

# Assessment of Metalaxyl migration through vadose zone of alluvial sandy soil using column experiment and HYDRUS numerical modeling

## Valutazione della migrazione di metalaxyl nella zona vadosa di un sistema sabbioso alluvionale tramite colonne sperimentali e modellazione numerica con HYDRUS

Nilesh Kumar MESHRAM<sup>a</sup>, Kalyan ADHIKARI<sup>a</sup> ✉, Rhitwik CHATTERJEE<sup>a</sup>

<sup>a</sup> Department of Earth and Environmental Studies, National Institute of Technology Durgapur, Durgapur, 713209, West Bengal, India. - email: [quilesh@gmail.com](mailto:quilesh@gmail.com); [rhitwikcu@yaboo.co.in](mailto:rhitwikcu@yaboo.co.in); email ✉ : [kalyan.adbhikari@ees.nitdgp.ac.in](mailto:kalyan.adbhikari@ees.nitdgp.ac.in)

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### Correspondence to:

Kalyan ADHIKARI ✉

[kalyan.adbhikari@ees.nitdgp.ac.in](mailto:kalyan.adbhikari@ees.nitdgp.ac.in)

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**Parole chiave:** acqua sotterranea, agricoltura, pesticidi, metalaxyl, HYDRUS.

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### Riassunto

La ricerca attuale è poco focalizzata sull'uso di pesticidi/fungicidi come potenziali fonti di contaminazione delle acque sotterranee, comprese le loro vie migratorie, in particolare nel bacino del Bengala occidentale (WBB). Il presente studio intende valutare la vulnerabilità delle acque sotterranee all'inquinamento da metalaxyl. Il metalaxyl è un fungicida aggiunto antropogenicamente ai terreni sabbiosi della WBB per la coltivazione di colture come pomodori, patate e senape. Lo studio esplora la meccanica dell'adsorbimento del metalaxyl nel suolo e la sua migrazione verso il sistema idrico sotterraneo. Le analisi chimiche mostrano alte concentrazioni di metalaxyl all'interno delle acque sotterranee (472.9 µg/L, valore massimo) provenienti dall'area di studio (distretto di Nadia nel WBB). Il *groundwater ubiquity score* del metalaxyl (4.6) suggerisce che è molto incline a lisciviare attraverso i terreni sabbiosi di WBB verso la falda sottostante. I risultati degli esperimenti di lisciviazione su colonna e la loro congruenza con i risultati dello studio di modellazione numerica con il software HYDRUS confermano il fatto. La resilienza per assorbimento dei terreni studiati verso il metalaxyl è insignificante (suoli di North Chandmari (S1) = 0.1087 mg/g, Ghoragacha (S2) = 0.21 mg/g e Khaldarpara (S3) = 1.771 mg/g). Tuttavia, la presenza di una concentrazione in eccesso di ferro può aumentare la capacità di adsorbimento del terreno del metalaxyl, limitando così la sua migrazione verso la zona satura.

### Abstract

Contemporary research on pesticides/fungicides as potential sources of groundwater contamination, including their migration pathways, especially in the Western Bengal basin (WBB), is scarce. The present research intends to study the vulnerability of groundwater towards pollution from metalaxyl. Metalaxyl is a fungicide added anthropogenically to the sandy soil of WBB for the cultivation of crops like tomatoes, potatoes and mustard. The study explores the mechanics of metalaxyl adsorption in soil and its migration to the associated groundwater system. Chemical analyses show high concentrations of metalaxyl within groundwater (472.9 µg/L, maximum amount) from the study area (Nadia district of WBB). The groundwater ubiquity score of metalaxyl (4.6) depicts that it is very much prone to leach through the sandy soils of WBB to the underlying groundwater system. The results of column leaching experiments and their congruence to the findings of numerical modelling study using HYDRUS software confirm the fact. The adsorptive resilience of the studied soils towards metalaxyl is insignificant (soils of North Chandmari (S1) = 0.1087 mg/g, Ghoragacha (S2) = 0.21 mg/g, and Khaldarpara (S3) = 1.771 mg/g). However, the presence of excess iron concentration may enhance the adsorptive capacity of the soil toward Metalaxyl, thereby limiting its migration toward the zone of saturation.

## Introduction

The non-judicious use of pesticides has been a growing issue in agricultural land and the associated environment as the residues of pesticides randomly produce the groundwater contamination (El Alfy & Faraj, 2017; Haddad et al., 2019). The leaching of pesticides from agricultural land right into groundwater has become the primary environmental concern (Besser et al., 2022). Pesticide remains can be discovered distant from the point of application within the dynamic soil water system (Yorlano et al., 2022). Vagi et al., (2022) state that the adsorption of pesticides by soils has a substantial impact on the fate of pesticides in the soil water profile (Vagi & Petsas 2022; Wu et al., 2011). There is a strong correlation between pesticide adsorption factors and soil characteristics (Rasool et al., 2022). Adsorption isotherms aid to understand the adsorptive behaviour of contaminants (pesticides) with different kinds of soils (Naboulsi et al., 2023). The *Groundwater Ubiquity Score* (GUS) of pesticide hints towards their leachability (Junior et al., 2023). The migration pathways of contaminants through vadose zone is frequently analysed with HYDRUS package as it offers several effective codes for the study of solute transport (Simunek et al., 2013).

Groundwater from shallow alluvial aquifers of Nadia district in WBB is highly vulnerable towards pesticide pollution (Duttgupta et al., 2020). The study area belongs to the intensive agricultural land of West Bengal, India, and was chosen for the present study. Poor surface runoff provides a greater opportunity for the contaminant-laden standing water in the farmland to infiltrate into the groundwater through the vadose zone (Yadav et al., 2003).

Metalaxyl was chosen for the present study because it is used as fungicide for the cultivation of vegetable crops in the study area (Alagh, 1988). Metalaxyl is an fungicide utilized to restrict the growth of fungus-like Oomycete, Pythium and Phytophthora (Sukul et al., 2001). Metalaxyl is responsible for increase in micronuclei and increase in

the frequency of micronuclei potentially results in genetic damage of individuals. Therefore, metalaxyl exposure can increase cancer risk (Bonassi et al., 2007; Saquib et al., 2021). Metalaxyl is readily soluble and poorly adsorbed to soil particles. Consequently, poor agricultural runoff may cause it to infiltrate and reach the saturated zone (Meite et al., 2018). A study was done in USA in which the concentration of metalaxyl was found to be more than 236 ppb (USEPA, 1994).

Previously no research has been done to study the transport mechanism of metalaxyl in the alluvial soil of this part of the world. Therefore, considering the likely carcinogenic character and extensive use of metalaxyl and the soil characteristics, it is important to study the potential of this fungicide to contaminate groundwater. The objectives of the present study are: (i) to understand the adsorptive behaviour of metalaxyl in the vadose zone, (ii) to assess the transport mechanism of metalaxyl through the alluvial sediments by lab-scale experimental study and (iii) to match the experimental results with the result of the numerical simulation with HYDRUS-1D code in order to predict the movement of the metalaxyl through vadose zone to reach aquifer under similar hydrogeological condition elsewhere.

## Material and methods

### Study area

Nadia district in West Bengal, India, is located between 22° 52' 253" and 24° 06' 033" North latitude and 88° 08' 113" and 88° 48' 083" East longitude (Fig. 1). The southern part of the district has been selected for the study. Because here, the yield of crops related to metalaxyl is high. The study area is approximately 748.480 km<sup>2</sup>. The district is divided into two halves by the Tropic of Cancer. It is situated around 14 metres above mean sea level on the fertile plains of the Hooghly River (Ahmed et al., 2012). The average annual precipitation is around 1400 mm (Biswas, 2022). The common pesticide uses

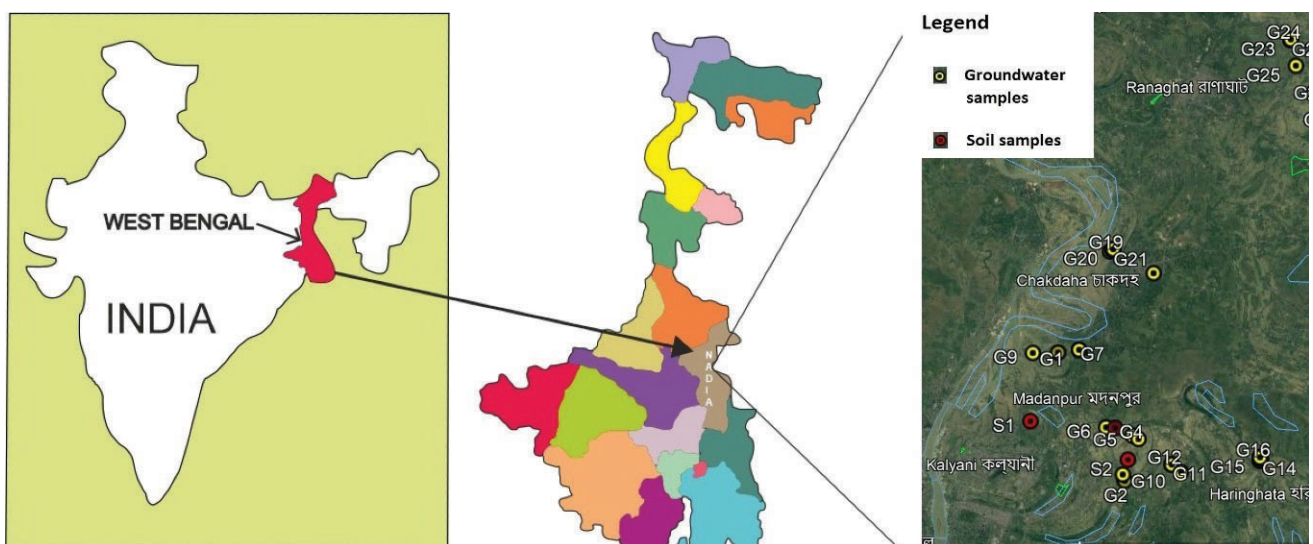


Fig. 1 - Schematic representation of the study area showing distribution soil and groundwater sampling point.

Fig. 1 - Rappresentazione schematica dell'area di studio raffigurante la distribuzione dei suoli e i punti di prelievo della falda.

in study area listed in Tab. 1S (supplementary information). The groundwater of this region occurs at very shallow depth within alluvial aquifer mostly under unconfined conditions. The average depth to pre monsoon water level varies between 0.6 to 4 m below ground level (bgl). The average depth to water level varies between 0.2 m to 2.5 m bgl. The average thickness of the vadose zone within the study area varies from 0.2 to 0.8 m (NAQUIM, 2016).

### Collection of groundwater samples and analysis

A total 32 number of groundwater samples (G1-G32) were collected from the different sites in the study area, detailed in (supplementary information). High-quality glass bottle of 500 ml capacity was used to collect the groundwater samples. To protect the collected samples from microbes 5 ml of chloroform was added in every bottle. The samples were transferred from the site to the laboratory by maintaining a temperature of 4°C using an ice box. The samples were filtered using Whatman 42 filter paper to remove any suspended particles.

### Gas Chromatography (GC) analysis

The groundwater sample was extracted using liquid-liquid-extraction (LLE) method (Mondal et al., 2018). These samples were then analysed quantitatively by GC using an Flame Ionization Detector (FID) detector and a TR-5 column (30 m 0.25 mm id. 0.25 μm). In the GC injector, one microliter of the sample was injected. Oven temperature was designed to climb from 60°C to 180°C at a rate of 6°C/min, and then to 225°C. The injector and detector temperature was maintained at 270 and 290°C respectively. Metalaxyl had a retention time (RT) of 13.11±0.5 min (Fig. 2).

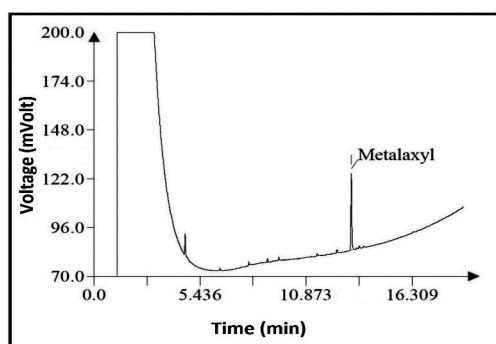


Fig. 2 - Chromatogram showing the peak of 10 mg/L concentration of metalaxyl at the retention time of 13.11 ± 0.5 minute.

Fig. 2 - Cromatogramma che mostra il picco di 10 mg/L di metalaxyl ad un tempo di ritenzione di 13.11 ± 0.5 minuti.

### Collection of Soil samples and analysis

Three soil samples were collected from North Chandmari (22°59'24"N, 88°27'36"E), Ghoragacha (22°58'12"N, 88°31'12"E) and Khaldarpara (22°59'24"N, 88°30'36"E) in the study area. Soils were sampled from 20 cm depth further air-dried, ground to pass through a 2 mm screen and preconditioned in an oven at 60°C for 24 hours.

Further for physicochemical analysis BIS guidelines were used (BIS, 1985). Specific gravity was determined utilizing a Pycnometer (Make-Testing Instruments Mfg. Co. Pvt. Ltd., India). Digital moisture metre (Model M-3A make- Advanced Research Instruments Co., India) was used to measure the natural moisture content, and a Casagrande apparatus (Make-Aimil Ltd., India) was used for liquid limit determination. The soil texture was analysed using sieve analysis and hydrometer testing. Bulk densities of the soil samples have been assessed, and proctor curves have been obtained for each soil sample to estimate its optimum moisture content (OMC) and maximum dry density (MDD) values. The capacity of oxides and hydroxide minerals, to adsorb cation or anion on their surfaces depends upon their surface charges, which in turn is dependent on the pH of point of zero charge (pH<sub>zpc</sub>) of the media (Parks and De Bruyn, 1962). Adsorption of anion is favoured when the pH < pH<sub>zpc</sub> and cation adsorption is favoured when pH > pH<sub>zpc</sub>. For the instant study, pH<sub>zpc</sub> of the soil samples were determined following the pH drift method (Karthikeyan et al., 2019).

### Groundwater Ubiquity Score (GUS)

It is an experimental calculated value that relates pesticide half-life ( $t^{1/2}$ , days) and pesticide's organic carbon sorption coefficient. The GUS is used to rank pesticides for their potential to move towards groundwater (Gustafson, 1989). GUS score was calculated using the following equation:

$$GUS = \log_{10} t^{1/2} \cdot [4 - \log_{10} (K_{oc})] \quad (1)$$

Where,  $K_{oc}$  (L kg<sup>-1</sup>) is the pesticide's organic carbon sorption coefficient normalized for organic carbon content and it is calculated with the equation below (Spadotto, 2002).

$$K_{oc} = \frac{K_D \cdot 100}{\%OC} \quad (2)$$

Where  $K_D$  (L kg<sup>-1</sup>) is the sorption coefficient and %OC is soil organic carbon content.

$K_D$  was calculated with the following equation

$$K_D = \frac{C_s}{C_w} \quad (3)$$

Where  $C_s$  (mg/kg) is concentration sorbed to the soil and  $C_w$  (mg/L) is the concentration remaining in the solution after achieving equilibrium.

A pesticide with a GUS score of less than 1.8 is termed as non-leacher, whereas a score of higher than 2.8 qualifies it as a leacher, and a score within 1.8 and 2.8 is called transitional (Hall et al., 2015).

### Scanning electron microscopy (SEM) and Energy Dispersive X-ray analysis (EDAX)

Soil particle characterization was done for all the three soil samples. Morphological analysis was done by Zeiss Sigma

Scanning Electron Microscope (SEM) imaging and Energy Dispersive X-ray analysis (EDAX) attached to the SEM was used for the detailed analysis of the elemental composition. Soil samples were also analysed with SEM and EDAX both before and after the column experiment.

### **Isotherm study and kinetic study**

The capacity of the chosen soil to adsorb the Metalaxyl were assessed through Isotherm studies or batch tests. It also helped to calculate different adsorption parameters and adsorption isotherms of metalaxyl onto the studied soil surfaces. The experiment involved optimization of the ranges of concentration, dose and time of the solute and the adsorbent following the Response Surface Methodology (RSM) (Rezić, 2011). Here, a statistical software "Design Expert" (Stat-Ease Inc) had been used to decide upon the design parameters of experiments. The Design-Expert supports comparative testing, optimization, screening, characterisation, mixed, robust-parameter, and combination designs using Design-Expert Box-Behnken model and ANOVA optimization technique. It produces the ramp plot by keeping the removal efficiency and initial concentration as maximum and soil dose and contact time as minimum (Fig. 1S supplementary information).

In the present research, the process parameters were optimized by taking the initial concentration of metalaxyl (mg/L), the soil dosage (g/L), and the contact duration as the input variables (minutes). The Box-Behnken model offered 15 distinct combinations, ranging from 2 to 1440 minutes of contact duration, 20 to 100 g/L of soil dosage, and 2 to 10 mg/L of starting metalaxyl concentration. Accordingly, 0.4 g of soil was mixed with variable metalaxyl concentrations (1, 2, 4, 6, 8, and 10 mg/L) in 250 mL conical flasks for equilibrium adsorption. The reaction mixtures were then agitated at 150 rpm on an orbital shaker for two hours (equilibrium period) at room temperature. After 2 hours, 15 mL of sample from each conical flask was collected and centrifuged at 10000 rpm for 5 minutes; and then filtered using 0.22 µm Whatman filter paper. The 5 ml supernatant was extracted three times with Ethyl acetate at a 1:1 (v/v) ratio. The solutions were then transferred to an ethyl acetate organic medium and subjected to GC- FID analysis (Trace GC 1110, Thermo Fisher Scientific) to obtain the residual metalaxyl concentrations. For GC analysis, extracted samples were re-concentrated to 1 ml through evaporation using a rotary vacuum evaporator. Each experimental set were removed from the shaker after the appropriate contact periods. The soil adsorption capacity was ascertained using three empirical adsorption models, viz., Freundlich, Langmuir and linear.

For kinetic study, in each 250 mL conical flask, 0.4 g of soil was added with 20 mL of 10 mg/L standard metalaxyl solution to evaluate kinetic adsorption. The reaction mixtures were then agitated at 150 rpm on an orbital shaker for three hours (equilibrium period) at room temperature. At intervals of 30, 60, 90, 120, 150, and 180 minutes, 15 mL samples were drawn from the flask. 15 mL of sample from the conical flask was taken and centrifuged at 10000 rpm for 5 minutes; the 5

mL supernatant was extracted three times with Ethyl acetate at a ratio of 1:1 (v/v). For GC analysis, extracted samples were re-concentrated to 1 ml through evaporation. Three isotherm models viz., pseudo-first-order, pseudo-second-order, and Elovich were considered to obtain the best fit of kinetic adsorption (Adhikary et al., 2022).

### **Transport study**

#### **Soil column experiment setup**

Three columns have been taken for three different soils of North Chandmari (S1), Ghoragacha (S2), and Khaldarpara (S3). The column had an inner diameter of 2.5 cm, where the soil was packed up to a height of 10 cm. To prevent any potential clogging during the experiment, a relative compaction level of 80% was employed (Adhikary et al., 2022). The bottom of the columns was lined with glass wool so that free water drainage could prevail. 600 mg/L of metalaxyl was applied from the top of the soil column on the start date. This experiment was made to simulate the actual condition; hence, a discontinuous flow of millipore milli-Q (mQ) water was applied manually from the top to maintain a constant hydraulic head of 5 cm. The leachate were collected at an interval of 2 days continuously for 30 days and were analysed quantitatively using gas chromatography (GC).

#### **HYDRUS-1D model calibration**

The hydraulic properties of the soil play a crucial role in determining the direct vertical percolation through the vadose zone (Ortenzi et al., 2022). In the present study, the HYDRUS-1D program was used to study metalaxyl migration in unsaturated zone (Šimůnek et al., 2008). Rosetta model (Schaap et al., 2001) uses input of particle size distribution and bulk density of the soil to estimate the unsaturated parameters residual water content ( $\theta_r$ , cm<sup>3</sup>/cm<sup>3</sup>), saturated water content ( $\theta_s$ , cm<sup>3</sup>/cm<sup>3</sup>), soil water retention functions [ $\alpha$  (cm<sup>-1</sup>) and  $n$ ] (Tab. 3S supplementary information). The saturated hydraulic conductivity ( $K_s$ , cm/day) used as an input parameter and was obtained from laboratory soil test. Longitudinal dispersivity ( $\alpha_L$ ) of metalaxyl was considered to be 10% of the height of the soil bed (Gelhar, 1986). The tortuosity was assumed as 0.5 (Muallem, 1976). Transport of a solute under equilibrium sorption is described using the following partial differential equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} \quad (4)$$

Where, C is solute concentration in aqueous phase (mg/L), S is solute concentration in solid phase (mg/kg), t is the time,  $\rho_b$  is bulk density of the sediment (kg/m<sup>3</sup> bulk soil), D is hydrodynamic dispersion coefficient (m<sup>2</sup>/day),  $\theta$  is porosity (-); v is mean pore velocity (m/day) and x is distance travelled in the direction of flow (m).

The sorption of metalaxyl with soil samples follows Langmuir isotherm (Li et al., 2002).

$$S = \frac{K_L S_m C}{1 + K_L C} \quad (5)$$

Where  $S_m$  is maximum sorption capacity (mg/kg) and  $K_L$  the Langmuir coefficient (-).

### Reaction of metalaxyl with major soil elements

Fe, Ca, Mg, and Al are significant elements present in the soil samples. An experiment is designed to understand the reaction whether any of the elements react with metalaxyl or not. We made S1, S2 and S3 (5 mg) to react with 20 mg/L of metalaxyl aqueous solution and then with Milli-Q water (MQ). Further, the samples were analysed in Atomic adsorption spectroscopy (AAS; Perkin Elmer model).

### Adsorption-reaction study of metalaxyl with Fe

#### Frontier orbitals

Computational chemistry has been applied to solve a number of problems related to environmental chemistry through the modelling of surfaces. The interaction of metals with metalaxyl can be better understood by simulation between the modelled metal surface and fungicide metalaxyl. In recent year insight of interaction, energy and adsorption quality has been analyzed by studying frontier orbitals, namely Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO), which plays a significant role in shaping the mechanism of interaction. The frontier orbitals were analysed in the D mol3 module of Materials studio, as shown in Fig. 3. The energy of HOMO and LUMO is provided in eV, and  $\Delta E_{LUMO-HOMO}$  is calculated and shown in Tab. 1. It was observed that the band gap was about 3.25 eV. The molecules would be more reactive and able to take part in a broader variety of chemical processes if the HOMO-LUMO band gap was smaller (Kareem et al., 2018).

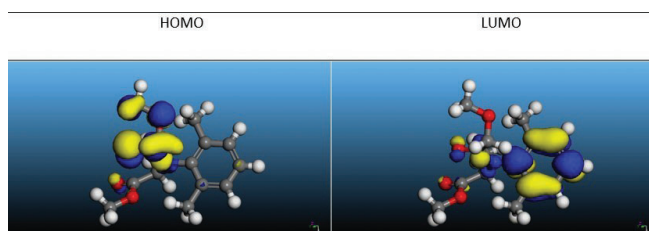


Fig. 3 - HOMO and LUMO images for the products.

Fig. 3 - Rappresentazione di HOMO e LUMO per i prodotti.

Tab. 1 - HOMO and LUMO data for the products.

Tab. 1 - Dati di HOMO e LUMO per i prodotti.

COMPOUND NAME	HOMO	LUMO	$\Delta E_{LUMO-HOMO}$
A	-8.75eV	-5.5eV	3.25

### Adsorption study using Material Studio

Iron surface was designed by for the adsorption of metalaxyl molecules. A plane of (1 1 0) has been constructed, and to this plane, a vacuum slab of a specific dimension was placed to

confine the simulation area in a box. The surface of Fe was set to be the target plane for the adsorption of water as solvent and metalaxyl as a reagent. The adsorption locator tool was selected, followed by simulation annealing to ultrafine quality. A single set of reagent molecules was added for adsorption, along with 1000 water molecules as solvent molecules. Then COMPASS III force field was equipped for the process Biovia Material Studio™ software 6.1. The force field is designed to find the most stable site for the adsorption of adsorbate molecules on the surface, giving the exact orientation of the reaction pathway (Abdelhameed et al., 2021).

### Molecular dynamics (MD)

The interaction between the Fe surface and the metalaxyl molecule in the presence of water as solvent was studied using simulation in a box model by molecular dynamics simulation; this was done by transforming the adsorption model into a reaction simulation area by providing the reaction conditions. At a varying temperature and NVT ensemble MD simulation was set up to 500 ps having a time interval of 1.0 fs. During the simulation, the dimensions of the Fe surface were constrained, and all the other molecules were left to move freely on the surface.

## Result and discussion

### Groundwater sample analysis

The European Union Council Directive 98/83/CE on the water for human consumption has set a maximum limit of 0.1  $\mu\text{g/L}$  for individual pesticides and 0.5  $\mu\text{g/L}$  for the total pesticide concentration (Anand et al. 2014). Table S2 (supplementary information) shows that 31 out of 32 samples contain metalaxyl concentrations greater than 0.1  $\mu\text{g/L}$ . G3, G30 and G31 show high concentration of metalaxyl.

### Soil characterization

The outcome of the physicochemical characterisation of the soil analyzed are presented in Tab. 2. The soil samples presenting higher permeability have a higher possibility of metalaxyl transport in the vadose zone. Metalaxyl is not affected by the pH value of 6.105 (median) of the soil as it is stable in the pH range of 1-8.5 (Sukul et al., 2000). All subsequent studies were conducted at a pH equal to the pH<sub>zpc</sub> value. The texture analysis of the soil samples reveals that it has less silt and clay particle. This means that the soil is texturally well sorted. Under such condition the porosity, become directly proportional to permeability. The higher porosity and permeability value promote sufficient drainage through the soil which facilitate transport of metalaxyl along with the water percolating through the vadose zone (Lassabatere et al., 2014), which made it close to well-sorted condition. The higher porosity and permeability values promote the water flow through the soils; thereby, the advective transport of metalaxyl may occur. Additionally, S2 and S3 are similar, and S1 have lower values of porosity and permeability, indicating metalaxyl transport through S1 would be slightly lower when compared to S2 and S3. In this

case, the Soil Organic Carbon (SOC) is low in percentage; hence, there is a very negligible possibility of SOC resisting metalaxyl transport.

Tab. 2 - Physicochemical properties of soil.

Tab. 2 - Proprietà fisico-chimiche dei suoli.

Properties	Soil samples		
	North Chandmari (S1)	Ghoragacha (S2)	Khaldarpara (S3)
Texture class	Loam sand	Sand	Sand
Sand (%)	82.4	93.31	93.48
Silt (%)	5.33	4.51	6.33
Clay (%)	12.26	2.18	0.16
Bulk density (g/cm <sup>3</sup> )	2.21	2.11	2.01
pH	6.07	6.16	6.085
Soil Organic Carbon (%)	0.791	0.790	0.788
Natural water content (%)	14.15	9.40	16.82
Porosity (%)	25.6	28.8	36.7
Saturated Hydraulic conductivity (cm/day)	4.85	64.75	95.84
Specific gravity	2.5	2.5	3.1
pH <sub>zpc</sub>	5.9	6.3	6.1
D <sub>50</sub> (micron)	600	300	300

### Adsorption isotherms and kinetics

The "Design expert" software solves the ANOVA optimization technique. It produces the ramp plot by keeping the removal efficiency and initial concentration as maximum and soil dose and contact time as minimum (Fig. 1S, supplementary information). The soil adsorption capacity was ascertained using three empirical adsorption models: Freundlich, Langmuir, and linear. The range of concentration, soil dose and time values was obtained from the ramp plot generated after RSM processes (Tab. 3).

Tab. 3 - The optimized result for Isotherm and Kinetic study.

Tab. 3 - Parametri ottimali per studio con isoterme e cinetico.

Variables	Isotherm study	Kinetic study
Concentration (mg/L)	1-10 mg/L	10 mg/L
Dose (g/L)	20	20
Time (hour)	2	0.5-3

However, the Langmuir model offered the most significant correlation for metalaxyl adsorption in the soil. The Langmuir equation may describe the formation of monolayers on surfaces with a certain number of homogeneously distributed similar sites (Kara et al., 2017). During adsorption, the system energy is taken to be constant, and the binding sites are uniformly distributed over the adsorbent surface (Awual et al., 2019).

Given that the model assumes a homogeneous surface and few interactions between sorbed molecules, Langmuir claims that the energy distribution is constant regardless of the degree of surface covering (García-Calzón & Díaz-García, 2007).

Because of their analytical formulas for expressing experimental isotherm data, numerical simulations of adsorptive separation processes, and parametric analyses of the processes, Langmuir's models are practically helpful (Sircar, 2017).

The maximum adsorption capacity of the samples used was found to be 0.1087, 0.21 and 1.771 mg/g for S1, S2 and S3, respectively (Tab. 4). All three soil samples showed a decreased adsorption capacity for metalaxyl resistance compared to the previous studies on clay soil (Suciu & Capri, 2009). The adsorption capacity of the adsorbent is primarily determined by the kind of adsorbent employed, the nature of the adsorbate, and the duration for which the adsorbent is used (Adhikary et al., 2022).

Tab. 4 - Isotherm model parameters.

Tab. 4 - Parametri del modello con isoterme.

Isotherm model			S1	S2	S3
Linear isotherm model	Regression coefficient	R <sup>2</sup>	0.84	0.88	0.78
	Isotherm coefficient	K <sub>d</sub> (L/g)=m	0.0105	0.0379	0.0524
Langmuir isotherm model	Isotherm coefficient	K <sub>L</sub> (L/mg) = 1/(m*Q <sub>0</sub> )	1.746	0.0184	2.606
	Regression coefficient	R <sup>2</sup>	0.9542	0.95	0.9786
Freundlich isotherm model	Isotherm coefficient	Q <sub>0</sub> (mg/g) = 1/C	0.1087	0.21	1.771
	Regression coefficient	R <sup>2</sup>	0.9513	0.9311	0.9369
Freundlich isotherm model	Isotherm coefficient	K <sub>f</sub> (mg/g) = eC	0.058	0.058	0.199
	Regression coefficient	n=(1/m)	2.844	1.3863	2.909

Adsorption kinetics is used to evaluate adsorbate diffusion in pores by measuring the adsorption uptake with respect to time at constant pressure or concentration (Peel et al., 1981). It is crucial for estimating the rate of solute absorption and the period of the adsorption process. These procedures give essential information on the adsorption efficiency and scalability of activities (Chatterjee et al., 2018).

The reaction kinetics was understood using three kinetic models: pseudo-first order, pseudo-second order and "Elovich" (Tab. 5). However, the pseudo-second-order model proved to be the best fit in this case. The pseudo-second-order rate expression was used to characterise chemisorption, includes valency forces via sharing or exchange of electrons as covalent forces as well as ion exchange between the adsorbent and adsorbate. The advantage of employing this model is that equilibrium capacity (q<sub>e</sub>) can be computed from the model

without knowing it from the experiment. Furthermore, the model may be used to assess the adsorption rate ( $K_2$ ; Tab. 5; Ho, 2006).

Tab. 5 - Kinetic model parameters.

Tab. 5 - Parametri del modello cinetico.

Kinetic model			S1	S2	S3
Pseudo-first order	Isotherm Coefficient	$K_1$ (L/min)	0.034	0.032	0.032
	Regression coefficient	$R^2$	0.96	0.96	0.88
Pseudo-second order	Isotherm coefficient	$q_e$ (mg/g)	0.1159	0.2392	0.2972
		$K_2$ (g/mg/min)	0.22	0.43	0.17
	Regression coefficient	$R^2$	0.99	0.95	0.93
Elovich	Isotherm coefficient	$\beta$ (g/mg)	27.69	39.38	26.59
		$\alpha$ (mg/g/min)	0.08	0.808	0.06
	Regression coefficient	$R^2$	0.99	0.95	0.93

**Metalaxyl transport**

**Lab-scale model**

The metalaxyl started coming out from the bottom outlet of the column on the 2<sup>nd</sup> day from each column. The metalaxyl-concentration of 14.56 mg/L, 54.02 mg/L, and 88.8 mg/L attains its highest peak at the 8<sup>th</sup>, 16<sup>th</sup>, and 8<sup>th</sup> day for S1, S2 and S3 respectively. It was observed that S3 has the least and S1 has the highest adsorbing capacity. The laboratory setup is shown in Fig. 4. The average particle size ( $D_{50}$ ) of the 3 soils have been analyzed and it was found that  $D_{50}$  of S2 (300  $\mu$ m) and S3 (300  $\mu$ m) are lower than S1 (600  $\mu$ m) which means that the average soil particle size is higher in case of S1 which might be a reason for the early breakthrough time as compared to S2 and S3. Though the  $D_{50}$  of S2 and S3 are same however the hydraulic conductivity of S3 is greater than S2 which can be attributed to the fact that higher effluent concentration was found in case of S3 (Mahmoodlu et al., 2021).

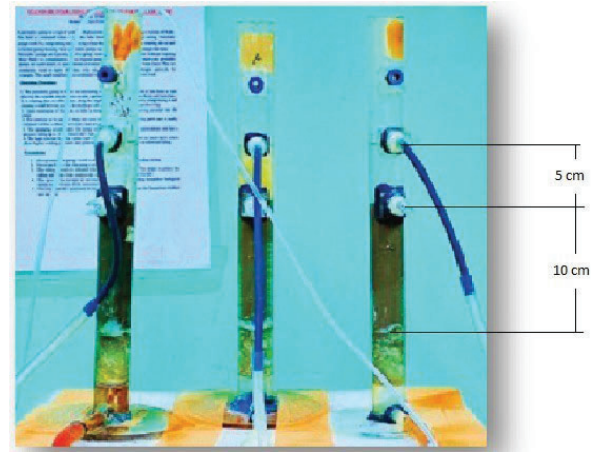


Fig. 4 - Laboratory setup of the soil-column.

Fig. 4 - Configurazione della colonna sperimentale di laboratorio.

**HYDRUS 1D modelling**

The same input concentration of metalaxyl (600 mg/L) as applied in column leaching experiment, was applied as input parameter in HYDRUS 1D soil column model to simulate the migration of metalaxyl through vadose zone. Three column representing HYDRUS model corresponds to the properties of three experimental soil columns. In both the laboratory experiment and the HYDRUS model, the maximum time period was set to be 30 days. The dimensions of the soil-column were the same as those in the laboratory. The simulation of metalaxyl migration through a vertical soil column correlates well with laboratory-scale results (Fig. 5).

**GUS results**

The metalaxyl GUS score was calculated using equation 1, and the  $K_{OC}$  values were obtained from equation 2. The average GUS score 4.6 was calculated by using values of  $K_D$ ,  $K_{OC}$ ,  $t^{1/2}$  and %OC provided in Tab. 4S (supplementary information). The GUS score of metalaxyl indicates its higher potential to leach into the groundwater.

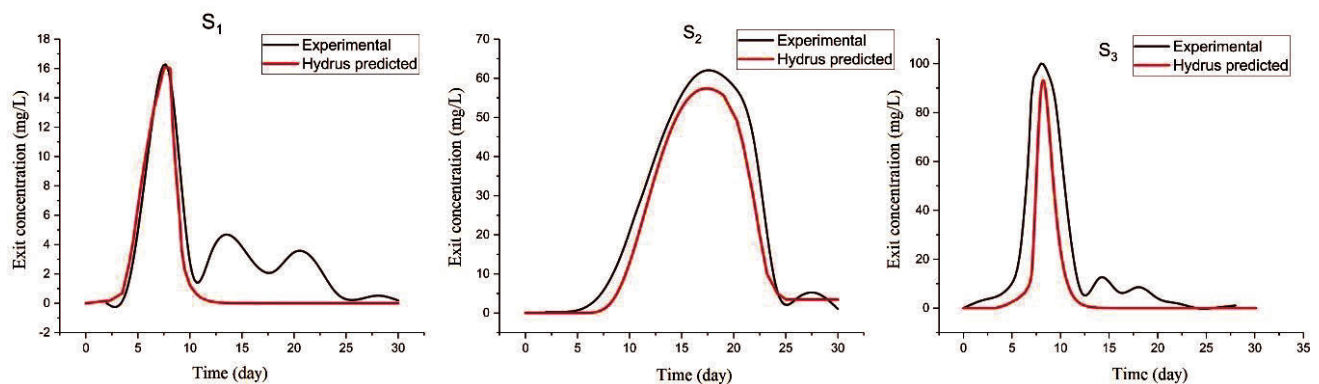


Fig. 5 - Comparison of laboratory-scale column study and HYDRUS predicted results of S1, S2 and S3.

Fig. 5 - Confronto fra i risultati ottenuti sperimentalmente in laboratorio e il modello per S1, S2 ed S3.

## SEM EDAX

SEM analysis proves that S1, S2 and S3 allow water to pass through themselves easily (Fig. 2S and Fig. 3S supplementary information). No significant changes were observed in the SEM images before and after the soil column experiment, indicating less adsorption capacity of the soil samples.

Owing to the highly permeable nature of the soils of the study area, metalaxyl or other pesticides, used continuously in such soils, are likely to reach groundwater, provided adsorption and reactions of the pesticides with soil water system do not act as a buffer against the transport.

In this study, the elemental concentration data before and after the soil column experiment are given in the Tab. 5S (supplementary information), where S1, S2 and S3 have  $Si > Al > Fe > Mg$  as major elements present in respective order of concentration in atomic percentage. These elements may be responsible for the adsorptive reaction with metalaxyl.

## Adsorption-reaction with soil elements

To understand the role of the major elements of the native soil with metalaxyl, the adsorption-reaction experiment was performed. Fe was found to be the most significant element that reacts with metalaxyl. Further, in S1, 69 % removal of metalaxyl with iron was observed, and 33 % removal was observed with S2 and S3 (Tab. 6). The removal percentage of metalaxyl was calculated using the following formula.

$$\text{Removal percentage} = \left( \frac{c_o - c_e}{c_o} \right) \cdot 100 \quad (6)$$

Previously (Sukul et al., 2013) have seen the effect of ferrite ( $Fe^{3+} 2O_3 \cdot 0.5H_2O$ ) over the metalaxyl (Sukul et al., 2013).

## Molecular dynamics simulation

The adsorption model provides the sites for adsorption which were used to carry out molecular dynamics simulation. As seen from Fig. 6(b), the molecule was adsorbed at Fe surface with a distance of 2.947, 2.871, and 3.025 angstroms; also, the molecule is surrounded by solvent molecules that stabilize the adsorbed state. AFM's results (Atomic Force Microscopy) found that the iron content is significantly reduced from the soil sample when washed with water. When chemisorption occurs between the Fe atoms and the metalaxyl, it was found that Fe from the soil, coordinates with metalaxyl and reduces its concentration in the aqueous medium.

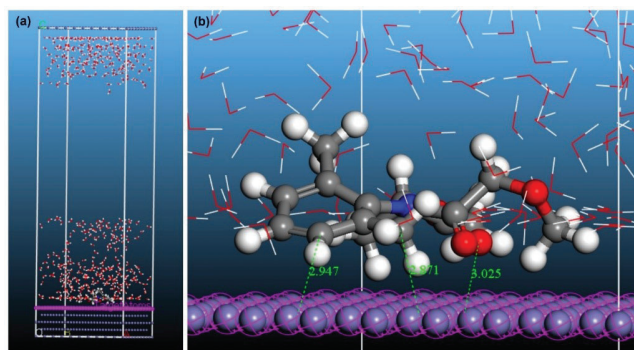


Fig. 6 - (a) Adsorption of metalaxyl molecules on the surface of Fe, (b) Molecular dynamics simulation studies of reagent molecules.

Fig. 6 - (a) Assorbimento di molecole di metalaxyl alla superficie di Fe; (b) Simulazione molecolare della dinamica delle molecole dei reagenti.

## Conclusion

Due to high permeable nature, lack of clay and lack of soil organic carbon (SOC), the sandy soils of the study area are susceptible to contaminant leaching. Metalaxyl being highly soluble in water with a GUS of 4.6, has a high potential to leach in sandy soils. Among 32 groundwater samples metalaxyl concentration of 31 samples was higher than the maximum permissible limit, and the concentration was high ( $G3 = 472.9 \mu\text{g/L}$ ,  $G30 = 395.79 \mu\text{g/L}$  and  $G31 = 181.81 \mu\text{g/L}$ ) in three groundwater samples. This significant finding of higher metalaxyl concentration in groundwater prompted to study the contaminant's transport and adsorptive pattern within the soil-water system. The isotherm study shows that metalaxyl manifests a weak tendency for adsorption ( $Q_0$ ) to sandy soils ( $S1 = 0.1087 \text{ mg/g}$ ,  $S2 = 0.21 \text{ mg/g}$  and  $S3 = 1.771 \text{ mg/g}$ ). However, the comparative study of the vertical soil column leaching experiment with HYDRUS shows significant adsorption of metalaxyl in all three-soil samples. Furthermore, the presence of clay plays an important role; with a significant presence of clay (12.26 %), a relatively lower concentration of metalaxyl in leachate was observed in S1 compared to S2 and S3. Metalaxyl of metalaxyl-laden water the surface while passing through the vadose zone was supposed to be significantly less adsorbed into the soil because of the poor clay and SOC content, but experimental results revealed significant adsorption of metalaxyl in the soil. In order to get an insight into this contrasting fact, the adsorption-reaction study was performed. The adsorption studies revealed that the metalaxyl

Tab. 6 - Table showing concentration (mg/L) of soil-element Fe, Al, Ca and Mg after reaction with metalaxyl and Milli-Q water.

Tab. 6 - Tabella che mostra la concentrazione (in mg/L) dei componenti del suolo Fe, Al, Ca e Mg dopo la reazione con il metalaxyl e acqua Milli-Q.

Element	S1		S2		S3	
	With metalaxyl	With MQ	With metalaxyl	With MQ	With metalaxyl	With MQ
Fe	0.533	0.71	0.635	0.949	0.441	0.89
Ca	3.652	5.125	2.628	3.593	4.951	4.372
Mg	0.051	0.049	0.041	0.066	0.06	0.062
Al	1.899	1.951	2.044	2.319	2.851	2.991



molecules are adsorbed towards the Fe surface through the O and C atoms of metalaxyl, which acts as the driving force for chemisorption to occur under optimal conditions. It was found that Fe from the soil, coordinates with metalaxyl and reduces its concentration in the aqueous medium. The result of this study vividly explains the mechanism of adsorption in the vadose zone. It indicates that the presence of Fe in the vadose zone hinders the transport of metalaxyl through the soil-water system. Overall, the study area soils are considerably less resistant to the transport of metalaxyl, thereby increasing the risk of extensive groundwater pollution and posing possible health risks to the local population. Moreover, the HYDRUS 1D model enables the metalaxyl contamination to be traced without evaluating a large number of soil samples. HYDRUS model may be used to predict metalaxyl movement through the soil and may also be used to understand the most sensitive parameters controlling the transport mechanism which in turn will help to formulate strategies to avoid or resist groundwater contamination. In order to establish a larger database, further research is required on the transport of metalaxyl through the alluvial soil of different river basins where metalaxyl is extensively used.

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#### Competing interest

The authors declare no competing interest.

#### Author contributions

All authors contributed to the study, conception and design. Material preparation, data collection and analysis were performed by Nilesh Kumar Meshram and Rhitwik Chatterjee. The draft was written by Nilesh Kumar Meshram and edited by Prof Kalyan Adhikari. Prof. Kalyan Adhikari supervised the entire research, and all authors commented on previous manuscript versions.

All authors read and approved the final manuscript.

#### Additional information

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