

UNDERSTANDING THE INTERACTION OF NANOAGROCHEMICALS WITH LEAFY VEGETABLES AND SOIL

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**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
APRIL 2023**

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VEGETABLES AND SOIL**

by

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DEPARTMENT OF CIVIL ENGINEERING

SUBMITTED

IN FULFILMENT OF THE REQUIREMENTS FOR THE

DEGREE FOR THE DOCTOR OF PHILOSOPHY

TO THE



INDIAN INSTITUTE OF TECHNOLOGY DELHI

APRIL 2023

DEDICATION

**To my parents, you are always the persons with whom I would like to share my
achievements.**

Both of you are my models of lifelong learning.

I am proud of being your daughter.

To my fiancé, you are the best thing happened in my life.

Let's accomplish more together.

I love you.

Certificate

This is to certify that the thesis entitled "**Understanding the interaction of nanoagrochemicals with leafy vegetables and soil**" submitted by **Shraddha Shahane** to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** is a bona fide record of research work carried out by her under my supervision. The content of this thesis, in full, or in part, has not been submitted to any other institute or university for the award of any degree or diploma.

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Acknowledgements

For all I have learned and experienced throughout my time as a PhD student at IIT Delhi, I am eternally thankful. Amazing people have entered my life and provided assistance in overcoming obstacles I've encountered in my studies and daily activities.

To Prof. Arun Kumar

My PhD has been very educative and has driven me through enormous scenarios, refining my view, approach, and maturity on the subject, leading to the requisite professional competence. In this process, I would like to dedicate my efforts to my guide, Dr. Arun Kumar, who has been guiding me relentlessly to perfection, also working beneath his wings. I have had a very fruitful experience with my PhD work. I want to express my deepest appreciation to my supervisor, Prof. Arun Kumar, Dept. of Civil Engineering at IIT Delhi. You are a great example, showing us that success depends not only on our talents, but also on our diligence, perseverance, and willpower. Your dedication gave me the opportunity to improve myself and become a competent research scholar. After working as a member of your research group, I believe that I have obtained greatly enhanced skills for my future career opportunities. Our research group is greatly fortunate to have you. I am extremely thankful for the privilege of being mentored by you. Thank you for guiding, understanding, and resolving problems.

To Dr. Babu Alappat, Dr. Zia and Dr. Alok Madan

I am thankful to have you all as my committee members. Thank you for showing your interest in guiding students to achieve success. I deeply appreciate your professional comments to improve my research work. Thank you so much for all your support.

To my parents and family:

I would like to convey my gratitude to my parents, Pradnya and Pravin Shahane. I am honoured to be your daughter. I would like to thank my entire family for understanding and supporting me during all the ups and downs of my life. With your support, I have overcome many difficulties in the past four years. You encouraged me to be independent, courageous and taught me how to tackle life's challenges and enjoy the journey. I love you forever.

To my grandparents, aunts, uncles, and cousins, thank you for always being there for me, no matter the distance. Your support has been invaluable, and I will forever cherish the memories we have created together. I am proud to belong to a family that values education and has supported me wholeheartedly in my academic pursuits. Thank you for believing in me and for helping me reach where I am today."

To my fiancé, Captain Shriniket Veer:

To have someone like you in my life is indeed a blessing. You are always encouraging and understanding. I really appreciate it. I'm lucky to have you as my best friend. I wouldn't have been able to reach this important milestone in my life without the aid and support of people like you.

To my extended family:

I would want to express my gratitude to everyone who works in the Civil and Engineering Department as well as the Environmental Engineering Laboratory. In addition, I would like to express my gratitude to Dr. Sanjay Gupta, Devsmita ma'am, and Deepak Bedwal for their assistance and guidance during the experimental sets. I'm grateful for my IIT Delhi buddy group. I would like to thank my friends and labmates, including Er. Shivraj, Er. Nikhil, Er. Sanket, Lt. Rahul Kumar, Lt. Lavesh, Lt. Aspin Raj, Lt. Sawan, Lt. Chetan, Dr. Rahul Gadakari, Er. Roshan, Er. Vikrant, Er.

Shiva, Smirthy, Arjita, Ajit, Divya, Angel, Ashish, Pratibha, Jyoti, Maliha, Kashish, Swapnil, D.P.Tripathi, Dr. Tanushree, and Dr. Preeti. I would like to express my sincerest gratitude to my friends, Dr. Mansi Bakshi, Radhika, Sagar, Samridhi, Sasi, Tribhuwan and Aparna who have been an integral part of my academic journey. I want to give a special thanks to Mansi, Sagar, Harshal for their unwavering support and constant encouragement during the most difficult times in my academic journey. I will always remember the small celebrations they organized to make me happy, even when I was struggling. To everyone who has supported me mentally, thank you for being a light in my life during the darkest moments. Your kindness, understanding, and support have been invaluable, and I am forever grateful."

"Dr. Sanjay Gupta's support during my academic journey was invaluable. He not only helped me with difficult problems in experimental sets, but he also created a comfortable and talkative environment, which made learning a pleasure. Moreover, his kind gestures like providing me with homemade food during my time away from home made me feel valued and cared for. I am deeply grateful for his mentorship, guidance, and support."

My colleagues and friends have led and pushed me throughout the process to bring out my best, and I am grateful to them for the remarkable recognition I have gained through this process.

Shraddha Shahane

Abstract

It is possible that simultaneous exposure to two distinct toxicants (nanoparticles (NPs) and pesticides or nanoparticle mixtures) would affect NP absorption and toxicity in plants. When wastewater that contains NPs is utilized as irrigation water, it is important to understand the interaction between herbicides and NPs and their impact on leafy vegetables. In addition, it is essential to have a good understanding of the levels of soil contamination that have been caused by the presence of NPs in partially treated wastewater or in wastewater effluent, as it may pose health risks. It is generally agreed that the soil system is the principal compartment via which NPs are gaining access to the plant root (when mode of application of NP via soil mixing). If nanoparticles are introduced into the soil in several ways, such as by soil amendment or foliar spray, the soil system might become polluted. In light of this, the following research questions were answered in the course of writing this thesis: (1) In what ways are leafy vegetables impacted by exposure to nanoparticles? (2) transgenerational pot study (3) When and how does the active component in the nanocarrier release takes place? (4) What are the dangers of consuming organic/inorganic nanoagrochemicals if human are eating green leafy vegetables and soil that has been contaminated? (5) How much of a nanoagrochemical solution may be safely sprayed on crops before it begins to harm both people and plants? (6) What happens to the soil when it's exposed to metal nanoparticles? This thesis reviews the literature on experimental and theoretical investigations to collect data on the current global use of nanoagrochemicals, existing toxicity data, application frequency, accumulation in plant tissues, soil, and a risk assessment methodology.

Over the course of two generations, we examined what happened to fenugreek when zinc oxide

nanoparticles (0.1-10 mg/L) were applied to the soil medium in which it was growing. Initial research indicated that zinc oxide nanoparticles stimulated growth. It was discovered that second-generation plants exposed to the ZnO NPs had increased shoot length, number of leaves, and plant biomass. Long-term cultivation using wastewater with 10 mg/L ZnO NPs was observed to promote the growth of plants grown in the second generation.

Recent years have seen an increase in the manufacturing and wide-spread application of nanoparticles in different sectors. One of the biggest gaps is what happens to soil matrix when its metal oxide nanoparticles pass through different soil depths. The present investigation aimed to use a soil column study to determine how the NP concentration and column depth affect the fate of ZnO and CuO NPs in soil. The quantity of Zn released from ZnO NPs (1 and 10 mg/L) in soil was found to be considerably larger than that in the control soil column ($p < 0.05$). Values of zinc and copper ions released in percolate at 10 mg/L ZnO/CuO nanoparticle concentrations were roughly 9 and 6% of the applied Zn and Cu contents in a soil column with 2 cm bed depth, respectively. Copper was observed to be less mobile in soil compared to zinc at the highest concentration of NPs and the shallowest bed depth ($p < 0.05$). Using the incorporation approach to apply NPs-containing wastewater or nanoagrochemicals to soil, this research reveals the degree to which particles are liberated from NPs in the top 10 cm of soil.

Zinc oxide nanoparticles interacting with atrazine in soil may provide a health concern. Zinc-contaminated soil's use, contamination, and health risks are unknown. The Toxicity Characteristics Leaching Procedure (TCLP) determines whether nanoparticle-contaminated soil may be safely disposed of or reused for agricultural growth. This study grew fenugreek plants in water containing 0.1 and 10 mg/L ZnO NPs for 55 days, observed effect on plant growth and soil metal content. The leaching procedure based on toxicity characteristics was performed to

determine metal leaching from the soil, and estimated soil metal exposure risks. Atrazine's effects were also examined. According to all soil measurements, ZnO NP has moderately contaminated the soil (Soil contamination factor ≤ 1 , Geo-accumulation index < 1). Adults are safe since soil intake and skin contact exposure hazard quotients (HQ) were less than one. TCLP findings indicate that this soil is safe to use.

A brief examination showed that nanoparticles such as CuO, Cu, Cu(OH)₂, and CuPRO 2005 are the most investigated copper-based nanoformulations. This study selected Cu(OH)₂ and CuO NPs for further evaluation based on nanoagrochemical toxicity and accumulation. This study proposed a "**NanoAgroChemRisk**" framework for analyzing risk to human health of two copper-based nanoagrochemicals. This research also found the safest copper-based nanoagrochemical concentration for farming. This study examines the risks of atrazine on nanocarriers and its release into the environment. In soil contamination, atrazine breakdown, volatilization, sorption and amount of active ingredient released from nanocarrier at t=0 and 4 days were considered. The "**NanopesticideRisk**" framework was presented in this study to analyze the dangers of soil- medium nanoatrazine. Time-dependent atrazine release in loam soil from various nanocarriers was utilized to determine the contaminated soil exposure dose. Accidental oral or topical nanoatrazine exposure from soil medium did not harm occupational workers. We found the safest nanocarrier atrazine application rate in our study.

सार

यह संभव है कि दो अलग-अलग विषाक्त पदार्थों के साथ-साथ संपर्क (नैनोपार्टिकल्स (NPs) और कीटनाशक या नैनोपार्टिकल मिश्रण) पौधों में एनपी अवशोषण और विषाक्तता को प्रभावित करेगा. जब अपशिष्ट जल जिसमें एनपी होता है, सिंचाई के पानी के रूप में उपयोग किया जाता है, तो जड़ी-बूटियों और एनपी के बीच बातचीत और पत्तेदार सब्जियों पर उनके प्रभाव को समझना महत्वपूर्ण है. इसके अलावा, मिट्टी के संदूषण के स्तर की अच्छी समझ होना आवश्यक है जो आंशिक रूप से उपचारित अपशिष्ट जल में या अपशिष्ट जल में एनपी की उपस्थिति के कारण हुआ है, क्योंकि यह स्वास्थ्य जोखिम पैदा कर सकता है. यह आम तौर पर सहमति है कि मिट्टी प्रणाली प्रमुख डिब्बे है जिसके माध्यम से एनपी संयंत्र जड़ (तक पहुंच प्राप्त कर रहे हैं जब मिट्टी मिश्रण के माध्यम से एनपी के आवेदन का तरीका). यदि नैनोकणों को कई तरीकों से मिट्टी में पेश किया जाता है, जैसे कि मिट्टी संशोधन या पर्ण स्त्रे, मिट्टी प्रणाली प्रदूषित हो सकती है. इसके प्रकाश में, इस शोध को लिखने के दौरान निम्नलिखित शोध प्रश्नों का उत्तर दिया गया था: (1) नैनोकणों के संपर्क में आने से पत्तेदार सब्जियां किस तरह से प्रभावित होती हैं? (2) ट्रांसजेनरेशनल पॉट स्टडी (3) नैनोकैरियर रिलीज में सक्रिय घटक कब और कैसे होता है? (4) अगर मानव हरी पत्तेदार सब्जियां और मिट्टी खा रहा है जो दूषित हो गया है तो जैविक / अकार्बनिक नैनो-रसायन के सेवन के क्या खतरे हैं? (5) एक नैनो-रासायनिक समाधान का कितना हिस्सा फसलों पर सुरक्षित रूप से छिड़काव किया जा सकता है इससे पहले कि यह लोगों और पौधों दोनों को नुकसान पहुंचाना शुरू कर दे? (6) धातु नैनोकणों के संपर्क में आने पर मिट्टी का क्या होता है? यह थीसिस नैनोएग्रोकेमिकल्स के मौजूदा वैश्विक उपयोग, मौजूदा विषाक्तता डेटा, अनुप्रयोग आवृत्ति, पौधों के ऊतकों में संचय, मिट्टी, पर डेटा एकत्र करने के लिए प्रयोगात्मक और सैद्धांतिक जांच पर साहित्य की समीक्षा करती है, और एक जोखिम मूल्यांकन पद्धति.

दो पीढ़ियों के दौरान, हमने जांच की कि जब जस्ता ऑक्साइड नैनोकणों (0.1-10 mg / L) को मिट्टी के माध्यम पर लागू किया गया था जिसमें यह बढ़ रहा था. प्रारंभिक शोध ने संकेत दिया कि जिंक ऑक्साइड नैनोकणों ने विकास को उत्तेजित किया. यह पता चला कि ZnO NPs के संपर्क में आने वाली दूसरी पीढ़ी के पौधों ने शूट की लंबाई, पत्तियों की संख्या और प्लांट बायोमास में वृद्धि की थी. दूसरी पीढ़ी में उगाए गए पौधों की वृद्धि को बढ़ावा देने के लिए 10 मिलीग्राम / एल ZnO एनपी के साथ अपशिष्ट जल का उपयोग करके दीर्घकालिक खेती देखी गई.

हाल के वर्षों में विभिन्न क्षेत्रों में नैनोकणों के विनिर्माण और व्यापक प्रसार के आवेदन में वृद्धि देखी गई है। सबसे बड़े अंतराल में से एक मिट्टी मैट्रिक्स के लिए होता है जब इसके धातु ऑक्साइड नैनोकणों को विभिन्न मिट्टी की गहराई से गुजरता है। वर्तमान जांच का उद्देश्य मिट्टी के स्तंभ अध्ययन का उपयोग करना है ताकि यह निर्धारित किया जा सके कि एनपी एकाग्रता और स्तंभ की गहराई मिट्टी में ZnO और CuO NPs के भाग्य को कैसे प्रभावित करती है। ZnO NPs (1 और 10 mg / L) से मिट्टी में जारी Zn की मात्रा नियंत्रण मिट्टी के स्तंभ ($p < 0.05$) की तुलना में काफी बड़ी पाई गई। 10 मिलीग्राम / एल ZnO / CuO नैनोपार्टिकल सांद्रता में छिद्र में जारी जस्ता और तांबे के आयनों के मूल्य लगभग 9 और 6% थे% क्रमशः 2 सेमी बिस्तर की गहराई के साथ एक मिट्टी के स्तंभ में लागू Zn और Cu सामग्री। एनपी की उच्चतम सांद्रता और उथले बिस्तर की गहराई ($p < 0.05$) पर जस्ता की तुलना में तांबे को मिट्टी में कम मोबाइल देखा गया। मिट्टी में एनपी युक्त अपशिष्ट जल या नैनो-रसायन को लागू करने के लिए निगमन दृष्टिकोण का उपयोग करते हुए, इस शोध से पता चलता है कि मिट्टी के शीर्ष 10 सेमी में एनपी से कणों को किस हद तक मुक्त किया जाता है।

मिट्टी में एट्राजीन के साथ बातचीत करने वाले जिंक ऑक्साइड नैनोपार्टिकल्स स्वास्थ्य संबंधी चिंता प्रदान कर सकते हैं। जस्ता- दूषित मिट्टी का उपयोग, संदूषण और स्वास्थ्य जोखिम अज्ञात हैं। विषाक्तता लक्षण लीचिंग प्रक्रिया (TCLP) यह निर्धारित करता है कि नैनोपार्टिकल-दूषित मिट्टी को कृषि विकास के लिए सुरक्षित रूप से निपटाया या पुनः उपयोग किया जा सकता है या नहीं। इस अध्ययन ने 55 दिनों के लिए 0.1 और 10 मिलीग्राम / एल ZnO एनपी वाले पानी में मेथी के पौधों को उगाया, पौधों की वृद्धि और मिट्टी की धातु सामग्री पर प्रभाव देखा। विषाक्तता विशेषताओं पर आधारित लीचिंग प्रक्रिया मिट्टी से धातु लीचिंग, और अनुमानित मिट्टी धातु जोखिम जोखिमों को निर्धारित करने के लिए की गई थी। एट्राजीन के प्रभावों की भी जांच की गई। सभी मिट्टी मापों के अनुसार, ZnO NP ने मिट्टी को दूषित किया है (मृदा संदूषण कारक ≤ 1 , भू-संचय सूचकांक < 1)। मिट्टी के सेवन और त्वचा के संपर्क जोखिम जोखिम वाले उद्घरणों के बाद से वयस्क सुरक्षित हैं (मुख्यालय) एक से कम थे। टीसीएलपी निष्कर्षों से संकेत मिलता है कि यह मिट्टी उपयोग करने के लिए सुरक्षित है।

एक संक्षिप्त परीक्षा से पता चला कि नैनोकणों जैसे कि CuO, Cu, Cu(OH)₂, और CuPRO 2005 सबसे अधिक जांच की गई तांबा-आधारित नैनो-संचालन हैं। इस अध्ययन ने नैनो <टोकेमिकल विषाक्तता और संचय के आधार पर आगे के मूल्यांकन के लिए Cu(OH)₂ और CuO NPs का चयन किया। इस अध्ययन ने दो तांबे-आधारित नैनो-रसायन के मानव

स्वास्थ्य के लिए जोखिम का विश्लेषण करने के लिए "नैनोएग्रोकेमिस्क" ढांचे का प्रस्ताव दिया. इस शोध में खेती के लिए सबसे सुरक्षित तांबा-आधारित नैनो-रासायनिक एकाग्रता भी पाया गया. यह अध्ययन नैनोकैरियर्स पर एट्राजीन के जोखिमों की जांच करता है और इसे पर्यावरण में जारी करता है. मिट्टी के संदूषण में, एट्राजीन ब्रेकडाउन, वाष्पीकरण, टांका लगाने और सक्रिय संघटक की मात्रा को नैनोकैरियर से टी = 0 और 4 दिनों में जारी किया गया था. मिट्टी के मध्यम नैनोट्राजाइन के खतरों का विश्लेषण करने के लिए इस अध्ययन में "नैनोपेस्टीसाइड रिस्क" रूपरेखा प्रस्तुत की गई थी. विभिन्न नैनोकैरियर्स से दोमट मिट्टी में समय पर निर्भर एट्राजीन रिलीज का उपयोग दूषित मिट्टी के संपर्क खुराक को निर्धारित करने के लिए किया गया था. मिट्टी के माध्यम से आकस्मिक मौखिक या सामयिक नैनोएट्राजीन जोखिम ने व्यावसायिक श्रमिकों को नुकसान नहीं पहुंचाया. हमने अपने अध्ययन में सबसे सुरक्षित नैनोकैरियर एट्राजीन आवेदन दर पाया.

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Abbreviations

NP	Nanoparticle	DNA	Deoxyribonucleic acid
WW	Wastewater	DW	Dry weight
TiO ₂	Titanium dioxide	DS	Digestive system
APHA	American Public Health Association	BAF	Bioaccumulation factor
TF	Translocation factor	LD	Lethal dose
SRF	soil retention factor	NOAEL	No-observed-adverse-effect-level
S1	Season one plant	TDI	Tolerable daily intake
S2	Season two plant	CI	Confidence interval
F1	1 st generation	POD	Point-of-departure
F2	2 nd generation	UF	Uncertainty factor
CuO	Copper oxide	WHO	World Health Organization
D50	The portions of particles with diameters smaller and larger than this value are 50%	IRIS	Integrated Risk Information System
CuO NPs	Copper oxide nanoparticle	ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
ADI _{soil}	Average daily intake of copper from soil	NPs	Nanoparticles
C _{soil}	concentration of agrochemicals in soil in terms of copper metal in soil	Pb	Lead
f	Dissolution factor	RfD	Reference dose
f _{soil}	Soil retention factor	ROS	Reactive oxygen species
IR _{soil}	Ingestion rate of soil	SRF	Soil retention factor
EF	Exposure frequency	TDI	Tolerable daily intake
IR _{veg}	Vegetable ingestion rate	TEM	Transmission Electron Microscopy
ED	Exposure duration	USEPA	United states Environmental Protection Agency
BW	Body weight	ECHA	European Chemicals Agency
f _{dissolution factor}	Dissolution factor for nanoagrochemicals on shoot which is dissolved in human digestive media	OECD	Organisation for Economic Co-operation and Development
f	Absorption factor for dietary copper	HSDB	Hazardous Substances Data Bank
AT	averaging time for non-carcinogens	UC	Uncovered
RfD	Reference dose value	WHO	World Health Organization
HQ	Hazard quotient	WW	Wastewater