

Chemistry Research and Applications

Cadmium

*Characteristics,
Sources of Exposure, Health
and Environmental Effects*

*Mirza Hasanuzzaman, Ph.D.
Masayuki Fujita, Ph.D.*
Editors

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CHEMISTRY RESEARCH AND APPLICATIONS

CADMIUM

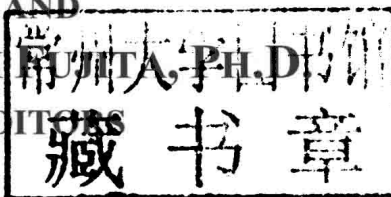
**CHARACTERISTICS, SOURCES
OF EXPOSURE, HEALTH
AND ENVIRONMENTAL EFFECTS**

MIRZA HASANUZZAMAN, PH.D.

AND

MASAYUKI FUJITA, PH.D.

EDITORS



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New York

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Library of Congress Cataloging-in-Publication Data

Cadmium : characteristics, sources of exposure, health and environmental effects / [edited by] Mirza Hasanuzzaman (Department of Agronomy, Faculty of Agriculture, Sher-e-Bangla Agricultural University, Dhaka, Bangladesh).

pages cm

Includes bibliographical references and index.

ISBN: 978-1-62808-722-2 (hardcover)

1. Plants--Effect of cadmium on. 2. Cadmium--Toxicology. I. Hasanuzzaman, Mirza.

QK753.C16C33 2013

571.9'54662--dc23

2013029195

Published by Nova Science Publishers, Inc. † New York

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PREFACE

The advancement of human civilization and fast growing industrialization are recognized as giving rise to various problems such as pollution, accumulation of heavy metals in soils, and reduction in water quality. These issues can result in severe deterioration of natural resources, disturbance of ecosystems, and deleterious effects on human health. Among these environmental problems, heavy metal toxicity is generating particular concern, and especially the toxicity caused by cadmium (Cd), one of the four metals that have been raising apprehension worldwide as environmental and health hazards. Human activities have dramatically changed the composition and organization of the soil on Earth. Industrial and urban waste deposition, in particular the uncontrolled disposal of wastes and the application of various substances to agricultural soils, has contaminated our ecosystem. Another oft-cited example is mining activity, which has resulted in the deposition of unusually high concentrations of Cd onto the soil surface. Plants and soil microorganisms must cope with the resulting elevated levels of Cd by developing sophisticated techniques for surviving and coexisting in these toxic environments. In addition, because Cd is easily translocated to food chain through these other organisms, human beings are readily affected. In recent decades, the number of publications focused on Cd toxicity in plants and animals has been growing exponentially, making this topic impossible to accommodate within the scope of a single volume. Some of the more detailed points have been omitted for brevity; yet, where conflicts exist, contrasting viewpoints are presented. Time may change these views, but it is the very nature of science to be in a continual state of flux and for the errors of one generation to be amended by the next.

In this book "Cadmium: Characteristics, Sources of Exposure, Health and Environmental Effects", the authors present a collection of 16 chapters written by 67 experts from 19 countries working in the field of Cd toxicity. In preparing this book, our aim was to provide the readers with a background for understanding Cd toxicity, its environmental and health aspects, and its remediation mechanisms. Various chapters included in this book provide a state-of-the-art account of the information as a resourceful guide suited for scholars and researchers working in the field of Cd. This book will be an invaluable resource for plant biologists, agriculturists, toxicologists, biochemists, environmental scientists, physiologists, pharmacologists, geneticists, molecular biologists; as well as graduate students in these disciplines.

This book begins with a chapter that deals with the generalized pictures on the overall effects of Cd toxicity and possible mitigation. The widespread distribution of Cd in the

environment is of great concern because of their toxic properties thus it is essential to find out the proper ways to alleviate Cd-induced adversities. The authors also point out the Cd-induced oxidative stress and antioxidant defense. Later, they describe the coordinated role of glutathione and glyoxalase system in mitigating Cd stress. Finally they nicely depicts the role of nutrient management in alleviating Cd toxicity in plants. Chapter 2 deals with morphophysiological, biochemical and molecular responses of Cd toxicity in plants. The authors describe many aspects of the mechanisms of Cd tolerance including morphological and ultrastructural alterations, antioxidant metabolism and chelation. The molecular mechanisms towards the plants tolerance to Cd stress is also highlighted. Phytoremediation technology has gained recent attention as strategies to clean-up contaminated soils and water which is a cost-effective 'green' technology based on the use of metal-accumulating plants to remove HMs from soil and water. Phytoremediation has recently become a subject of intense public and scientific interest and a topic of many recent reviews. Both in Chapter 1 and Chapter 2, the authors clearly describes the potential use of phytoremediation technology in mitigating Cd levels. Chapter 3 exclusively presents a full characterization of the toxic effect of Cd in plants and of the main mechanisms plants use against oxidative stress induced by this heavy metal. In Chapter 4, the authors highlighted the effects of Cd on plant growth, metabolism and lignin production. Chapter 5 highlights the Cd assimilation by biota and physiological and molecular consequences of the same on animals, plants and microbes. In Chapter 6, the authors provided the results on influence of Cd on microbial behaviour under Argentina's perspective. They showed the research results of the screening of Cu, Cd, Zn and Pb resistant/tolerant and culturable microbiota and depicted an interesting feature to understand microbial behaviour under metal exposure. Chapter 7 narrates the overview of toxicity and tolerance in microalgal cells under Cd exposure. The authors also analyzed the potential use of these microorganisms in bioremediation of Cd-contaminated environments. In Chapter 8, the authors summarize the current knowledge concerning the mechanisms of Cd accumulation and detoxification in *Solanum nigrum* and how this hyperaccumulator remediates Cd from contaminated soil. The authors also discuss the latest study on the transcriptomics of the *S. nigrum* response to Cd, highlight its mechanisms of phytoremediation, and discuss the future application of this hyperaccumulator plant for the decontamination of Cd. Chapter 9 focuses on the application of living microorganisms ubiquitous in wastewaters, specifically *Sphaerotilus natans* and *Zoogloea ramigera*, or dead microbial biomass of *Arthrospira (Spirulina) platensis* or even cellulosic biomass such as *Agave americana* fibers in searching a potential way to remove Cd from aqueous solutions by biosorbents. Chapter 10 focuses the use of zeolitic tuff nanoparticles as immobilizing agent. This chapter provides an indication of using nanoscale zeolitic tuff as an promising candidate for heavy metal. It narrates the results on the effect of this soil amendment on metal uptake of Zn, Cd, and Pb in plants and on metal fractionation in soil as well as the effect of amendments on the uptake of essential elements such as P, Fe, and Mn by summer barley. Chapter 11 provides a deliberate review of characteristics of Cd based devices and the possible material alternatives that could replace Cd in the devices. Chapter 12 uncovers the potential ways to treat dissolved toxic metals is by using ionizing radiation. The authors explore the methods utilizing ionizing radiation are very promising and could even be single-stage, followed only by the filtering of the precipitated product. Chapter 13 narrates the Cd binding properties of surface waters and special emphasize is given on the role of dissolved and suspended matter. The authors reveal that suspended matter (high concentration of particulate) plays a major

role in binding dissolved lead and Cd, thus contributing to the auto-depuration of the aqueous phase. Chapter 14 sheds light on Cd exposure from food and the important factors underlying the risk assessment. This chapter narrates several aspects viz. Cd use and source of exposure, Cd absorption and metabolism, symptoms and signs of intoxication and the mechanism of Cd toxicity, bioindicators of Cd exposure, body burden and toxic effects and safe Cd levels. In Chapter 15, the authors attempt to provide an overview of the existing scientific literature on the Cd levels in the red meat and edible offal and they provided the notion that the concentration of Cd in meat and especially in edible offal may be used as an indicator of environmental contamination by Cd. Lastly, it is important to highlight major dietary sources of Cd, provide estimates of exposure as well as its biomagnification and absorption through the food chain using available data from research papers. Chapter 16, draws particular attention to Cd exposure via food chain in livestock, certain wild plants and seafoods as well as the bioavailability or absorption of Cd as Cd-MT in foods. The editors and authors hope that this book will serve as a practical update on our knowledge on Cd toxicity in plants and animals and will lead to new discussions and efforts in the use of various techniques for the mitigation of Cd-induced toxicity and environmental hazards.

The authors are grateful to all the authors for their valuable contributions. The authors are also indebted to our research group members, especially, Mrs. Kamrun Nahar, Mr. Md. Mahabub Alam, Laboratory of Plant Stress Responses, Faculty of Agriculture, Kagawa University, Japan for their valuable helps in formatting and incorporating editorial changes in the manuscripts. The authors are highly thankful to Prof. Dr. Md. Fazlul Karim; Mr. Anisur Rahman and Mr. Md. Hasanuzzaman, Department of Agronomy, Faculty of Agriculture, Sher-e-Bangla Agricultural University, Dhaka, Bangladesh for their critical reading of the manuscripts. The authors mourn the passing of one of our contributors, Margarita V. Savina, I.M. Sechenov Institute of Evolutionary Physiology and Biochemistry of Russian Academy of Sciences, St.-Petersburg, Russia, who departed from the world during the preparation of the manuscript and could not complete the task. The authors appreciate Mrs. Carra Feagaiga, Department of Acquisitions, Nova Science Publishers, Inc. for her prompt help, suggestions and punctuality in publication of this collective volume. Despite conscientious efforts by all concerned, the chapter authors, the editor, and the publisher cannot assume any liability for errors that this book may contain though every effort has been made to keep the error rate as low as possible. This book is dedicated to all of the researchers who spent significant times in searching the fact of Cd.

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Chapter 1

ADVERSE EFFECTS OF CADMIUM ON PLANTS AND POSSIBLE MITIGATION OF CADMIUM-INDUCED PHYTOTOXICITY

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ABSTRACT

Increasing population together with fast industrialization causes serious environmental problems, including the production and release of considerable amounts of toxic metals into the environment. Cadmium (Cd) has assumed importance as an environmental contaminant only within the past 60 years. The effects of Cd on plants have been widely studied by researchers. The regulatory limit for Cd in agricultural soil is 100 mg kg⁻¹ soil. Plants grown in soil containing high Cd concentrations demonstrate chlorosis, necrosis, leaf rolling, root growth inhibition, stunted plant growth, altered stomatal action, decreased water potential, cation efflux, alterations in membrane functions, photosynthesis inhibition, altered metabolism, altered activities of several key enzymes, and even death. Therefore, understanding the responses of plants to Cd stress is essential for holistic perception of plant resistance mechanisms under Cd stress conditions. Improvement of the antioxidant defense system of plants has shown to provide better protection to Cd-induced oxidative stress. Among the antioxidants, glutathione (GSH) plays an important role because of its involvement in the chelation of Cd and as a substrate of the glyoxalase system. The coordinated effects of antioxidant defense and glyoxalase systems have provided better protection against Cd-induced

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damage in many plants species. Recent studies have showed that various plant nutrients provide differing levels of protection against Cd-induced damage in plants. It is also necessary to explore eco-friendly techniques to remediate Cd-affected soils. Recent studies have indicated a wider success of phytoremediation on Cd removal from contaminated sites. In this chapter, we focus on the major effects of Cd on plant growth and productivity, as well as possible mechanisms through which to mitigate Cd-induced damage.

INTRODUCTION

In the era of climate change, plants have continuously suffered from environmental adversity that prevents them from reaching their full genetic potential and limits crop productivity worldwide (Hasanuzzaman et al., 2009, 2010a, b; Hasanuzzaman and Fujita, 2011; Hasanuzzaman et al., 2011a, b; 2012a–c; 2013a–d). In recent decades, contamination of soil by toxic metals has become a serious problem in crop production worldwide. The rapid increase in population together with fast industrialization has caused serious environmental problems, including the production and release of considerable amounts of toxic metals into the environment (Sarma, 2011; Hasanuzzaman and Fujita, 2012a, b; Hasanuzzaman and Fujita, 2013). Of all heavy metals (HMs), cadmium (Cd) ranks the highest in terms of damage to plant growth and productivity (Nouairi et al., 2009). It accumulates in the soil naturally or through anthropogenic activities, including mining, industrial waste disposal, use and disposal of batteries and sludge, application of pesticides, and phosphate fertilizers (Wright and Welbourn, 2002; Hasanuzzaman and Fujita, 2012a).

Cadmium is generally released into the soil through various industrial processes, and due to its phytotoxic nature, it causes severe damage to plants. Cadmium is easily taken up by plant roots and transported to different plant parts, causing various phytotoxic symptoms (Bernard, 2008). It also obstructs almost all of the physiological and metabolic processes of the plants. Cadmium also diminishes water and nutrient uptake (Li et al., 2008), as well as causes chlorosis and necrosis of the leaves and roots with reduced growth. The photosynthetic apparatus is one of the target sites of Cd, and it can directly or indirectly interfere with different components of the photosynthetic apparatus. It inhibits biosynthesis of photosynthetic pigments, can decrease electron transport efficiency, inhibits the enzymes involved in photosynthesis, reduces photosynthetic carbon assimilation, and causes oxidative damage to sub-organelles (Maksymiec et al., 2007). The Cd-induced oxidative stress also causes various complications in plant physiological processes. As a consequence the growth and development of plant are impeded, which is evidenced by Cd-induced reduced and abnormal seed germination, reduced and irregular growth, chlorosis and necrosis, anomalous development of reproductive organs and yield components, and reduced yield (Gill and Tuteja, 2011). Moreover, the phytotoxicity of Cd is so high that higher Cd accumulation than 5–10 $\mu\text{g Cd g}^{-1}$ leaf dry weight leads to plant death, except in Cd-hyperaccumulators (White and Brown, 2010).

Considering the severity of Cd toxicity, researchers are thinking of alternative ways to lessen its toxicity in plants and to lessen Cd content in the soil as well. Despite Cd toxicity, many plants have developed different mechanisms to cope with Cd, including antioxidant defense, metal exclusion, active excretion, restricted distribution of the metal in sensitive

tissues, metal binding to the cell wall, chelation by organic molecules, and compartmentalization in vacuoles (Benavides et al., 2005; Gratião et al., 2005). Cadmium accumulation in plants depends on plant species and growth stages, Cd concentration and its various forms, types and condition of soil, weather, and the environment (Singh et al., 2012; Hasanuzzaman and Fujita 2012a). Thus, reducing Cd toxicity through exploring phytoremediation and phytoextraction, exogenous protectants, and nutrient management are potential new areas of study (Verbruggen et al., 2009). In this chapter, various impairments of Cd to plant growth and developmental processes are illustrated, as well as an overview of different aspects of remediation technologies for reducing Cd toxicity.

CADMIUM STRESS: A WORLDWIDE PROBLEM

With the advancement of human civilization, fast industrialization has given way to various problems. Among these, HM toxicity is generating great concern. Among the HMs, Cd is one of four metals that have been raising apprehension worldwide with respect to deteriorating environmental quality and causing health hazards (di Toppi and Gabbrielli, 1999). As a result of anthropogenic activity, a large amount of Cd has been added to the environment. It is widespread in atmosphere, soil, and water due to non-sensible production, use, and cycling of various industrial materials. Heating systems, metallurgic industries, waste incinerators, advanced transport systems, cement factories, and the fertilizer industry are some of the major sources of Cd production (di Toppi and Gabbrielli, 1999; Benavides et al., 2005; Gratião et al., 2005). Due to a strong demand for Cd worldwide, particularly in the nickel-Cd battery industry, approximately 30,000 t of Cd are released into the atmosphere each year. It is estimated that 4,000–13,000 t of Cd is produced via industrial activities (ATSDR, 2005). Compared with anthropogenic sources, 840 t of Cd is added from natural sources, including volcanic eruption (Wright and Welbourn, 2002). The major sources of Cd in soil are illustrated in Figure 1. The emission of Cd in soil greatly varied depending on the sources (Hasanuzzaman and Fujita, 2012a; Figure 2).

Cadmium toxicity is a major agricultural problem in soil and has been intensively studied in plants. Generally, the normal concentration of Cd in soil ranges from 0–1 mg kg⁻¹. In Cd-polluted soil, the concentration ranges from 3–10 mg kg⁻¹ soil. The lethal level of Cd concentration is around 100 mg kg⁻¹, which is present in soil containing treated sewage sludge (Rodriguez-Flores and Rodriguez-Castellon, 1982). Although Cd is not essential for plant growth (di Toppi and Gabbrielli, 1999), it is readily taken up and accumulates in traces in plants (Amani, 2008) but due to its high mobility and hydrophilic nature (Pinto et al., 2004), which poses a source of potential damage to plants. Cadmium through the soil is taken up by plants, and this is the primary reason that Cd enters the trophic chain (Wuana and Okieimen, 2011).

The bioaccumulation of Cd in the food chain can be highly dangerous (Raskin et al., 1997; di Toppi and Gabbrielli, 1999), and it is a great threat for humans and wildlife (Jarup and Akesson, 2009). The FAO/WHO recommended maximum tolerable intake of Cd is 400–500 µg week⁻¹ or 70 µg d⁻¹. Other studies reveal that in urban areas, 60–80% of HM toxins found in human bodies were due to the consumption of contaminated foods rather than due to air pollution (Wuana and Okieimen, 2011; Irfan et al., 2013).

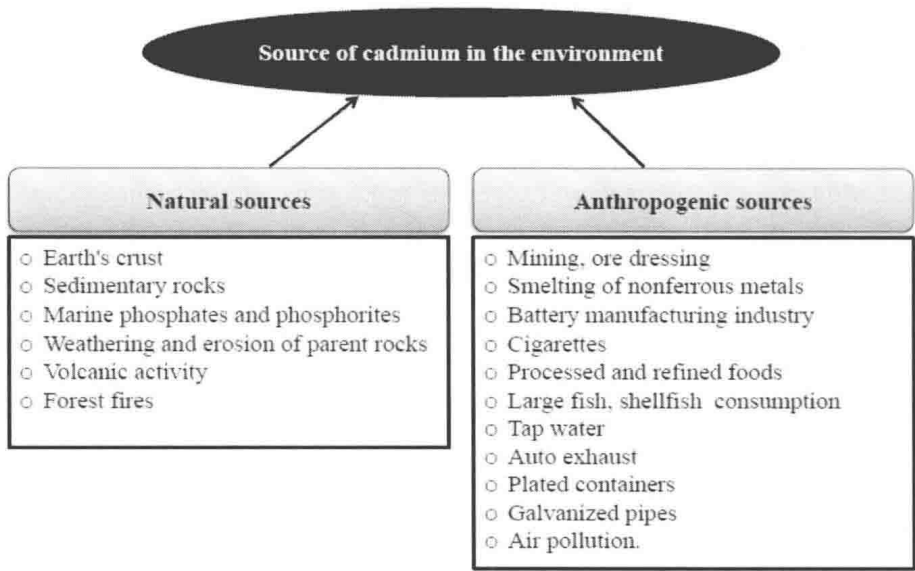


Figure 1. Major sources of cadmium in the environment.

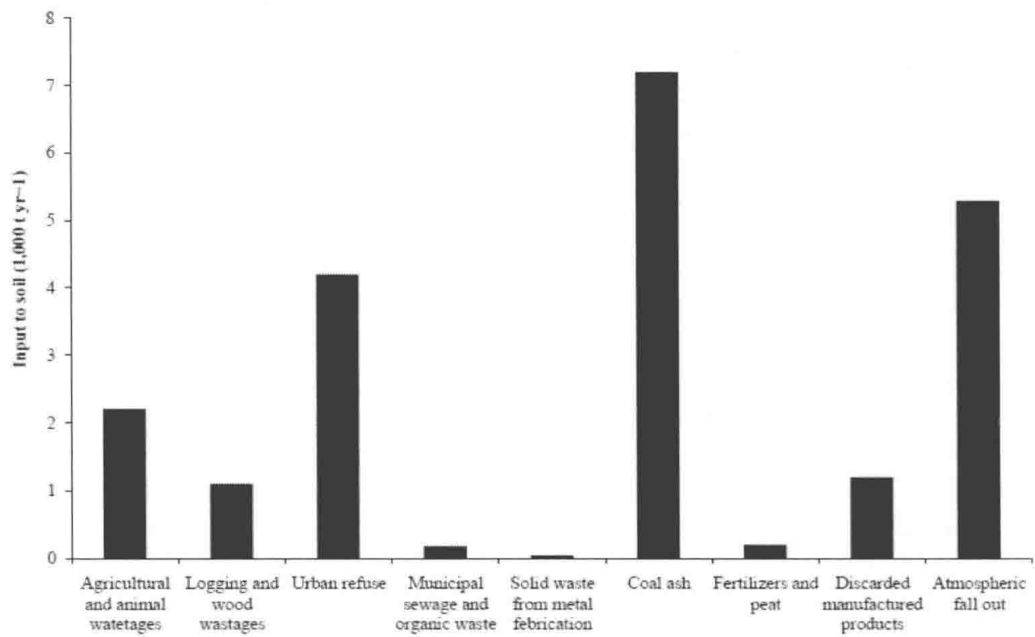


Figure 2. Worldwide input of cadmium in soil.

Among all the toxic HMs, Cd ranks the highest in terms of damage to plant growth and human health (Heyes, 1997). Cadmium toxicity is a great threat for normal plant growth and development.

The excessive intake of Cd from soil creates dual problems in plants. First, the crops, which are sources of the human diet, are contaminated. Second, the crop yield declines due to inhibition of metabolic processes (Singh and Aggarwal, 2006).

Daily consumption of Cd-contaminated foods poses a risk to human health, although it is considered weakly genotoxic (Beyersmann and Hartwig, 2008). For instance, Cd causes both acute and chronic poisoning. Cadmium toxicity induces mitochondrial damage and culminates in cell death either by apoptosis or by necrosis; later, it causes tissue inflammation and fibrosis (Thijssen et al., 2007). It has adverse affects on human bones, kidney, liver, heart, reproductive system, vascular, and immune system. Cadmium is considered a class 1 human carcinogen by the International Agency for Research on Cancer (IARC, 1993). More seriously, through mutation effects, Cd exposure can cause chromosomal aberration and birth defects (Cui et al., 2006; Nouairi et al., 2009).

Cadmium is such a dangerous HM that it is generating great concern among the general population, plant scientists, environmentalist, and policymakers. The sources of Cd, its mode of spread within the food chain, as well as its adverse effects on plants, animals, and humans should be studied intently. Simultaneously, how this acute problem can be solved should be determined. As part of this attempt, we try to gain insight into the effect of Cd on plant growth and developmental processes, as well as to understand plants' mitigation mechanisms when faced with Cd toxicity.

PLANT RESPONSE TO CADMIUM STRESS

Plants exhibit various physiological responses to Cd toxicity, including reduced root activity, tissue chlorosis, stunting, impaired photosynthesis, lower water transportation, and decreases in dry matter accumulation and yield (Cao et al., 2007; Gill et al., 2013a, b).

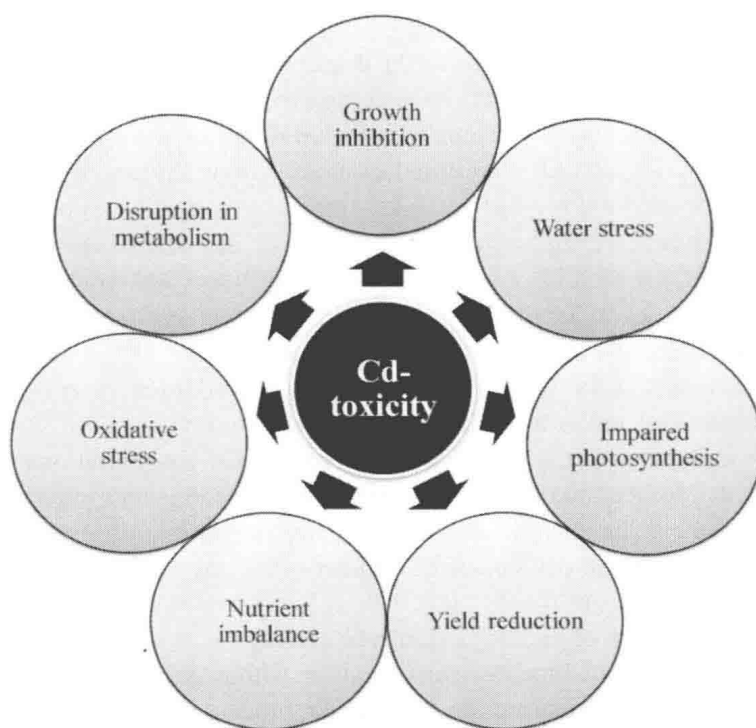


Figure 3. Common effects of cadmium in plants.

The degree of Cd toxicity varies depending upon the dose of Cd, duration of exposure, plant genotypes, and their stress tolerance capacity (Groppa et al., 2008; Daud et al., 2009; Niu, 2009). Cadmium leads to multifarious physiological and biochemical alterations in plant, which results in decreases in growth and yield (Figure 3; Table 1). However, these effects depend on the plant species, genotypes, and the dose and duration of Cd exposure. It also depends on how much Cd in total accumulates. The amount of Cd that accumulates in plants is governed by a variety of factors: (i) availability of Cd within the root zone, (ii) rates of Cd transport into roots through apoplastic and symplastic pathways, (iii) proportion of Cd fixed within the roots as a Cd-phytochelatin complex and accumulated within the vacuole; (iv) rates of xylem loading and translocation of Cd (Nazar et al., 2012).

GERMINATION

Seed germination and subsequent seedling growth are important stages of plant life because better seedling establishment is critical for desirable plant growth and yield. The germination stage is highly sensitive to Cd, as the germinating seed is the first interface of material exchange between the plant development cycle and environment (Bewley and Black, 1994). When the seed's surroundings are contaminated with a toxic HM such as Cd, it prevents water uptake and water movement in the embryo axis; this may be one of the main reasons for the low germination rate (Vijayaragavan et al., 2011), delayed germination, and poor seedling development (Rahoui et al., 2008; 2010). Impaired germination under Cd is also associated with several other disorders in germinative metabolism.

Ample examples of Cd toxicity impairing the germination of different plants could be presented. In rice (*Oryza sativa* L.), the plant germination index, vigor index, radical length, and amylase activities of the variety Xiushui 11 decreased more significantly with increasing Cd (CdCl_2 , 1, 5, 10, 25, 75 and 200 μM) level compared with Xiushui 110. Furthermore, Cd accumulated in a higher amount in Xiushui 11, which diminished the mitotic index in the root tips and amylase activities, as well as resulted in more serious Cd toxicity (He et al., 2008). Additionally, Cd hampered the seed germination rate, root elongation, shoot elongation, and seedling growth of wheat (*Triticum aestivum*) (Chen et al., 2010). As another example, following germination, the seedling survival percentage of beans was gradually reduced from the control as Cd stress levels increased; the survival percentage of seedlings in the control and in Cd 50, 100, 200, 300, and 400 mg kg^{-1} soil samples was 89.0 and 83.0, 76.0, 70.0, 62.0, and 54.0%, respectively (Shekar et al., 2011). In addition, seeds of *Glycyrrhiza uralensis* were germinated and grown with different concentrations of Cd (Cd-acetate 0, 0.05, 0.1, 0.2, and 0.4 mM). Relative to the control, increased Cd concentrations led to gradual decreases in growth, surface area, and fresh weight of cotyledons and hypocotyls. Reduced shoot elongation, radical length, and seedling biomass were also observed (Zheng et al., 2010). Finally, the germination percentage of *Suaeda salsa* was reduced from 88.0% to 18% under different CdCl_2 treatment (0, 0.1, 0.5, 1.0, 2.0, 4.0, and 6.0 mg L^{-1}). Cadmium also reduced shoot and root length of seedlings (Liu et al., 2012).

Various physiological and biochemical alteration within germinating seeds have been identified as being due to Cd impairing the germination process. Cadmium toxicity was found to impair capacity for moisture absorption, resumption of respiration, activity of hydrolases, and availability of nutrients. These facts were identified to reduce germination rate and