

**INVESTIGATION OF THE FATE AND TRANSPORT OF
PHARMACEUTICALS AND PERSONAL CARE PRODUCTS
(PPCPS) IN SUBSURFACE ENVIRONMENTS**

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**SCHOOL OF INTERDISCIPLINARY RESEARCH
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by

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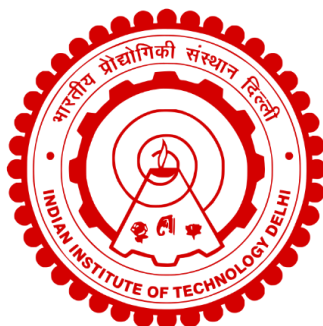
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DEDICATED

TO

MY SON

CERTIFICATE

This is to certify that the thesis entitled “**Investigation of the Fate and Transport of Pharmaceuticals and Personal Care Products (PPCPs) in Subsurface Environments**”, being submitted by **Ms. Maliha Ashraf** to the **Indian Institute of Technology, Delhi** for the award of the degree of ‘**Doctor of Philosophy**’ in the School of Interdisciplinary Research is a record bonafide research work carried out by him under our supervision and guidance. The thesis work, in our opinion, has reached the requisite standards fulfilling the requirement for the Degree of Doctor of Philosophy.

The material contained in the thesis is original and has not been submitted in part or full to any other University or Institute for the award of any other degree or diploma.

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ABSTRACT

Over recent decades, the widespread presence of pharmaceutical and personal care products (PPCPs) in the environment has raised global concern due to their potential adverse effects on ecological and human health. These emerging contaminants (ECs) pose significant risks to ecosystems and human well-being, even at trace levels. Understanding the origin, interactions, and transport behaviour of PPCPs is crucial for effective environmental management. Field monitoring programs, supported by advanced analytical techniques like gas and liquid chromatography coupled with mass spectrometry, have been pivotal in detecting and quantifying these contaminants. The fate and transport of PPCPs in the subsurface involve complex interactions shaped by physical, chemical, and biological processes. Numerical modeling emerges as a valuable tool for investigating the mobility of PPCPs, offering advantages like cost efficiency, broader spatial and temporal insights, and reduced manpower requirements. Developing such models requires a comprehensive understanding of the fate and transport dynamics of PPCPs in the subsurface. Thus, the thesis investigates the fate and transport dynamics of two PPCPs, metformin (MTN) and erythromycin (ETM), in subsurface environments, i.e. sediments and underlying compacted subsurface soil. These PPCPs, once discharged from wastewater treatment plants (WWTPs) into adjacent rivers, partition into the underlying sediments and subsequently migrate into the underlying saturated subsurface soil. This process is of significant concern due to the potential risk these contaminants pose to drinking water sources. Notably, studies on the migration of PPCPs at environmentally relevant concentrations within sediments and real subsurface compacted soil cores remain limited.

The study commences by analysing the migration of these two PPCPs numerically in a saturated sandy soil column using temporal moment analysis. Key flow and transport parameters, including Darcy velocity, longitudinal dispersivity, adsorption, and degradation coefficients, were analyzed to understand the plume dynamics of MTN and ETM in saturated porous media. Results reveal that MTN, a highly mobile contaminant, is eliminated from the system in approximately 40 d, whereas ETM exhibits substantial adsorption, attributed to its hydrophobicity and strong affinity for the soil matrix. The study underscores the critical role of Darcy velocity and adsorption coefficient in governing the transport of PPCPs within porous media, as evidenced by variations in solute mass recovery at the column outlet.

Further, to comprehend the adsorption coefficients and the adsorption characteristics of MTN and ETM in sediments and subsurface soils with different fractions of organic matter and soil particle composition, the study investigates sorption kinetics (single and competitive), isotherms, thermodynamic properties, and the effect of pH and soil moisture content at environmentally relevant concentrations. Notably, the high adsorption coefficients observed for MTN (6.14 L.Kg⁻¹ in sand and 245.70 L.Kg⁻¹ in silty loam) and ETM (8.28 L.Kg⁻¹ in sand and 488.13 L.Kg⁻¹ in silty loam) underscore the significant sorption capacity of these compounds, unlike to as revealed in previous studies. The thermodynamic analysis confirms the feasibility, exothermic nature, and physical characteristics of ETM and MTN adsorption at 293K. A positive impact on adsorption was observed with reduced soil moisture content in the sediments, leading to higher K_d or Q_t values for the studied contaminants. These findings improve our understanding of the fate and transport of MTN and ETM in soil-water systems, thereby aiding the development of effective management strategies to mitigate their environmental impacts.

Additionally, a sandy soil column representing sediments was utilised to understand the migration of targeted PPCPs in sediments. The migration potential of the contaminants in sediments at environmentally relevant concentrations has been studied, thereby prompting the accurate migration potential of the contaminants in the sediments. MTN displayed higher mobility, appearing earlier at sampling ports, while ETM appeared later due to its lower mobility. MTN had a recovery rate exceeding 90%, with a recovery rate exceeding 90 %. In contrast, ETM showed a delayed appearance due to its lower mobility, with a recovery rate of less than 15 %. Fate and transport parameters were determined using experimental breakthrough curves and inverse optimization in HYDRUS 1D, revealing a dispersivity of 0.4 cm and a saturated hydraulic conductivity of 0.75 cm.h^{-1} . MTN's adsorption coefficient was notably lower than ETM's, highlighting concerns about groundwater contamination due to its higher mobility.

Additionally, the mobility of MTN and ETM in subsurface aquifers was examined using 2D soil core samples sourced from the Micromodel Lab at IIT Delhi. Using a 2D tank setup with a constant groundwater table, the study monitors the fate and mobility of PPCPs over a 365 d period. The research offers insights into MTN and ETM transport behaviour, highlighting limited horizontal and vertical migration. Results suggest that MTN travels approximately 40 cm horizontally and 10 cm vertically over one year, while ETM exhibits slow migration due to its strong sorption potential. The study emphasizes the role of soil characteristics and attenuation processes in controlling PPCPs' fate, aiding risk assessment, and environmental management decisions.

Overall, this study provides valuable insights into the transport and fate of MTN and ETM in sediments and subsurface soils. The results revealed that, unlike previous studies, MTN and ETM exhibited higher adsorption potential in both sediments and compacted subsurface soils. Furthermore, the reduced mobility of these polar contaminants within compacted soil matrices

indicates a lower potential for rapid groundwater contamination. These findings provide essential insights for risk assessment, aiding policymakers and environmental professionals in addressing contaminated sites by illuminating the behaviour and transport mechanisms of PPCPs in subsurface environments. Future research should aim to validate numerical models with larger-scale, field-based experiments to better capture PPCPs' transport behaviour under diverse environmental conditions. Additionally, exploring flow and transport dynamics in the unsaturated zone is essential for understanding PPCPs' movement in subsurface environments. Extending the study to include a wider variety of contaminants beyond MTN and ETM will contribute to a more comprehensive understanding of PPCPs' transport patterns and environmental risks. Incorporating multidisciplinary methods, such as molecular biology and isotopic tracing, will further elucidate the interactions among physical, chemical, hydrological, and biological processes.

शोध प्रबंध का शीर्षक: फार्मास्युटिकल्स और पर्सनल केयर प्रोडक्ट्स (पीपीसीपी) के भूमिगत परिवेश में भाग्य और परिवहन की जांच।

छात्र का नाम: मलीहा अशरफ

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सार

पिछले कुछ दशकों में, पर्यावरण में फार्मास्युटिकल्स और पर्सनल केयर प्रोडक्ट्स (पीपीसीपी) की व्यापक उपस्थिति ने पारिस्थितिक और मानव स्वास्थ्य पर उनके संभावित प्रतिकूल प्रभावों के कारण वैश्विक चिंता बढ़ा दी है। ये उभरते प्रदूषक (इमर्जिंग कंटामिनेंट्स) यहां तक कि सूक्ष्म स्तरों पर भी पारिस्थितिक तंत्र और मानव कल्याण के लिए गंभीर जोखिम पैदा करते हैं। पीपीसीपी की उत्पत्ति, परस्पर क्रियाओं और परिवहन व्यवहार को समझना प्रभावी पर्यावरण प्रबंधन के लिए अत्यंत महत्वपूर्ण है। गैस और लिक्विड क्रोमैटोग्राफी को मास स्पेक्ट्रोमेट्री के साथ जोड़ने जैसी उन्नत विश्लेषणात्मक तकनीकों द्वारा समर्थित क्षेत्र निगरानी कार्यक्रमों ने इन प्रदूषकों का पता लगाने और मात्रा निर्धारित करने में महत्वपूर्ण भूमिका निभाई है। पीपीसीपी का भूमिगत परिवेश में भाग्य और परिवहन भौतिक, रासायनिक और जैविक प्रक्रियाओं द्वारा आकार लिए गए जटिल अंतःक्रियाओं में शामिल होता है। संख्यात्मक मॉडलिंग पीपीसीपी की गतिशीलता की जांच के लिए एक मूल्यवान उपकरण के रूप में उभरता है, जो लागत-प्रभावशीलता, व्यापक स्थानिक और कालिक अंतर्दृष्टि, और कम जनशक्ति की आवश्यकता जैसे फायदे प्रदान करता है। ऐसे मॉडल विकसित करने के लिए भूमिगत परिवेश में पीपीसीपी की भाग्य और परिवहन गतिकी की व्यापक समझ की आवश्यकता होती है। इस प्रकार, यह शोध प्रबंध भूमिगत परिवेशों, जैसे कि तलछट और अंतर्निहित संघनित भूमिगत मिट्टी में, दो पीपीसीपी, मेटफॉर्मिन (एमटीएन) और एरिथ्रोमाइसिन (ईटीएम), की भाग्य और परिवहन गतिकी की जांच

करता है। ये पीपीसीपी, जब अपशिष्ट जल उपचार संयंत्रों (डब्ल्यूडब्ल्यूटीपी) से समीपवर्ती नदियों में छोड़े जाते हैं, तो तलछट में विभाजित हो जाते हैं और फिर अंतर्निहित संतृप्त भूमिगत मिट्टी में प्रवास करते हैं। यह प्रक्रिया पेयजल स्रोतों के लिए इन प्रदूषकों के संभावित जोखिम के कारण महत्वपूर्ण चिंता का विषय है। विशेष रूप से, पर्यावरणीय रूप से प्रासंगिक सांद्रता पर तलछट और वास्तविक भूमिगत संघनित मिट्टी के कोर के भीतर पीपीसीपी के प्रवास पर अध्ययन सीमित हैं।

यह अध्ययन संतृप्त रेतीली मिट्टी के स्तंभ में दो पीपीसीपी के प्रवास का संख्यात्मक विश्लेषण करके प्रारंभ होता है, जिसमें टेम्पोरल मोमेंट एनालिसिस का उपयोग किया गया है। मुख्य प्रवाह और परिवहन मापदंडों, जैसे डार्सी वेग, अनुदैर्घ्य विसरणशीलता, सोखना, और अपघटन गुणांक, का विश्लेषण किया गया ताकि संतृप्त छिद्रयुक्त माध्यम में एमटीएन और ईटीएम के प्लूम गतिकी को समझा जा सके। परिणाम बताते हैं कि एमटीएन, जो एक अत्यधिक गतिशील प्रदूषक है, लगभग चालीस दिनों में प्रणाली से समाप्त हो जाता है, जबकि ईटीएम में महत्वपूर्ण सोखना प्रदर्शित होता है, जो इसकी हाइड्रोफोबिसिटी और मिट्टी के मैट्रिक्स के लिए मजबूत आकर्षण के कारण होता है। यह अध्ययन छिद्रयुक्त माध्यम के भीतर पीपीसीपी के परिवहन को नियंत्रित करने में डार्सी वेग और सोखना गुणांक की महत्वपूर्ण भूमिका को रेखांकित करता है, जैसा कि स्तंभ के आउटलेट पर सॉल्यूट मास रिकवरी में विभिन्नताओं से प्रमाणित होता है।

इसके अतिरिक्त, विभिन्न जैविक पदार्थ अंशों और मिट्टी कण संरचना वाले तलछट और भूमिगत मिट्टी में एमटीएन और ईटीएम के सोखना गुणांक और सोखना विशेषताओं को समझने के लिए, अध्ययन पर्यावरणीय रूप से प्रासंगिक सांद्रता पर सोखना गतिकी (एकल और प्रतिस्पर्धात्मक), आइसोथर्म, ऊष्मागतिक गुण, और पीएच तथा मिट्टी की नमी सामग्री के प्रभाव की जांच करता है। विशेष रूप से, एमटीएन (रेत में छह दशमलव एक चार लीटर प्रति किलोग्राम और सिल्टी दोमट में दो सौ पैंतालीस दशमलव सात शून्य लीटर प्रति किलोग्राम) और ईटीएम (रेत में आठ दशमलव दो आठ लीटर प्रति किलोग्राम और सिल्टी दोमट में चार

सौ अट्टासी दशमलव एक तीन लीटर प्रति किलोग्राम) के लिए देखे गए उच्च सोखना गुणांक इन यौगिकों की महत्वपूर्ण सोखना क्षमता को रेखांकित करते हैं, जो पूर्ववर्ती अध्ययनों में प्रकट की गई क्षमता से भिन्न है। ऊष्मागतिक विश्लेषण दो सौ तिरानवे केल्विन पर ईटीएम और एमटीएन के सोखना की व्यवहार्यता, उष्माक्षेपी प्रकृति और भौतिक विशेषताओं की पुष्टि करता है। तलछट में कम मिट्टी की नमी सामग्री के साथ सोखना पर सकारात्मक प्रभाव देखा गया, जिससे अध्ययन किए गए प्रदूषकों के लिए उच्च केडी या क्यूटी मान प्राप्त हुए। ये निष्कर्ष मिट्टी-पानी प्रणालियों में एमटीएन और ईटीएम के भाग्य और परिवहन को समझने में सुधार करते हैं, जिससे इनके पर्यावरणीय प्रभावों को कम करने के लिए प्रभावी प्रबंधन रणनीतियों के विकास में सहायता मिलती है।

इसके अतिरिक्त, तलछट का प्रतिनिधित्व करने वाले रेतीली मिट्टी के स्तंभ का उपयोग लक्षित पीपीसीपी के तलछट में प्रवास को समझने के लिए किया गया। पर्यावरणीय रूप से प्रासंगिक सांद्रता पर तलछट में प्रदूषकों के प्रवास क्षमता का अध्ययन किया गया, जिससे तलछट में प्रदूषकों की सटीक प्रवास क्षमता का पता चला। एमटीएन ने अधिक गतिशीलता प्रदर्शित की, जिससे यह नमूना बिंदुओं पर पहले दिखाई दिया, जबकि ईटीएम कम गतिशीलता के कारण बाद में दिखाई दिया। एमटीएन का रिकवरी दर नब्बे प्रतिशत से अधिक थी, जबकि ईटीएम ने कम गतिशीलता के कारण विलंबित उपस्थिति दिखाई, जिसमें रिकवरी दर पंद्रह प्रतिशत से कम थी। भाग्य और परिवहन मापदंडों को प्रायोगिक ब्रेकथ्रू वक्र और एचवाईड्रस एक-डी में इनवर्स ऑप्टिमाइजेशन का उपयोग करके निर्धारित किया गया, जिसमें शिथिलता शून्य दशमलव चार सेंटीमीटर और संतृप्त हाइड्रोलिक चालकता शून्य दशमलव सात पांच सेंटीमीटर प्रति घंटा पाई गई। एमटीएन का सोखना गुणांक ईटीएम की तुलना में उल्लेखनीय रूप से कम था, जिससे इसकी उच्च गतिशीलता के कारण भूजल प्रदूषण की चिंताओं को उजागर किया गया।

इसके अतिरिक्त, भूमिगत जलभृतों में एमटीएन और ईटीएम की गतिशीलता की जांच आईआईटी दिल्ली के माइक्रोमॉडल लैब से प्राप्त २डी मिट्टी के कोर नमूनों का उपयोग करके की गई। एक स्थिर भूजल स्तर के साथ २डी टैंक सेटअप का उपयोग करते हुए, अध्ययन पीपीसीपी के भाग्य और गतिशीलता की ३६५ दिनों की अवधि में निगरानी करता है। यह शोध एमटीएन और ईटीएम के परिवहन व्यवहार में अंतर्दृष्टि प्रदान करता है, जिसमें क्षैतिज और ऊर्ध्वाधर प्रवास सीमित पाया गया। परिणाम बताते हैं कि एमटीएन एक वर्ष में लगभग चालीस सेंटीमीटर क्षैतिज और दस सेंटीमीटर ऊर्ध्वाधर दिशा में यात्रा करता है, जबकि ईटीएम अपने मजबूत सोखना क्षमता के कारण धीमी प्रवास दर्शाता है। यह अध्ययन मिट्टी की विशेषताओं और मंदन प्रक्रियाओं की भूमिका को पीपीसीपी के भाग्य को नियंत्रित करने, जोखिम मूल्यांकन में सहायता करने और पर्यावरणीय प्रबंधन निर्णयों में जोर देता है।

समग्र रूप से, यह अध्ययन तलछट और भूमिगत मिट्टी में एमटीएन और ईटीएम के परिवहन और भाग्य के बारे में मूल्यवान अंतर्दृष्टि प्रदान करता है। परिणामों ने खुलासा किया कि, पूर्ववर्ती अध्ययनों के विपरीत, एमटीएन और ईटीएम ने तलछट और संकुचित भूमिगत मिट्टी दोनों में उच्च सोखना क्षमता प्रदर्शित की। इसके अतिरिक्त, इन ध्रुवीय प्रदूषकों की संकुचित मिट्टी मैट्रिक्स के भीतर कम गतिशीलता ने तेजी से भूजल प्रदूषण की संभावना को कम दर्शाया। ये निष्कर्ष जोखिम मूल्यांकन के लिए आवश्यक अंतर्दृष्टि प्रदान करते हैं, जिससे नीतिनिर्माताओं और पर्यावरण पेशेवरों को दूषित स्थलों को संबोधित करने में सहायता मिलती है, क्योंकि यह भूमिगत वातावरण में पीपीसीपी के व्यवहार और परिवहन तंत्र को उजागर करता है। भविष्य के शोध को बड़े पैमाने पर, क्षेत्र-आधारित प्रयोगों के साथ संख्यात्मक मॉडलों को सत्यापित करने का लक्ष्य रखना चाहिए, ताकि विभिन्न पर्यावरणीय परिस्थितियों के तहत पीपीसीपी के परिवहन व्यवहार को बेहतर ढंग से समझा जा सके। इसके अलावा, भूमिगत क्षेत्र में प्रवाह और परिवहन गतिकी की जांच करना आवश्यक है ताकि भूमिगत वातावरण में पीपीसीपी की गति को समझा जा सके। अध्ययन को एमटीएन और ईटीएम

के अलावा अधिक विविध प्रकार के प्रदूषकों को शामिल करने के लिए विस्तारित करना पीपीसीपी के परिवहन पैटर्न और पर्यावरणीय जोखिमों की अधिक व्यापक समझ में योगदान देगा। अंतःविषय विधियों को शामिल करना, जैसे आणविक जीव विज्ञान और समस्थानिक ट्रेसिंग, भौतिक, रासायनिक, जलविज्ञान और जैविक प्रक्रियाओं के बीच अंतःक्रियाओं को और अधिक स्पष्ट करेगा।

TABLE OF CONTENTS

CERTIFICATE	i
ACKNOWLEDGEMENTS	ii
ABSTRACT	iv
TABLE OF CONTENTS	xiii
LIST OF FIGURES	xix
LIST OF TABLES	xxiii
LIST OF ABBREVIATIONS	xxv
CHAPTER 1	1
INTRODUCTION: BACKGROUND AND PROBLEM STATEMENTS	1
1.1 Background	2
1.2 Problem statement	8
1.3 Objectives of the study	10
1.4 Scope of the study	11
1.5 Dissertation structure	11
CHAPTER 2	144
LITERATURE REVIEW AND BIBLIOMETRIC STUDY	144
2.1 Background	155
2.2 Methodology	166
2.2.1 Raw data extraction	177
2.2.2 Data analysis	188
2.2.3 Data visualizations and interpretation: Tools used	188
2.3 Occurrence of PPCPs in the environment.....	199

2.4 Sources of PPCPs in water resources	211
2.4.1 Point sources of PPCPs.....	222
2.4.2 Diffused sources of PPCPs.....	233
2.5 Fate and transport of PPCPs in subsurface soils and groundwater: adsorption and degradation	244
2.6 Understanding contaminant migration in the aquifers: Experimentally	277
2.7 Mathematical modeling of contaminant migration in the saturated porous media	299
2.7.1 Advection	30
2.7.2 Diffusion and Mechanical Dispersion: Hydrodynamic Dispersion	311
2.7.3 Adsorption	322
2.7.4 Degradation	333
2.7.5 Modeling advection-dispersion, adsorption and degradation of contaminants in porous media.....	344
2.7.5.1 Chemical non-equilibrium: one-site sorption model.....	355
2.7.5.2 Chemical non-equilibrium: two-site sorption model.....	366
2.8 Temporal moment-based approach to understanding the migration of contaminants in the porous media	377
2.9 Study of metformin and erythromycin for its fate and transport in the subsurface	4040
2.10 Research growth trend in the area of fate and transport of PPCPs.....	466
2.11 Data analysis of bibliometric information on the fate and transport of PPCPs.....	477
2.11.1 Text mining: Identification of research themes.....	477
2.11.2 Author keywords of fate and transport	533
2.11.3 Index keywords of fate and transport study	555
2.11.4 Sankey Diagrams: Three field plots on fate and transport.....	555
2.12 Conclusions	566

2.13 Identified research gaps.....	599
CHAPTER 3	611
IMPLEMENTATION OF TEMPORAL MOMENTS TO ELUCIDATE THE REACTIVE TRANSPORT OF METFORMIN AND ERYTHROMYCIN IN THE SATURATED POROUS MEDIA	611
3.1 Background	622
3.2 Materials and methodology.....	655
3.2.1 Numerical modeling.....	68
3.2.1.1 Initial and boundary conditions	699
3.2.2 Computation of temporal moments.....	699
3.3 Verification of the numerical modeling approach.....	711
3.4 Results and Discussion	72
3.4.1 Temporal variation of the PPCP concentration profile	722
3.4.2 Effect of conceptual models on temporal moments of contaminant concentration	733
3.4.3 Mechanistic insights into temporal moments of PPCP concentration.....	777
3.4.3.1 Effect of Darcy velocity	777
3.4.3.2 Effect of longitudinal dispersivity	80
3.4.3.3 Effect of adsorption coefficient	83
3.4.3.4 Effect of degradation coefficient	866
3.5 Conclusions.....	899
CHAPTER 4.....	92
UNRAVELING SORPTION DYNAMICS: EXPLORING METFORMIN AND ERYTHROMYCIN COMPETITIVE BEHAVIOUR IN SOILS USING BATCH STUDY .	92
4.1 Background	933
4.2 Materials and methodology.....	955

4.2.1 Procurement and characterisation of soil samples	955
4.2.2 Chemicals and reagents	966
4.2.3 Experiment methodology	97
4.2.3.1 Sorption kinetics experiment.....	97
4.2.3.2 Experimentation on Sorption Isotherms.....	97
4.2.3.3 Experiments on varying temperature and pH.....	988
4.2.3.4 Moisture content.....	988
4.2.4 Analytical methods.....	98
4.2.5 Data Processing.....	100
4.3 Results and discussion	1022
4.3.1 Sorption kinetics	1022
4.3.2 Sorption Isotherms	104
4.3.3 Effect of temperature on adsorption of MTN and ETM: Thermodynamic studies	107
4.3.4 Influence of pH on the adsorption of MTN and ETM onto soils.....	1088
4.3.5 Impact of soil moisture content	110
4.4 Conclusions.....	111
CHAPTER 5.....	1133
EXAMINING THE TRANSPORT OF METFORMIN AND ERYTHROMYCIN IN	
SEDIMENTS IN A 1D SATURATED SANDY SOIL COLUMN: EXPERIMENTAL	
INVESTIGATION AND MODELING ANALYSIS.....	113
5.1 Background.....	114
5.2 Materials and methodology.....	115
5.2.1 Material preparation: Compound selection and soil conditioning	115
5.2.2 Column setup	1166
5.2.3 Analytical methods.....	1188

5.2.4 Numerical modeling.....	118
5.2.4.1 Initial and boundary conditions.....	119
5.2.4.2 Numerical modeling approach	120
5.3 Results and discussion	122
5.3.1 Transport of Bromide tracer and VGM parameters	122
5.3.2 Co-transport of PPCPs in the sediments	1244
5.3.3 Simulation of PPCPs using HYDRUS 1D	1266
5.3.4 Desorption study and temporal moments	129
5.4 Conclusions	132
CHAPTER 6.....	134
INVESTIGATING THE MOBILITY OF METFORMIN AND ERYTHROMYCIN IN THE	
SUBSURFACE SOIL: A 2D SOIL CORE EXPERIMENT	134
6.1 Background	135
6.2 Materials and methodology.....	137
6.2.1 Soil core collection for the 2D tank setup	140
6.2.2 2D-soil tank setup.....	141
6.2.3 Soil characterisation: bulk density and porosity.....	144
6.3 Results and Discussions	147
6.3.1 Mobility of metformin in the 2D subsurface saturated soil core.....	147
6.3.2 Mobility of erythromycin in the 2D subsurface saturated soil core.....	153
6.4 Conclusions	157
CHAPTER 7	1599
CONCLUSIONS AND FUTURE SCOPE.....	159
7.1 Concluding Remarks.....	160

7.2 Future Scope	1633
REFERENCES	166
PUBLICATIONS	207
BIODATA	209

LIST OF FIGURES

Fig. 1.1 Potent sources of groundwater and drinking water supplies- Rural and urban activities.	3
Fig. 2.1 Pictorial representation of the research framework to find the research trails and hotspots in the area of fate and transport of PPCPs.	17
Fig. 2.2 Detection of PPCPs in various environmental settings in the past decade.	19
Fig. 2.3 Advection, dispersion, adsorption and degradation processes affecting contaminant migration in the porous media.	30
Fig. 2.4 Analysis of breakthrough curve for its solute mass recovery, residence time, variance, and skewness.	38
Fig. 2.5 The publication growth trend in fate and transport research.	46
Fig. 2.6 The co-occurring author keywords of fate and transport research.	53
Fig. 2.7 Density visualization of top Index keywords based on 30 co-occurrences.	56
Fig. 2.8 Tree plot of top thirty Index Keywords.	57
Fig. 2.9 Three Field Plot Keywords (Left), Author (middle), and Source/Journal (Right).	58
Fig. 3.1 Flowchart of the methodology adopted for the numerical modeling and temporal moment analysis of PPCPs.	67
Fig. 3.2 Spatial concentration profile for non-reactive contaminant at time, $T = 2.5$ d.	71
Fig. 3.3 Concentration profile of MTN (left) and ETM (right) at different time levels ($T = 0, 1, 5, 10, 15, 20, 25, 30, 35, 40, 45,$ and 47.5 d).	72
Fig. 3.4 Spatial distribution of (a, e) solute mass recovery, (b, f) mean residence time, (c, g) variance of the breakthrough curve and (d, h) coefficient of skewness of MTN and ETM in the sandy porous system with different conceptual models.	74

Fig. 3.5 Spatial distribution of (a, e) solute mass recovery, (b, f) mean residence time, (c, g) variance of breakthrough curves, and (d, h) coefficient of skewness of MTN and ETM for different values of Darcy velocity. 79

Fig. 3.6 Spatial distribution of (a, e) solute mass recovery, (b, f) mean residence time, (c, g) variance of the breakthrough curve, and (d, h) coefficient of skewness of MTN and ETM for different values of longitudinal dispersivity. 82

Fig. 3.7 Spatial distribution of (a, e) solute mass recovery, (b, f) mean residence time, (c, g) variance of the breakthrough curve, and (d, h) coefficient of skewness of MTN and ETM for different values of sorption distribution coefficient..... 85

Fig. 3.8 Spatial distribution of (a, e) solute mass recovery, (b, f) mean residence time, (c, g) variance of BTC, and (d, h) coefficient of skewness of MTN and ETM for different values of degradation coefficient..... 88

Fig. 4.1 Calibration curve in solvents for (a) MTN and (b) ETM obtained from LC/TQ..... 99

Fig. 4.2 Sorption kinetic curves for MTN and ETM in the two soils are shown: both in single systems (a) sandy soil and (b) silt loam; and in competitive systems (c) sandy soil and (d) silt loam. Symbols represent measured data, while solid lines depict model fits..... 102

Fig. 4.3 Sorption isotherms of MTN and ETM at various concentrations examined on (a) Sandy soil and (b) Silt loam..... 106

Fig. 4.4 Effect of pH values on the sorption of (a) MTN and (b) ETM onto the sandy soil and silt loam..... 109

Fig. 4.5 Effect of soil moisture content on the sorption of (a) MTN and (b) ETM onto sandy soil. 110

Fig. 5.1 Experimental setup of 1D column to study the mobility of MTN and ETM in sandy soil.	116
Fig. 5.2 Detailed map of the column study (1) Stock solution; (2) Peristaltic pump; (3) Headspace; (4) saturated sandy soil; (5) sampling ports 5(a)-Port A, 5(b)-Port B and 5(c)-Port C located at 10cm, 20cm and 30cm from topmost soil layer; (6) MTN and ETM samples; (7) Ultivo LC/TQ for sample analysis by direct injection.	117
Fig. 5.3 Schematic diagram of the mathematical model of saturated porous system describing the boundary conditions.....	120
Fig. 5.4 Schematic diagram of the methodology adopted for studying the fate and transport of MTN and ETM. (BTCs = breakthrough curves).	121
Fig. 5.5 Breakthrough curve of bromide transport in sandy soil; points representing the experimental data and lines depicting the simulated data using HYDRUS 1D.....	122
Fig. 5.6 Breakthrough curve of the competitive transport of MTN and ETM in sandy soil obtained at 10cm, 20cm and 30 cm from the uppermost soil layer.	124
Fig. 5.7 Breakthrough curve- experimental and simulated using two-site sorption model in HYDRUS 1D; experimental data represented by points and numerical data represented by lines.	129
Fig. 5.8 Desorption of MTN (left) and ETM (right) from the sandy soil on the discontinuation of PPCPs source and introduction of water.....	130
Fig. 5.9 Variation of mass recovery, mean residence time and variance of the breakthrough curve of MTN (orange) and ETM (green) for ports A, B and C positioned at 10cm, 20cm and 30cm, respectively, below the soil surface in the column.	131

Fig. 6.1 Sample collection site from IIT Delhi region located using map of India, Delhi Region and IIT Delhi.....	138
Fig. 6.2 The methodology adopted for the soil core collection to investigate the mobility of PPCPs in the subsurface.	139
Fig. 6.3 Soil samples were collected in rings after the removal of the 50cm topsoil.	139
Fig. 6.4 Gradual collection of 2D soil core to desired depth from Micromodel lab, IIT Delhi, Delhi.	140
Fig. 6.5 Laboratory Setup of 2D Tank Experiment.....	142
Fig. 6.6 Schematic diagram of 2D Tank Setup for examining fate and transport of PPCPs in the subsurface soil.....	143
Fig. 6.7 Soil core samples submerged in water to achieve complete saturation of the soil cores.	144
Fig. 6.8 Determination of particle density using pycnometer.	146
Fig. 6.9 Concentration profiles of MTN migration in the upper ports (i.e. Ports 1 to Port 5) of the soil core spatially and temporally in a 365-d period.....	148
Fig. 6.10 Concentration profiles of MTN migration in the lower ports (i.e. Ports 6 to Port 10) of the soil core spatially and temporally in a 365-d period.....	151
Fig. 6.11 Concentration profiles of ETM migration in Ports 2, 3, 4 and 5 of the soil core spatially and temporally in 365 d period.	154
Fig. 6.12 Concentration profiles of ETM migration in Ports 1, 6, 9 and 10 of the soil core spatially and temporally in 365 d period.	155

LIST OF TABLES

Table 2.1 Literature reported on the fate and transport studies conducted for MTN and ETM. .	41
Table 2.2 Physio-chemical properties of MTN and ETM in the subsurface.....	42
Table 2.3 Fate and transport parameters of the selected MTN and ETM.	43
Table 2.4 Top three author keywords in each cluster of the co-occurrence network. Average Publishing Year (APY); Starting Year (SY); Ending Year (EY).	54
Table 3.1 Model parameters used in COMSOL Multiphysics for fate and transport modeling of MTN and ETM.	66
Table 4.1 The physio-chemical characteristics of the soils.....	95
Table 4.2 Physio-chemical properties of MTN and ETM in the subsurface.....	96
Table 4.3 Multiple reaction monitoring (MRM) for MTN and ETM.	99
Table 4.4 Limit of detection (LOD) and limit of quantification (LOQ).	100
Table 4.5 The kinetic model parameters and regression coefficients for MTN, and ETM sorption onto the two soils. (SS = sandy soil; SL = silt loam; MS = single solutes; CS = competitive solutes).	104
Table 4.6 The isotherm sorption model parameters and coefficients of regression for MTN and ETM sorption onto the two soils (SS = Sandy soil; SL = Silt loam).....	105
Table 4.7 Thermodynamic parameters of the sorption of the MTN and ETM onto the two soils.	107
Table 5.1 Fitting parameters of equilibrium and non-equilibrium adsorption isotherms obtained on inverse optimisation of the MTN and ETM breakthrough curves using HYDRUS 1D; units of linear distribution coefficient (K_d), Freundlich coefficient (K_f) and Langmuir Coefficient (K_i) is [$L.kg^{-1}$] and degradation coefficient (k) [d^{-1}] while other parameters being dimensionless.	127

Table 6.1 Observation table for calculating the bulk density of collected subsurface soil. 145

Table 6.2 Observation table for calculating the particle density of collected subsurface soil (B = Pycnometer bottle; C = Cap; S = Soil; W = Water)..... 147

LIST OF ABBREVIATIONS

Acronyms	Expanded form
2D	Two-dimensional
ADE	Advection dispersion equation
ADES	Advection dispersion sorption
ADESD	Advection dispersion sorption degradation
ECs	Emerging contaminants
ESI	Electron spray ionisation
ETM	Erythromycin
LC/TQ	Liquid chromatography triple quadrupole
LCMS	Liquid chromatography mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
MRM	Multiple reaction monitoring
MTN	Metformin
PPCPs	Pharmaceuticals and personal care products
SOM	Soil organic matter
VGM	Van-Genuchten-Mualem
WWTPs	Wastewater treatment plants