1016/j-jes.2017.12.022.

John, L.J., Claudiana, M.D., Cleber, J.J. and Jorge, A.G. (2013). Photosynthetic capacity and water use Efficiency in sugarcane genotypes subject to water deficit during early growth phase. *Brazillian archives of Biology and Technology,* 56(5):735-748.

Kadar A.A., Stevens M.A., Albright-Holton, M., Morris, L. and Algazi M. (1999). Effect of fruit Ripeness when picked on flavor and composition in fresh market tomatoes. *Journal of the American Society for Horticultural Science*, 102: 724 -731.

Kamali, M., Jafari, L., Rezvani, P. and Moghaddam, L. (2013). "Phytotoxicity and stimulatory impacts of nanosized and bulk titanium dioxide on fennel (*Foeniculum vulgare* Mill)," *Chemosphere*, 91(4): 506–511.

Karamushka, V.I. and Gadd, G.M. (1999). Interaction of *Saccharomyces cerevisiae* with gold: toxicity and accumulation, *BioMetals*, 12(4): 289–294,

Karkleliene, R., Dambrauskiene, E., Juskeviciene, D., Radzevicius, A., Rubinskiene, M., and Viskelis, P. (2014). Productivity and nutritional value of dill and parsley. *Horticultural Sciences* (*Prague*), 41(3): 131 -137.

Katherine, W.S, Guangshu, Z., David, W.P., Pedro J.A.A. and Jerald, L.S. (2014). Transport of gold nanoparticles through plasmodesmata and precipitation of gold Ions in woody poplar, *Environment science Technology Letter*, 1 (2): 146–151.

Keltjens, W., Rodriguez, D., and Goudriaan, J. (1998). Plant leaf area expansion and assimilate production in wheat *Triticum aestivum* .L.) Growing under low Phosphorus conditions. *Journal of plant and soil*, 200:227-228.

Khodakovskaya, M. V. B., Kim, B., and Kim, J.N. (2012).Carbon nanotubes as plant growth regulators: effects on tomato growth, reproductive system, and soil microbial community, Small, 9, (1):115–123.

Kimberly, .W. and Victor, B.K. (2010). Canning, Picking and Preserving: *Tools, Techniques and Recipes*, 1:88.

Klaus, M.G.A. Van der Heijden, S., De Bruin, L., Luckerhoff, R.S.P. and van Logtestijn, J. (2016).Wide spread plant-fungal-bacterial symbiosis promotes plant biodiversity, plant nutrition and seedling recruitment. *The ISME journal* 10 (2): 389-399.

Klein, B.P. and Perry, A.K. (1982). Ascorbic acid and vitamin A Activity in selected vegetables from different Geographical areas of the United States Journal of Food Science, 47:941-945.

Kreider, V. and W. Halperin. (2010). "Engineered nanomaterials: learning from the past, planning for the future," *Journal of Occupational and Environmental Medicine*, 53: (6) S108–S112.

Kritchevski S.B. (1999). β-Carotene, carotenoids and the prevention of coronary heart disease. *Journal of Nutrition*, 7(129): 5 -8.

Kulkarni, N., Muddapur, U. (2014).Biosynthesis of metal nanoparticles. *Journal of Nanotechnology* 2(1): 1-8.

Kumar, A., Pandey, A. K., Singh, S. S., Shanker, R., and Dhawan, A. (2011). Engineered ZnO and TiO2 nanoparticles induce oxidative stress and DNA damage leading to reduced viability of Escherichia coli. *Free Rad. Biol. Med*, 51:1872−1881.

Kuppusamy P, M., Yusoff, G. P., Maniam, N. and Govindan, M. (2016). Biosynthesis of metallic nanoparticles using plant derivatives and their new avenues in pharmacological applications-An updated report. *Saudi Pharmaceutical Journal*, 24(4): 473-484

Kureh, I., Segun, A., Lagoke, S.T.O. and Mohammed, S. (2005b). Host Plant resistant and anti-transpirant for the control of Alectra vogelli in Soybean. *Journal of food Agriculture and Environment*, 3(2):176-180.

Lagriffoul, A., Mocquot, B., Mench, M. and Vangronsveld, J. (1998). Cadmium toxicity effects on growth, mineral and chlorophyll contents and activities of stress related enzymes in young maize plants (*Zea mays* L.). *Plant and Soil*, 200 (2):241-250.

Lee, W., An, Y., Yoon, H., and Kweon, H. (2005). "Toxicity and bioavailability of copper nanoparticles to the terrestrial plants mung bean (*Phaseolus radiatus*) and wheat (*Triticum aestivum*): plant agar test for water-insoluble nanoparticles," *Environmental Toxicology and Chemistry*, 27(9):1915–1921.

Lee, W., Kwak, J.I. and An, Y. (2012). "Effect of silver nanoparticles in crop plants *Phaseolus radiatus* and Sorghum bicolor: media effect on phytotoxicity*". Chemosphere,* 86(5): 491–499.

Lenore, A., and Susan, S. (2000). Lycopene and cardiovascular disease. *American Journal of Clinical Nutrition*, 71(6):1691s-1695s.

Leonardi, .C. Ambrosino, P., Esposito, F., and Fogliano, V. (2000). Antioxidative activity and carotenoid and tomatine contents in different typologies of fresh consumption tomatoes. *Journal of Agricultural and Food Chemistry*, 48: 4723–4727.

Leyva, J. and Yoa, S. (2014). The functions of tomato-Lycopene and its role in human health. *Journal of the American Botanical Council*, 62:49-56.

Li, H. (2000). Principles and Techniques of Plant Physiological, Biochemical Experiment. Higher Education Prss, Beijing, pp.260-263.

Lidén, G. (2011).The European commission tries to define nanomaterials, *Annals of Occupational Hygiene*, 55(1): 1–5.

Lin, D. and Xing, B. (2007). (Phytotoxicity of nanoparticles: inhibition of seed germination and root growth, *Environmental Pollution*, 18(21):98-100

Lombi, E., Nowack, B., Baun, A. and McGrath, S. P. (2012). *Evidence for effects of manufactured nanomaterials on crops is inconclusive*, Proceedings of the National Academy of Sciences of the United States of America, 109:49.

Loureiro, S., VanGestel, C.A. and Lofts, S. (2018). Metal based Nanoparticles in soil: Fate, Behaviour and Effects on soil invertebrates. Journal of Environmental Toxicology, 29(10):79.

Luisa, L. M. and Miguel P. M. (2006). Effect of Excess Copper on Tomato Plants: Growth Parameters, Enzyme activities, chlorophyll, and mineral Content. *Journal of plant nutrition,* 29 (12):28-30.

Ma, Bertsch, M., Glenn, T.C., Kabengi, N.J.AND Williams, P.L. (2009). Toxicity of manufactured zinc oxide nanoparticles in the nematode *Caenorhabditis elegans, Environmental Toxicology and Chemistry*, 28(6):1324-1330.

Ma, X., Geiser-Lee, J., Deng, Y. and Kolmakov, A. (2010). Interactions between engineered nanoparticles (ENPs) and plants: Phytotoxicity, uptake and transport: *Science of the Total Environment,* 408(16):3053-3061.

Makeen, K., Babu, G.S., Lavanya, G.R. and Abraham, G. (2007). Studies of chlorophyll content by different methods in Black Gram (*Vigna mungo* L.). *International journal of Agricultural research*, 2:651-655.

Maphosa, Y. and Jideani, A.V. (2017).The role of Legumes in human nutrition, functional food-improves helth through adequate food. https://www.intechopen,com/books/functional food.

Masfaraud, J., Foltête, V., Bigorgne, E. (2011). "Environmental impact of sunscreen nanomaterials: ecotoxicity and genotoxicity of altered TiO_2 nanocomposites on *Vicia faba*," *Environmental Pollution*, 159(10):2515–2522.

Milka, O., Montes-holgguin, J., Peralta-videa, G., Alejandro Martinez, M., Guadalupe de la rosa, H. A., Castillo, M and Jorge Gardea-torresdey, L. (2006). Biochemical and spectroscopic studies of the response of *Convolvulus arvensis* L. to chromium (iii) and chromium (iv) stress. *Environmental Toxicology and Chemistry*, 25 (1):220-226.

Minfang, Q., Yufeng, L., and Tianlai, L. (2013). Nano-TiO_2 improves the photosynthesis of tomato leaves under mild heat stress. *Biological trace elements research*, 156(1):323-328.

Mitchell, G.A., Bingham, F.T. and Page, F.A. (1999). Yield and metal composition of lettuce and wheat grown on soils amended with sewage sludge enriched with cadmium, copper, nickel, and zinc. *Journal of Environmental Quality*, (2):165–171.

Monteiro-Riviere, N.A, Xia, X., and Riviere, J. E. (2010). An index for characterization of nanomaterials in biological systems. *Nature Nanotechnology*, 5(9) 671–675.

Mouldgil, B.M., Kevin, W. P., Scott, C. B., Vijay, B. K. Scott, C. W. and Roberts, S. M.(2006). Research strategies for safety evaluation of nanomaterials. Part VI. Characterization of nanoscale particles for toxicological evaluation, *Toxicological Sciences*, 90(2): 296–303.

Mukherjee, A., De la Torre-Roche, R., Hamdi, H., and White, J. C. (2015). A review of the use of engineered nanomaterials to suppress plant disease and enhance crop yield. *Journal of nanoparticle research*, 45(17):92.

Mukherjee, A., Peralta-videa, J.R., Bandyopadyay, S., Rico, C.M., Zhao, L, L., and Gardea Torresdasy, J.L. (2013). Physiological effects of nanoparticulate ZnO in green peas (*Pisum sativum* L.) cultivated in soil.*Metallomic*, 10(10):39.

Munzuroglu, J. and Geckil, H. (2002). Effects of metals on seed germination, root elongation, and coleoptile and hypocotyl growth in *Triticum aestivum* and *Cucumis sativus. Archives of Environmental Contamination and Toxicology*, 43(2):203–213.

Nadiminti, Y. D., and Dong, C. (2013). Nanostructured liquid crystalline particles as an alternative delivery vehicle for plant agrochemicals. *Applied Materials and Interfaces*, 5(5):1818–1826.

Nagata, M. and Yamashita, I. (1992). Simple Method for Simultaneous Determination of Chlorophyll and Carotenoids in Tomato Fruit. Journal of Food Science Technology, 39:925-928.

Naeem, M., Abid, A.A., Sarvajeet, S.G. (2017). Essential plant nutrients uptake, use efficiency and management. eBooks by Springer:978-3-31186488-4.

Nair, P.M.G and Chung, I.M. (2010). Impact of copper oxide nanoparticles exposure on *Arabidopsis thaliana* growth, root system development, root lignification, and molecular level changes. *Environmental Science Pollution Resources*, 113(56):3210-3215

Nakano, Y. and Asada, K. (1981). Hydrogen peroxide is scavenged by ascorbate-specific peroxidase in spinach chloroplasts. Plant Cell Physiology, 22:867-880.

Nevious, B. A., Chen, Y. P., Ferry, J. L. and Decho, A. W. (2012).“Surface-functionalization effects on uptake of fluorescent polystyrene nanoparticles by model biofilms,” *Journal*

of Ecotoxicology, 21: (8) 2205–2213. View at Publisher· View at Google Scholar· View at Scopus.

Nguyen, B. D., Brar, S.D., Bui, B. C, Nguyen T.V, L. N. Pham, P.B and Nguyen O.S (2015). Environmental Effects of Nanoceria on seed production of common Beans (*Phaseolus vulgaris*). A proteomic Analysis. *Environmental Science Technology*, (XXXX) XXX: XXX−XXX.

Niklasson, G. A. and Granqvist, C. G. (1999). New approach to the origin of lognormal size distributions of nanoparticles. *Nanotechnolog*, 4(10): 25–28.

Nwaichi, E.O., and Anosike, E.O. (2016). Plant response on exposure to Ag Nanoparticles. Astudy with *Vigna subterranean. Journal of Biochemistry.*5:29

Ogunkunle, C.O., Folarin, O.O., Olorunmaiye, K.S.,Fatoba, P.O. (2017). Bioaccumulation of copper and tissue partitioning of selected mineral elements in German Pea (Kleine Rheinlanderin) under the influence of copper nanoparticles.

Ogunkunle, C.O., Jimoh, M.A., Asogwa, N.T., Viswanathan, K., Vishwakarma, V., and Fatoba, P. O., (2018). Effects of manufactured nano-copper on copper uptake, bioaccumulation and enzyme activities in cowpea grown on soil substrate. *Ecotoxicology and Environmental Safety*, 155: 6-93

Oh, W. C., M. L. Chen., and Lim, C. S. (2007). Preparation with different mixing ratios of anatase to activated carbon and their photocatalytic performance. *Journal of Ceramic Processing Resource, 8*: 119 – 124.

Olayinka, B.U. and Emmanuel, E.O. (2015). Growth analysis and yield of two varieties of groundnut (*Arachis hypogeae.*L.) as influenced by different weed control methods. *Indian Journal of Plant Physiology,* 20(2):130-136.

Olga, O., Mykola, V., Nataliya, T., Lyudmla, B. and Inna, K. (2016). The effects of copper and zinc nanoparticles on the growth parameters, contents of scorbic acid and quantitative composition of amino acids and acylcarnitines in Pistia stratiotes L. (Araceae).65-70.

Omenn, G.S., Goodman, G.E., Thornquist, M.D, Balmes, J., Cullen, M.R, Glass, A., Keogh. J.P, Meyskens, F.L, Valanis, B., Williams, J.H, Bamhart, S. Cherniack, M.G, Brodkin, C.A and Hammer, S. (1996). Risk factors for lung cancer and for intervention effects in CARET, The Beta-carotene and Retinol Efficacy. *Journal of the National Cancer Institute,* 88(21):1550-1559.

Oniga, I., Tamas, M., Toiu, A., Fodorea, C., Vostinaru, O., Popovici, E.J., Vadan, M. (2004). Cercetari asupra unor pigmenti din mere tratate cu ozon. Clujul Medical, 77(4):789-792.

Ozgur, U., Alivov, Y. I., Liu, C., Teke, A., Reshchikov, M. A., Dogan, S. (2005). A comprehensive review of ZnO materials and devices. *Journal of Applied Physics,* 98:041301.

Page, A.L., Miller, R.H and Keeney, D.R. (Ed., 1982):Methods of soil analysis;Chemical and microbiological properties, 2.Aufl. 1184 S., Ameriican Society of Agronomy (Publ.), Madison, Wisconsin, USA, gebunden

Patel, H.V, Paemar S.R, Chidasama and Mangrola A.V. (2013). Interactive studies of zinc with cadmium and arsenic on seed germination and antioxidant properties of *phaseolus aureus roxb. International journal of plant animal and environmental sciences,* 3(1):2231-4490.

Peltry, N., Egli, I., Gahrutu, J. B., Tugirimana, P.L., Boy, E. and Hurrell, R. (2012). Stable iron isotope studies in Rwandese women indicate that the common bean has limited potential as a vehicle for iron biofortification. *Journal of nutrition,* 142:492-497.

Perreault. F. Bogdan, N., Morin, M., Claverie, J., and Popovic, R. (2012). Interaction of gold nanoglycodendrimers with algal cells (*Chlamydomonas reinhardtii*) and their effect on physiological processes. *Nanotoxicology*, 6 (2):109–120.

Phillips, R. D., Mcwatters, K. H., Chinnan, M. S., Hung, Y. C., Beuchat, L. R., Sefa-dedeh, S., Saki-dawson, E., Ngoddy, P., Nnanyelugo, D., and Enwere, J. (2003). Utilization of cowpeas for human food. *Field crops Resource.* 82**(**1): 193-198.

Potera, C. (2010). Nanomaterials: Transformation of Silver Nanoparticles in Sewage Sludge. *Journal of Environmental Health perspective*, 118 (12): A526-A527.

Radiman, R., Abd-Shukor, A. and Chia, C. H. (2011). Capping effect of palm-oil based organometallic ligand towards the production of highly monodispersed nanostructured material, in palm oil: nutrition, uses and impacts, *Nova Science*, 1:189–219.

Rai, M., Ingle, A., Pandit, R., Paralikar, P., Shende, S. and Gupta, I. (2018). Copper and copper nanoparticles: Role in management of insect-pests and pathogenic microbes. *Nanotechnology Reviews,* 7:303-315.

Raliya, R., Biswas, P., Tarafada, J.C. (2015).TiO_2 nanoparticles biosynthesis and its physiological effect on mung bean (*Vigna radiate* L.). *Biotechnology reports*, 5, 22-26.

Raliya, R., Saharan, V., Dimpka, C. and Biswas, P. (2017). Nanofertilizer for precision and sustainable agriculture: current state and future perspectives. *Journal of Agricultural*

and Food Chemistry, 66(26):6487-6503.

Rayhaneh, A., Norouzi. M., Saeri. M.(2016). Impact of zinc and zinc oxide nanoparticles on

the physiological and biochemical processes in tomato and wheat. *Journal of Botany.* 01-04.

Ramesh, R., Tarafdarl., J.C. and Sharma., S. (2015). Nanotechnology: Interdisciplinary

Science of applications. *African Journal of Biotechnology,* 1684-5315.

Rajput, K., Rai, S.K., Bhatt, A. and Agrawal, P.K. (2017). Biosynthesis and application of silver nano-particles: a review. *International journal of current microbiology and applied Science*, 6(7):1513-1528.

Reddy, K. M., Feris, K., Bell, J., Wingett, D. G., Hanley, C. and Punnoose, A. (2016) "Selective toxicity of zinc oxide nanoparticles to prokaryotic and eukaryotic systems," *Applied Physics Letters*, 90, (21): 213902.

Rizzello, L., and Pompa, P.P. (2014). Nanosilver-based antibacterial drugs and devices: mechanisms, methodological drawbacks, and guidelines, *Chemical Society Reviews,* 43 (5): 1501–1518.

Rousk, J., Erland Baath and Fierer., N. (2009). Soil bacterial and fungal communities across a Ph gradient in an arable soil. ISME Journal, 4, 13401351

Shekhawati, S., Arshad, M., Chaudhari, S.K (2014). Zinc oxide nanoparticles for revolutionilizing agriculture: *Science world journal*, 115 (92-94).

Sahar, M. O. (2014). "Antifungal activity of silver and copper nanoparticles on two plant pathogens, *Alternaria alternata* and *Botrytis cinerea*," *Research Journal of Microbiology*, 9: 34–42.

Sanchis, F.J., Manzanares, M., Eusebio, F., De, A., Tenorio, J.L. Ayerbe, L. (1998). Turgor maintenantce, osmotic adjustment and soluble sugar and proline accumulation in 49 pea cultivars in response to water stress. *Field Crops Resource*, 59**:**225–235.

Sanghamitra, M., Almeida, E.A., Arigi, E.A., Choi, N.C and VerBekmoes *et al*

(2015).Environmental Effects of Nanoceria on seed production of common bean Sohaebuddin (Phaseolus vulgaris): A proteomic Analysis. *Environmental Science and Technology*, 49(22), 13283-13293.

Savage, N., Thomas, T.A., and Duncan, J.S. (2007). Nanotechnology applications and implications research supported by the US Environmental Protection Agency STAR grants programme. *Journal of Environmental Monitoring*, *Science Technology*, 40: 4336–4345.

Selivanov, V.N., and Zorin, E.V. (2009). Sustained Action of Ultrafine Metapowders on seeds of grain crops, *Perspekt Materialy*, 4:66-69.

Sharma, V., Shukla, R. K., Saxena, N. D., Parmar, M. D., and Dhawan, A. (2009). "DNA damaging potential of zinc oxide nanoparticles in human epidermal cells." *Toxicology Letters*, 185(3): 211–218.

Shekhawat, M.S., Ravindran, C.P., and Manokari, M. (2014). Biogenic production of zinc oxide nanoparticles from aqueous extracts of *Duranta erecta* L. *International Journal of Green and Herbal Chemistry*, 3 (2): 518-523.

Shi, Z., Liu, F., Yao, S. (2012). Adsorptive removal of phosphate from aqueous solutions using activated charcoal. *Journal of Environmental Pollution*, 159(2): 1277–1282.

Simon, J.A (1997). Recent developments in cleanup technologies. *Remediation Journal*, 8(1):129–136.

Singh, B. B., Ehlers, J. D., Sharma, B., and Freire, F. R. (2002). *Recent Progress in Cowpea Breeding*. International Institute of Tropical Agriculture (IITA). 22-40

Singh, B.B., Ajeigbe, H.A., Tarawali, S.A., Fernandez-Riveria, S. and Musa, A. (2003). Improving the production and utilization of cowpea as food and fodder, *Field Crop Resource*, 84:169-177.

Sivasankar, R., Kalaikandhan, R and Vijayarengan, P. (2012). Phytoremediating capability of four plant species under zinc stress. *International Journal of Environmental Science and Technology*, 2(1): 1-9.

Slade, S. J., and Pegg, G. F. (1993) "The effect of silver and other metal ions on the in –vitro growth of root-rotting Phytophthora and other fungal species," *Annals of Applied Biology*, (122)2: 233–251.

Smalle, J.A., Wang, S. J., Kurepa, (2011). Ultra-small TiO_2 nanoparticles disrupt microtubular networks in Arabidopsis thaliana Plant. *Cell & Environment*, 34(5): 811–820.

Sohaebuddin, S.K., Thevenot, P. T., Baker, D,. Eaton, J.W. and Tang, L. (2010). Nanomaterial cytotoxicity, composition, size, and cell type dependent. *Particle and fibre Toxicology*, 7 (22):20.

Somashekaraiah, B. V. Padmaja, K. and Prasad, A. R. K.(1992) ."Phytotoxicity of cadmium ions on germinating seedlings of mung bean (*Phaseolus vulgaris*): involvement of lipid peroxides in chlorphyll degradation." *Physiologia Plantarum*, 5(1):85–89.

Soni, D., Naoghare, P.K., Saravanadevi, S. and Pandey, R.A. (2015). Release, Transport and Toxicity of Engineered Nanoparticles. In D.M Whitacre (Ed.), Reviews of Environmental Contamination and Toxicology (pp1-47). Cham: Springer International Publishing.

Song, J. Y., Kim, B.S. (2013). Rapid Biological synthesis of silver nanoparticles using plant leaf extracts. Bioprocess Biosystem ngineer 32(1)78-84.

Sooyeon, L., Sunghyun, K., Saeyeon, K. and Insook, L. (2013). Assessment of phytotoxicity Of ZnO NPs on a medicinal plant, *Fagopyrum esculentum*. *Environmental Science and Pollution Research*, 20(2): 848–854.

Sreenivasulu, Y., Prasad, T.N., Sudhkar, V.P (2012) ''Effects of nanoscale zinc oxide particles on the germination, growth and yied of peanut. Journal of plant nutrition 35(6):905-927.

Stamm, H., Gibson, N., and Anklam, E. (2012). "Detection of nanomaterials in food and consumer products: bridging the gap from legislation to enforcement*," Food Additives and Contaminants* 29(8):1175–1182.

Stella, T., Y. L., Priscilla, A.B., Djurišić, M. Y. L. and Kenneth, L. (2010). "Toxicities of nano zinc oxide to five marine organisms: influences of aggregate size and ion solubility.," *Analytical and Bioanalytical Chemistry*, 396 (2): 609–618.

Sturikova, H., Krystofova, O., Huska, D. and Adam, V. (2018). Zinc, zinc nanoparticles and plants. Journal of Hazardous Materials, 349:101-110.

Szyndler, M.W., Haynes, K.F, Potter, M.F, Corn, R.M and Loudan, C. (2013).Entrapment of Bedbugs by leaf trichomes inspires microfabrication of biomimetic surfaces, Journal of the Royal Society Interface, 1:9.

Taiz, L. and Zeiger, E. (1998). Plant physiology 2nd edn, pp. 2551-286.Sinaeur, Sunderland, M.A, USA.

Tani, F. H., and Barrington, S. (2005). "Zinc and copper uptake by plants under two transpiration rates. Part I. Wheat (Triticum aestivum .L.)," *Environmental Pollution,* 138(3):538–547.

Taylor, G. J. and Foy, C. D. (1985). "Differential uptake and toxicity of ionic and chelated Copper in *Triticum aestivum*,." *Canadian Journal of Botany*, 63 (7):1271–1275.

Taylor, R. A., Otanicar, T. P., Herukerrupu, Y., Bremond, F., Rosengarten, G., Hawkes, E., Jiang, X. and Coulombe, S. (2013). *Feasibility of nanofluid-based optical filters. Applied Optics*, 52 (7): 1413–22

Thandavan, T. M. K., Gani, S. M. A., San Wong, C. and M.D., Nor, R. (2015). Enhance Photoluminescence and raman properties of Al-Doped ZnO nanostructures prepared using thermal chemical vapour deposition of methanol assisted with heated brass. *Journal of Pone*, 10(10):371-372.

Tiede, K., Boxall, A.B., Tear, S.P., Lewis, J., David, H. and Hassellov, M. (2008). Detection and Characterization of Engineered Nanoparticles in food and the environment. Food additives and contaminants: part A: Chemistry, Analysis, Control, Exposure and Risk Assessment, 25:(795-821).

Tonucci, L.H., Holden J.M., Beecher, G.R., Khachik, F., Davis C.S. and Mulokozi, G. (1995). Carotenoid content of thermally processed tomato-based food. Journal of Agric, Food Chemistry, 43:579-586.

Tyagi, P. (2013). Synthesis of metal nanoparticles. A biological prospective for analysis. *IJPRS Soil Screening Guidance*: 2(4) USEPA. User's Guide.

UNFAO (2010). Food and Agriculture Organisation of the United Nations.

USDA(2013). USDA National Nutrient Data base for Standard eference.http;//ndb.nal.usda.gov/ndb/search/list

USEPA(1996). Soil Screening Guidance: User's Guides ospublication.co.in/downloadapp.php/?id..

USEPA (2007). Nanotechnology white paper. Document Number EPA 100/B-07001 1 www.epa.gov/osa

Venkatesan, M., Fitzgerald, C. B., Lunney, J. G. and Coey, J. M. D. (2004). Anisotropic ferromagnetism in substituted zinc oxide. *Phys. Rev. Lett*, 93:177206.

Verma, S., and Dubey, R. S. (2001). Effect of cadmium on soluble sugars and enzymes of their metabolism in rice. *Biol. Plant*, 44:117–123.

Vinit-Dunand., F., Daniel, E., Badr, A.S., and Pierre, M.B. (2002). Effects of copper on growth and on photosynthesis of mature and expanding leaves in cucumber plants.163 (1): 53-58.

Viskelis, P., Audrius, R., Dalia, U., Jonas, V., Rasa, K. and Ceslovas, B. (2015). Biochemical Parameters in tomato fruits from different cultivars as functional foods for Agricultural, Industrial and Pharmaceutical uses. *Plants for the future*, 10:5772-60873

Viskelis, P., Vilkauskaite, G., and Noreika, R. K. (2005). Chemical composition, functional properties and consumption of tomatoes. *Journal of Food Balt*, 24(4):182 -192.

Wagner, S.C. (2011).''Biological Nitrogen Fixation''.*Nature Education Knowledge*, 3(10):15

Walker, N. J., and Bucher J. R. (2009). A 21st century paradigm for evaluating the health hazards of nanoscale materials? *Toxicological Sciences*, 110(2): 251–25.

Wang, F., Liu, X., Shi, Z., Tong, R., Adams, C.A. and Shi, X. (2016 a).Abuscular mycorrhizae alleviate negative effects of zinc oxide nanoparticle and zinc accumulation in maize plants- a soil microcosm experiment. Chemosphere, 147, 88-97.

Wang, K. (1996). "Comparative study on Cd phytotoxicity to different genes of rice," Rural Eco-Environment, vol. 12, no. 3, pp. 18–23.

Wang, Q., and Yang, S. (2017). ''Host-secreted antimicrobial peptide enforces symbiotic selectivity in Medicago truncatula DNA'', *Journal of Hungarian Academy of Sciences and Agricultural Biotechnology*, (26):6854-6859.

Wang, X., Summers, C. J., and Wang, Z. L. (2004). "Large-scale hexagonal-patterned growth of aligned ZnO nanorods for nano-optoelectronics and nanosensor arrays". *Nano Letters*, 4(3):423–426.

Wang, X., Yang, X., Chen, S., Li, Q., Wang, W., Hou, C., Gao, X. Wang, L., and Wang, S. (2016 b). Zinc oxide nanoparticles affect biomass accumulation and photosynthesis in Arabidopsis. Front. Plant Sci.https//doi.org/10.3389/fpls.2015.01243.

Wuncheng, W. (1986). Toxicity tests of aquatic pollutants by using common duckweed, Journal of *Environmental Pollution B*, 11(1):1–14.

Yang, F., Hong, F.S., You, W.J., Liu, C., Gao, F.Q. Wu, C. and Yang, P. (2006). Influence of nano-anatase TiO_2 on the nitrogen metabolism of growing spinach, *Biological Trace Element Research*, 110: 179–190.

Yin, L., Cheng, Y., Espinasse, B. (2011). “More than the ions: the effects of silver nanoparticles on *Lolium multiflorum*.” *Environmental Science and Technology*, 45(6) 2360–2367.

Yin, L., Colman, B. P., McGill, B. M., Wright, J. P., and Bernhardt, E. S.(2012).“Effects of silver nanoparticle exposure on germination and early growth of eleven wetland plants, *Plos one Journal*, 7 (10):2-8.

You, J., and Reid, J.R. (2006) Manufactured nanoparticles in the enivironment: multimethod dete mination of particle sizes: 43(19):7277-7284.

Zhang, L., Gu, F., Chan, J., Wang, A., Langer, R.S., and Faroichzad, O.C. (2008). Nanoparticles in Medicinal: Therapeutic applications and Developments.*Clinical Pharmacology Therapy*, 83:761-769.

Zhao, L., Peralta-Videa, J.R., Ren, R., Varela-Ramirez, A., Li, C., Hernandez-VIezcas, J.A.Aguilera, R.J. and Gardea-Torresday, J.L. (2012). Transport of Zn in a sandy loam soil treated with ZnO NPs and uptake by common plants: electron microprobe and confocal microscopy studies. *Chemical Engineering Journal*, 184:1-8.

Zheng, L., Hong,F., and Chao, L. (2005). Effects of Nano TiO_2 on strength of naturally aged seeds and growth of spinach. *Biological Trace Element Research*, 104(1):83-91.

Zuvervza-Mena, N., Medina-Velo, I.A., Barrios, A.C., Tan, W.P., Peralta-Videa, J.R. and Gardea-Torresdey, J.L. (2015). Copper nanoparticles/compounds impact gronomic and physiological parameters in cilantro (*Coriandrum sativum*). *Environmental Science: Processes and Impacts*, 17:1783-1793.



Figure 5: Bean plants



Figure 6: Tomato plants



Figure 7: Bean and tomato plants



Figure 8: Bean plant showing the pod and the inflorescence

UNIVERSITY OF ILORIN, ILORIN, NIGERIA

UNIVERSITY ETHICAL REVIEW COMMITTEE

Vice Chancellor: Prof. S.A. Abdulkareem
B.Che, M.ChE, (Detroit); Ph.D. (Louisville),
MNAICh, MNSE, MACS, R.Eng. (COREN).
Registrar: Dr, (Mrs) F.M. Olowoleni
B.Sc (Zaria); MBA, M.Sc. PGDE (Ilorin)

E-mail: P.M.B. 1515, Ilorin
uerc@unilorin.edu.ng
unilorin.uerc@gmail.com
Website: ethicalrview.unilorin.edu.ng
www.unilorin.edu.com

Our Ref: UIL/UERC/10/68ER001

Date: 12th April, 2018

Protocol Identification Code: UERC/LSC/148
UERC Approval Number: UERC/ASN/2018/1218

EFFECTS OF COPPER AND ZINC-OXIDE NANOPARTICLES ON THE GROWTH AND PRODUCTIVITY OF SOLANIUM LYCOPERSICUM AND *PHASEOLUS VULGARIS PLANTS*.

Name of applicant/Principal Investigator:	**AKANBI-GADA,** Mariam Abiola
Address of Applicant:	Department of Plant Biology Faculty of Life Sciences University of Ilorin, Ilorin.
Type of Review:	Full Committee Review
Date of Approval:	12/04/2018

Notice of Full Committee Approval

I am pleased to inform you that the research described in the submitted proposal has been reviewed by the University Ethical Review Committee (UERC) and given full Committee approval.

This approval dates from 12/04/2018 to 11/04/2021, and there should be no participant accrual or any activity related to this research to be conducted outside these dates.

You are requested to inform the committee at the commencement of the research to enable it appoints its representative who will ensure compliance with the approved protocol. If there is any delay in starting the research, please inform the UERC so that the dates of approval can be adjusted accordingly.

The UERC requires you to comply with all institutional guidelines and regulations and ensure that all adverse events are reported promptly to the UERC. No charges are allowed in the research without prior approval by the UERC. Please note that the UERC reserves the right to conduct monitoring/oversight visit to your research site without prior notification.

Thank You,

Ismaila Isah
For: University Ethical Review Committee

"....If it's not ethical, it's not scientific, if it's not scientific it's not ethical"