

Article

Retention of Ammonia in Soils: Mechanisms and Implications for Agronomic Uses of Anhydrous Ammonia Injection

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Abstract

Ammonia injection into soils is used both to supply N to field crops and to reduce soil-borne pests and weeds. Ammonia efficacy depends on its persistence in the soil environment following application. Hence, the extent of ammonia binding in six thermic, xeric Mediterranean soils, varying widely in texture, was evaluated at three moisture contents. Fitting the experimental retention data for each of the six oven-dry soils to the Langmuir isotherm yielded apparent maximum retention capacities (S_{MAX}) ranging from 440 to 1730 mg NH_3 -N kg^{-1} , and Langmuir binding coefficients (k) ranging from 0.08 to 4.31 L mg^{-1} . The S_{MAX} correlated strongly and linearly with clay content ($r^2 = 0.946$, $p < 0.01$). The S_{MAX} of the six soils increased with moisture content, likely due to ammonia dissolution in the liquid phase and the adsorption of its cationic derivative. The expected reduction in ammonia binding to the solid phase upon wetting, due to competition with water, was reflected in a sharp, unanimous decrease in the Langmuir model coefficients. A reduction in ammonia retention (but not in S_{MAX}) due to moistening occurred only in the very-fine clayey montmorillonitic soil. While anhydrous ammonia may act as an effective slow-release N source in heavier-textured soils, its tendency to remain in the gas phase in sandy soils is advantageous for pest control.

Keywords: ammonia retention; clay content; Langmuir model parameters; soil moisture content

1. Introduction

Ammonia (NH_3) injection is a commonly used method for application of available nitrogen to soils [1]. Ammonia is also formed in soils, following the application of ammonium (NH_4^+) and urea-containing fertilizers (e.g., [2–6]). Losses of applied ammonia through volatilization may be considerable and are affected by factors such as loading rate and soil properties, including mineralogy, CEC, moisture content, solution pH, temperature, and salinity [7–9]. Thus, NH_3 losses from calcareous soils treated with ammonium sulfate were reported to reach 80% of the amount applied. The extent of loss was inversely related to the soil's CEC and clay content [7]. One may expect rapid equilibration between the fraction of applied NH_3 that remains in the gas phase and the NH_3 , as well as cationic NH_4^+ , which are dissolved or sorbed in the liquid and solid phases of the soil, respectively. The equilibrium ratio between the above two species is controlled by factors such as solution pH and temperature, as described, for example, by the Henderson-Hasselbalch equation (e.g., [10]). The higher the pH, the higher the $[NH_3]/[NH_4^+]$ ratio in the soil solution. The



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extent of retention of the nitrogen added as ammonia is affected in part by the degree to which the added NH_3 is converted to the ammonium ion, and that in turn, strongly affects the availability of the added N to the crop.

Injection of NH_3 has also been shown to be an effective method for eradicating various soil-borne pests and weeds [11–15]. While loss of gaseous ammonia to the atmosphere reduces its efficiency as a source of N, a high concentration of NH_3 in the soil's atmosphere improves its efficacy as a pesticide.

The often-observed large differences among soils in the effectiveness of ammonia injection, either as a nitrogen source or as a plant protection agent [12,16,17], motivated the effort to determine the soil properties that most strongly influence ammonia retention and its partitioning between soil and atmosphere. The most thoroughly investigated parameters include texture, carbonate content, and organic matter content [18–20]. Understanding the relationship between soil properties and ammonia uptake is essential for determining which soil types may benefit from ammonia injection, for what purpose, and under what conditions. The suitability of applied ammonia for either N-supply or pest control depends mainly on the rate and extent of its binding to the soil's solid and liquid phases. Forecasting ammonia partitioning among soil phases will enable informed decisions on whether to utilize ammonia for N fertilization and/or pest control, and on the required load.

In a laboratory study, Gips (2008) [13] exposed soil-borne fungal pathogens to ammonia concentrations up to 30 mg L^{-1} at 25°C . Fungal mycelia tested were of *Sclerotium rolfsii*, *Verticillium dahliae*, *Sclerotinia sclerotiorum*, *Rhizoctonia solani*, and *Fusarium oxysporum* f.sp. *lycopersici*. and of resting spores/sclerotia (propagules) of some of these fungi. Fungal suppression was influenced by the interaction between ammonia concentration and exposure time. Hence, the two extremes were *S. rolfsii*, which was eliminated within 15 min of exposure to $1.2 \text{ mg L}^{-1} \text{ NH}_3\text{-N}$, and *V. dahliae*, which required 30 min of exposure to $16 \text{ mg NH}_3\text{-N L}^{-1}$. The resting spores/sclerotia were somewhat more resistant to ammonia, requiring longer exposure times and higher concentrations to achieve the same results. Similarly, Ben-Yephet et al. (2006) [12] tested the effect of ammonia on the viability of propagules of four soil-borne fungal pathogens (*V. dahliae*, *S. rolfsii*, *S. sclerotiorum*, and *F. o. dianthi*). Ammonium sulfate was added to 50 g portions of pre-limed soil ($\text{pH} \geq 10$) at $0.21 \text{ mg NH}_4\text{-N g}^{-1}$ soil. The soil was spray-moistened to field capacity, and the vessels were sealed and incubated at 25°C for 96 h. This resulted in a 100% kill of all four fungal species. Notably, pH per se had no effect on fungal viability.

Soil is a non-homogeneous medium, containing a variety of sorption sites that vary within and among soils [21]. Hence, precise modeling of sorption in the soil, or more generally of retention of a species by the soil, is rather complex. In the present paper, empirical relationships between soil properties and ammonia uptake were estimated using the Langmuir isotherm. It is recognized that the total simultaneous retention through the various uptake pathways does not exhibit a straightforward Langmuir-type behavior [22]. Still, evaluating apparent maximum retention capacity and binding strength by fitting the data to a Langmuir isotherm has been shown to reasonably describe ammonia/ammonium uptake by soils [19,23].

The overall objective of the present study was to determine, through an understanding of the uptake behavior of injected anhydrous ammonia, in which soils and under what conditions ammonia injection is an effective means for either nitrogen fertilization or pest control.

2. Materials and Methods

2.1. Soils

Six semi-arid Mediterranean soils, ranging in texture from sand to very fine clay, were tested (Table 1). The soils were oven-dried at 105 °C overnight, ground to pass a 2 mm sieve, and stored in sealed glass vessels at room temperature.

Table 1. General data and selected properties of the investigated soils.

Location and Name			Texture	Coordinates					Soil Classification (USDA-ARS)		
Rishon Lezion			Quartzitic sand	31°58'58.99" N 34°43'24.60" E					Coastal dune		
Bet-Dagan			Loamy sand	31°59'49.20" N 34°48'43.55" E					Typic Haploxerept		
Gilat			Sandy loam	31°19'59.77" N 34°39'54.23" E					Calcic Haploxeralf		
Nahal Oz			Sandy clay loam	31°28'30.82" N 34°29'32.87" E					Calcic Haploxeralf		
Netanya-6 (B _{t2} horizon)			Sandy clay	32°17'19.72" N 34°50'49.93" E					Typic Palexeralf		
Golan-4			Very fine clay	32°46'17.65" N 35°42'26.35" E					Chromic Haploxerert		
Soil	pH	CEC (cmol _c kg ⁻¹)	Specific Surface Area ⁽¹⁾ (m ² g ⁻¹)	Sand	Silt	Clay	CaCO ₃	Organic Carbon	Water ⁽²⁾ at 33 Pa	Water ⁽²⁾ at 15 atm	Available Water
Dune sand	8.8	1.6	2.3	958	12	30	28	0.5	62	19	43
Bet-Dagan	7.8	8.2	53.2	833	49	118	0.6	6.6	116	62	54
Gilat	8.0	13.2	90.2	570	248	182	172	4.6	187	75	112
Nahal Oz	7.9	22.0	148.0	450	268	282	129	5.2	200	87	113
Netanya 6	6.4	24.8	188.4	503	145	352	1.0	2.7	263	141	122
Golan 4	7.2	79.6	415.0	150	106	744	37	16	490	343	147

⁽¹⁾ Calculated based on [24]. ⁽²⁾ Water content measured at 33 kPa and 1.5 MPa corresponds to field capacity and wilting point, respectively. The difference between the two is the plant-available water.

2.2. Determination of Ammonia Retention and Its Concentration in the Soil Gaseous Phase

Five grams of oven-dried soil samples were placed in 50 mL glass beakers, and every four beakers were placed in 1 L glass containers. Into the sealed containers, anhydrous ammonia was injected through a rubber stopper. The ammonia concentrations applied ranged from 0 to 40 mg N L^{−1} air. The concentration was calibrated by injecting 0–80 mL of ammonia gas (in 5 mL increments up to 20 mL, and 10–20 mL increments thereafter) into 1 L glass containers containing four empty beakers. It was ascertained that ammonia adsorption to the glass walls was negligible. A preliminary run with the Golan fine clay showed that 4 h were sufficient for the ammonia concentration in the gas phase to stabilize; this duration was used thereafter before assuming equilibrium was attained. Each treatment, i.e., a specific soil type exposed to a given initial concentration of ammonia, was run in four 1 L replicate containers, all at a constant temperature of 25 °C.

Following the 4 h incubation period, 60 mL gas samples were withdrawn from the sealed containers using a glass syringe equipped with a two-way valve. The gas samples were injected into 5 mL of 0.01 M HCl solution, and the concentration of ammonium-N was determined colorimetrically using an autoanalyzer (Lachat, Milwaukee, WI, USA). The amount of ammonia retained by the soil was calculated by subtracting the final ammonia amount in the container's gas phase from the amount injected into the container.

2.3. The Effect of Soil Moisture Content on Ammonia Retention

Each soil was tested at three moisture contents: oven-dryness, field capacity (FC), and 50% of the available water (50–AW). The latter is the difference between FC and point (WP) moisture content. The FC and WP of the six soils were determined at 33 kPa and 1.5 MPa, respectively, using pressure plates. Wetting of the 5 g oven-dry soil samples was achieved by evenly spraying the designated amount of deionized water over the soils. The beakers containing moist soil were covered with a Parafilm sheet and kept at 25 °C for an hour to ensure uniform water distribution within the soil. Then, these beakers were treated as described above (Section 2.2).

2.4. Statistics

Statistical analyses and model fitting were performed using JMP 16 [25]. Non-linear regression analysis was used to fit the NH₃ retention data to the Langmuir isotherm [Equation (1)], and the resulting parameters were evaluated for relationships with the clay content of the six soils. Specifically, these parameters are the apparent maximum retention capacity (S_{MAX}) and the Langmuir binding coefficient (k). Within each soil, these were derived at three soil moisture contents.

Differences in Langmuir parameters (S_{MAX} and k) within each soil at the three moisture contents were evaluated using a 95% confidence interval (CI) approach based on the standard errors obtained from the nonlinear regression of JMP. The 95% CI values were calculated as parameter estimate $\pm t \cdot SE$, where t , the critical value of the t-distribution at the 0.05 significance level, equals 1.96. Non-overlapping confidence intervals were used to indicate statistically significant differences among soils (e.g., in Table 2).

Table 2. Langmuir isotherm parameters for ammonia binding to soils (± 1 standard error) as affected by the soil texture and moisture content ⁽¹⁾.

Parameter	Soils and Their Langmuir Parameters		
	Oven Dry	50% Available Wat.	Field Capacity
Dune sand			
k (L mg ^{−1} NH ₃ -N)	0.08 $\pm$ 0.03	0.05 $\pm$ 0.01	0.11 $\pm$ 0.03
S_{MAX} (mg NH ₃ -N kg ^{−1})	440 $\pm$ 110	871 $\pm$ 122	597 $\pm$ 88
R-Square	0.85	0.97	0.95
Retained fraction (%) ⁽²⁾	24 $\pm$ 2 c	36 $\pm$ 0.5 b	46 $\pm$ 1.5 a
Bet Dagan, loamy sand			
k	0.13 $\pm$ 0.04	0.07 $\pm$ 0.02	0.06 $\pm$ 0.02
S_{MAX}	817 $\pm$ 110 b	1700 $\pm$ 232 a	2260 $\pm$ 436 a
R-Square	0.87	0.97	0.96
Retained fraction (%)	41 $\pm$ 1.5 c	58 $\pm$ 2 b	62 $\pm$ 1.5 a
Gilat, sandy loam			
k	0.34 $\pm$ 0.07 a	0.1 $\pm$ 0.02 b	0.09 $\pm$ 0.02 b
S_{MAX}	769 $\pm$ 51 b	2083 $\pm$ 256 a	2466 $\pm$ 336 a
R-Square	0.90	0.95	0.96
Retained fraction (%)	46 $\pm$ 0.5 c	69 $\pm$ 1 b	73 $\pm$ 1 a

Table 2. Cont.

Parameter	Soils and Their Langmuir Parameters		
	Oven Dry	50% Available Wat.	Field Capacity
Nahal Oz, clay loam			
k	0.67 ± 0.15 a	0.19 ± 0.02 b	0.24 ± 0.03 b
S_{MAX}	1107 ± 65 b	1738 ± 101 a	1803 ± 108 a
R-Square	0.88	0.97	0.97
Retained fraction (%)	69 ± 0.5 c	73 ± 0.5 b	76 ± 0.5 a
Netanya, sandy clay			
k	0.35 ± 0.05	0.25 ± 0.03	0.20 ± 0.03
S_{MAX}	1015 ± 55 b	1265 ± 58 a	1456 ± 93 a
R-Square	0.87	0.95	0.95
Retained fraction (%)	58 ± 0.5 c	64 ± 0.25 b	67 ± 0.5 a
Golan, very fine clay			
k	4.31 ± 0.74 a	0.79 ± 0.12 b	0.54 ± 0.05 b
S_{MAX}	1732 ± 75 b	1921 ± 101 ab	2305 ± 92 a
R-Square	0.88	0.92	0.94
Retained fraction (%)	91 ± 0.05 a	85 ± 0.1 c	87 ± 0.25 b

⁽¹⁾ Same letters in a row (k or S_{MAX} within a soil), or their absence, denote no significant difference between the respective means at 95% confidence interval. ⁽²⁾ "Retained fraction" is the percent of added ammonia that was retained by the soil. It was calculated from the reduction in the NH_3 content in the vessel's gas phase. It is shown for the highest applied soil-gas-phase concentration, which, per soil, was the same across all three water contents.

The Langmuir S_{MAX} parameter was regressed against the soils' clay content using ordinary least squares linear regression (Fit Y by X), and the k parameter was similarly regressed using linear regression after natural-log transformation of the k values (i.e., $\log(y)$ by x). Model performance was evaluated using the coefficient of determination (r^2) and significance parameter (p -value).

3. Results

Figure 1 presents ammonia retention by the investigated soils as a function of the final ammonia concentration in the gas phase and the soils' water content. Recall that three moisture contents were tested: oven-dryness, field capacity, and 50% AW (Table 1). The amount of NH_3 -N retained by the soil was calculated from its disappearance from the gas phase.

The NH_3 -N retention data were fitted to the Langmuir isotherm:

$$Q = \frac{k * S_{MAX} * C}{1 + k * C} \quad (1)$$

where Q is the amount of NH_3 -N that was retained ($mg\ kg^{-1}$ soil), C is the NH_3 -N concentration in the gas phase at equilibrium ($mg\ L^{-1}$), k is the Langmuir binding coefficient, a parameter related to binding strength or affinity ($L\ mg^{-1}$), and S_{MAX} is the apparent maximum retention capacity namely, the maximum NH_3 -N the soil can apparently retain ($mg\ kg^{-1}$). Equation (1) was fitted to each of the data sets presented in Figure 1, using the nonlinear regression of JMP 16 [25]. The S_{MAX} and k values thus calculated are presented in Table 2. As discussed below, the total retained NH_3 -N is the sum total of gaseous NH_3

taken up by the soil in multiple pools, including NH_3 physisorbed to solids, NH_3 dissolved in the soil solution, and NH_4^+ formed and retained via cation exchange.

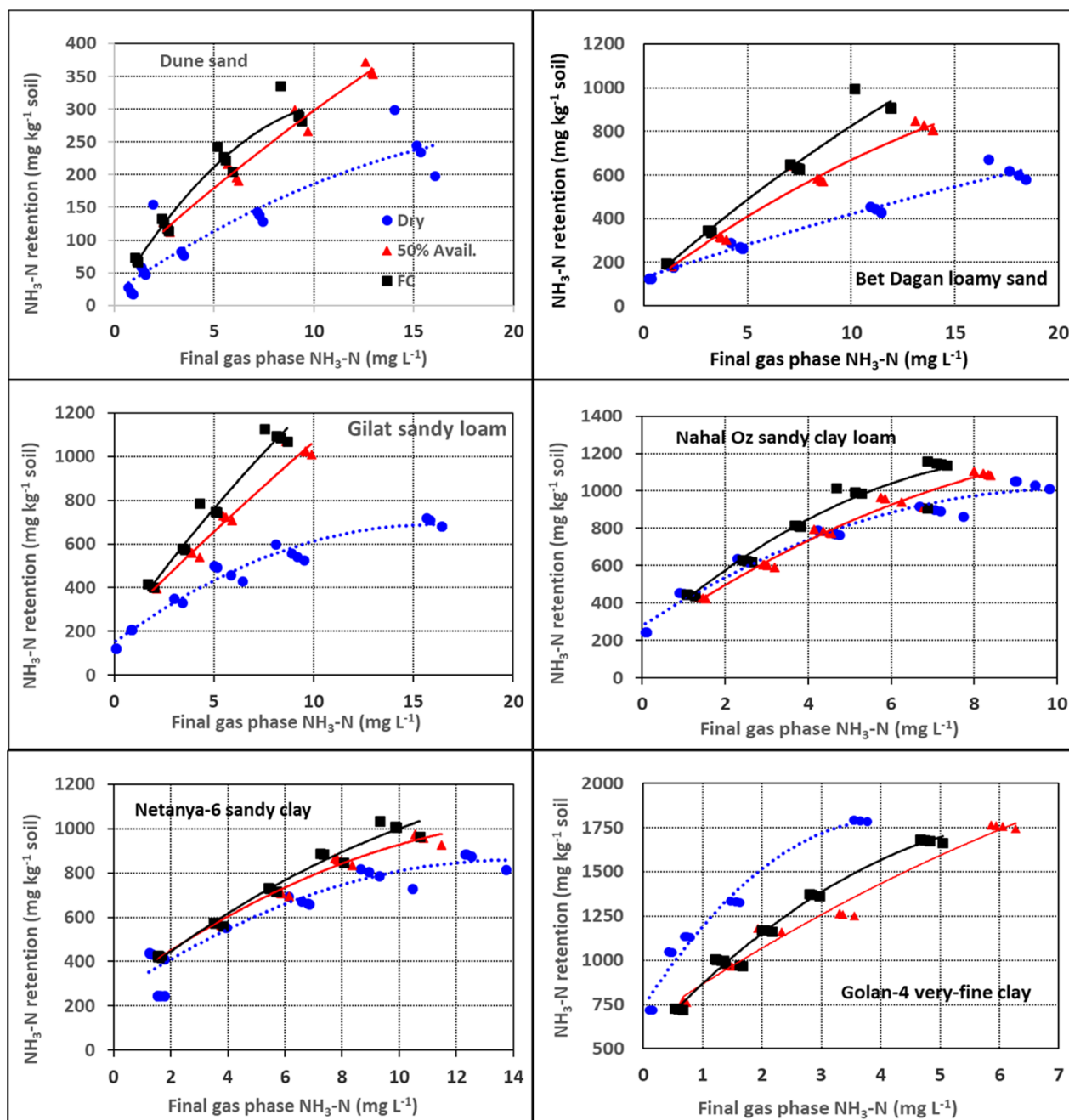


Figure 1. Ammonia retention by the six investigated soils as a function of the final concentration of ammonia (mg L^{-1}) in the gas phase and the soils' moisture content (oven dry, 50% of plant available water, and field capacity).

The S_{MAX} values (in $\text{mg NH}_3\text{-N kg}^{-1}$ soil) of the dry soils ranged from 440 ± 110 in the dune sand to 1732 ± 75 in the Golan soil (Table 2). The S_{MAX} parameter strongly and linearly correlated with the clay content ($r^2 = 0.946$, $p < 0.01$) (Figure 2). S_{MAX} increased with soil moisture content, but in the presence of a water phase, it correlated much less well with soil clay content (Table 2, Figure 2), probably due to the distinctive properties of the aqueous phase of the various soils. The k parameter ranged in the oven-dry soils from 0.08 in the dune sand to 4.31 in the fine-clayey Golan soil (Table 2), and it correlated strongly with the clay content of the soils (Figure 3; $r^2 = 0.859$; $p < 0.01$). The relationships

regarding the k values at the other two moisture contents are also shown in Figure 3. For most soils, the k value in the dry state was higher than in the moist state, and within each moisture content, the k tended to increase with soil clay content (Table 2 and Figure 3). This behavior of the k parameter seems to reflect ammonia's strong affinity for clay surfaces and the blocking influence of adding water on its binding affinity to solid surfaces [21,26].

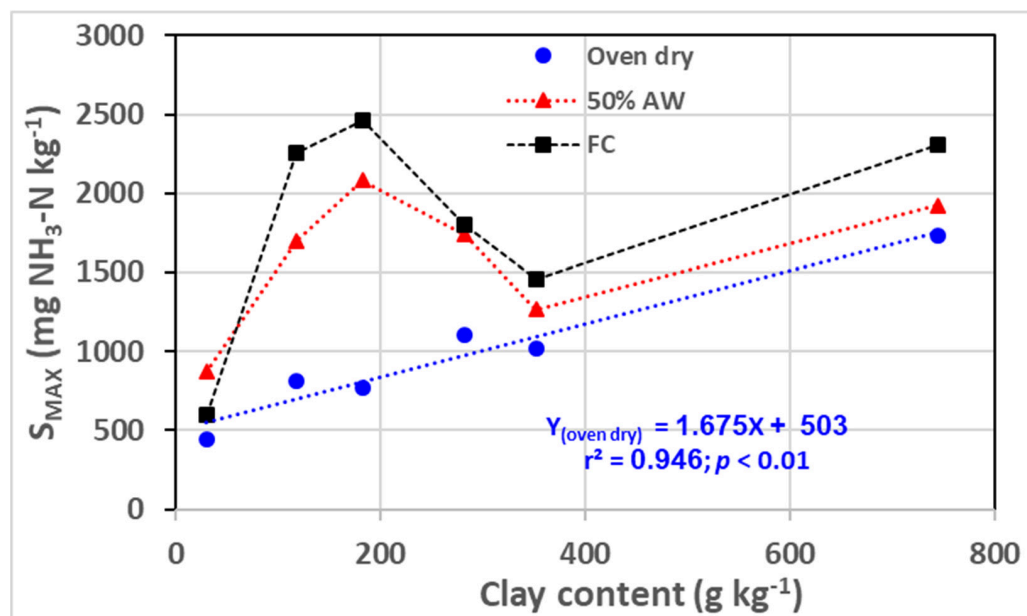


Figure 2. The relationship between the ammonia S_{MAX} (the Langmuir model's apparent maximum retention capacity) and the clay content of the six investigated soils. The soil moisture contents were oven-dryness, 50% of the available water (50% AW), and field capacity (FC).

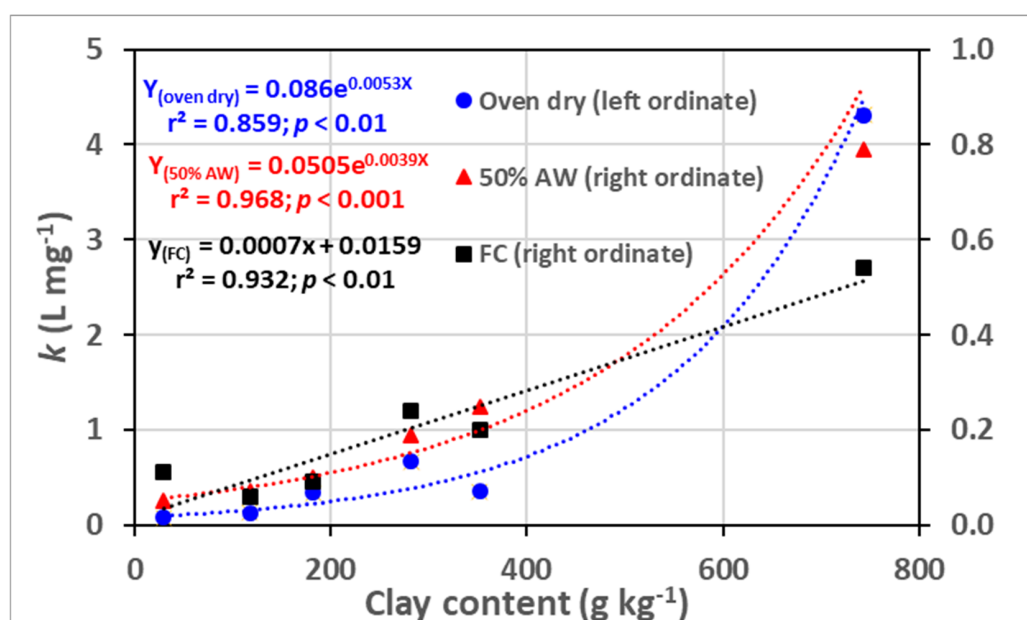


Figure 3. The relationship between the ammonia k (the Langmuir binding coefficient) and the clay and moisture contents of the six investigated soils. The soil moisture contents were oven-dryness (k units on the left Y-axis), 50% of the available water (50% AW), and field capacity (FC) (k units on the right Y-axis).

In general, significantly more of the applied ammonia was retained by the moist soil than by the same oven-dry soil at the range of ammonia concentrations investigated in the present study (Table 2). The only exception was the very fine clayey Golan soil, in which

ammonia retention in moist samples was lower than in oven-dry soil. This phenomenon is discussed in the Discussion section.

The above data demonstrate the primary role of the soil clay fraction in Mediterranean soils [24] in binding anhydrous ammonia to the soil's solid phase. The implication is that ammonia will be more available to crops (albeit via controlled release) in finer-textured soils, whereas in coarse-textured soils, most of the ammonia will remain in the gas phase and be susceptible to volatilization [27].

4. Discussion

A number of mechanisms were proposed to explain the uptake pattern of ammonia in soils. Thus, Nommik and Vahtras [19] proposed that this uptake occurs mainly through adsorption onto clay minerals and organic matter, via both physical adsorption and chemisorption. Physical sorption is reversible and usually takes place shortly after ammonia is added to the soil [19,27]. Chemisorption may become the dominant mechanism for the long-term uptake of ammonia in soils.

Some of the NH_3 taken up is converted in the soil to NH_4^+ , and that cation is being adsorbed mainly by organic matter and clays through cation exchange [28,29]. Yet, since the base dissociation constant of ammonium hydroxide (the product of ammonia association with pure water) is around 1.77×10^{-5} (though probably somewhat higher due to enhanced polarization at the soil–water interface [29]), indicating a weak base, only a fraction of that added ammonia, which was converted to NH_4^+ , is likely to exist in the soil system as the free ammonium cation (rather than as the ammonium hydroxide base). The size of this fraction will depend on the pH value of the soil solution following the application of the anhydrous ammonia. Nonetheless, it has been demonstrated that soils rich in clay or organic matter exhibit a high capacity for ammonia/ammonium uptake [29,30], indicating that ammonia per se is readily taken up by soil.

In mineral soils, such as those tested in this study, the role of organic matter in binding ammonia is expected to be overshadowed by the much higher clay mineral content. Also, another, often dominant, pathway for the retention of ammonia and its derivatives in soil (other than binding to the soil's solid phase) is dissolution in the soil's aqueous phase. This pathway is discussed below.

The Langmuir model was employed to quantify the extent of ammonia retention by the soils through the estimation of the S_{MAX} and k parameters (Equation (1)). Due to the complexity of the soil system (see Section 1), the use of that model for this purpose should be regarded as a phenomenological tool rather than a mechanistic description of the retention process. Accordingly, the Langmuir S_{MAX} and k are empirical, composite parameters—not solid-phase adsorption constants. Namely, the precision of the calculated S_{MAX} and k parameters should be assessed with the understanding that the Langmuir isotherm does not rigorously describe ammonia retention in soil. Also, in gauging the validity of the data in Table 2, one should consider the artificial inverse correlation between the k and S_{MAX} parameters that may be surmised from the structure of Equation (1). Thus, Freiberg et al. [31] pointed out a strong inverse relationship between S_{MAX} and the Langmuir binding coefficient (k) for phosphate binding in seven Mediterranean soils. In addition to the numerous ammonia retention modes existing in soils, k and S_{MAX} estimates may be biased by the fact that due to the relatively rapid conversion of NH_3 to NH_4^+ and vice versa, the Langmuir model is used here in an attempt to estimate the overall retention of a number of related species (the added NH_3 and its derivatives), rather than of the uptake of one sorbate by a solid medium containing one type of sorbing sites.

As shown in Table 2 and notwithstanding the above qualifications, a good fit was usually obtained between the measured data and the computed Langmuir isotherms.

Also, the S_{MAX} values obtained herein are consistent with published data. Thus, Khengre and Savant [32] reported an uptake capacity of $1620 \text{ mg NH}_3\text{-N kg}^{-1}$ soil, in a clay soil (CEC $53 \text{ cmol}_c \text{ kg}^{-1}$). Mineral soils with organic matter and clay contents of 20–90 and 80–560 g kg^{-1} , respectively, displayed ammonia uptake capacities of 425 to 1445 mg kg^{-1} soil [33].

It is stipulated that ammonia retention by dry soils occurs largely through strong H-bonding with the hydroxyl groups of the 1st hydration shell of cations on the surface of clay particles. Brown and Bartholomew [26] reported that dry clays (bentonite and halloysite) adsorbed more ammonia than the clays at 2.5% (W/W) moisture content. They concluded that the ammonia, which would have been sorbed on the dry clays, is replaced in the wetted soil by water molecules, which become part of the hydration shells of the positively charged species at the clay's surface. The hydration energy of the 2nd hydration shell of cations is apparently higher than the energy of interaction of the 1st hydration shell water molecules with ammonia, and hence, the exchangeable cations–ammonia interaction contributes more to ammonia uptake in the absence of an aqueous phase [21]. The above-discussed differences in binding energies are reflected in the steep reduction in the ammonia Langmuir binding coefficient (k) upon wetting the investigated soils (Table 2 and Figure 3). Yet, increasing the moisture content of the soils investigated in the current study increased the extent of ammonia uptake (due to dissolution in the aqueous phase) in all soils except for the very fine clay Golan soil (Figure 1).

The seeming contradiction between the effect of the moisture content on ammonia uptake by the Golan and by the rest of the soils is a consequence of the relative contributions of two competing pathways of ammonia retention in soils, namely sorption on the solid phase and dissolution in the aqueous phase. While ammonia can sorb onto the solid phase of the soil, it can also dissolve in the liquid phase. Ammonia is one of the most soluble gases in water (solubility at 25°C is 450 g L^{-1}). This is primarily due to its ability to form strong hydrogen bonds with the hydroxyl group of water. But, as discussed above, water molecules compete effectively with ammonia for adsorption on sites in the soil's solid phase and, in addition, water molecules occupy soil pores, blocking ammonia diffusion towards potentially binding solid surfaces. It is, therefore, suggested that adding moisture to the soils decreased the extent of ammonia adsorption to the soil solid phase, a decrease which is compensated for by ammonia dissolution in the expanding soil's liquid phase. Whenever the sorption on the soil's solid phase is high enough, such as in the Golan very fine-clayey soil (Figure 1), the dissolution of ammonia in the aqueous phase (when such a phase is present) may not be sufficient to fully compensate for the diminished adsorption—owing to competition with water—at the clay (or organic matter) surfaces. Thus, at the highest ammonia concentration added in the present study (40 mg N L^{-1}), the amount of ammonia dissolved was still insufficient to offset the steep decline in the amount adsorbed onto the clay-rich soil's solid phase. It is hard to predict at what clay content the phenomenon of decreased ammonia retention with increased moisture content will commence, among other reasons, since it depends on the nature of the clay surfaces. However, in montmorillonitic soils, our results indicate that this phenomenon starts to appear at clay contents greater than 35% but lower than 75% (Table 1 and Figure 1). Inasmuch as the difference in clay content between the very fine clay and the Netanya-6 soil (the soil with the next lower clay content tested in the present study) was rather large (Table 1), it is not possible to estimate more precisely at what clay content the inversion of the wetting effect on ammonia retention starts.

As is evident from the above discussion and the data summarized in Table 2, while in coarse and medium-textured soils, wetting will increase the amount of ammonia retained in the soil, wetting may have the opposite effect in fine-textured soils (Table 2). Yet, the

S_{MAX} values of the moistened Golan soil were higher than those of the same soil when oven-dried. This may seem at first like a paradox, but it simply implies that, had a sufficient amount of ammonia been added, the dissolved ammonia would have overcompensated for the reduction in the amount adsorbed to the solid phase. In the range of ammonia concentrations applied in the present study, even if all retained ammonia (Figure 1) were dissolved in the aqueous phase of the wetted soils, the concentration of dissolved ammonia (and the derivative ammonium) in the aqueous phase would have been, depending on the soil, in the range of 5–10 g L⁻¹. This is more than an order of magnitude lower than the aqueous solubility of ammonia.

The discussion concerning the role of clay in ammonia uptake should also hold for ammonia uptake by the soil's organic matter, of which the Golan soil is relatively rich (Table 1). H-bonds with ammonia molecules would, in this case, also be obstructed by competition for the adsorption sites on the organic matter between the ammonia and the water molecules in the water phase, when such a phase is present.

As shown above, both S_{MAX} and k for ammonia retention by the six investigated soils increased with the soil's clay content (Table 2). Accordingly, an inverse relationship between soil CEC and the extent of NH₃ volatilization from soils is expected, and, indeed, this has been demonstrated [20,27]. The former authors also reported that a significant reduction in NH₃ evaporation occurred only in soils with CECs above 25 cmol_c kg⁻¹. Others also published similar findings [34–37]. It should be noted, however, that in soils with low clay and organic matter content, a reduction in the rate of ammonia loss can be achieved, for example, by sprinkler irrigation over the soil after being treated with ammonia-forming fertilizers [38].

In summary, the properties of the solid phase of the soil (e.g., specific surface area, CEC, carbonate content, and solubility), and the properties of its aqueous phase (primarily pH and ionic strength and composition), will determine the extent to which injected anhydrous ammonia will dissolve in the soil solution or adsorb to the soil's solid phase. The added ammonia will partially convert to the cationic form, NH₄⁺, causing the pH to rise (to an extent determined by the buffer capacity of the soil solution) [39]. Both the NH₃ and NH₄⁺ forms will adsorb onto and dissolve in the soil, causing a significant portion of the added ammonia to be retained by the soil's non-gaseous phases. Accordingly, ammonia-based pest control (which may require a high concentration of NH₃ in the gas phase) will be both technically simpler and more cost-effective in light-textured soils. In medium-textured soils, it is preferable to apply ammonia for pest control when the moisture content is below field capacity (well after irrigation has stopped). At any event, the soil solution pH should be adjusted to exceed the pK_a of the NH₃/NH₄ system [15]. In heavy-textured soils, pest control via NH₃ addition should be avoided, given the high dose required for effective control. The actual quantity of ammonia to be added is, of course, dependent not only on the soil's properties but also on the sensitivity to ammonia of the target pathogen. Injecting anhydrous ammonia into heavy-textured soils may serve as an effective slow-release mode of N addition as a supplemental N fertilizer.

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Data Availability Statement: All relevant data are included in the paper. Additional data will be made available upon reasonable request.

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

Abbreviations

CEC, cation exchange capacity; FC, field capacity moisture content; 50–AW, 50% of the available water; k , Langmuir binding equilibrium constant; S_{MAX} , Langmuir apparent maximum retention capacity; WP, wilting point.

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