

**A STUDY ON SOIL POLLUTION AND ASSOCIATED
FOOD CONTAMINATION DUE TO PESTICIDE USE
IN AGRICULTURE**

SANDHYA GUPTA



**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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FOOD CONTAMINATION DUE TO PESTICIDE USE
IN AGRICULTURE**

by

SANDHYA GUPTA

Department of Civil Engineering

Submitted

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CERTIFICATE

This is to certify that the thesis entitled, "**A Study on Soil Pollution and Associated Food Contamination Due to Pesticide Use in Agriculture**" being submitted by Ms. Sandhya Gupta to the Indian Institute of Technology, Delhi, India, for the award of the degree of DOCTOR OF PHILOSOPHY, is a record of bona fide research work carried by her under my supervision and guidance. This thesis work, in my opinion, has reached the standard, fulfilling the requirement of DOCTOR OF PHILOSOPHY degree. The research report and results presented in this thesis have not been published, in part or in, to any other university or institute, for the award of any degree or diploma.

Manika Gupta

Dr. Manika Gupta

(Co-supervisor)

Department of Geology

Delhi University

New Delhi-110007, India

N K Garg

Prof. N. K. Garg

(Supervisor)

Civil Engineering Department

Indian Institute of Technology

New Delhi-110016, India

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ABSTRACT

The present study was carried out to study the mobility and persistence of the pesticides-carbendazim and paraquat in soil (half-life 1-13 years) for the wheat crop along with their translocation from soil into the wheat grains as no field studies are available for these pesticides. The experiments for the two crop seasons (2018-19 and 2019-20) were conducted at the plot scale in the agricultural fields Pusa, Delhi, India. The soil texture was classified as sandy loam. Paraquat dichloride 24% SL (herbicide) and carbendazim 50 wp (fungicide) were applied at the recommended doses on five fields; four fields were kept under different irrigation treatments and the fifth field was held at the rain-fed condition. Carbendazim and paraquat in soil and in the wheat grains were analyzed using HPLC. The Spatio-temporal variation of the soil moisture contents and pesticide's residue in soil in the each of the five fields were determined for both the seasons.

Carbendazim was found either to be degraded or in traces in the soil at the harvest time of the wheat crop seasons. Also, no traces of carbendazim residue in the wheat grains were found in any of the fields for both the seasons. Therefore, carbendazim was not found to be contaminating the soil and the wheat grains and was not considered in the numerical simulation and regulation studies.

Paraquat was found in the background concentration before its application in all the five fields and at all the four soil depths (0-15 cm, 15-30 cm, 30-45 cm, 45-60 cm) in both the seasons. After paraquat application, it was found to be persistent in the top 15 cm soil layer with almost no mobility beyond 15 cm soil depth in all the five fields and in both the crop seasons irrespective of the irrigation treatments. The final concentration of paraquat at the harvest time was found to be more than its initial concentration in the top 15 cm soil depth in all the five fields for both the seasons leading to soil pollution.

The moisture flow and transport of paraquat was also simulated using numerical model, HYDRUS-1D to find out the sustainable doses of paraquat to avoid the soil contamination. The moisture flow model was validated using the field moisture data for all the fields and for both the seasons. There was a good agreement as the relative Root Square Mean Errors (RMSEr) values for the moisture simulations varied from 0.05 to 0.26 and the model efficiencies varied from 0.65-0.95. For paraquat transport modeling, the solute transport parameters were first optimized using inverse modeling with the field data of the Season 1. The temporal variations of the concentrations of paraquat in the soil were then calibrated with the optimized solute transport parameters for the Season 1. The RMSEr values for the paraquat transport simulations varied from 0.015 to 0.167 and the model efficiencies varied from 0.61-0.97, indicating good concentration simulations. Paraquat transport model was further validated, using the optimized solute transport parameters of the Season1, on the field data of the Season 2. There was a good agreement, and the RMSEr values for paraquat transport simulations for the Season 2 varied from 0.012 to 0.139 and the model efficiencies varied from 0.64-0.98. After the model validation, the numerical model was further used for paraquat regulation strategies under different scenarios for different irrigation treatments. It was seen that paraquat contaminated the soil even at the reduced doses as it was found to be persisted in the soil at the end of the wheat crop seasons under all the simulations.

Paraquat residue in the wheat grains was also found in all the fields and in both the seasons, ranging between 21.6 to 49.02 mg kg⁻¹ against the maximum residue level of 0.1 mg kg⁻¹. From the multiple linear regression analysis, paraquat residue in the wheat grain was not found to be sensitive to the depth of irrigation water whereas % clay in soil was found to be the predominant factor. In view of the longer persistence of paraquat in the soil, alarming paraquat residue in the wheat grains and its associated toxic impact on human health, paraquat use is not recommended for the wheat crop based on the present study.

Keywords: Pesticide concentration, Soil pollution, Wheat grain contamination, Numerical modeling, Inverse modeling, Pesticide regulation

सार

वर्तमान अध्ययन गेहूं की फसल के लिए मिट्टी में कीटनाशकों- कार्बेन्डाजिम और पैराक्वाट (आधा जीवन 1-13 वर्ष) की गतिशीलता और दृढ़ता का अध्ययन करने के लिए किया गया था, साथ ही मिट्टी से गेहूं के दानों में इनके स्थानांतरण के साथ-साथ इन कीटनाशकों के लिए कोई क्षेत्र अध्ययन उपलब्ध नहीं है। दो फसल मौसमों (2018-19 और 2019-20) के लिए प्रयोग कृषि क्षेत्रों पूसा, दिल्ली, भारत में भूखंड पैमाने पर आयोजित किए गए थे। मिट्टी की बनावट को रेतीले दोमट के रूप में वर्गीकृत किया गया था। पैराक्वाट डाइक्लोराइड 24% एसएल (हर्बिसाइड) और कार्बेन्डाजिम 50 डब्ल्यूपी (कवकनाशी) पांच क्षेत्रों पर अनुशंसित खुराक पर लागू किए गए थे; चार खेतों को विभिन्न सिंचाई उपचारों के तहत रखा गया था और पांचवें खेत को वर्षा-सिंचित स्थिति में रखा गया था। एचपीएलसी का उपयोग करके मिट्टी और गेहूं के दानों में कार्बेन्डाजिम और पैराक्वाट का विश्लेषण किया गया था। पांच क्षेत्रों में से प्रत्येक में मिट्टी में नमी सामग्री और कीटनाशक के अवशेषों की स्थानिक-अस्थायी भिन्नता दोनों मौसमों के लिए निर्धारित की गई थी। कार्बेन्डाजिम गेहूं की फसल के मौसम कीकटाई के समय मिट्टी में या तो समाप्त या निशान में पाया गया था। साथ ही, दोनों मौसमों में किसी भी खेत में गेहूं के दानों में कार्बेन्डाजिम अवशेष का कोई निशान नहीं पाया गया। इसलिए, कार्बेन्डाजिम को मिट्टी और गेहूं के दानों को दूषित नहीं पाया गया और संख्यात्मक अनुकरण और विनियमन अध्ययनों में इस पर विचार नहीं किया गया।

पैराक्वाट सभी पांच क्षेत्रों में इसके आवेदन से पहले पृष्ठभूमि की सांद्रता में पाया गया था और दोनों मौसमों में सभी चार मिट्टी की गहराई (0-15 सेमी, 15-30 सेमी, 30-45 सेमी, 45-60 सेमी) में पाया गया था। पैराक्वाट के प्रयोग के बाद, यह शीर्ष 15 सेमी मिट्टी की परत में स्थिर पाया गया, जिसमें सभी पांच क्षेत्रों में 15 सेमी मिट्टी की गहराई से परे लगभग कोई गतिशीलता नहीं थी और दोनों फसल मौसमों में सिंचाई उपचार के बावजूद। फसल कटाई के समय पैराक्वाट की अंतिम सांद्रता दोनों मौसमों के लिए सभी पांच क्षेत्रों में शीर्ष 15 सेमी मिट्टी की गहराई में इसकी प्रारंभिक एकाग्रता से अधिक पाई गई, जिससे मृदा प्रदूषण हुआ।

पैराकेट की नमी प्रवाह और परिवहन को संख्यात्मक मॉडल, एचवाईडीआरयूएस -1 डी का उपयोग करके भी अनुकरण किया गया था ताकि मिट्टी के संदूषण से बचने के लिए पैराकेट की स्थायी खुराक का पता लगाया जा सके। नमी प्रवाह मॉडल को सभी क्षेत्रों और दोनों मौसमों के लिए क्षेत्र नमी डेटा का उपयोग करके मान्य किया गया था। नमी सिमुलेशन के लिए सापेक्ष रूट स्क्वायर मीन एरर (आरएमएसईआर) मान 0.05 से 0.26 तक भिन्न थे और मॉडल क्षमता 0.65-0.95 से भिन्न थी। पैराकेट परिवहन मॉडलिंग के लिए, विलेय परिवहन मापदंडों को पहले सीजन 1 के क्षेत्र डेटा के साथ व्युत्क्रम मॉडलिंग का उपयोग करके अनुकूलित किया गया था। मिट्टी में पैराकेट की सांद्रता के अस्थायी विविधताओं को तब सीजन 1 के लिए अनुकूलित विलेय परिवहन मापदंडों के साथ कैलिब्रेट किया गया था। पैराकाट परिवहन सिमुलेशन के लिए आरएमएसईआर मान 0.015 से 0.167 तक भिन्न थे और मॉडल क्षमता 0.61-0.97 से भिन्न थी, जो अच्छी एकाग्रता सिमुलेशन का संकेत देती है। पैराकाट ट्रांसपोर्ट मॉडल को सीज़न 1 के अनुकूलित विलेय परिवहन मापदंडों का उपयोग करके सीज़न 2 के फील्ड डेटा पर और अधिक मान्य किया गया था। एक अच्छा समझौता था, और सीजन 2 के लिए पैराकाट परिवहन सिमुलेशन के लिए आरएमएसईआर मान 0.012 से 0.139 तक भिन्न थे और मॉडल क्षमता 0.64-0.98 से भिन्न थी। मॉडल सत्यापन के बाद, संख्यात्मक मॉडल का उपयोग विभिन्न सिंचाई उपचारों के लिए अलग-अलग परिदृश्यों के तहत पैराकेट विनियमन रणनीतियों के लिए किया गया था। यह देखा गया कि पैराकेट ने कम खुराक पर भी मिट्टी को दूषित कर दिया क्योंकि यह सभी सिमुलेशन के तहत गेहूं की फसल के मौसम के अंत में मिट्टी में बना हुआ पाया गया था।

गेहूं के दानों में पैराकेट अवशेष भी सभी खेतों में और दोनों मौसमों में पाए गए, जो 0.1 मिलीग्राम किलोग्राम⁻¹ के अधिकतम अवशेष स्तर के मुकाबले 21.6 से 49.02 मिलीग्राम किलोग्राम⁻¹ के बीच थे। एकाधिक रैखिक प्रतिगमन विश्लेषण से, गेहूं के दाने में पैराकेट अवशेष सिंचाई के पानी की गहराई के प्रति संवेदनशील नहीं पाया गया था जबकि मिट्टी में % मिट्टी प्रमुख कारक पाई गई थी। मिट्टी में पैराकेट की लंबी दृढ़ता, गेहूं के दानों में खतरनाक पैराकेट अवशेषों और मानव स्वास्थ्य पर इसके संबंधित विषाक्त प्रभाव

को देखते हुए, वर्तमान अध्ययन के आधार पर गेहूं की फसल के लिए पैराक्वेट उपयोग की सिफारिश नहीं की जाती है।

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ACRONYMS AND ABBREVIATIONS

Symbol	Expansion
a.i.	Active ingredient
ASMC	Available soil moisture content
DAP	Diammonium Phosphate
Delta	Total depth of water applied
HPLC	High Performance Liquid Chromatography
IPS	Initial Pesticide residue
LAI	Leaf area index
MAD	Maximum allowable depletion of the ASMC
MOP	Muriate of Potash
MSE	Mean Square Error
OM	Organic Matter
P1	Field maintained at 25% of MAD
P2	Field maintained at 50% of MAD
P3	Field maintained at 75% of MAD
P4	Fully irrigated field
P5	Rain-fed field
PM	Penman Monteith
RMSEr	Relative Root Mean Square Error
S1	Season 1
S2	Season 2
SL	Soluble Liquid
SMRC	Soil moisture retention curves
USDA	United States Department of Agriculture
WHO	World Health Organisation
WP	Wettable Powder

NOTATIONS AND SYMBOLS

Symbols	Description	Unit
C_t	Total pesticide concentration	mg cm^{-3}
D	Soil depth	cm
E	Nash Sutcliffe efficiency	-
ET_o	Reference evapotranspiration	mm day^{-1}
G	Soil heat flux	$\text{MJ m}^{-2} \text{day}^{-1}$
H	Soil water matric potential	Bar, cm
h_w	Pressure head at permanent wilting point	cm
h_a	Anaerobiosis point	cm
h_b and h_c	Pressure heads between which normal water uptake exist	cm
h_s	Maximum pressure head	cm
IE	Irrigation efficiency	-
L	Rooting depth	cm
N	Curve fitting parameters	-
N	number data points	-
NT	Maximum number of temporal observation	-
N_x	No. of observational points in the vertical direction at a particular t	-
R	Growth rate of root lengths	day^{-1}
R^2	Coefficient of determination	-
$RMSEr$	Relative root mean error	-
S	Root water extraction	$\text{cm}^3 \text{cm}^{-3} \text{day}^{-1}$
S_m	Maximum root water extraction rate	$\text{cm}^3 \text{cm}^{-3} \text{day}^{-1}$
T	Mean daily air temperature	$^{\circ}\text{C}$
T	Time	Day
U	Wind velocity	m s^{-1}
V	Pore water velocity	cm day^{-1}
α	Curve fitting parameters	cm^{-1}
α_1	Dimensionless water stress reduction function	-

θ	Volumetric moisture content	% , v/v
D_h	Hydrodynamic dispersion coefficient	$\text{cm}^2 \text{ day}^{-1}$
D_e	effective dispersion coefficient	$\text{cm}^2 \text{ day}^{-1}$
D_l^s	Diffusion coefficient in soil	$\text{cm}^2 \text{ day}^{-1}$
D_l^w	Diffusion coefficient in free water	$\text{cm}^2 \text{ day}^{-1}$
J_h	Hydrodynamic dispersive flux	cm day^{-1}
J_a	Advective or convective flux	cm day^{-1}
J_d	Diffusive flux	cm day^{-1}
J_s	Total solute flux	cm day^{-1}
K	Unsaturated hydraulic conductivity	cm day^{-1}
K_d	Distribution coefficient	$\text{cm}^3 \text{ mg}^{-1}$
K_s	Saturated hydraulic conductivity	cm day^{-1}
MSE	Mean square error	$[\text{mg cm}^{-3}]^2$
M_i	measured data (moisture, pesticide concentration)	$\text{cm}^3 \text{ cm}^{-3}, \text{mg cm}^{-3}$
NS_i	numerically simulated data (moisture, pesticide concentration)	$\text{cm}^3 \text{ cm}^{-3}, \text{mg cm}^{-3}$
R_n	Net radiation at the crop surface	$\text{MJ m}^{-2} \text{ day}^{-1}$
S'	Sink term for pesticide	$\text{mg cm}^{-3} \text{ day}^{-1}$
T_p	Potential transpiration rate	cm day^{-1}
c_i	Initial pesticide concentration	mg cm^{-3}
c_i	Model predicted concentration	mg cm^{-3}
c_i^*	Pesticide concentration observed in the field	mg cm^{-3}
c_s	Pesticide's concentration in the soil	mg mg^{-1}
c_w	Pesticide's concentration in the water	mg cm^{-3}
e_a	Average diurnal ambient vapour pressure	kPa
e_s°	Mean saturated vapour pressure	kPa
fr	Root growth parameters	-
l_0	Initial root depth	cm
lm	Maximum rooting depth	cm
w_{MAD}	Volumetric moisture content at MAD	%
w_f	Volumetric moisture content at field capacity	%

w_i	Weighting function	-
w_w	Volumetric moisture content at wilting point	%
α_2	Extinction coefficient of radiation	-
β_1	Normalized depth of moisture uptake that depends on the root distribution function	cm^{-1}
γ	Psychrometric constant	$\text{kPa } ^\circ\text{C}^{-1}$
$\theta_{initial}$	Initial moisture content	$\text{cm}^3 \text{ cm}^{-3}$
θ_r	Residual moisture content	$\text{cm}^3 \text{ cm}^{-3}$
θ_s	Saturated moisture content	$\text{cm}^3 \text{ cm}^{-3}$
λ	Dispersivity	Cm
μ	First order decay rate constant for pesticides	day^{-1}
ξ	Tortuosity factor	-
ρ_b	Soil bulk density	g cm^{-3}
ρ_d	Particle density	g cm^{-3}

