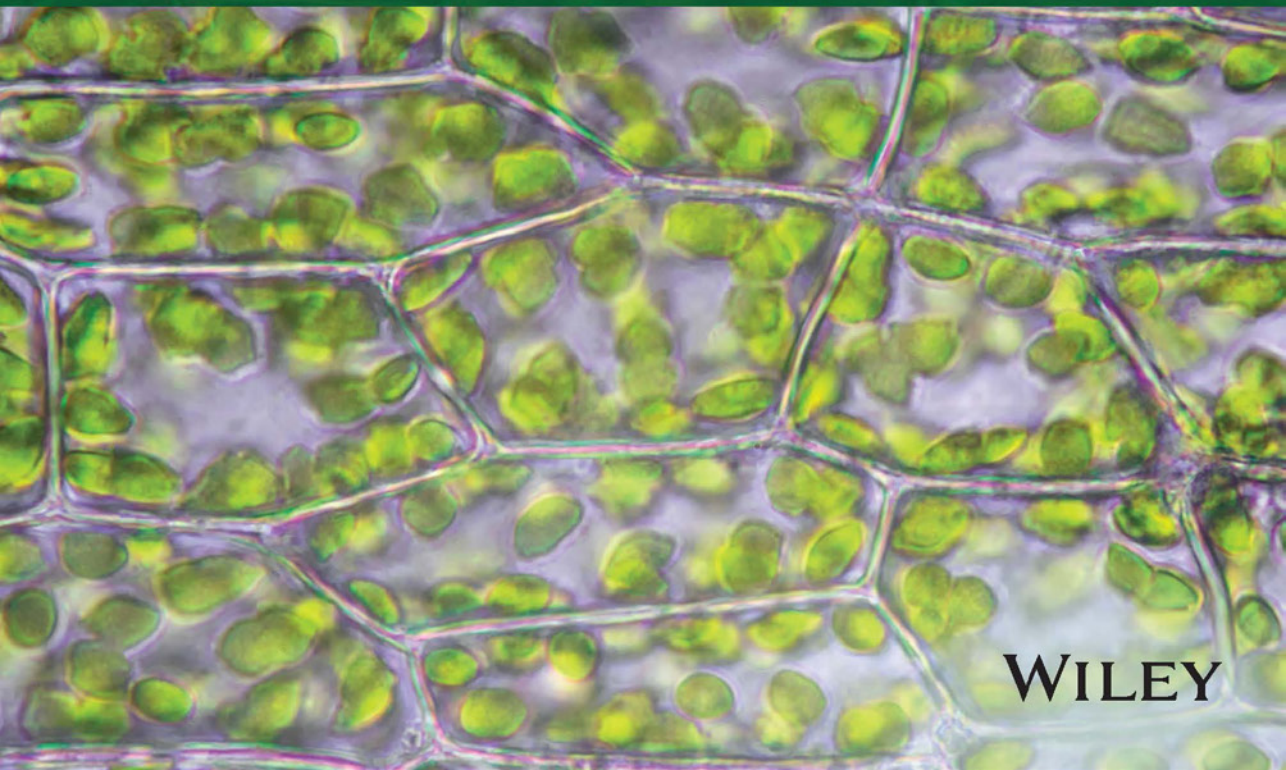


Plant Ionomics

**Sensing, Signaling and
Regulation**

Edited by

Vijay Pratap Singh • Manzer H. Siddiqui



WILEY

Plant Ionomics

Plant Ionomics

Sensing, Signaling, and Regulation

Edited by

*Vijay Pratap Singh
University of Allahabad
Prayagraj
India*

*Manzer H. Siddiqui
King Saud University
Riyadh
Saudi Arabia*

WILEY

This edition first published 2023
© 2023 John Wiley & Sons Ltd

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at <http://www.wiley.com/go/permissions>.

The right of Vijay Pratap Singh and Manzer H. Siddiqui to be identified as the editors of this work has been asserted in accordance with law.

Registered Offices

John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Wiley also publishes its books in a variety of electronic formats and by print-on-demand. Some content that appears in standard print versions of this book may not be available in other formats.

Trademarks: Wiley and the Wiley logo are trademarks or registered trademarks of John Wiley & Sons, Inc. and/or its affiliates in the United States and other countries and may not be used without written permission. All other trademarks are the property of their respective owners. John Wiley & Sons, Inc. is not associated with any product or vendor mentioned in this book.

Limit of Liability/Disclaimer of Warranty

While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials or promotional statements for this work. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

Library of Congress Cataloging-in-Publication Data applied for
Hardback ISBN 9781119803010

Cover Design: Wiley

Cover Image: © Pasottee/Shutterstock

Set in 9.5/12.5pt STIXTwoText by Straive, Pondicherry, India

Contents

List of Contributors *xii*

Preface *xvi*

1 Regulation of Metabolites by Nutrients in Plants 1

Akash Tariq, Fanjiang Zeng, Corina Graciano, Abd Ullah, Sehrish Sadia, Zeeshan Ahmed, Ghulam Murtaza, Khasan Ismoilov, and Zhihao Zhang

Introduction 1

Nitrogen (N) 2

Phosphorus (P) 3

Potassium (K) 5

Sulfur (S) 7

Magnesium (Mg) 7

Calcium (Ca) 8

Boron (B) 9

Chlorine (Cl) 10

Copper (Cu) 11

Iron (Fe) 11

References 12

2 Agricultural Production Relation with Nutrient Applications 19

Sehrish Sadia, Muhammad Zubair, Akash Tariq, Fanjiang Zeng, Corina Graciano, Abd Ullah, Zeeshan Ahmed, Zhihao Zhang, and Khasan Ismoilov

Introduction 19

Soil as a Basic Element in Agriculture 21

Constituents and Ingredients of Soil 21

Essential Nutrients in Agriculture Especially in Plants 23

Beneficial/Valuable Nutrients 24

Some Other Valuable Nutrients 24

Plant Nutrient Sources 24

Plant Nutrients Supply and Nature 24

Compost 25

Biosolids 25

Manure of Livestock 25

Crop Residues 25

Atmospheric Deposition 26

Synthetic Fertilizers 26

Issues Related to Plant Nutrition 26
Fertilizers and Fertilization Strategies 27
References 28

3 Role of Nutrients in the ROS Metabolism in Plants 30

Muhammad Arslan Ashraf, Rizwan Rasheed, Mudassir Iqbal Shad, Iqbal Hussain, and Muhammad Iqbal

Introduction 30
Oxidative Defense System 31
Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) 33
ROS Generation and Functions in Plants 34
RNS and ROS Signaling in Plants in Response to Environmental Stresses 35
Antioxidant Compounds 36
Antioxidant-Mediated RNS/ROS Regulation 37
Role of Nutrients in ROS Metabolism Under Salinity 39
Role of Nutrients in ROS Metabolism Under Drought 40
Role of Nutrients in ROS Metabolism Under Heavy Metal Stress 42
Role of Nutrients in ROS Metabolism Under Low- and High-Temperature Stress 43
References 45

4 Polyamines Metabolism and their Regulatory Mechanism in Plant Development and in Abiotic Stress Tolerance 54

Savita Bhardwaj, Tunisha Verma, Monika Thakur, Rajeev Kumar, and Dhriti Kapoor

Introduction 54
Distribution, Biosynthesis, and Catabolism of Polyamines 55
 Distribution 55
 Polyamine Biosynthesis 55
 Catabolism 57
Role of Polyamines in Plant Development 57
Polyamines as Biochemical Markers for Abiotic Stress Tolerance 59
 Drought Stress 59
 Salinity Stress 60
 Heavy Metal Stress 61
 Temperature Stress 62
Crosstalk of Polyamines with Other Signaling Molecules 63
 Nitric Oxide 63
Plant Growth Regulators 64
Conclusion 65
References 65

5 Mycorrhizal Symbiosis and Nutrients Uptake in Plants 73

Kashif Tanwir, Saghir Abbas, Muhammad Shahid, Hassan Javed Chaudhary, and Muhammad Tariq Javed

Introduction 73
Mycorrhizal Association and Its Types 74
 Endomycorrhiza 74

Ectomycorrhiza (ECM)	75
Establishment of Arbuscular Mycorrhiza in Soil	76
Growth of Asymbiotic Hyphae	76
Presymbiotic Stage	77
Different Symbiotic Stages of Fungal Mycelium Growth	77
Root Modifications for Accumulation of Nutrients	79
Nitrogen Uptake Mechanisms of Mycorrhizal Symbionts	80
Phosphorus Accumulation Mechanisms of Mycorrhizal Fungus	81
Potassium (K) and Sodium (Na) Uptake Mechanisms of Mycorrhizal Fungi	83
Metabolism of Sulfur in Mycorrhizal Symbiosis	83
Role of Mycorrhizal Lipid Metabolism in Nutrients Accumulation	84
Mechanism of Micronutrients and Heavy Metal Uptake in Mycorrhizae	85
Carbons-Based Triggering of Nutrients Accumulation in Mycorrhizal Symbiosis	86
Conclusion	87
References	87
6 Nutrient Availability Regulates Root System Behavior	96
<i>Salar Farhangi-Abriz and Kazem Ghassemi-Golezani</i>	
Introduction	96
Nutrients Importance in Root Growth and Development	98
Morpho-Physiological Responses of Plant Roots to Nutrients Availability	99
Macronutrients	99
Nitrogen	99
Phosphorus	101
Potassium	103
Calcium	104
Magnesium	105
Sulfur	105
Micronutrients	106
Zinc	106
Boron	108
Copper	108
Iron	109
Nano Nutrients and Root System Modifications	110
Management Strategies for Maximizing Root Systems	110
Soil Management	110
Plant Management	111
Conclusions and Future Perspectives	111
References	112
7 Potassium Transport Systems at the Plasma Membrane of Plant Cells. Tools for Improving Potassium Use Efficiency of Crops	120
<i>Jesús Amo, Almudena Martínez-Martínez, Vicente Martínez, Manuel Nieves-Cordones, and Francisco Rubio</i>	
Potassium (K ⁺) as a Macronutrient for Plants	120
Functions of K ⁺ and Its Concentration in Plant Cells	120

Concentrations of K ⁺ in Soil, K ⁺ -Deficient Soils, and Presence of Environmental Conditions that Affect K ⁺ Nutrition	121
K ⁺ Transport Systems	122
HAK/KT/KUP Transporters	123
Voltage-Gated K ⁺ Channels	124
HKT Transporters	125
Cyclic Nucleotide Gated Channels	126
Key Points for K ⁺ Homeostasis and Transport Systems Involved	127
General Mechanisms of Regulation	129
Transcriptional Regulation	129
PostTranslational Regulation	131
Multimerization and Regulatory Subunits	131
Regulation by Phosphorylation	131
Agriculture for the Future: K ⁺ Use Efficiency and Stress Tolerance	132
K ⁺ Use Efficiency	132
Abiotic Stress Affecting K ⁺ Homeostasis	133
Salinity	133
Drought	134
Waterlogging	134
Toxic Ions	135
Biotic Stress Affecting K ⁺ Homeostasis	136
Biotechnological Approaches and Emerging Techniques for Crop Improvement	136
Models Versus Crops and Translational Research	136
Natural Variation Exploitation	137
New Alleles Generated in the Lab	138
Genome Editing	138
References	139
8 Role of Nutrients in Modifications of Fruit Quality and Antioxidant Activity	148
<i>Tomo Milošević and Nebojša Milošević</i>	
Introduction	148
Short Overview About Fruit Quality	149
Main Role of Mineral Elements on Trees Growth, Development, and Fruit Quality	150
The Ionic Analysis of Fruit Crops	152
Requirements of Fruit Trees to Chemical Elements	153
The Role of Elements in the Metabolism of Fruit Trees and in Improving Quality	155
Macroelements	155
Nitrogen (N)	155
Phosphorus (P)	156
Potassium (K)	156
Calcium (Ca)	157
Magnesium (Mg)	157
Sulfur (S)	158
Microelements	158

	Iron (Fe)	158
	Manganese (Mn)	159
	Copper (Cu)	159
	Zinc (Zn)	159
	Boron (B)	159
	Other Essential Microelements	160
	Conclusion and Future Prospects	161
	References	162
9	Nutrients Use Efficiency in Plants	171
	<i>Neda Dalir</i>	
	Introduction	171
	Nutrient Use Efficiency (Concepts and Importance)	172
	Role of Nutrient-Efficient Plants for Improving Crop Yields	172
	Physiological Mechanisms in Plant Nutrient Use Efficiency	173
	Uptake Efficiency	173
	Acquisition of Available Nutrients	173
	Increasing Nutrient Availability	174
	Utilization Efficiency	175
	Conclusion and Future Prospects	175
	References	176
10	Nutrients Uptake and Transport in Plants: An Overview	180
	<i>Neda Dalir</i>	
	Introduction	180
	Routes from the Soil to the Stele	181
	Apoplastic Pathway	181
	Symplastic Pathway	183
	Movement of Solutes Across Membranes	183
	Passive Transport	184
	Simple Diffusion	184
	Facilitated Diffusion	184
	Osmosis	185
	Active Transport	185
	Primary Active Transport	185
	Secondary Active Transport	185
	Radial Transport of Mineral Ions	186
	Long Transport of Mineral Ions	186
	Conclusion and Future Prospects	187
	References	187
11	Regulation of Phytohormonal Signaling by Nutrients in Plant	191
	<i>Harshita Joshi, Nikita Bisht, and Puneet Singh Chauhan</i>	
	Introduction	191
	Phytohormones: Structure, Sites of Biosynthesis, and its Effects	192
	Interaction between Nutrient Availability and Phytohormone Signaling	195

Nutrients in Cytokinin (CK) Signaling	197
Nutrients in Ethylene (ETH) Signaling	198
Nutrients in Auxin Signaling	199
Nutrients in Gibberellic Acid (GA) and Abscisic Acid (ABA) Signaling	201
Nutrient Availability and Signaling of other Phytohormones	201
Jasmonic Acid (JA)	202
Brassinosteroids (BR)	202
Salicylic Acid (SA)	202
Polyamines and Strigolactones	203
Transcriptional Interrelation between Nutrient Deprivation and Phytohormones	203
Conclusions and Prospects	204
Acknowledgments	204
References	204
12 Nutrients Regulation and Abiotic Stress Tolerance in Plants	209
<i>Nikita Bisht, Harshita Joshi, and Puneet Singh Chauhan</i>	
Introduction	209
How Abiotic Stresses Affect Plants	210
Plant's Response to Abiotic Stress	211
Mineral Nutrients in the Alleviation of Abiotic Stress in Plants	213
Macronutrients	213
Micronutrients	215
Plant Growth-Promoting Rhizobacteria (PGPR), Mineral Nutrients, and Abiotic Stress	216
Conclusion	217
Acknowledgments	217
References	219
13 Nutrient Management and Stress Tolerance in Crops	224
<i>Saghir Abbas, Kashif Tanwir, Amna, Muhammad Tariq Javed, and Muhammad Sohail Akram</i>	
Introduction	224
Implications of Abiotic Stress in Plants	226
Salinity Stress	226
Drought	227
Toxic Metals	228
Other Stresses	228
Role of Nutrients in Stress Tolerance	229
Nitrogen	229
Nitrogen Role in Stress Tolerance	230
Potassium	230
Role of Potassium in Stress Tolerance	231
Phosphorus	232
Role of Phosphorus in Stress Tolerance	232

Calcium	233
Role of Calcium Under Stress	233
Sulfur	234
Role of Sulfur in Stress Tolerance	234
Magnesium	234
Role of Mg in Stress Tolerance	235
Boron	235
Role of Boron Under Stress	236
Iron	236
Role of Iron in Stress	236
Zinc	237
Role of Zn Under Stress	237
Copper	238
Role of Copper in Stress Tolerance	238
Manganese	238
Role of Mn in Stress Tolerance	239
Molybdenum	239
Molybdenum Role Under Stress	239
Conclusion	240
References	241
Index	253

List of Contributors

Saghir Abbas

Department of Botany
Faculty of Life Sciences
Government College University
Faisalabad, Pakistan

Zeeshan Ahmed

Xinjiang Key Laboratory of Desert Plant
Roots Ecology and Vegetation Restoration
Xinjiang Institute of Ecology and Geography
Chinese Academy of Sciences
Urumqi, China

State Key Laboratory of Desert and
Oasis Ecology
Xinjiang Institute of Ecology and
Geography

Chinese Academy of Sciences
Urumqi, China

Cele National Station of Observation and
Research for Desert-Grassland Ecosystems
Cele, China

and

University of Chinese Academy of Sciences
Beijing, China

Amna

Department of Plant Sciences
Faculty of Biological Sciences
Quaid-i-Azam University
Islamabad, Pakistan

Jesús Amo

Departamento de Nutrición Vegetal
Centro de Edafología y Biología Aplicada
del Segura-CSIC
Murcia, Spain

Muhammad Arslan Ashraf

Department of Botany
Government College University Faisalabad
Faisalabad, Pakistan

Savita Bhardwaj

Department of Botany
School of Bioengineering and Biosciences
Lovely Professional University
Phagwara, Punjab, India

Nikita Bisht

Microbial Technologies Division
Council of Scientific and Industrial
Research-National Botanical Research
Institute (CSIR-NBRI)
Lucknow, Uttar Pradesh, India

Puneet Singh Chauhan

Microbial Technologies Division
Council of Scientific and Industrial
Research-National Botanical Research
Institute (CSIR-NBRI)
Lucknow
Uttar Pradesh, India

Neda Dalir

Department of Soil Science
Tarbiat Modares University
Tehran, Iran

Salar Farhangi-Abriz

Department of Plant Eco-physiology
Faculty of Agriculture
University of Tabriz
Tabriz, Iran

Kazem Ghassemi-Golezani

Department of Plant Eco-physiology
Faculty of Agriculture
University of Tabriz
Tabriz, Iran

Corina Graciano

Instituto de Fisiología Vegetal

Consejo Nacional de Investigaciones
Científicas y Técnicas

Universidad Nacional de La Plata
Buenos Aires, Argentina

Iqbal Hussain

Department of Botany
Government College University Faisalabad
Faisalabad, Pakistan

Mudassir Iqbal Shad

Department of Botany
Government College University Faisalabad
Faisalabad, Pakistan

Muhammad Iqbal

Department of Botany
Government College University Faisalabad
Faisalabad, Pakistan

Khasan Ismoilov

University of Chinese Academy of Sciences
Beijing, China

and

CAS Key Laboratory of Biogeography and
Bioresource in Arid Land
Chinese Academy of Sciences
Urumqi, China

Hassan Javed Chaudhary

Department of Plant Sciences
Faculty of Biological Sciences
Quaid-i-Azam University
Islamabad, Pakistan

Harshita Joshi

Microbial Technologies Division
Council of Scientific and Industrial
Research-National Botanical Research
Institute (CSIR-NBRI)
Lucknow, Uttar Pradesh, India

Dhriti Kapoor

Department of Botany
School of Bioengineering and Biosciences
Lovely Professional University
Phagwara, Punjab, India

Rajeev Kumar

Department of Botany
School of Bioengineering and Biosciences
Lovely Professional University
Phagwara, Punjab, India

Vicente Martínez

Departamento de Nutrición Vegetal
Centro de Edafología y Biología Aplicada
del Segura-CSIC, Murcia, Spain

Almudena Martínez-Martínez

Departamento de Nutrición Vegetal
Centro de Edafología y Biología Aplicada
del Segura-CSIC, Murcia, Spain

Nebojša Milošević

Department of Pomology and Fruit Breeding
Fruit Research Institute Čačak
Čačak, Republic of Serbia

Tomo Milošević

Department of Fruit Growing and
Viticulture
Faculty of Agronomy
University of Kragujevac
Čačak, Republic of Serbia

Ghulam Murtaza

Faculty of Environmental Science and
Engineering
Kunming University of Science and
Technology, Kunming, PR China

Manuel Nieves-Cordones

Departamento de Nutrición Vegetal
Centro de Edafología y Biología Aplicada
del Segura-CSIC
Murcia, Spain

Rizwan Rasheed

Department of Botany
Government College University Faisalabad
Faisalabad, Pakistan

Francisco Rubio

Departamento de Nutrición Vegetal
Centro de Edafología y Biología Aplicada
del Segura-CSIC, Murcia, Spain

Sehrish Sadia

Department of Biological Sciences
University of Veterinary and Animal
Sciences-Lahore, Pattoki, Pakistan

Muhammad Shahid

Department of Bioinformatics and
Biotechnology
Government College University
Faisalabad, Pakistan

Muhammad Sohail Akram

Department of Botany
Faculty of Life Sciences
Government College University
Faisalabad, Pakistan

Kashif Tanwir

Department of Botany
Faculty of Life Sciences
Government College University
Faisalabad, Pakistan

Muhammad Tariq Javed

Department of Botany
Faculty of Life Sciences
Government College University
Faisalabad, Pakistan

Akash Tariq

Xinjiang Key Laboratory of Desert Plant
Roots Ecology and Vegetation Restoration
Xinjiang Institute of Ecology and Geography
Chinese Academy of Sciences
Urumqi, China

State Key Laboratory of Desert and
Oasis Ecology

Xinjiang Institute of Ecology and
Geography
Chinese Academy of Sciences
Urumqi, China

Cele National Station of Observation and
Research for Desert-Grassland Ecosystems
Cele, China
and University of Chinese Academy of
Sciences, Beijing, China

Monika Thakur

Division Botany
Department of Bio-Sciences
Career Point University
Hamirpur, Himachal Pradesh, India

Abd Ullah

Xinjiang Key Laboratory of Desert Plant
Roots Ecology and Vegetation Restoration

Xinjiang Institute of Ecology and
Geography, Chinese Academy of Sciences
Urumqi, China

State Key Laboratory of Desert and
Oasis Ecology

Xinjiang Institute of Ecology and
Geography

Chinese Academy of Sciences
Urumqi, China

Cele National Station of Observation and
Research for Desert-Grassland Ecosystems
Cele, China

and

University of Chinese Academy of Sciences
Beijing, China

Tunisha Verma

Department of Botany
School of Bioengineering and Biosciences
Lovely Professional University
Phagwara, Punjab, India

Fanjiang Zeng

Xinjiang Key Laboratory of Desert Plant
Roots Ecology and Vegetation Restoration
Xinjiang Institute of Ecology and
Geography

Chinese Academy of Sciences
Urumqi, China

State Key Laboratory of Desert and
Oasis Ecology

Xinjiang Institute of Ecology and
Geography

Chinese Academy of Sciences
Urumqi, China

and

Cele National Station of Observation and
Research for Desert-Grassland and
Ecosystems
Cele, China

Zhihao Zhang

Xinjiang Key Laboratory of Desert Plant
Roots Ecology and Vegetation Restoration

Xinjiang Institute of Ecology and
Geography

Chinese Academy of Sciences
Urumqi, China

State Key Laboratory of Desert and
Oasis Ecology

Xinjiang Institute of Ecology and
Geography

Chinese Academy of Sciences
Urumqi, China

Cele National Station of Observation and
Research for Desert-Grassland Ecosystems
Cele, China

and

University of Chinese Academy of Sciences
Beijing, China

Muhammad Zubair

Discipline of Zoology
University of Veterinary and Animal
Sciences-Lahore, Pattoki, Pakistan

Preface

Ionome includes the role of mineral nutrients, namely phosphorus (P), nitrogen (N), calcium (Ca), potassium (K), sulfur (S), magnesium (Mg), etc., and trace metals namely iron (Fe), copper (Cu), manganese (Mn), molybdenum (Mo), cobalt (Co), zinc (Zn), etc. in plant growth and development. Although all mineral nutrients and trace elements are essential for growth and developmental processes of plants, concentration greater than the required level becomes toxic to the plants. Apart from posing toxicity at higher concentration, nutrients under safe limit play important role in alleviating toxicity induced by various stresses.

Appropriate and adequate amount of any nutrient is required at specific stage of development and time to sustain the life of the plant. Hence, in the past decade, much progress has been made in understanding the regulation of nutrients homeostasis under normal and stressed conditions. Further, on one hand an approach has been developed for generating biofortified grains and on other hand nutrients have been successfully employed for managing stress challenges in plants. Taking into account the progress made in ionomics and plants, this book has compiled recent knowledge on sensing, signaling, and regulation of nutrients uptake in plants under changing environment.

A total of 13 chapters have been compiled in this book. Chapter 1 has comprehensively complied information on the regulation of metabolites by nutrients in plants. Chapter 2 deals with agricultural production relation with nutrient applications. Chapter 3 deals with the role of nutrients in ROS metabolism in plants. Chapter 4 deals with polyamines metabolism and their regulatory mechanism in plant development and in abiotic stress tolerance. Chapter 5 narrates the mycorrhizal symbiosis and nutrients uptake in plants. Chapter 6 deals with nutrient availability and root system behavior. Chapter 7 describes in detail the potassium transport systems at the plasma membrane of plant cells and their potential roles in improving potassium use efficiency of crops. Chapter 8 narrates the role of nutrients in modifications of fruit quality and antioxidant activity. Chapter 9 deals with the nutrients use efficiency in plants. Chapter 10 describes the nutrients uptake and their transport in plants. Chapter 11 comprehensively deals with the regulation of phytohormonal signaling by nutrients in plants. Chapter 12 gives details on the nutrients regulation and abiotic stress tolerance in plants. Chapter 13 deals with nutrient management and stress tolerance in crops. Overall, we believe that this book will serve as an important source of information for students, researchers, and academicis.

Vijay Pratap Singh
Manzer H. Siddiqui

1

Regulation of Metabolites by Nutrients in Plants

Akash Tariq^{1,2,3,4}, Fanjiang Zeng^{1,2,3}, Corina Graciano⁵, Abd Ullah^{1,2,3,4}, Sehrish Sadia⁶, Zeeshan Ahmed^{1,2,3,4}, Ghulam Murtaza⁷, Khasan Ismoilov^{4,8}, and Zhihao Zhang^{1,2,3,4}

¹Xinjiang Key Laboratory of Desert Plant Roots Ecology and Vegetation Restoration, Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences, Urumqi, China

²State Key Laboratory of Desert and Oasis Ecology, Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences, Urumqi, China

³Cele National Station of Observation and Research for Desert-Grassland Ecosystems, Cele, China

⁴University of Chinese Academy of Sciences, Beijing, China

⁵Instituto de Fisiología Vegetal, Consejo Nacional de Investigaciones Científicas y Técnicas, Universidad Nacional de La Plata, Buenos Aires, Argentina

⁶Department of Biological Sciences, University of Veterinary and Animal Sciences, Lahore, Pakistan

⁷Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, PR China

⁸CAS Key Laboratory of Biogeography and Bioresource in Arid Land, Chinese Academy of Sciences, Urumqi, China

Introduction

Mineral nutrients are required for plant growth and metabolism. Seventeen nutrients that are essential for plant growth have been identified to date. Macronutrients or essential elements such as nitrogen (N), phosphorus (P), potassium (K), sulfur (S), and magnesium (Mg) are required in large amounts, whereas micronutrients or trace elements including chloride (Cl), copper (Cu), manganese (Mn), iron (Fe), zinc (Zn), cobalt (Co), molybdenum (Mo), and nickel (Ni) are required in smaller amounts. Some researchers also consider sodium (Na) and silicon (Si) as essential micronutrients because of their role in certain crop plants; however, whether they are essential for plant growth and metabolism remains unclear (Maathuis 2009; Marschner 2012). Plants acquire these nutrients from the soil through the roots and carbon (C) and oxygen (O₂) from the air. The concentrations of the available forms of these nutrients in the soil solution are low; for example, N can be readily absorbed by plant roots in nitrate (NO₃⁻) and ammonium (NH₄⁺) forms and P in orthophosphate (HPO₄²⁻ and H₂PO₄) forms (Soetan et al. 2010; Mazid et al. 2011). Their availability can be further altered in both time and space because of several environmental factors, such as precipitation, temperature, wind, and soil properties. Consequently, plants have evolved various flexible physiological and morphological mechanisms to facilitate the

Plant Ionomics: Sensing, Signaling, and Regulation, First Edition.

Edited by Vijay Pratap Singh and Manzer H. Siddiqui.

© 2023 John Wiley & Sons Ltd. Published 2023 by John Wiley & Sons Ltd.

uptake of nutrients. Each mineral carries equal importance and a deficiency of any of them can affect growth and disrupt the plant life cycle.

Metabolites are chemical compounds produced during metabolism and catalyzed by different naturally occurring enzymes in the cell. Plants can produce a variety of metabolites ranging from 0.1 to 1 million, which help plants survive in diverse environments, as these metabolites play important roles in structure, defense, energy, signaling, and interactions with other organisms (Rai et al. 2017). Plant metabolites are divided into two categories (primary and secondary) according to their functions. Primary metabolites (PMs) are directly involved in growth and cellular functions; they are thus also referred to as vital metabolites because they are generally common in all plant species. These are the intermediate products of anabolic metabolism and are formed in the growth phase. PMs are produced in large amounts and can be easily extracted. Examples of PMs include carbohydrates, protein, nucleic acids, lipids, and vitamins. Secondary metabolites (SMs) are the derivatives of PMs, and they are not directly involved in growth and development, but they are ecologically relevant. SMs are formed in the stationary phase; they are also called “natural products” and are different in every plant species because of environmental and genetic differences. There are more than 30 000 SMs, but they are produced in small concentrations, and extracting them can be difficult (Baranauskiene et al. 2003). Plant SMs have diverse applications and have been used in pharmaceuticals, flavoring compounds, antimicrobial agents, dyes, antioxidants, and agrochemicals. Examples of SMs include alkaloids, terpenoids, phenolic compounds, and glycosides.

There is a strong linkage between plant metabolites and mineral nutrients, but understanding the large diversity of plant metabolites requires knowledge of their biosynthesis, degradation, regulation, and transportation processes. Their biosynthesis involves various metabolic pathways such as absorption, assimilation of C, photosynthesis, protoplast formation, respiration, transpiration, translocation, and storage, and these pathways are regulated by mineral nutrients available in different forms in the soil solution (Soetan et al. 2010). Mineral nutrient availability and composition have a profound effect on the type and amount of PMs and SMs produced. Plants growing in soil with an unbalanced composition and limited nutrient concentrations experience serious morphological, biochemical, physiological, and molecular disruptions (Amtmann and Armengaud 2009). There is an increased interest in unraveling the regulatory roles of mineral nutrients in the biosynthesis of plant metabolites. The aim of this chapter is to improve our understanding regarding the regulatory roles of mineral nutrients in the biosynthesis of plant metabolites.

Nitrogen (N)

N is a key plant macronutrient that accounts for nearly 4% of the total dry matter of plants. It is an important structural component of several organic compounds, including amino acids, proteins, chlorophyll pigments, and nucleic acids. N is also involved in the biochemistry of several nonprotein compounds such as polyamines, co-enzymes, SMs, and photosynthetic pigments. N is an important plant macronutrient that is necessary for the biosynthesis of various PMs (i.e. amino acids, chlorophyll, nucleic acids, lipids, proteins, and enzymes) and SMs (i.e. flavonoids and phenolic compounds) in plants (Kováčik

and Klejdus 2013; Shiwakoti et al. 2016). N availability controls plant metabolism and alters the N-based metabolites into C-based plant metabolites (Strissel et al. 2005; del Mar Rubio-Wilhelmi et al. 2012a). C-based plant metabolites mostly contain phenolic acids, anthocyanins, flavonoids, and coumarins (Kováčik et al. 2011). Phenolics consist of thousands of nonenzymatic antioxidants that are ubiquitous in plants and an integral part of human nutrition (Balasundram et al. 2006). The concentrations of flavonoid produced in the secondary metabolism of plants are affected by N, which regulates flavonoid biosynthesis by affecting the C flow allocation between primary and secondary metabolism. For example, excessive N application reduces the content of flavonoids in plants (Ballizany et al. 2012; Shiwakoti et al. 2016), and low N increases the content of carbohydrates (e.g. starch and fructose) but decreases the content of N-rich metabolites (e.g. proteins, free amino acids, and polyamines) in plants (Paul and Driscoll 1997; Coruzzi and Bush 2001).

Soil solution carries N mainly in the form of nitrate (NO_3^-) and ammonium (NH_4^+), but, NO_3^- -N is readily available for plants uptake (at high pH). Plants absorb NO_3^- , which is then reduced to NH_4^+ through enzymatic action of glutamine synthetase/glutamate synthase (GS/GOGAT) enzymes. Scheible et al. (2004) reported downregulation of most genes responsible for chlorophyll and plastid protein synthesis, photosynthesis, and upregulation of many genes involved in secondary metabolism following two days of N deprivation in *Arabidopsis thaliana*. It is noted that N limitation mainly governs the shift from N-based to C-based plant metabolites (Kováčik et al. 2011; del Mar Rubio-Wilhelmi et al. 2012b). This effect of N limitation on phenolic metabolites is thought to be the result of reductions in other macronutrients, such as the depletion of K, and does not increase phenolic metabolites and vice versa (Nguyen et al. 2010).

Leaf N limitation generally alters the pattern of N allocation in photosynthetic organs and directly regulates the content and enzymatic activity of ribulose 1,5-bisphosphate carboxylase/oxygenase (Rubisco) and chlorophyll, thereby affecting the photosynthetic rate. Kováčik and Klejdus (2013) noted that concentrations of phenolic metabolites (especially chlorogenic acid) and free amino acids (mainly proline and arginine) increased in *Matricaria chamomilla* plants upon NH_4^+ application. Coumarin-related metabolites showed a similar increase under N limitation, and herniarin mainly accumulated in plants under NO_3^- addition and umbelliferone under NH_4^+ addition.

Phosphorus (P)

P does not exist in elemental form but is firmly fixed (>90%) in soil minerals, therefore it is unavailable to plants. P is assimilated by the plants as phosphate (H_2PO_4^-) at a pH of 5, and it is unevenly distributed because it is relatively immobile in soils. In addition, inorganic phosphate (Pi) is an important part of several biological compounds, such as sugar phosphates, phospholipids, DNA, RNA, and nucleotides. P has a crucial role in energy metabolism and activation of various intermediates in the C cycle of photosynthesis. These are the reasons why plant growth and yield depend on the availability of P.

Aside from its structural roles, P is involved in reversible protein phosphorylation (facilitated by kinases and phosphatases) to modulate protein activity. In this mechanism,

terminal Pi from ATP or GTP nucleotide is transferred to Ser or the protein residues. ATP is an important energy compound with a pyrophosphate bond. Pyrophosphate is an energy-rich bond and participates in active ion uptake and the synthesis of various PMs and SMs during hydrolysis (30 kJ mol^{-1}). GTP, CTP, and UTP are energy-rich phosphonucleotides which also regulate the nucleic acid metabolism. CTP provides energy during phospholipid biosynthesis, and UTP is the main structural constituent of sucrose, starch, and cellulose (Maathuis and Diatloff 2013). Pi also regulates various enzymes involved in carbohydrate metabolism (Ashihara and Stupavska 1984; Avigad and Bohrer 1984). P is a constituent of energy metabolism, and the phospho groups are responsible for the activation of enzymes and metabolic intermediates. For example, P activates intermediates in the photosynthetic carbon cycle and during the entire primary metabolism. P limitations have a substantial effect on plants at the morphological, physiological, biochemical, and molecular levels (Secco et al. 2013; Pant et al. 2015). Morcuende et al. (2007) determined the metabolite levels, transcripts, and maximum enzyme activity in the seedlings of *Arabidopsis* grown under P-added and P-depleted liquid culture. Reduction occurred in the levels of ATP and hexose phosphates (Glc6P, Fru6P, and Glc1P), owing to P limitation, recovered immediately after restocking with a knock-on effect on UDP-glucose, which took few hours for its completion. Tricarboxylic acids such as 3-phosphoglyceric acid (3PGA) and phosphoenolpyruvate (PEP), accumulated due to P limitation, are rapidly used after restocking and lead to the quick initiation of glycolysis. However, reduction in organic acids (malate, 2-oxoglutarate, citrate, and fumarate) and storage carbohydrates (starch and sucrose) due to P limitation did not get back to their normal state within 24 hours of restocking. These findings clearly show that in response of P restocking, plants do modifications to retrieve their energy stores and the biosynthesis of phosphorylated substrates for glycolysis.

Soil contains extremely low concentrations of Pi ($\sim 0.1\text{--}1 \text{ mM}$), and P limitation is likely widespread in agriculture. Several studies revealed that P deficiency affects numerous PMs and SMs in soybean and *Arabidopsis* (Hurry et al. 2001; Morcuende et al. 2007; Hernandez et al. 2009). However, how the metabolite profile during P limitation and in mutants is affected during the P-deprivation response remains unclear.

Morcuende et al. (2007) noted that P limitation in *A. thaliana* can induce or suppress more than 1000 genes involved in many metabolic processes. P limitation leads to the accumulation of carbohydrates, amino acids, and organic acids. P-limited plants also show significant variations in the expression of many genes associated with secondary metabolism and carbon assimilation. Upon P deficiency, plants generally recycle P from organic molecules (Yuan and Liu 2008). P limitation can induce substantial variations in gene expression in plants, but the diversity of these metabolic alterations and their regulation procedure have been poorly studied. Pant et al. (2015) profiled nearly 350 PMs and SMs of P-added and P-deficient *A. thaliana*, wild-type, and mutants of the central P-signaling components (PHR1 and PHO2, and microRNA399 overexpressor). P availability has a significant effect on the metabolite profile in the roots and shoots of *A. thaliana* wild-type, *phr1*, *pho2*, and *miR399OX* seedlings. The concentrations of many glucosinolates, phenylpropanoids, flavonoids, flavonoid glycosides, esculetin, ferulic acid, caffeic acid, kaempferol glucuronide, kaempferol 3-*O*-glucoside, kaempferol 3-*O*-rutinoside, and many other glucosinolates markedly increased in wild-type *A. thaliana* under P limitation.

Potassium (K)

K is a vital macro-mineral element (inorganic cation) that is necessary for the optimal growth and development of plants. K being an abundant cation in plant tissues plays fundamental role in numerous biochemical and biophysical processes, such as osmoregulation, ion homeostasis, enzyme activation, and protein formation. Nonstomatal inhibition of photosynthesis, such as the inhibition of chlorophyll synthesis, is often observed during unfavorable conditions, and the K supply can positively affect chlorophyll biosynthesis (Tiwari et al. 1998), the chloroplastic CO₂ level, and the electron transport system. The free ionic form of K (K⁺) plays a fundamental role in regulating many physiological processes, such as membrane polarization, protein synthesis, and osmotic adjustments, and thus controls osmotically driven processes such as phloem transport and stomatal function (Zorb et al. 2014). When K⁺ is sufficient, carboxylation and the overall photosynthetic rate lead to normal growth and yield. K-limitation reduces photosynthetic rates because of the low concentration of CO₂ stemming from stomatal closure (Jin et al. 2011). In contrast, a sufficient K level can improve the photosynthetic rate by regulating stomatal and gas exchange attributes and enzymes such as Rubisco (Erel et al. 2015). Furthermore, K-induced increases in photosynthesis might also stem from a reduction in reactive oxygen species. For example, the K supply can decrease oxidative damage by increasing the activities of key enzymes of the antioxidant system, such as SOD, POD, and CAT (Ahanger and Agarwal 2017a, 2017b). Plants have developed efficient mechanisms for K uptake to guarantee normal growth under K-limited conditions. For example, main strategies for efficient K uptake capacity include potassium redistribution between cytosol and vacuole for cellular homeostasis and adaptation of the root system. Execution of these strategies needs accurate regulatory signaling pathways and mechanisms. The accumulation of sugars and amino acids increased in both leaves and roots, but organic acids showed reduction upon low K stress. Moreover, amino acids with negative charges (Asp and Glu) and most organic acids were decreased while amino acids carrying positive charge (Lys and Gln) increased in all three genotypes (Ashley et al. 2006). The selective reductions in acidic amino acids can facilitate the maintenance of the charge balance upon low K stress. Armengaud et al. (2009) noted the responses of shoot and roots of two-week old *Arabidopsis* (*A. thaliana*) plant species to K availability. The concentrations of nitrate, pyruvate, organic acids (2-oxoglutarate and malate), glutamate, and aspartate (negatively charged amino acids) were significantly reduced in the roots, but the concentrations of soluble carbohydrates (e.g. glucose, sucrose, and fructose) and numerous amino acids such as glycine, arginine, and glutamine (positively charged amino acids) and those with a high N:C ratio were significantly increased in the roots. In addition, metabolite alterations under K depletion were observed later in the shoots than in the roots. Carbohydrates (sucrose and reducing sugars) and organic acids were increased in the shoots. Moreover, N-rich and basic amino acids like arginine, glutamine, asparagine, lysine, and histidine largely increased in shoots relative to the roots.

Although K is not metabolized, but there are numerous metabolic processes that are highly K-dependent. For example, (i) direct enzyme activation of enzymes: vacuolar PPase isoforms, which are responsible for the accumulation of protons in the vacuolar lumen, are largely dependent on the K⁺ level; (ii) translation: ribosome-mediated protein synthesis

also depends on a sufficient K^+ concentration; and (iii) transportation: both across membranes and over long distances, among other important roles (Wyn Jones and Pollard 1983; Marschner 1995). These processes assist in observing the metabolic impairments especially under K-deficient conditions.

K^+ limitation can lead to low chlorophyll and photosynthetic activity, the accumulation of simple carbohydrates, and a decrease in plant growth and yield. Therefore, sufficient K^+ must be present in the soil to facilitate sufficient absorption and transportation, since its distribution to different plant organs depends on its availability and significantly affects the biosynthesis, conversion, and allocation of plant metabolites (Sorger et al. 1965; Evans and Sorger 1966). K^+ -deficient conditions can also increase the sensitivity of plants to unfavorable environmental conditions. The plant K level decreases the occurrence of pests and diseases by regulating the production of organic compounds having large molecular weight, such as proteins, cellulose, and starch (Marschner 1995). The availability and level of K^+ also regulate plant metabolism through transcriptional and posttranscriptional regulation of metabolic enzymes. Studies on K^+ -deficient *A. thaliana* plants gave insight into the induction of GS/GOGAT pathway, malic enzyme, and the suppression of nitrate uptake (Amtmann and Blatt 2009; Armengaud et al. 2009). K limitation in cultivated land has emerged as a major factor negatively affecting the sustainable growth and production of crop plants worldwide. K-sufficient conditions help sustain the normal metabolism and growth of plants (Sharma et al. 2006). K-limited plants accumulate numerous basic or neutral amino acids, show minor rise in total amino acids and proteins, and contain few acidic amino acids and nitrate. K also plays a key role as an inorganic osmotic solute as well as in the synthesis of other compatible solutes required for stomatal movement and maintenance of water relations. Potassium also governs the loading of photo-assimilates and the functioning of key metabolic enzymes (Ahanger et al. 2014; 2015; Erel et al. 2015). Furthermore, a significant reduction in pyruvic acid was observed in the roots. Most metabolites returned to their prealteration levels within 24 hours of K re-stocking; the exception was sucrose, glucose, and fructose in the shoots. However, in roots, pyruvic acid recovered within minutes, but 2-oxoglutaric acid and malic acid recovered more slowly. K limitation also reversibly changed the activities of many enzymes engaged in sugar metabolism (glucokinase, fructokinase, and invertase), glycolysis (glyceraldehyde 3-phosphate dehydrogenase [GAPDH]), Krebs cycle (malic enzyme), and N assimilation (NR, GS, GDH, and Fd-GOGAT). The noticeable build-up of sugars, the reduction of pyruvic acid in the root cells, and the swift restoration of root sugar and pyruvic acid level suggest that K level in root cytoplasm could be the first one to be recovered upon K re-supply (Leigh and Wyn Jones 1984). Alterations in the shoot metabolite profile (e.g. sugar accumulation and nitrate reduction) are likely derived from the same alterations in the roots. However, following K re-supply, changes in some amino acids were specific to the shoots and took place even before K accumulated, specifying the presence of a root/shoot signal from K itself. Based on the determined metabolite profile, glutamic acid appears to play a vital role in the long-distance signaling of tissue K status (Lacombe et al. 2001; Davenport 2002). K limitation has also been shown to decrease the scopolin content in sunflower (Lehman and Rice 1972), oxylipins in *A. thaliana* (Troufflard et al. 2010), and galanthamine in Narcissus bulbs (Lubbe and Verpoorte 2011). These findings suggest that K availability has crucial role in regulating the production of SMs in plants. Low K also induces oxidative stress owing to overproduction of

reactive oxygen species (ROS), which damages cell membrane stability. Proline and ascorbate, which are important nonenzymatic antioxidants, have been found to mount up in plants against low K stress to protect plants from oxidative stress damage (Zeng et al. 2018).

Sulfur (S)

S is another essential mineral element and a central component of plant metabolism. Autotrophic organisms require sulfur for the biosynthesis of various PMs and SMs for their growth and development. The acquisition and assimilation of S in plants have received increased research interest, especially in the context of crop improvement. Any changes in S acquisition and assimilation can lead to drastic metabolic changes that affect sulfur-containing pools of both PMs and SMs.

Sulfur is an integral part of an array of plant metabolites including proteins and amino acids (cysteine, methionine), antioxidants (reduced glutathione), phytohormones, vitamins, sulfolipids, phytochelatin, iron-sulfur (Fe-S) clusters, glucosinolates, and cofactors (biotin and thiamine) having ability to potentially modify the physiological processes in plants (Takahashi et al. 2011; Asgher et al. 2014; Fatma et al. 2016). S application decreases the production of excess ROS and thus protects plants from oxidative damage (Fatma et al. 2014; Khan et al. 2015). Once absorbed by the roots, S becomes assimilated into some key organic metabolites, such as thiol (-SH) groups in cysteine or nonprotein thiol such as glutathione. Glutathione helps to remove excess ROS, which protects the cells from oxidative damage.

S limitation inhibits chlorophyll biosynthesis, Rubisco content, photosynthesis, N assimilation, and protein synthesis and eventually disturbs plant metabolism (Honsel et al. 2012). Lunde et al. (2008) reported that S limitation decreases the concentrations of glucose, fructose, and the glycolytic intermediate PEP but increases the content of starch, flavonoids, and anthocyanins. The consumption of carbohydrates was more strongly inhibited compared with photosynthesis in S-limited plants. The reduction in monosaccharides can be linked to the reduction in photosynthesis, and the increase in starch accumulation is considered a general response to nutrient deficiency. S-limitation has been shown to markedly decrease the concentration of lipids (especially sulfolipids), protein, RNA, S-adenosyl-methionine (SAM), and chlorophyll (which requires SAM for biosynthesis), as well as the photosynthetic rate (Nikiforova et al. 2005). S deprivation decreases total glucosinolates and downregulates the genes involved in glucosinolate biosynthesis (Aghajanzadeh 2015). Indole-acetonitrile, a breakdown product of glucosinolate, is produced from Trp and it acts as a precursor in the biosynthesis of indole-3-acetic acid (auxin), which is also upregulated by S-deficiency (Kutz et al. 2002). The increase in the auxin level could explain the increase in lateral root growth in S-deficient plants.

Magnesium (Mg)

Low Mg availability negatively affects morphogenesis, development, and the productivity of plants. Mg is another essential macronutrient element required for plant growth and development. Mg has vital role in carbon fixation being a key constituent of chlorophyll

molecule. Mg^{2+} holds central place in the chlorophyll molecule, surrounded by four N atoms from the porphyrin ring. The important regulatory role of Mg^{2+} in photosynthesis is well established. Changes in Mg^{2+} concentration in the chloroplast control the functioning of many important enzymes involved in photosynthesis. Mg^{2+} plays an important role in photosynthesis because it can promote light reactions operating in the stroma. Light triggers the entry of Mg^{2+} into the stroma of the chloroplast in exchange for H^+ , thus establishing an optimum level for the carboxylase reaction. Mg^{2+} acts as a cofactor and activates the ribulose bisphosphate carboxylase (RuBP carboxylase,) and fructose-1,6-bisphosphatase. Thus, Mg^{2+} plays a fundamental role in CO_2 assimilation and related metabolic processes, such as sugar and starch production (Marschner 2012). Mg^{2+} also acts as a cofactor in almost all the enzymes activating phosphorylation processes. Mg^{2+} links the pyrophosphate structure of ATP or ADP to the enzyme molecule. Hence, the activation of ATPase by Mg^{2+} is brought about by this linking function (Balke and Hodges 1975). Mg^{2+} is also required for the activation of dehydrogenases and enolase, the aggregation of ribosomes, the modulation of ionic currents across the chloroplast, and vacuolar membranes (i.e. the organelle that regulates ion balance in the cell and stomatal opening (Maathuis and Diatloff 2013).

Mun et al. (2020) examined the effects of excess Mg on *Perilla frutescens* leaves and noted higher chlorophyll, carbohydrates (glucose, xylose, maltose, adonitol, xylitol, glycerol, gluconic acid, glyceric acid, maltose, and fructose), and amino acids (threonine, glycine, serine, and GABA) but low antioxidant metabolites (ABTS, DPPH, and FRAP). In contrast, tryptophan, sucrose, and some organic acids (oxoglutaric acid and lactic acid), flavonoids (apigenin-7-*O*-diglucuronide, apigenin-7-*O*-glucuronide, luteolin-7-*O*-diglucuronide, apigenin-6,8-diglucoside, luteolin-7-*O*-glucoside, and liquiritigenin), sagerinic acid, cinnamic acid derivatives (dimethoxycinnamic acid, caffeic acid, and salvianolic acid C), and triterpenoids (tormentic acid and corosolic acid) were significantly reduced in Mg-oversupplied plants compared to control plants. In contrast, previous studies have shown that plant SMs (flavonoids and phenolic compounds) also serve the purpose of antioxidants and assist in reducing the oxidative damage induced by abiotic stress (Nakabayashi et al. 2014).

Calcium (Ca)

Ca is an abundant element existing in the lithosphere having a mean value of approximately 3.5% Ca. However, soils composed of chalk or limestone are usually rich in $CaCO_3$ (calcite) and possess 50% Ca. Plant roots absorb Ca in the form of divalent ion (Ca^{2+}) and account for approximately 0.5% of plant dry matter. Inside plant tissues, Ca^{2+} has a high affinity for plant metabolites with a negative charge. Therefore, Ca cannot be remobilized from old plant organs; hence, if Ca availability is low in the soil solution, the Ca concentration can decrease below critical levels and have negative effects on growth and productivity. A sharp decrease in Ca levels, especially in fast-growing tissues, can lead to diseases such as “blossom end rot” in tomatoes, “black heart” in celery, “tip burn” in lettuce, or “bitter-pit” in apples, even when plants are growing in the presence of sufficient amounts of Ca in soil (White 2000; Demidchik and Maathuis 2007; Bárcena et al. 2019).

Ca has a crucial role in cell division, structure and permeability of plasma membrane, cell transduction and elongation, translocation of carbohydrate, and nitrogen metabolism (White 2000; El-Beltagi and Mohamed 2013). Ca plays a role in maintaining the structure of the cell wall and membranes. It readily forms complexes with several anionic substances such as the phosphates and carboxyls of phospholipids, sugars and proteins. For example, in plant cell walls, the cross-linking of pectins and glycans occurs through electrostatic coordination of Ca. Ca acts as “glue” that not only contributes to cell wall structure and strength but also decreases the risk of pathogen penetration (Marschner 1995; Maathuis and Diatloff 2013).

This complexation mainly occurs outside the cell membrane and requires a high concentration of apoplastic Ca. Replacement of Ca with other cations or elimination of apoplastic Ca can compromise membrane strength and lead to cellular electrolyte leakage. Since Ca can form insoluble salts with phosphates and sulfates easily, therefore concentration of free Ca in the cytoplasm is normally kept low nearly around ca. 100 nM. This makes Ca an ideal secondary messenger, and various stimuli have been shown to evoke rapid changes in cytosolic free Ca in plants, including responses to biotic and abiotic stress, stomatal regulation, and physical damage (Haynes 1980; Wallace and Mueller 1980). Ca also participates in photosynthetic water oxidation in PSII, which requires a metal cluster that contains a Ca ion (Hochmal et al. 2015). In contrast, optimal amounts of Ca have been shown to significantly improve the production of chlorophylls and carotenoids and maintain high photosynthetic efficiency and stomatal conductance (Elkelish et al. 2019). Ca also plays a role in polyphenolic metabolism. For example, Ca takes part in the biosynthesis of polyphenolic compounds. The application of Ca can increase the phenylalanine ammonia-lyase activity, which leads to the accumulation of polyphenols (Castaneda and Perez 1996; Juric et al. 2020).

In addition, Ca deprivation has been reported to inhibit the photosynthesis and N metabolism of spinach plants by reducing the content of chlorophyll and activities of Rubisco, GDH, GS, and GPT (Chao et al. 2008). Under Ca deficiency, plants face the problem of an enhanced electrolyte leakage rate and decreased AsA content (da Silva et al. 2021). The increase in malondialdehyde might enhance the activity of pectolytic enzymes (Olle and Bender 2009) and lipid peroxidation (Chao et al. 2009).

Boron (B)

B is an important trace mineral nutrient necessary for physiological processes in higher plants. B plays important roles in cell division and elongation, sugar transport, carbohydrate metabolism, N metabolism, cytoskeletal proteins, cell wall synthesis, and lignification, as well as in maintaining the integrity of bio-membranes. Ions (K^+ , H^+ , Ca^{2+} , KPO_4^{3-} , and Rb^+) are transported across the membranes, and plasmalemma-bound enzymes, polyamines, nucleic acids, ascorbic acid, and phytohormones (indoleacetic acid) are important for mediating ion transport (Shireen et al. 2018). Plant growth and metabolism are adversely affected due to B deficiency. B deficiency or toxicity usually leads to carbohydrate accumulation (hexose sugars (glucose, fructose) and starch contents become high, but the accumulation of sucrose is low. Ruuhola et al. (2011a) reported that B availability affects