

Article

Effects of Natural Zeolites on Nitrate and Ammonium Leaching in Sandy-Loam Soils

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Abstract

Nitrogen applied in excess of plant demand in intensive agricultural systems can be lost through runoff and leaching into surface and groundwater, with potentially negative effects on water quality. Zeolites, due to their high cation exchange capacity and internal porosity, can adsorb ammonium (NH_4^+) and help mitigate excessive nitrate (NO_3^-) leaching. Owing to such properties, zeolites can play an important role in reducing the potential negative impact associated with the extensive use of nitrogen-based fertilizers. In this study, we investigated the effects of two commercial natural zeolites on selected hydraulic properties, water storage, and solute transport parameters of three sandy-loam soils with different pedological characteristics. Laboratory experiments were conducted on disturbed soil columns. The leaching of NO_3^- and NH_4^+ ions was monitored using ion-selective electrode analysis. The results indicate that zeolite application reduces the mobility of nitrate and ammonium. This effect can be attributed to changes in the original pore size distribution of the investigated soils, characterized by a reduction in macropore regions and a corresponding increase in meso- and micropore regions. In the case of ammonium, adsorption mechanisms are also involved, which further contribute to retarding its mobility. These effects were consistently observed across the investigated soils. For a given soil, the magnitude of the observed effects depended on both the type of zeolite used and the amount of zeolite mixed with the soil. Finally, ANOVA tests and multivariate analyses were applied to the full dataset to provide statistical support for the observed changes in the selected parameters.

Keywords: zeolites; soil transport; soil hydraulic properties; nitrate leaching; ammonium retention



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1. Introduction

In agronomic systems, nitrogen management plays a crucial role in ensuring both crop productivity and environmental sustainability. Excess nitrogen compounds applied beyond the actual requirements of intensive agricultural systems are transferred to surface and groundwater, inducing eutrophication, algal blooms, and high fish mortality rates [1–5].

Surplus nitrogen can also be released into the atmosphere as inert gas (N_2), contributing to anthropogenic climate change through nitrous oxide (N_2O) emissions [6,7]. Ammonium (NH_4^+) and nitrate (NO_3^-) constitute the main inorganic forms of nitrogen.

Caicedo [8] reported that their assimilation by plants can account for up to 70% of the total absorbed cations and anions.

In agricultural systems, nitrogen losses by leaching become significant when water inputs exceed the soil's storage capacity, leading to downward water movement that transports soluble nitrogen species. Among these, nitrate is particularly mobile and easily leached, since its negative charge results in electrostatic repulsion (i.e., anion exclusion) between nitrate ions and the negatively charged surfaces of soil particles. As a result, NO_3^- ion is poorly retained within the soil matrix and readily move with percolating water [9–11].

By contrast, ammonium, being positively charged, interacts with cation exchange sites on clays and soil organic matter. Consequently, its mobility can be limited in fine-textured soils, whereas in sandy or coarse-textured soils, ammonium leaching may become more pronounced [12–14].

From a practical perspective, improving the retention of nitrate and ammonium in agricultural soils is of primary importance. Enhanced retention reduces nutrient losses through leaching, thereby increasing nitrogen use efficiency and lowering fertilizer requirements.

Over the years, numerous studies have focused on identifying practices that both enhance soil fertility and mitigate nutrient losses to water bodies [15,16]. Farmers adopt a variety of strategies to minimize these losses, such as splitting nitrogen applications, using controlled-release fertilizers, or incorporating soil amendments that enhance the retention of NO_3^- and NH_4^+ [17,18]. Due to their high cation exchange capacity, zeolites can be used as an inexpensive cation exchanger to control NH_4^+ release [16,19]. To retard the movement of anionic species, zeolites with high affinity for anions are required. It has been shown that surfactant-modified zeolites, when used as amendments, can effectively control NO_3^- release and meet these requirements [20,21]. However, the interactions between these modified zeolites and soils remain poorly understood and clearly warrant further investigation [22,23].

Zeolites are hydrated aluminosilicates characterized by a three-dimensional network of SiO_4 and AlO_4 tetrahedrons linked by oxygen atoms. The open three-dimensional framework is a negatively charged network characterized by open channels (30–40%) of nanometric dimensions (0.1–0.4 μm), where different kinds of polar and non-polar molecules can be adsorbed and exchanged.

It has been extensively shown [24–28] that the reduced mobility of both anionic and cationic species in soils mixed with zeolites can be attributed to their ability to alter soil porosity, particularly by increasing meso- and microporosity, as well as modifying soil tortuosity, and connectivity, since a finer fraction (i.e., zeolite) is added to the soil matrix. Such multifactorial interactions among all the distinct phases involved can ultimately modify soil hydraulic and solute transport properties.

Several studies have shown that the impact of zeolites may vary depending on soil type, zeolite characteristics, and application rate. In particular, the addition of fine zeolitic materials may reduce macroporosity and, in some cases, limit water availability for plants, especially at higher application rates. The magnitude of these effects is controlled by multiple interacting factors, including soil mineralogical composition, texture and structure, zeolite type, and water characteristics [29–31]. Consequently, soil–zeolite interactions may produce complex hydraulic and transport responses that are not always easily predictable [19,32,33].

Despite the growing body of literature on the use of zeolites as soil amendments, several knowledge gaps still remain. Most studies have primarily focused on ammonium adsorption or nitrate leaching reduction, often considering these processes separately [17,21,27]. However, the combined effects of natural zeolites on soil hydraulic properties and solute transport processes are still not fully understood, particularly in

sandy-loam soils characterized by relatively high permeability [29,30]. Furthermore, although several investigations have demonstrated the potential of zeolites in reducing nitrogen losses under agricultural conditions, most studies have focused either on field-scale agronomic responses or on specific adsorption processes, without explicitly linking soil structural modifications to hydraulic and solute transport behavior [34,35]. In this context, a more integrated analysis relating soil structural changes, hydraulic behavior, and solute transport mechanisms is needed to better understand the role of zeolites in controlling nitrogen dynamics in agricultural soils.

Based on this evidence, and with the aim of establishing a rational experimental framework, we hypothesize that (i) the addition of natural zeolites modifies the soil pore structure, leading to measurable changes in soil hydraulic and transport properties, and (ii) these structural modifications reduce nitrate and ammonium mobility within the soil matrix. Furthermore, we hypothesize that the magnitude of these effects depends on both the type of zeolite used and the application rate. Accordingly, the objectives of the present study were defined to evaluate, through a series of laboratory experiments, the effect of two natural zeolites (namely chabazite and clinoptilolite), mixed with sandy-loam soils of different pedological features, on selected soil hydraulic and transport properties influencing NO_3^- and NH_4^+ leaching. Sandy-loam soils were specifically selected for this study because they are characterized by moderate-to-high permeability, making them particularly vulnerable to nitrogen leaching processes.

To investigate soil transport properties, specific experiments were carried out using potassium chloride (KCl) as a conservative tracer, together with potassium nitrate (KNO_3) and ammonium chloride (NH_4Cl). Changes in soil hydraulic properties were independently evaluated through modifications in the measured soil water retention curves (SWRCs), allowing subsequent analysis of key hydraulic parameters and derived soil water storage parameters (SWSPs). Statistical analyses, including ANOVA and multivariate methods, were conducted on the experimental dataset to provide statistical validation of the changes observed in the selected parameters.

2. Materials and Methods

2.1. Physico-Chemical Characterization of Selected Soils and Zeolites

In the present research, several laboratory experiments were carried out on repacked soil samples collected from the Ap horizon (~0–20 cm below the soil surface). According to [36], three sandy-loam soils were considered, hereafter referred to as ME (i.e., Metaponto site, latitude: 40.37° N, longitude: 16.81° E), GE (Genzano site, latitude: 40.85° N, longitude: 16.03° E), and FE (San Ferdinando site, latitude: 41.30° N, longitude: 16.07° E).

The principal physico-chemical characteristics of these soils, including texture, organic carbon (OC), pH , and bulk density (ρ_b), are summarized in Table 1. These parameters were determined using standard procedures described by [37–40].

Table 1. Principal physico-chemical properties and pedological classification of the investigated soils.

Soil ID	Soil Texture and Classification (USDA)				Soil Pedological Classification	ρ_b (g/cm ³)	OC (g/kg)	pH
	Texture	Sand (%)	Silt (%)	Clay (%)				
ME	Sandy loam	53.81	34.94	11.25	Haplic Calcisol	1.10	17.2	7.9
GE	Sandy loam	57.43	31.95	10.62	Dystric Luvisol	1.10	7.7	7.7
FE	Sandy loam	60.38	28.88	10.74	Haplic Luvisol	1.10	12.3	8.2

Regarding the zeolites, two commercial natural types were used, namely Chabazite (Zeolite® Italia, Gioia Tauro, Italy) and Clinoptilolite (Heiltropfen® Lab, Markovci, Slove-

nia). Details on the selected zeolites are reported in Table 2. Mineralogical characterization of zeolitic material was performed by X-ray diffraction (XRD) analysis.

Table 2. (a) Qualitative and quantitative analysis of Chabazite and Clinoptilolite materials. (b) Chemical analysis of Chabazite and Clinoptilolite materials.

(a)			
Chabazite	% in weight		
Chabazite	64.2		
Phillipsite	1.5		
Analcime	0.65		
K-Feldspar	11.9		
Plagioclase	5.5		
Muscovite/illite	5.2		
Pyroxene	2.75		
Clinoptilolite	% in weight		
Clinoptilolite	91.3		
Feldspar (K-Feldspar + Plagioclase)	4.8		
Cristobalite/Quartz	2.5		
Mica (Muscovite/Illite)	0.9		
Accessory minerals (e.g., Pyroxene, traces of Calcite)	0.5		
(b)			
Chabazite			
Component	%	Component	ppm
SiO ₂	55.05	Ba	578
TiO ₂	0.44	Ce	198
Al ₂ O ₃	16.60	Co	3
Fe ₂ O ₃	3.31	Cr	n.d.
MnO	0.11	Cu	2
MgO	1.27	Ni	22
CaO	5.46	Pb	94
Na ₂ O	0.46	Sr	1120
K ₂ O	4.63	Zn	56
P ₂ O ₅	0.10	Zr	613
Clinoptilolite			
Component	%	Component	ppm
SiO ₂	68.40	Ba	515
TiO ₂	0.22	Ce	165
Al ₂ O ₃	12.40	Co	2.8
Fe ₂ O ₃	1.25	Cr	n.d.
MnO	0.08	Cu	3.0
MgO	0.85	Ni	18
CaO	3.60	Pb	10
Na ₂ O	0.75	Sr	945
K ₂ O	2.80	Zn	49
P ₂ O ₅	0.12	Zr	587

2.2. Estimation of Soil Hydraulic Properties and Soil Water Storage Parameters

For this set of laboratory experiments, the SWRCs were determined via the hanging water column technique, a widely adopted method for determining SWRCs in the low suction range investigated in the present study, and particularly suitable for reconstructed laboratory samples [41,42].

Following the procedure proposed by [43], the soil samples were oven dried at 105 °C, passed through a 2 mm sieve, and then combined by weight with zeolite at concentrations

of 2% and 5% (hereafter referred to as Z2 and Z5). Once mixed, soil samples were built in PVC cylinders (8 cm in diameter and 7 cm in length) by gradually adding known weights of soil and slightly shaking the cylinder to settle the soil in a fixed height increment to reach a predefined final bulk density of the soil sample.

In addition, for each soil type, a control sample without zeolite (Z0) was prepared. In all, including Z0 samples, 60 soil samples were prepared (3 soils $\times$ 5 treatments $\times$ 4 replicates, where the five treatments are Z0, chabazite Z2, chabazite Z5, clinoptilolite Z2, and clinoptilolite Z5).

The RETC software (version 6.02, USDA-ARS U.S. Salinity Laboratory, Riverside, CA, USA) [44], based on the van Genuchten model [45], was specifically utilized for post-processing the acquired SWRCs. For the sake of completeness, Equation (1) reports the van Genuchten (vG) equation:

$$\theta = \theta_r + \frac{\theta_s - \theta_r}{[1 + \alpha|\psi|^n]^m}, \quad (1)$$

where θ , θ_s , and θ_r are respectively the volumetric water content, the volumetric water content at saturation, and the residual water content, and ψ (hPa) is the matric potential. The parameters n (-), m ($=1 - 1/n$), and α (hPa^{-1}) are shape parameters.

A MATLAB (version R2024a, The MathWorks, Inc., MA, USA) code developed by the authors was used to calculate variations in soil porosity due to the addition of zeolite to soils. These variations were obtained using the equation proposed by [46]:

$$W = \frac{1}{|\psi_f - \psi_i|} \int_{\psi_f}^{\psi_i} \theta(\psi) d\psi, \quad (2)$$

where W represents the potential weighted average water content between the matric potentials ψ_f and ψ_i , which are the boundary limits. With reference to these limits, in the present research, we adopted the value of $\psi = -100$ hPa as a threshold between macro- and mesoporosity regions, and the value of $\psi = -15,000$ hPa to separate the mesoporosity domain from the microporosity domain [47–52].

Available water content (AWC) was calculated as the difference between the volumetric water content at field capacity, θ_{FC} (measured at $\psi = -100$ hPa), and the volumetric water content at the permanent wilting point, θ_{PWP} (measured at $\psi = -15,000$ hPa):

$$AWC = \theta_{FC} - \theta_{PWP}. \quad (3)$$

To estimate the readily available water content (RAWC), we adopted the method proposed by [53,54]. Following these authors, RAWC was evaluated within the matric potential interval between $\psi = -100$ hPa and $\psi = -1000$ hPa:

$$RAWC = \theta_{FC} - \theta_{-1000}. \quad (4)$$

Finally, saturated hydraulic conductivity (K_s) was determined on the same soil samples using the constant head method [55] under room temperature conditions. In particular, the hydraulic gradient was fixed at 1.25 cm/cm.

2.3. Estimation of Soil Solute Transport Parameters

For this set of laboratory measurements, soil–zeolite mixtures were prepared according to the experimental protocol described in the previous section. In this latter case, the samples were repacked in PVC cylinders 8 cm in diameter and 11 cm in length. To determine the soil solute transport parameters of the selected soil–zeolite mixtures, solute transport tests were conducted using potassium chloride (KCl) as a tracer, and to monitor nitrate and ammonium dynamics we adopted potassium nitrate (KNO_3) and ammonium

chloride (NH_4Cl). For the above experiments, the laboratory apparatus (Figure 1) mainly consisted of: (i) a Mariotte system for water application, (ii) a peristaltic pump (set at a flow rate of approximately 25 mL min^{-1}) associated with a drip applicator for solute application, (iii) a fraction collector system located at the column outflow, (iv) an ion-selective electrode (ISE) apparatus, and (v) a data acquisition system.

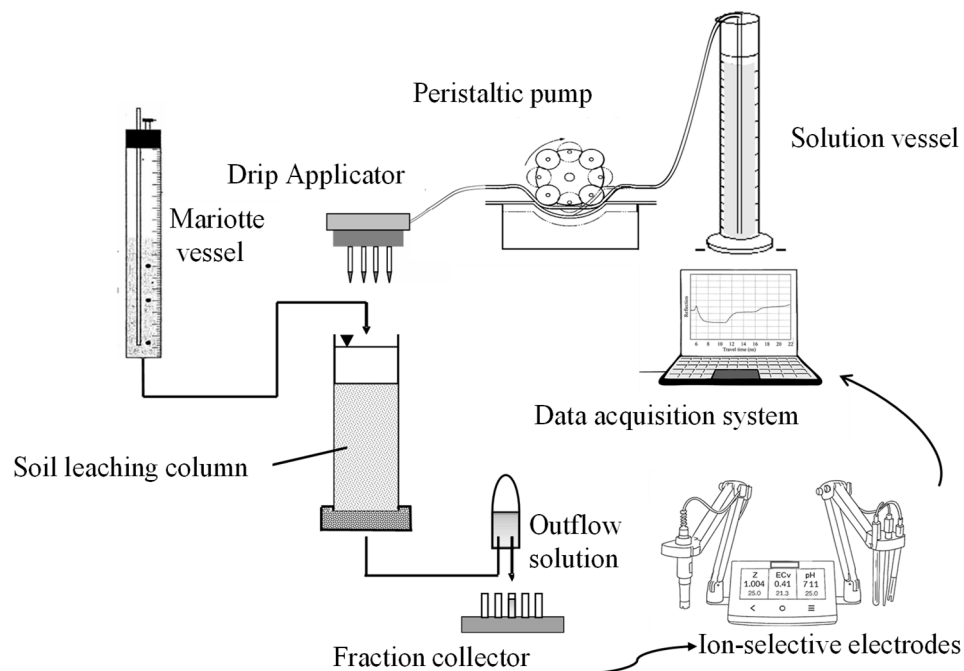


Figure 1. Schematic diagram of the laboratory apparatus developed for the miscible flow tests (adapted from [56]).

At the beginning of the leaching tests, the soil sample was fully saturated with water from the bottom. Once saturation was achieved, water was applied from the top of the soil sample. The Mariotte apparatus was adjusted to maintain a constant ponding level of approximately 2 cm. After steady-state flow had been established (steady-state conditions were assumed when consecutive outflow measurements exhibited negligible variations), the water supply was stopped and the ponded water at the soil surface was allowed to drain completely. Subsequently, 20 cm^3 of a test solution was applied, in a few seconds, to the top of the sample using the drip applicator. After the solution pulse had fully infiltrated the soil surface, the Mariotte system was re-opened to allow the solute to leach downward. For each soil type, experiments were first performed on a sample without zeolite (Z0), which served as the control. Solute transport experiments were then conducted sequentially using a solution of 20 g/L of KCl , KNO_3 and NH_4Cl .

During the experiments, the ion concentration of Cl^- , NO_3^- and NH_4^+ was determined on the eluate collected at the bottom of the soil column using ion-selective electrodes connected to the data acquisition system (Hanna Instruments, Villafranca Padovana, Italy, model HI6000).

The experimental breakthrough curves (BTCs: concentration vs. time curves) were then analyzed by means of a MATLAB code developed by the authors to estimate solute transport parameters, such as soil pore water velocity, v (cm/min), soil dispersivity, λ (cm), which represents the spreading of the solute caused by mechanical dispersion within the soil pore network, coefficient of dispersion $D = \lambda v$ (cm^2/min), and retardation factor R (-), which quantifies the delay of solute transport relative to water flow.

These parameters were obtained using the time moment analysis approach [57] which is known to allow the interpretation of experimental BTCs without the assumption of a

specific process in the soil, and thus, of a specific model (e.g., a convection–dispersion equation, CDE; [58–60]). Temporal moments were numerically evaluated by integrating the experimental BTCs over time.

Briefly, the temporal moments of the experimental BTC at a position z and for a pulse input of a mass solute (non-reactive or reactive) are defined as:

Zeroth-order moment (area under the curve):

$$m_0 = \int_0^{\infty} C(t) dt. \quad (5)$$

First-order moment (mean travel time):

$$m_1 = \frac{1}{m_0} \int_0^{\infty} (t - m_1)^2 C(t) dt. \quad (6)$$

Second-order moment (variance of travel times):

$$m_2 = \frac{1}{m_0} \int_0^{\infty} t C(t) dt. \quad (7)$$

In the above, C is the solute concentration and t is the time variable.

Once these moments are calculated, the soil pore water velocity, v , can be determined as

$$v = \frac{z}{m_1}, \quad (8)$$

and the dispersivity λ by using

$$\lambda = \frac{z}{2} CV^2, \quad (9)$$

CV being the coefficient of variation (i.e., m_2/m_1^2). It is worth noting that the λ values were determined through chloride transport tests [61–63].

Finally, in the case of ammonium, for a fixed soil–zeolite mixture, the retardation factor R was calculated from the ratio of the travel time variance of NH_4^+ and that of Cl^- [62]:

$$R = \frac{m_1^{NH_4^+}}{m_1^{Cl^-}}. \quad (10)$$

2.4. Statistical Analysis of Soil Hydraulic, SWSP, and Transport Parameters

Experimental data were collected with four replicates ($n = 4$) and analyzed using SPSS software (version 30.0, SPSS Statistics for data analysis, IBM Corp., Armonk, NY, USA) and OriginPro software (version 2026, OriginLab Corporation, Northampton, MA, USA). Results are reported as mean values. The effects of zeolite on hydraulic and transport parameters across the three soils were assessed using a one-way ANOVA statistical test to compare zeolite treatments within each soil group. A two-way ANOVA statistical test was performed to evaluate the main effects of soil (S), treatment (T), and their interaction ($S \times T$). For both analyses, a Tukey post hoc test was employed for multiple comparisons between means. Statistical significance was defined at the significance level of $p \leq 0.05$. The assumptions of normality and homogeneity of variance were verified using the Shapiro–Wilk ($p \leq 0.05$) and the Levene ($p \leq 0.05$) tests, respectively. Results were presented using the classical Compact Letter Display (CLD) method.

To identify homogeneous groups within a dataset comprising measurements from various samples subjected to specific treatments, a multivariate statistical approach was also adopted. A k -means clustering algorithm was applied to partition the observations into five distinct groups (Cluster 1, 2, 3, 4 and 5) based on the Euclidean distance between points

in the principal component space [64,65]. The analysis was performed on all individual replicates, allowing the algorithm to account for internal variability and ensuring that the resulting clusters were robust and representative of the overall dataset distribution. Before processing, a z-score normalization was necessary to scale the variables into a common range (mean = 0, standard deviation = 1). The optimal number of clusters (k) was determined by cross-referencing the results of two complementary methodologies, namely the Elbow Method [66] and Silhouette Analysis [67]. The analysis identified $k = 5$ as the most robust partition for the given dataset. Finally, to visualize the fingerprint of each cluster, a radar chart was generated.

3. Results and Discussions

3.1. Effects of Zeolite on Soil Hydraulic and Soil Water Storage Parameters

The influence of zeolite on the shape of the SWRCs can be observed in Figure 2a–f, which illustrate both the experimental data and the corresponding vG fitting curves obtained for each soil type and zeolite content. Figure 2a also reports the $|\psi_{FC}|$ and $|\psi_{PWP}|$ values (dashed vertical lines), which represent the limits between the macropore and mesopore domains, and between the mesopore and micropore domains, respectively.

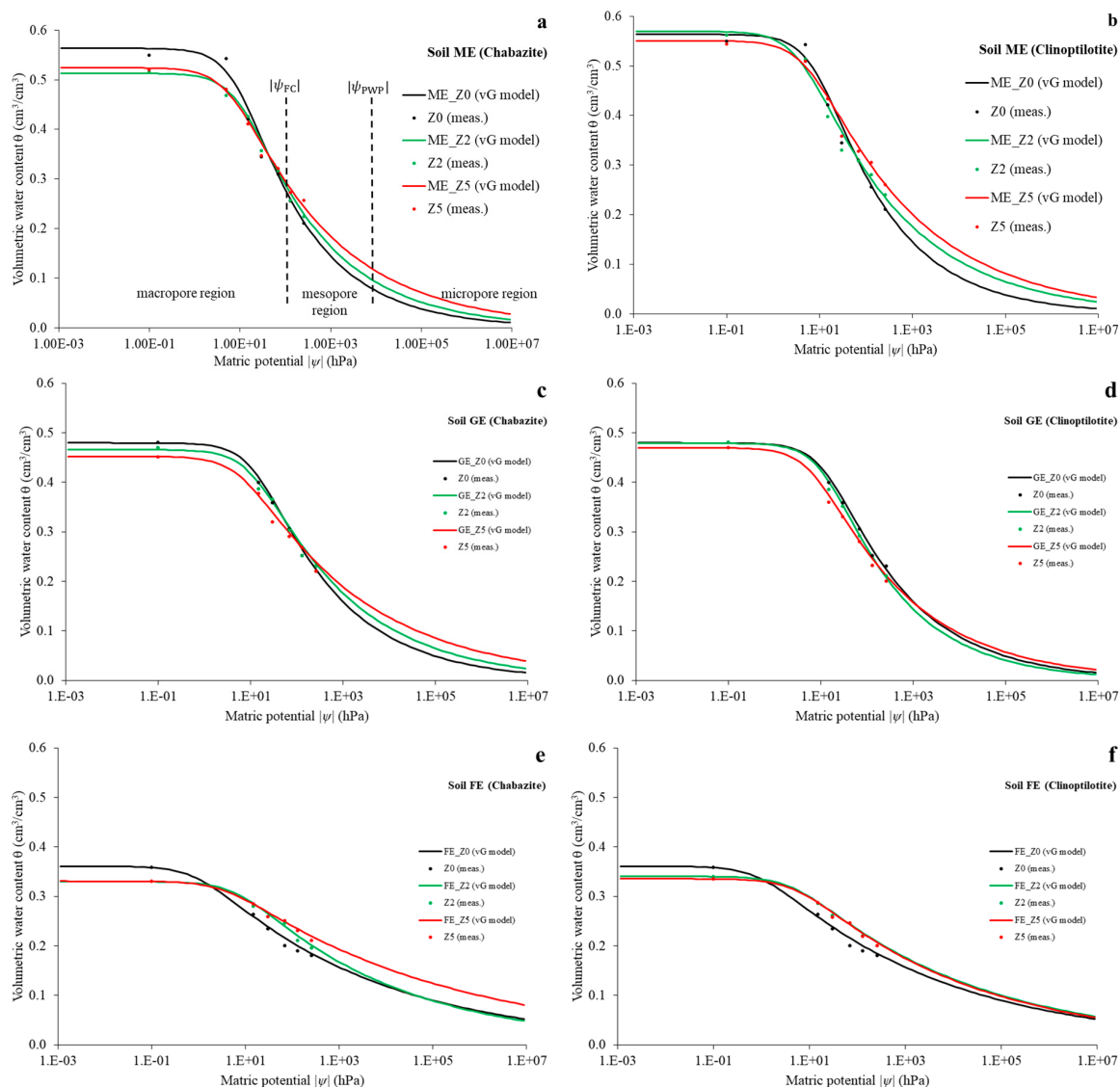


Figure 2. SWRCs measured and modeled by the vG Equation (1) of all soil–zeolite treatments: (a,b) ME, (c,d) GE, and (e,f) FE soils.

The results show that zeolite addition affects the overall shape of the SWRCs, leading to a substantial modification of the soil pore size distribution. For a given soil, increasing zeolite content results in a decrease in soil total porosity [67,68]. In general, the magnitude of this effect is proportional to the amount of zeolite applied.

Table 3 shows changes in the soil porosity fractions (macro-, meso-, and microporosity) induced by the addition of chabazite and clinoptilolite to the three soils (i.e., ME, GE and FE), and for the sake of completeness, the related vG parameters (α , n and m), along with the coefficient of determination (r^2) indicating the quality of the fit between the measured and modeled SWRCs. These soil porosity modifications were determined, by means of Equation (2), as the ratio between the soil–zeolite mixture and the untreated control (i.e., Z0). The data reveal a consistent and notable trend across soil types, characterized by a decrease in macroporosity (all negative values) and an increase in meso- and microporosity (mostly positive values). This systematic change in pore size distribution can be attributed to two primary mechanisms: (i) the physical rearrangement of soil particles, where fine zeolite particles fill existing macropores, and (ii) the intrinsic microporous nature of the zeolites themselves, which directly contributes a significant additional volume of smaller pores to the soil matrix. For these reasons, in the resulting soil–zeolite mixture, the microporosity fraction is the sum of the neo-formed microporosity and that intrinsic to the zeolite [33]. Such pore size redistribution likely altered pore connectivity and flow path tortuosity, thereby contributing to the observed changes in water and solute transport behavior.

Table 3. α , n , and m vG-shape parameters, coefficient of determination r^2 , obtained from experimental SWRCs with reference to the selected soils and zeolites, and changes in porosity fractions (macro-, meso- and microporosity) for all soil–zeolite treatments and soil types.

Soil ID	Zeolite ID	Treatment	α (hPa ^{−1})	n (−)	m (−)	r^2	Macroporosity (%)	Mesoporosity (%)	Microporosity (%)
ME	Soil	Z0	0.128	1.285	0.223	0.99	−	−	−
		Z2	0.108	1.250	0.200	0.99	−3.25	+1.78	+1.50
		Z5	0.175	1.207	0.172	1.00	−2.74	+3.74	+2.76
	Clinoptilolite	Z2	0.268	1.216	0.177	0.98	−0.70	+2.83	+2.22
		Z5	0.194	1.196	0.164	0.99	−0.50	+5.33	+3.64
GE	Soil	Z0	0.085	1.256	0.204	0.99	−	−	−
		Z2	0.098	1.218	0.179	0.99	−0.78	+3.06	+2.24
		Z5	0.176	1.173	0.147	1.00	−2.86	+4.18	+4.09
	Clinoptilolite	Z2	0.091	1.275	0.215	1.00	−0.55	−0.12	+0.19
		Z5	0.162	1.220	0.180	0.99	−2.20	+1.17	+1.63
FE	Soil	Z0	1.149	1.121	0.108	0.99	−	−	−
		Z2	0.161	1.137	0.120	0.99	−1.15	+1.05	−0.16
		Z5	0.313	1.096	0.087	0.99	−1.17	+3.63	+3.26
	Clinoptilolite	Z2	0.235	1.123	0.110	0.99	−0.31	+2.01	+0.92
		Z5	0.201	1.126	0.112	1.0	−0.74	+1.81	+0.64

A comparable trend was observed across all the investigated soils. Comparison between the two zeolites reveals a clear dose-dependent response for both zeolites, and that chabazite generally induced more pronounced changes than clinoptilolite. Particularly at the higher application rate (Z5), chabazite led to the greatest reductions in macroporosity (−3.25% in ME soil and −2.86% in GE) and the most substantial increases in meso- (+5.33% in ME soil) and microporosity (+4.19% in GE). Clinoptilolite also followed the general trend but often with lower intensity, especially at low doses (Z2). A notable exception was the GE soil treated with a low dose of clinoptilolite (Z2), which showed a negligible variation

in mesoporosity (-0.12%) and a very limited increase in microporosity ($+0.19\%$), indicating a minimal effect on the soil structure under these specific conditions.

These results are consistent with previous studies [29,31,69,70], which reported that zeolite addition generally imparts a “clay-like” behavior to soils by slowing water and solute mobility due to the increased presence of smaller pores.

The above effects of zeolite can also be inferred by observing θ_s and K_s values reported in Table 4. The results clearly indicate that zeolite addition modifies the hydraulic behavior of all investigated soils. Again, the magnitude of the effects depends on both soil type and zeolite characteristics.

Table 4. Soil hydraulic properties: (i) soil hydraulic conductivity at saturation (K_s), (ii) water content at saturation (θ_s), (iii) water content at field capacity (θ_{FC}), (iv) water content at permanent wilting point (θ_{PWP}), (v) water content at $\psi = -1000$ hPa (θ_{-1000}), (vi) available water content (AWC), and (vii) readily available water content (RAWC). Values are means ($n = 4$). Data were analyzed by one-way ANOVA followed by Tukey’s post hoc test. For single soil, means in columns without a common superscript letter differ ($p \leq 0.05$).

Soil ID	Zeolite ID	Treatment	K_s (cm min^{-1})	θ_s ($\text{cm}^3 \text{cm}^{-3}$)	θ_{FC} ($\text{cm}^3 \text{cm}^{-3}$)	θ_{PWP} ($\text{cm}^3 \text{cm}^{-3}$)	θ_{-1000} ($\text{cm}^3 \text{cm}^{-3}$)	AWC ($\text{cm}^3 \text{cm}^{-3}$)	RAWC ($\text{cm}^3 \text{cm}^{-3}$)
ME	Soil	Z0	0.123 ^a	0.563 ^b	0.268 ^d	0.064 ^e	0.139 ^e	0.204 ^a	0.129 ^a
		Z2	0.074 ^b	0.513 ^e	0.280 ^c	0.081 ^d	0.159 ^d	0.199 ^b	0.121 ^b
		Z5	0.070 ^b	0.524 ^d	0.288 ^b	0.103 ^b	0.180 ^b	0.185 ^d	0.108 ^d
	Clinoptilolite	Z2	0.074 ^b	0.570 ^a	0.280 ^c	0.095 ^c	0.171 ^c	0.184 ^d	0.109 ^d
		Z5	0.044 ^c	0.551 ^c	0.306 ^a	0.115 ^a	0.196 ^a	0.191 ^c	0.111 ^c
GE	Soil	Z0	0.049 ^a	0.480 ^a	0.274 ^b	0.077 ^d	0.154 ^c	0.197 ^a	0.120 ^a
		Z2	0.022 ^c	0.466 ^b	0.280 ^a	0.095 ^b	0.171 ^b	0.185 ^c	0.109 ^b
		Z5	0.007 ^e	0.453 ^c	0.274 ^b	0.116 ^a	0.185 ^a	0.159 ^e	0.089 ^d
	Clinoptilolite	Z2	0.040 ^b	0.479 ^a	0.258 ^c	0.066 ^e	0.138 ^d	0.192 ^b	0.119 ^a
		Z5	0.018 ^d	0.470 ^b	0.253 ^d	0.085 ^c	0.153 ^c	0.169 ^d	0.100 ^c
FE	Soil	Z0	0.047 ^a	0.361 ^a	0.203 ^d	0.111 ^e	0.154 ^d	0.092 ^c	0.049 ^d
		Z2	0.024 ^b	0.330 ^d	0.224 ^c	0.114 ^d	0.164 ^c	0.111 ^a	0.060 ^a
		Z5	0.019 ^c	0.331 ^d	0.237 ^a	0.147 ^a	0.191 ^a	0.090 ^d	0.047 ^e
	Clinoptilolite	Z2	0.023 ^b	0.341 ^b	0.231 ^b	0.125 ^b	0.174 ^b	0.106 ^b	0.056 ^c
		Z5	0.010 ^d	0.336 ^c	0.229 ^b	0.122 ^c	0.172 ^b	0.107 ^b	0.057 ^b

In the ME soil, a decrease in θ_s values was observed with chabazite additions in the range of approximately 6.90–8.90%, whereas clinoptilolite amendments showed no effect at Z2, and at Z5 the effect was $\sim 2.0\%$. As regards K_s , the effects were more evident with both zeolites used, ranging from ~ 8.70 – 9.40% for chabazite and from approximately ~ 8.70 – 14.0% for clinoptilolite. For the GE soil mixed with chabazite, θ_s varied between approximately 3.0% and 5.60%, while the effect of clinoptilolite was very modest ($\sim 2.0\%$ at Z5). Changes in K_s values were very similar to those observed for the ME soil, except for Z2 clinoptilolite, where K_s values decreased by only $\sim 2\%$ compared to Z0. Finally, for FE soil, while the changes in K_s values were very similar to those observed for ME, θ_s decreased more substantially in all examined cases. For chabazite, the effect at Z2 and Z5 was approximately $\sim 8.5\%$, whereas for clinoptilolite it ranged between $\sim 5.7\%$ and $\sim 7.0\%$. Similar results were also observed by [71–73].

It is evident that the observed reductions in K_s with increasing zeolite content should be considered not only in terms of changes in soil hydraulic behavior, but also with respect to their practical implications under agricultural conditions. From a practical perspective, the observed reductions in K_s indicate a slower movement of water through the soil profile, resulting in increased water residence time and reduced rapid drainage pathways. Such effects may contribute to limiting nitrate and ammonium leaching under agricultural

conditions. However, excessive reductions in hydraulic conductivity could potentially impair soil drainage and aeration, particularly under high water input conditions.

Selected SWSPs of agronomic interest, such as θ_{FC} , θ_{PWP} , q_{-1000} , AWC, and RAWC are also reported in Table 4. From analysis of the above parameters, it can be inferred that the impact of zeolite on water availability was highly soil-dependent, reflecting a complex balance between θ_{FC} and θ_{PWP} . In ME and GE soils, both AWC and RAWC were highest in the control and decreased as zeolite content increased. This occurs because, although zeolite may increase θ_{FC} , it raises θ_{PWP} to an even greater extent, thereby reducing AWC and RAWC values and indicating a net increase in microporosity relative to macroporosity. This mechanism is consistent with the findings of [26,74], who observed similar trends and suggested that increases in fine pore fractions can enhance total water retention while simultaneously reducing plant-available water. Conversely, FE soil, characterized by the lowest initial water retention (i.e., at Z0), responded positively to zeolite addition (especially at lower doses), with AWC and RAWC values increasing by about 18% on average.

The impact of zeolite on AWC appears to be closely linked to the baseline soil texture. In FE soil, characterized by the highest sand content (60.4%), zeolite incorporation effectively promoted a more favorable pore size distribution. Conversely, in ME and GE soils, which have higher silt and clay fractions, the amendment led to an increase in microporosity. These findings support a site-specific approach to zeolite application.

Notably, this evidence suggests that, even in coarse-textured or poorly retentive soils, zeolite can promote a beneficial pore structure that enhances soil water retention in the θ_{FC} - θ_{PWP} domain. Comparable improvements in sandy or coarse-textured soils have also been documented by [28,69,73], who reported increased plant-available water due to zeolite incorporation. However, the use of zeolite in finer sandy loams soils (like ME and GE) may be focused on its chemical benefits (e.g., increased CEC and nitrogen retention) rather than hydraulic ones. In these cases, the slight reduction in AWC is an acceptable compromise for reduced leaching and improved fertilizer efficiency [75,76].

These results are further supported by the two-way ANOVA analysis reported in Table 5, which indicates that soil (S) and treatment (T) factors, as well as their interaction ($S \times T$), have a highly significant effect (even at a significance level of $p \leq 0.001$) on all measured hydraulic properties.

Table 5. Two-way ANOVA statistical test of soil type and zeolite treatment effects on water content at saturation (θ_s), water content at field capacity (θ_{FC}), water content at permanent wilting point (θ_{PWP}), water content θ_{-1000} , available water content (AWC), readily available water content (RAWC), and soil hydraulic conductivity at saturation (K_s).

Source	Sum of Squares	Degrees of Freedom	Mean Square Error	F-Ratio	p-Value
θ_s					
Soil	0.428	2	0.214	39,788.78	≤ 0.0001
Treatment	0.011	4	0.003	492.47	≤ 0.0001
Soil $\times$ Treatment	0.004	8	0.000	85.76	≤ 0.0001
θ_{FC}					
Soil	0.038	2	0.019	10,468.48	≤ 0.0001
Treatment	0.002	4	0.001	343.78	≤ 0.0001
Soil $\times$ Treatment	0.006	8	0.001	400.14	≤ 0.0001
θ_{PWP}					
Soil	0.016	2	0.008	23,825.36	≤ 0.0001
Treatment	0.01	4	0.002	7495.67	≤ 0.0001
Soil $\times$ Treatment	0.006	8	0.001	2105.2	≤ 0.0001

Table 5. Cont.

Source	Sum of Squares	Degrees of Freedom	Mean Square Error	F-Ratio	p-Value
θ_{-1000}					
Soil	0.001	2	0.001	791.5	≤ 0.0001
Treatment	0.009	4	0.002	2824.06	≤ 0.0001
Soil $\times$ Treatment	0.007	8	0.001	1048.5	≤ 0.0001
AWC					
Soil	0.099	2	0.049	75,440.54	≤ 0.0001
Treatment	0.003	4	0.001	1283.54	≤ 0.0001
Soil $\times$ Treatment	0.003	8	0.000	645.7	≤ 0.0001
RAWC					
Soil	0.045	2	0.022	98,990.3	≤ 0.0001
Treatment	0.002	4	0.001	2687.76	≤ 0.0001
Soil $\times$ Treatment	0.002	8	0.000	1173.9	≤ 0.0001
K_s					
Soil	0.035	2	0.017	5055.32	≤ 0.0001
Treatment	0.017	4	0.004	1216.92	≤ 0.0001
Soil $\times$ Treatment	0.004	8	0.000	142.11	≤ 0.0001

The high significance of the $S \times T$ interaction confirms that the efficacy of zeolite amendments is intrinsically linked to the starting physical properties of the soil matrix. This is consistent with previous research demonstrating that the interaction between soil type and zeolite treatment exerts a statistically significant influence on soil hydraulic behavior. In particular, Ref. [27] showed that both the main factors (soil and zeolite amount) and the relationships among them significantly affected soil physical quality indices and hydraulic responses. Similar conclusions were reached by [33], who observed that variations in hydraulic conductivity and pore size distribution in response to zeolite addition depended strongly on soil texture, confirming a clear $S \times T$ interaction effect. While the S factor emerged as the predominant factor of water retention capacity and total porosity (F-ratio = 39,789 for θ_s ; F-ratio = 75,440 for AWC; F-ratio = 98,990 for RAWC), the T factor modulates these values in ways that can either enhance or diminish plant water availability depending on the soil's original texture and pore size distribution.

3.2. Effects of Zeolite on Soil Solute Transport Properties

Estimated v and λ values are shown in Figure 3a–c, a'–c'. For each soil, the parameters were grouped according to the ion used in the transport test (i.e., chloride, nitrate, and ammonium), allowing the variations observed to be clearly identified as a function of the treatment. In the same graphics, letters displayed above the bars illustrate the results of the one-way ANOVA statistical test.

In general, v was observed to decrease with increasing zeolite addition. Under control conditions (Z0), ME soil showed the highest v values (0.17–0.19 cm min^{−1}), followed by GE (0.07–0.08 cm min^{−1}) and FE (0.05–0.08 cm min^{−1}), indicating a more dynamic pore system in ME soil. In all Z0 soils, as expected, Cl^- and NO_3^- behaved similarly, consistent with their quasi-conservative nature, whereas NH_4^+ generally exhibited slightly lower velocities, suggesting the effect of cation exchange interactions. The addition of chabazite significantly reduced velocities in all soils, particularly at the Z5 level, with the strongest effects observed in GE and ME soils, where NH_4^+ reached minimum values (down to 0.01–0.02 cm min^{−1}), reflecting both structural changes (favoring meso- and microporosity regions) and enhanced adsorption mechanisms.

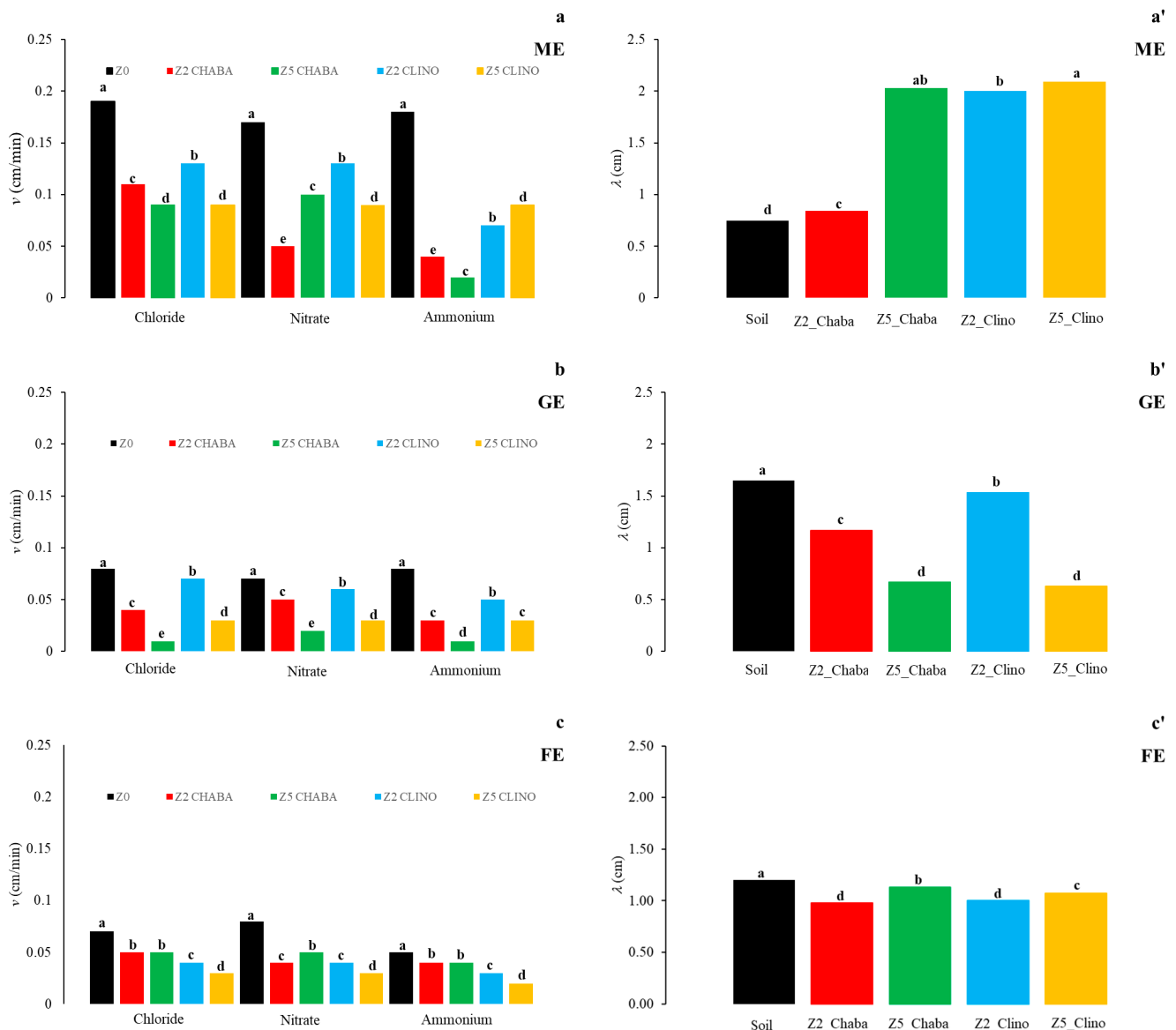


Figure 3. Effects of zeolite treatments on solute transport parameters: (a–c) pore water velocity v , and (a'–c') soil dispersivity λ . Values are means ($n = 4$). Data presented in each graph were analyzed by one-way ANOVA statistical test. Letters indicate that differences among treatments are statistically different at a significance level of $p \leq 0.05$.

For a given treatment, differences in the magnitude of v among soils are undoubtedly related to the type of zeolite. An additional effect may arise from the initial soil texture. Although all soils are classified as sandy-loam, the sand fraction, particularly the fine (0.10–0.25 mm) and very fine (0.05–0.10 mm) fractions (see Appendix A for details), varies among the three soils. In particular, in GE and FE soils, the fine and very fine sand fractions are substantial, accounting for approximately 45–50% of the total sand fraction; in ME, these fractions are approximately 25%. Therefore, it is plausible that this textural difference, together with the complex interactions among the soils, their mineralogical composition, and the zeolite (which is not an inert material), may lead to distinct structural arrangements in the resulting soil–zeolite mixtures, thereby promoting the development of different proportions of meso- and micropores [33]. ME soil, which initially has the lowest percentage of fine and very fine sand (and therefore likely contains larger pore spaces at Z0 than GE and FE soils), is the one in which the addition of zeolite tends to produce fewer meso- and micropores, with consequent effects on the observed velocities.

These complex interactions between soil and zeolite may also play a role in the changes in soil dispersivity which are, to some extent, soil-dependent. Indeed, while for GE and FE soils, λ generally decreases with increasing zeolite content—the reduction ranging from ~5% (Z5_CHABA, FE soil) to ~60% (Z5_CLINO, GE soil)—for ME soil, λ values tend to increase with increasing zeolite fraction. In particular, in ME, both Z2 and Z5 levels of clinoptilolite resulted in λ values greater than 2 cm, which are significantly higher, up to ~170%, than Z0. For chabazite, λ increased by approximately 12% and 160% for Z2 and Z5, respectively. This trend is consistent with the findings of [52] who, working on sandy soils mixed with zeolite, reported increases in λ values (compared to the controls) of up to 28%. Similarly, Ref. [33], using a synthetic zeolite, observed increases in λ values.

Overall, the addition of zeolite to ME soil resulted in a more heterogeneous structure, creating additional interstitial spaces that enhanced mechanical dispersion [18,19]. Conversely, in GE and FE, the observed reduction in λ values suggests that the zeolites produced a more hydraulically uniform medium.

From this perspective, Ref. [32] suggested that the effects of zeolites on soils are highly specific: each zeolite exerts a distinct influence on a given soil, and such behavior may not necessarily be observed in other soil types. Nevertheless, this is an aspect that certainly warrants further investigation to fully understand the underlying mechanisms.

Further indications of zeolite-induced changes in soil transport properties may be drawn from additional parameters reported in Table 6, showing the mean travel time t_{mean} (i.e., the average time required for solute particles to pass through the system, that is the centroid of the temporal distribution of the solute mass), the peak solute arrival time t_{peak} (i.e., the time needed by the solute peak concentration to pass through the system, that is to reach the bottom of the column at $L = 11$ cm), the peak solute velocity $v_{peak} = (L/t_{peak})$, the dispersion coefficient (D), and the retardation factor (R). The data are grouped by soil type and zeolite treatment. For each soil–zeolite combination, the estimated transport parameters are reported for every monitored ion.

Table 6. Mean time (t_{mean}), peak solute arrival time (t_{peak}), peak solute velocity (v_{peak}), dispersion coefficient (D), and retardation factor (R), determined from the experimental (Cl^- , NO_3^- , and NH_4^+) C/C_0 breakthrough curves, referring to the selected soil (Z0) and soil–zeolite mixtures (Z2 and Z5). Letters indicate that differences among treatments are statistically different at a significance level $p \leq 0.05$.

Soil ID	Treatment	Ion	t_{mean} (min)	t_{peak} (min)	v_{peak} (cm/min)	D (cm ² /min)	R
ME	Z0	Cl^-	57.51 ^d	45 ^e	0.250	0.14	1.00
	Z2 Chaba		96.72 ^b	80 ^b	0.137	0.10	1.00
	Z5 Chaba		120.45 ^a	90 ^a	0.122	0.18	1.00
	Z2 Clino		81.95 ^c	50 ^d	0.220	0.26	1.00
	Z5 Clino		119.75 ^a	75 ^c	0.146	0.19	1.00
	Z0	NO_3^-	64.17 ^e	45 ^e	0.250	0.12	1.00
	Z2 Chaba		132.0 ^b	85 ^b	0.129	0.05	1.00
	Z5 Chaba		136.20 ^a	100 ^a	0.110	0.20	1.00
	Z2 Clino		114.98 ^d	75 ^d	0.146	0.26	1.00
	Z5 Clino		116.72 ^c	80 ^c	0.138	0.20	1.00
	Z0	NH_4^+	60.07 ^e	45 ^e	0.250	0.13	1.20 ^e
	Z2 Chaba		182.90 ^c	90 ^d	0.122	0.03	1.90 ^d
	Z5 Chaba		385.12 ^a	330 ^a	0.030	0.04	3.20 ^a
	Z2 Clino		220.14 ^b	135 ^c	0.080	0.14	2.70 ^b
	Z5 Clino		120.19 ^d	140 ^b	0.070	0.19	2.00 ^c

Table 6. Cont.

Soil ID	Treatment	Ion	t_{mean} (min)	t_{peak} (min)	v_{peak} (cm/min)	D (cm ² /min)	R
GE	Z0	Cl^-	130.85 ^e	75 ^e	0.146	0.14	1.00
	Z2 Chaba		265.66 ^c	165 ^c	0.060	0.04	1.00
	Z5 Chaba		808.45 ^a	815 ^a	0.010	0.01	1.00
	Z2 Clino		146.96 ^d	85 ^d	0.129	0.11	1.00
	Z5 Clino		331.60 ^b	275 ^b	0.040	0.02	1.00
	Z0	NO_3^-	149.52 ^e	95 ^e	0.116	0.12	1.00
	Z2 Chaba		233.65 ^c	165 ^c	0.060	0.06	1.00
	Z5 Chaba		773.62 ^a	830 ^a	0.010	0.01	1.00
	Z2 Clino		181.92 ^d	125 ^d	0.090	0.10	1.00
	Z5 Clino		329.18 ^b	290 ^b	0.040	0.02	1.00
	Z0	NH_4^+	140.58 ^e	95 ^d	0.116	0.15	1.20 ^b
	Z2 Chaba		306.34 ^c	165 ^c	0.060	0.04	1.20 ^b
	Z5 Chaba		909.74 ^a	915 ^a	0.010	0.01	1.20 ^b
	Z2 Clino		190.16 ^d	165 ^c	0.070	0.08	1.30 ^a
	Z5 Clino		385.96 ^b	335 ^b	0.030	0.02	1.20 ^b
FE	Z0	Cl^-	156.93 ^d	125 ^e	0.080	0.08	1.00
	Z2 Chaba		241.90 ^c	200 ^c	0.060	0.04	1.00
	Z5 Chaba		243.20 ^c	205 ^b	0.050	0.05	1.00
	Z2 Clino		263.73 ^b	180 ^d	0.060	0.04	1.00
	Z5 Clino		301.02 ^a	570 ^a	0.020	0.03	1.00
	Z0	NO_3^-	157.57 ^e	125 ^e	0.080	0.10	1.00
	Z2 Chaba		245.00 ^d	200 ^c	0.060	0.04	1.00
	Z5 Chaba		310.19 ^a	210 ^b	0.050	0.05	1.00
	Z2 Clino		265.11 ^c	184 ^d	0.050	0.04	1.00
	Z5 Clino		310.15 ^b	575 ^a	0.020	0.03	1.00
	Z0	NH_4^+	190.80 ^e	140 ^e	0.070	0.17	1.20 ^d
	Z2 Chaba		298.69 ^c	205 ^d	0.060	0.04	1.24 ^c
	Z5 Chaba		317.39 ^b	245 ^c	0.040	0.04	1.30 ^b
	Z2 Clino		284.19 ^d	275 ^b	0.040	0.03	1.10 ^e
	Z5 Clino		597.03 ^a	605 ^a	0.020	0.02	1.98 ^a

Under control conditions (Z0), clear differences among soils were observed for all the selected parameters. ME soil showed the lowest t_{mean} values for all ions (~57–64 min), confirming its higher hydraulic conductivity and faster solute transport compared to GE and FE, where t_{mean} values were approximately two to three times higher. The addition of chabazite markedly increased both t_{mean} and t_{peak} values, especially at the highest dose (Z5). In GE soil, the NH_4^+ test (for Z5 Chaba) showed an extreme increase in t_{mean} (up to 909.74 min), with a strong reduction in v_{peak} ($=0.010\text{ cm min}^{-1}$), and the highest R value of 3.20, highlighting intense chemical retention combined with reduced flow velocity. The high retardation factors observed for NH_4^+ suggest that adsorption and cation exchange processes played a major role in controlling ammonium transport within the soil–zeolite mixtures. However, the magnitude of the observed R values may also reflect the complex interaction between chemical retention processes and the simultaneous reduction in pore water velocity induced by pore network reorganization.

The t_{mean} , t_{peak} and v_{peak} values for Cl^- and NO_3^- were also strongly affected by the soil–zeolite mixtures.

In FE soil, chabazite and clinoptilolite induced a moderate increase in t_{mean} (up to ~317 min and ~597 min for the Z5 Chaba- NH_4^+ test and Z5 Clino- NH_4^+ test, respectively)

and a more progressive and gradual decrease in v_{peak} values, ranging from $0.080 \text{ cm min}^{-1}$ down to $0.020 \text{ cm min}^{-1}$, suggesting a more buffered structural response compared to GE and ME.

Regarding the coefficient of dispersion, D values tended to decrease under high chabazite doses in GE and FE soils, reflecting reduced mechanical dispersion associated with lower flow velocities, whereas in ME soil some treatments (e.g., Z2 Clinoptilolite) showed increased D values, suggesting, in this case, enhanced spreading under intermediate flow conditions.

Overall, soil-specific responses were evident: ME soil displayed the widest range of variation and strongest chemical retardation under chabazite treatment, GE soil showed the most pronounced structural slowdown at high doses, and FE exhibited a more gradual and buffered response, indicating the complex interactions between soils and zeolites that depend on the intrinsic physico-chemical properties of soils and of these natural amendments.

3.3. Multivariate Analysis

To synthesize the complex interactions between soil texture, zeolite treatment, and hydraulic behavior, a multivariate statistical approach was adopted. The application of the k-means algorithm using Euclidean distance was specifically chosen because the dataset was standardized through z-score normalization (mean = 0, standard deviation = 1). This ensures that the distance in the principal component (PC) space reflects actual geometric similarity across variables of different units [65]. The identification of five distinct clusters, validated by the Elbow and Silhouette approaches, highlights the structural reorganization induced by zeolite. As shown in Figure 4, the first two principal components capture 77.5% of the total variance, revealing a clear segregation based on soil provenance and treatment.

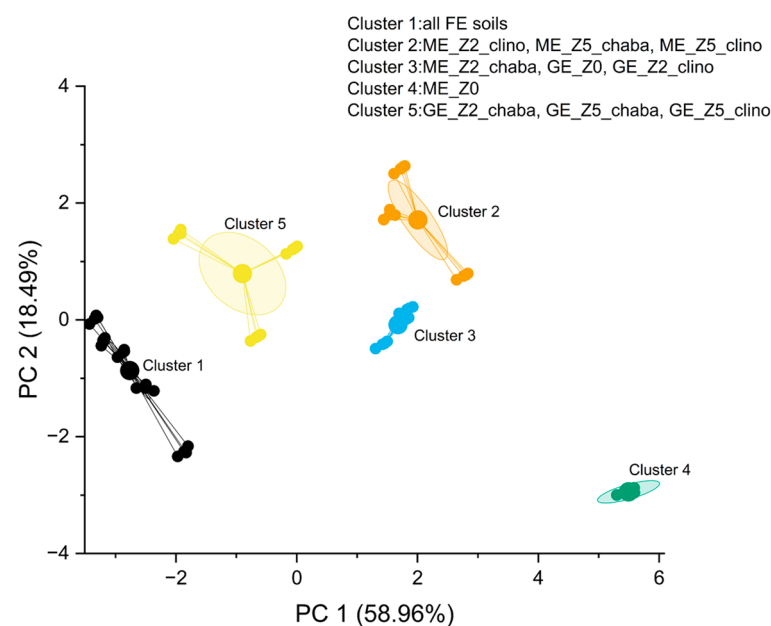


Figure 4. Spatial distribution and partitioning of soil samples into five distinct groups identified through k -means clustering ($k = 5$). The axes represent the first two dimensions of the multivariate dataset, accounting for 58.96% (PC1) and 18.49% (PC2) of the total variance. Solid ellipses denote the 95% confidence intervals for each cluster.

Cluster 1 primarily groups all FE soil samples, is positioned at negative PC1 values, and shows high internal cohesion and distinct separation from the others. In contrast, the proximity of clusters 2, 3, and 5 suggests shared hydraulic characteristics across the ME and GE sandy loams, though they remain statistically distinct. Cluster 4 (exclusively

ME Z0) is isolated at the extreme positive end of PC1, representing the native macropore-dominated state before amendment. The spatial distribution of these clusters reveals clear segregation based on soil provenance and the impact of zeolite amendments. It is important to acknowledge that the identified clusters represent behavior patterns rather than rigid, isolated categories. Soil properties are inherently continuous, and the proximity of clusters 2, 3, and 5 suggests the existence of transitional hydraulic behavior. We argue that while grouping is a simplification, it is a necessary tool for categorizing soil management zones and providing practical agronomic recommendations. Further analysis, as shown in the radar chart in Figure 5, serves as a multivariate functional profile, highlighting the structural modifications induced by zeolite amendments in the studied soils. Because z-scores for the radar plot were used, the center of the radar plot represents the dataset mean, while the vertices show deviations in terms of standard units, allowing for a balanced comparison of heterogeneous variables like hydraulic conductivity and retention. Cluster 4 exhibits the highest K_s and velocity values for all monitored ions. This pattern, a distinctive feature among the analyzed soils, reflects a macropore-dominated structure that facilitates nutrient leaching and represents the condition most vulnerable to solute losses. In contrast, cluster 1 is mainly characterized by low θ_s and θ_{FC} values, reduced saturated hydraulic conductivity, low dispersivity, limited ion velocities, but relatively high values of θ_{PWP} and θ_{-1000} . Such features indicate a pore network that restricts water flow and solute movement. This configuration reduces the risk of ion leaching while simultaneously enhancing water availability for plants.

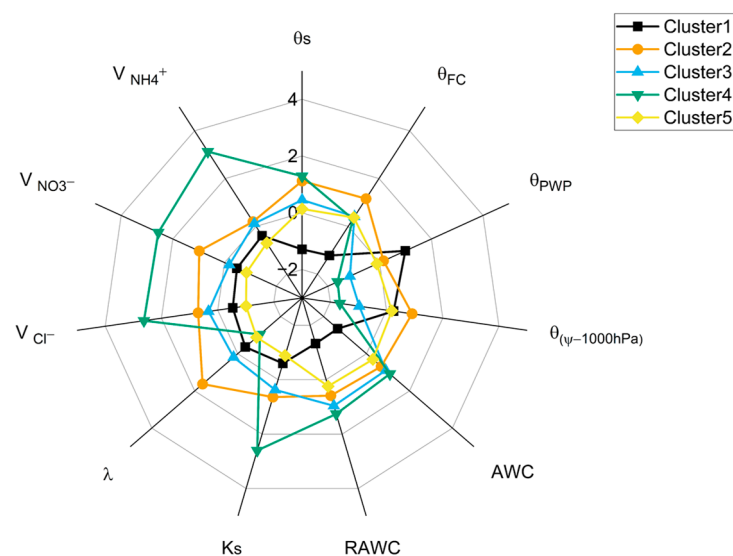


Figure 5. Radar diagram illustrating the multivariate functional profiles (centroids) of the five *k*-means clusters.

Cluster 2 shows elevated θ_{FC} and AWC values, relatively high dispersivity, and moderate ion velocities. This configuration indicates a pore network promoting water storage within plant-available pore classes, while maintaining sufficient permeability for drainage. Cluster 3 displays intermediate K_s , AWC, and RAWC values, along with moderate-to-low ion velocities and intermediate l values. These characteristics suggest a pore network with reduced flow path variability and moderate dispersive transport behavior. Cluster 5 represents a condition with moderate pore network reorganization that proportionally affects most parameters, and is associated with relatively contained ion velocities.

Ultimately, our findings demonstrate that there is no universal approach to zeolite application; rather, its role fundamentally depends on the baseline physical structure of the

soil. In coarser-textured soils (sand $\geq 60\%$, such as the FE soil), zeolite acts primarily as a hydraulic enhancer by increasing plant-available water (AWC). Conversely, in medium-textured soils (with higher silt and clay content, such as ME and GE soils), the agronomic value of zeolite shifts toward nutrient conservation and environmental protection. Although zeolite may not increase the water available due to the narrowing of the AWC window, it restricts the leaching of fertilizers toward groundwater. These distinct behaviors, visually summarized by the spatial segregation in Figure 4 and the functional fingerprints in the radar chart (Figure 5), confirm that zeolite is a versatile tool for soil management [76].

4. Conclusions

The present research illustrated the effects of two commercial zeolites on several hydraulic and transport properties of three selected sandy-loam soils in southern Italy. It primarily showed that the addition of these natural zeolites affects soil pore structure, influencing the entire set of hydraulic and solute transport parameters. Such structural changes reduce the velocity of water and solutes in soils, limiting rapid flow pathways.

Between the two investigated zeolites, chabazite generally induced more pronounced modifications in hydraulic and transport properties, whereas clinoptilolite showed similar trends but typically with lower intensity, particularly at lower application rates.

As sandy-loam soils are characterized by moderate-to-high mobility for water and solutes, such modifications may have important environmental implications for nitrogen compound dynamics in such soils. The general increase in meso- and microporosity reduced the mobility of nitrates. Ammonium transport was further constrained by adsorption processes, resulting in increased retardation and prolonged residence time within the soil matrix. These effects were quantitatively reflected by the observed reductions in pore water velocity and peak solute velocity, together with the increase in retardation factors under the different zeolite treatments.

Together, these mechanisms contribute to retaining NO_3^- and NH_4^+ in the root zone, thereby reducing nutrient losses and mitigating risks of groundwater contamination.

The results demonstrate that even relatively low zeolite application rates (as tested in this study) were sufficient to produce measurable effects on both soil hydraulic and solute transport properties. This finding highlights the efficiency of zeolite amendments, indicating that significant reductions in nitrogen leaching can be achieved without the need for high application rates. From both an agronomic and economic perspective, this supports the practical feasibility of zeolite use under field conditions and further reinforces their potential as a promising strategy to enhance nutrient use efficiency and minimize the environmental impacts associated with intensive fertilization.

Future research should focus on long-term field validation and performance under different climatic and irrigation conditions to support their adoption in sustainable agricultural management.

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Data Availability Statement: The data presented in this study are openly available in Zenodo at 10.5281/zenodo.18874001.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Appendix A.1. Haplic Calcisols (Metaponto, Basilicata, Southern Italy)

USDA Classification: Sandy-Loam

Table A1. Particle size analysis.

Sand Texture	Sand (%)
Very coarse sand	0.92
Coarse sand	2.83
Medium sand	24.78
Fine sand	21.55
Very fine sand	3.73

Soil description: Soils developed on flat and well-preserved, sometimes gently or moderately sloping, surfaces of marine terraces. These areas are locally characterized by alluvial and colluvial deposits of modest thickness and are intersected by some deep incisions from the secondary hydrographic network. The parent materials are sands with lenses of gravel and limestone pebbles. The elevation ranges between 10 and 140 m above sea level.

These soils are widely found in gently sloping areas limited by strongly skeletal horizons. They are highly calcareous with abundant surface stoniness. Due to erosion, the calcic horizon is shallow, sometimes outcropping. The texture is loam or sandy-loam, with common coarse fragments, good drainage, and moderately high permeability. They are moderately calcareous in the plowed horizon and very calcareous in the underlying horizons. They have a very alkaline reaction.

Appendix A.2. Dystric Luvisols (Genzano, Basilicata, Southern Italy)

USDA Classification: Sandy-Loam

Table A2. Particle size analysis.

Sand Texture	Sand (%)
Very coarse sand	0.30
Coarse sand	1.38
Medium sand	7.05
Fine sand	28.8
Very fine sand	19.9

Description: Soils on the rugged mountainous relief of the alternations of sandstones and marly clays.

The morphology is characterized by moderately steep to very steep slopes, often interrupted by steep tectonic scarps, at the base of which lie depressed areas with gentler gradients. The elevations range between 100 and 1100 m above sea level; the most represented altitudinal range is between 700 and 900 m.

The most widespread soils have a moderately differentiated profile due to brunification and partial carbonate removal, and show significant variability related to the prevalence of different lithological components. In areas with a predominant clay component, fine-textured soils are present, while on slopes dominated by the arenaceous (sandy) component, there are loam-textured soils. These are highly evolved and very deep soils, with a distinct argillic horizon. The Dystric Luvisol unit has a sandy-loam texture at the surface and a sandy clay loam texture at depth, and is free of coarse fragments. Non-calcareous, such soils have a neutral or slightly acidic reaction and medium or low base saturation. They have mediocre drainage and moderately low permeability.

Appendix A.3. Haplic Luvisol (San Ferdinando di Puglia, Puglia, Southern Italy)

USDA Classification: Sandy-Loam

Table A3. Particle size analysis.

Sand Texture	Sand (%)
Very coarse sand	3.93
Coarse sand	8.28
Medium sand	14.2
Fine sand	29.03
Very fine sand	9.48

Description: This soil presents the classic Luvisol profile, with a light-colored, clay-leached surface horizon (E) over a denser, clay-enriched subsoil (B_t). Developed on calcareous alluvial and marine deposits of the Tavoliere plain, it is found on flat to gently sloping landscapes. The soil is generally well-drained but can have temporary waterlogging above the clay pan. Reaction is neutral in the surface and becomes alkaline with depth due to the calcareous parent material. The sandy-loam texture of the surface layer makes it very easy to work with and allows rapid water infiltration. The underlying clay-enriched horizon acts as a reservoir for moisture and nutrients.

Source:

<https://www.regione.basilicata.it/siti/suoli-basilicata/index.htm> (accessed on 1 January 2026).

<https://pugliacon.regione.puglia.it/web/sit-puglia-sit/sistema-informativo-dei-suoli> (accessed on 1 January 2026).

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