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Review

Too Salty or Toxic for Use: A Tale of Starter Fertilizers in Agronomic Cropping Systems

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Abstract: The rising shortage of fertilizer resources in crop-producing regions worldwide and the need for fertilizer use optimization to minimize the impact of salt injuries and ammonia toxicity are at the centre of a brewing storm call for sustainable fertilizer savings. The allocation of fertilizers will be an ever-increasing pressure source because of vast agricultural demands under changing climatic conditions. Therefore, starter fertilizers must complement their efficiency and aim to boost productivity and improve food quality to reduce its toxicities, and these observations are corroborated by an analysis of past and ongoing short-, medium-, and long-term experiments. Concurrently, to counterbalance nutrient uptake, fertilizing products containing select nutrients are commonly placed through soil–seed or soil–fertilizer–seed systems to enhance crop production and productivity. Knowledge of the importance of starter fertilizers and their implications as influenced by frequent environmental conditions and management practices remains essential for sustainable and socio-economics of human livelihoods and successful global agronomic food systems under climate change. Therefore, this review takes a closer look at the detailed starter fertilizers' (N, P, and K) placement approaches exploring their implications on crop production cycles and integrating them with environmental and agronomic management practices that could help to tailor the appropriate fertilizer recommendations and minimise fertilizer toxicity. We explored the mechanisms by which fertilizer salt injury and ammonia toxicity interfere with the morpho-physiological and biochemical processes in most agronomic seed crops. Beyond this, we show the advances that have already been made, as well as suggestions and recommendations concerning managing fertilizer salt injuries and ammonia toxicity potentials in the agricultural industry.

Keywords: agronomic crops; ammonia toxicity; salt injury; starter fertilizers; sustainable food systems

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1. Introduction

The world's human population has increased four times in the last century alone. This booming demography, partly due to improved agricultural and industrial techniques, places continued pressure on food production to feed the growing numbers [1,2]. Therefore, agricultural intensification is required to provide for the growing and increasingly demanding human population, and this entails increasing substantial fertilizers use and other inputs, applied as efficiently as possible, i.e., with a concurrent increase in resource use and resource use efficiency [1]. Despite the advantages of fertilizer application, increased emphasis is now being placed on the problem of plant damage, which takes a toll on both the health and quality of agricultural soils and crops [2–4]. With an understanding that most agronomic crops are the main global food sources for human consumption, a considerable gap still exists where access to fertilizers and their efficient use are among the major significant challenges towards ending poverty, hunger and improving human health [5,6]. These fertilizers are one of the greatest consumptive materials that, when applied to the soil, can affect the seeds or seedlings through soil–fertilizer, seed–fertilizer, or soil–fertilizer–seed placement systems (Figures 1 and 2) [7]. Starter fertilizers, which are "foster fathers" that contribute to improved crop seed-seedling establishment and development and enhance sustainable food production systems, have recently gained significant global courtesy on their placement since The Green Revolution [8–10]. However, its detrimental effects on seed-crop growth and development have drawn international attention due to fertilizer salt injury and ammonia (NH_3) toxicity being associated with different fertilizer salt indexes, NH_3 production, and various susceptible plant developmental stages [11–13]. In the meantime, increasing crop productivity per given area of land to meet future food and fibre demand increases soil nutrient removal, which determines the importance of replenishing soil fertility through efficient use and placement of starter fertilizers without damaging the seed and/or seedlings, and this becomes astronomical in the sustainability of agricultural systems, food, and nutritional security [14,15].

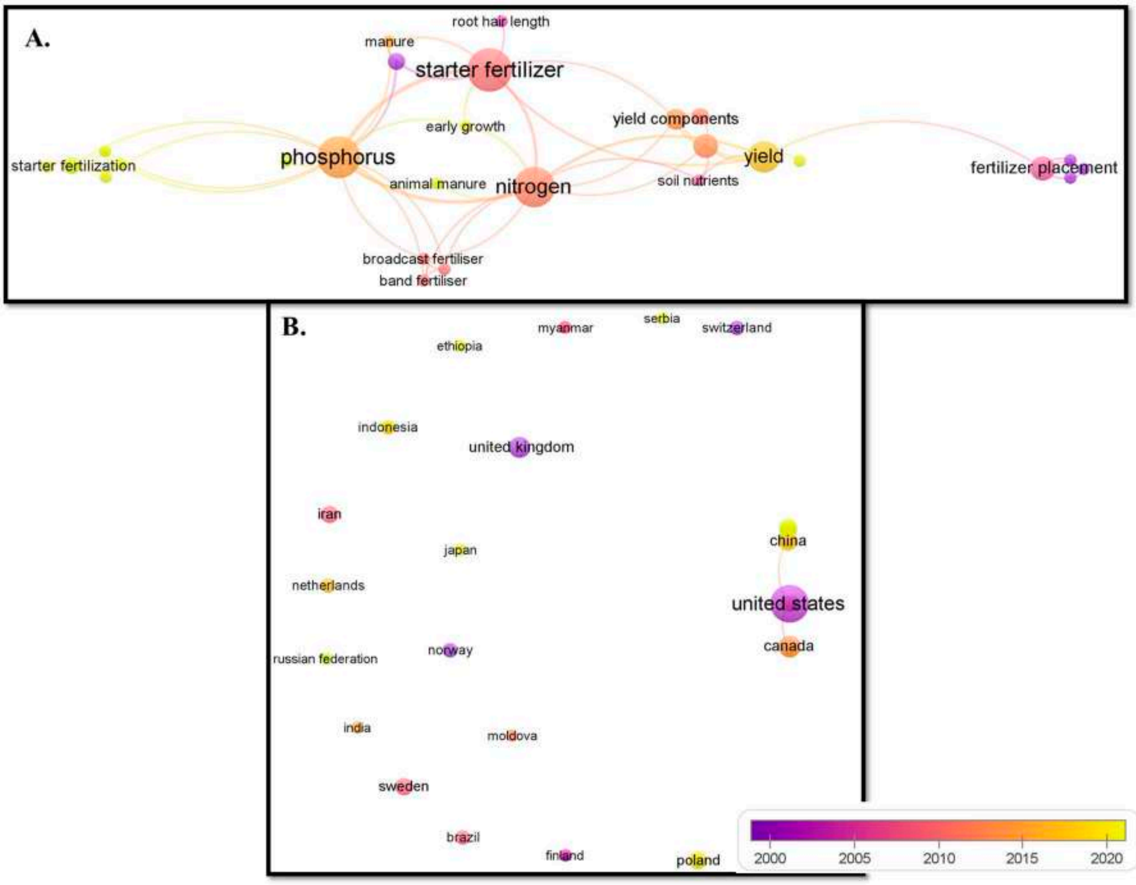

Figure 1. (**A**) Authors keywords maps: Global network-overlay visualization of authors' keywords co-occurrence and thematic evolution in research on starter fertilizer placement on agronomic crop production. (Map produced by VOSviewer); (**B**) Country collaboration network researching starter fertilization in agronomic crop production and productivity. A and B were prepared following the screening criteria of relevant papers about starter fertilizer toxicity, with pertinent focus on fertilizer salt and ammonia toxicity. This resulted in generating a total number of 490 research articles reported in the Web of Science and Scopus, out of which 210 were universally related to all aspects of fertilizer toxicity on soil and crop production and productivity.

The fundamental role of starter fertilizers in providing immediate nutrient access to emerging crop roots, increasing the concentration of relatively immobile nutrients (P and K) in the rhizosphere, improving early-season nutrient uptake, inducing root growth and favourable rhizospheric compounds, limiting nutrient losses and enhancing crop production and productivity is well documented [9,16–18]. Learning from the soil's memory, starter fertilizers take advantage of placement, formulation, and timing to impact seed-crop growth and development [17,19–21]. These different starter fertilizer placements include broadcast, banded (subsurface) starter, or in-furrow (fertilizer–seed contact or pop-up), and a combination of banded and seed placement (Figure 2), which are super-imposed based on various fertilizer recommendations [22–25]. However, little is known pertaining to the fertilizer placement rates that provide safety to the seeds and seedlings due to variability in fertilizer toxicity levels.

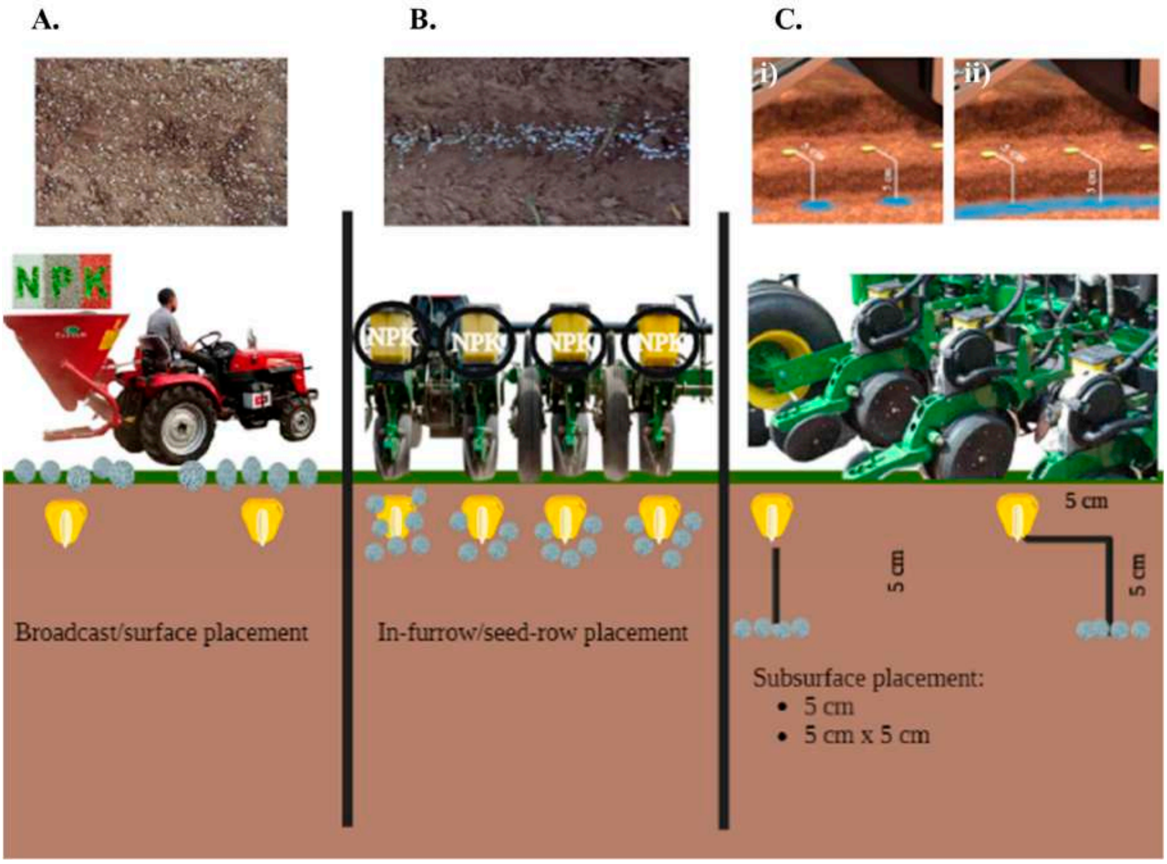

Figure 2. Most typical methods of placing starter–fertilizer in the soil. (**A**) Broadcast placement using a trailed and mounted machine; (**B**) in-furrow placement using a seed-drill tractor-mounted system; (**C**) (**i**) 5 cm below the seed (**ii**) 5 cm away from the seed × 5 cm below the seed (5 cm × 5 cm) placement (**C**(**i**,**ii**) were adapted from Drazic et al. [26]).

The awareness of fertilizer toxicity, which encompasses both inorganic fertilizers and organic-rich amendments capable of generating high salt and NH_3 levels with the potential to elicit toxicity symptoms, has been outstanding since the 1920s when the whole crop production cycle was affected beyond sustainability boundaries [11,27–29]. This brought an interest in establishing and standardizing fertilizer salt indices and their potential NH_3 toxicity [30,31]. The objective was to capacitate agronomists, practitioners, farmers, the fertilizer industry, fertilizer dealers, researchers, and politicians about the consequences of placing N-P-K fertilizer near seeds and seedlings with an increasing focus on the effectiveness of fertilizer use for different placement methods, as well as providing an economical and convenient operation [24,32–34]. However, extra attention is required to avoid seed and seedling damage due to the magnified fertilizer salt accumulation, NH_3 production, and toxicity within the seeding zone from different formulations and sources [24,35,36]. The reason is that most established fertilizer–salt-index table references [30] are currently misleading [37].

From the fertilizer scientist's perspective, improper fertilizer recommendation, placement, and management in crop production may become the primary factors limiting global plant stand and its establishment, with the most substantial consequences in crop yields. Therefore, efforts to improve crop stand and lessen the severity and incidence of salt injury, pH changes in the seed germination zone, and ammoniacal-N toxicity needs balanced starter fertilization, which becomes the fulcrum for sustainable global food crop production [5,6,11,19,38,39]. Knowledge of the importance of starter fertilizers and their implications as influenced by frequent environmental conditions and management practices remains essential for sustainable and socio-economics of human livelihoods for successful global food production and productivity under climate change. Therefore, in this review, we aim (i) to provide a comprehensive review of broadcast, in-furrow, and subsurface N-P-K fertilizer placement methods and their effects on agronomic production cycles and toxicity risks engendered by these fertilizers; (ii) to summarize the mechanisms of fertilizer toxicity on the phenological and biochemical response of crops focusing on salt injury and NH_3 toxicity; and (iii) to establish the alleviation and/or mitigation measures that counterbalance the effects of salt injury and NH_3 toxicity. This manuscript's motivation was to help navigate between historical and new concepts of starter–fertilizer placement implications on sustainable agricultural cropping systems and to help all stakeholders tailor adapting good fertilization practices.

2. Starter N-P-K Fertilization Placement and Its Efficiency on Crop Production Cycles

2.1. Broadcast Effects on Agronomic Crop Development

The importance of fertilizer placement is not expected to be the same for N as for P and K due to their different chemical properties determined by different soil test levels [34,36,39]. This, in turn, affects crop response under various fertilizer sources/types, placements, and rates (Table 1). Also, the efficiency of typical starter–fertilizer placement methods depends highly on soil physicochemical characterisation where soil test P (STP) and soil test K (STK) levels have a pivotal role. One ex ante study obtained an increased winter-wheat (*Triticum aestivum* L.) yields when starter N, P, and K fertilizers (urea: 45 kg N ha^{-1}; TSP: 0-45-0, 20 kg P ha^{-1} and muriate of potash (MOP): 0-0-50 at 37 kg K ha^{-1}) were broadcast and incorporated as compared to when pre-plant P applied alone followed by the top-dress N application [40]. Corresponding findings indicated that broadcasting 22 kg ammonium sulphate (AS) ha^{-1} was ideal for early rice (*Oryza sativa* L.) establishment when applied to Sharkey clay (very fine, smectitic, thermic Chromic Epiaquerts) soils prior to field flooding [41]. It is interesting to note a 34% increment in early maize (*Zea mays* L.) establishment and growth and 2.4% yield increase under low STP (<16 mg kg^{-1} Bray-1 P) following P (61–114 kg P_2O_5 ha^{-1}) and K (108–145 kg K_2O ha^{-1}) broadcast [42–44]. Remarkably, broadcast applications of K were 73% as effective as in-furrow placement and significantly contributed to reduced maize lodging, especially at low STK values (<163 kg K_2O ha^{-1}), and vice versa when fertilizer K rate or STK increased [45]. These findings contradict placing fertilizers on horticultural crops; for instance, broadcasting calcium ammonium nitrate (CAN) at 125 and 250 kg N ha^{-1} equivocally caused a reduction in vegetable crop establishment (calabrese [*Brassica oleracea* L.], carrot [*Daucus carota* L.], onion [*Allium cepa* L.], and red beet [*Beta vulgaris* L.]) whilst P or K fertilizers (applied at 126, 252 kg P_2O_5 ha^{-1} and 127, 253 kg K_2O ha^{-1}) had optimum plant establishment, respectively [46].

2.2. In-Furrow Fertilizer Placement Effects

In-furrow placement is recognised as the most effective method for starter fertilization in most agronomic crops and has been acknowledged in the historical wheat varietal development program (1920–2016), where an average yield increase of 200–400 kg ha^{-1} irrespective of the variety release year was recorded, whilst grain N-removal increased nonlinearly with the year of release, which significantly increased between 1966 and 2000 [47]. Seed-placed NP starter fertilizer in southern Indiana soils enhanced early growth and increased maize yield in both ploughed and no-tillage systems at low P and K pre-plant fertilization on low STP and STK [48,49]. This corroborates with Wortmann et al. [44], who revealed a 48% maize increase in early establishment and growth in 5/7 trials with low STP (Bray-P1 $\leq$ 15 mg kg^{-1}) following seed-placed N + P and N + P + S. Likewise, Bermudez and Mallarino [50] globally obtained 27% early-season growth, 1.1% maize grain-yield increase, and 30% plant N and P uptake respectively. Contrary to dribble over-the-row and subsurface placement, $\geq$22 kg N ha^{-1} in the in-furrow significantly reduced plant stand and had little maize yield benefits [23]. In addition, 50 kg DAP ha^{-1} in-furrow fertilization placement using a knife point furrow opener at 28 cm row spacing reduced wheat plant establishment by nearly 20% and yielded from 3.94 to 3.44 t ha^{-1} [51,52]. In pulse crops, their sensitivity to different rates and starter N fertilizers varied among the species. For instance, lentils (*Lens culinaris* L.) had a minor plant establishment when in-furrow (10 kg N ha^{-1} rate) placed (sourced from MAP + urea and MAP + AS), followed by pea, chickpea (*Cicer arietinum* L.), soyabean, black bean (*Phaseolus vulgaris* L.), and faba bean, respectively [53]. Seed-placed ammonium polyphosphate (APP: 10-37-0) on commerce silt loam soil (STP: 130–150 mg kg^{-1} Bray-1 P) had 2–36% maize plant height increment, reduced silking-interval by 3–5 days, 5–10% increase in grain yield and 7–14 g kg^{-1} grain moisture content reduction [54–56]. A low rate of liquid in-furrow starter fertilizer placed on Lamberton (average pH 5.5 and 17 Bray-1 P year^{-1}) and Waseca (pH 6.4 and 18 Bray-1 P year^{-1}) loam soils increased early-season maize establishment, height, decreased time to silking and maize grain moisture at harvest [57–59]. On the other hand, 93.5 L APP (10–34–0) ha^{-1} seed-placed fertilizer in sandy soils strongly reduced maize establishment whilst the placement of 4-10-10 and 3-18-18 had no impact on plant establishment [60]. A three-year experiment that evaluated agronomic and economic responses of maize to in-furrow starter fertilizer (65 kg ha^{-1} of 10-34-0) for hybrids reflected an improved maize crop uniform establishment [59]. This agrees with Kaiser et al. [57], who showed a more significant response to in-furrow starter fertilizer when Bray-P1 STP was <16 mg kg^{-1}. These findings suggest that the combination of N, P, and K fertilizer products may impart some additional seed safety requirements concerning fertilizer toxicities.

2.3. Subsurface Starter N-P-K Fertilization Placement

On subsurface placement, determining the proper depth plays a pivotal role in minimizing environmental-related issues (e.g., greenhouse gas: NH_3, N_2O, or CH_4 emissions; eutrophication) and reducing the competitiveness of weeds in crops [61–63]. For example, starter N fertilizer (classical and slow-release urea) deep placement reduced CH_4 emissions in comparison with surface broadcasting [64], which is a result of an increase in CH_4 oxidation stimulated by the high NH_4^+-N in localized bands and promoted by root growth in the deep soil [65,66]. The use of a self-propelled spoke wheel applicator to inject and deep place liquid fertilizer dissolved from crystalline of $(NH_4)_2HPO_4$ (21-53-0) has increased maize establishment, production, and productivity [67]. In the cane study, maximum yields were observed when a cam-crank rocker combination mechanism deep placed the liquid fertilizer (ammonium nitrate mixed with water: 0.21 kg N L^{-1}) at a rate of 100 kg N ha^{-1} [14,68,69]. Nash et al. [70] endorsed that deep band placement of N fertilizer in a strip-tillage system produced significantly greater maize emergence, establishment, and yield, especially in poorly drained claypan soils. Comparative studies indicated an increasing rate of early-season growth of maize at the 3-leaf stage to 4-leaf stage, which was proportional to 0–24 kg N ha^{-1} starter fertilizers (AN and urea) following 5 cm $\times$ 5 cm placement [18,57,71,72]. In low STP (<15 ppm M_3) and STK soils, 5 cm $\times$ 5 cm P and K fertilizers (10-20-10; 16-40-53 and 15-20-18) applied at 37 kg ha^{-1} were ideal for 107.6 kg ha^{-1} global soyabean (*Glycine max* L.) yield benefits compared to high STP and STK levels from any fertilizer placement [73]. Nevertheless, similar predominant Corn Belt soils (16–20 mg P kg^{-1} Bray-P1 or 90–130 mg K kg^{-1} M3P) had registered the maximum soybean yield benefits from broadcast P and K fertilizers ([liquid: 3–18–18 at 12–16 kg P_2O_5 ha^{-1} and 12–17 kg K_2O ha^{-1}, granulated P-K: 112–151 kg P_2O_5 ha^{-1}, 135–169 kg K_2O ha^{-1}]) [57]. Likewise, seed-^{15}N urea placement (5 cm × 10 cm) at the range of 60–240 kg ha^{-1} resulted in ≥10% wheat yield gain, with better nutrient uptake and recovery of total N [74]. An empirical study by Vann et al. [28] registered that banded organic materials (feather meal and poultry litter: 80 and 12 kg N ha^{-1}) following a rye and hairy vetch cover crop yielded less grain and N uptake than a no fertilizer treatment. In terms of the crop nutrient recovery, banded urea-^{15}N applied to wheat at the rate of 60 kg ha^{-1} had higher N recovery compared to 240 kg ha^{-1} [75] and this was consistent with the work of Ju et al. [76], who found 54% N recovery at 120 kg N ha^{-1} and 32% at 360 kg N ha^{-1} when deep placed. On the contrary and in comparison, with 8-cm deep placement, cattle slurry combined with $(^{15}NH_4)_2SO_4$ placed in a thick-centred layer 2 or 5 cm below the seed did not affect nitrogen use efficiency (NUE) and ^{15}N recovery [77].

Concerning P and K starter fertilization, a preliminary two-year field study (characterized by pH_{water} 5.72, organic matter 18.25 g kg^{-1}, total N 1.10 g kg^{-1}, 18.23 mg kg^{-1} Olsen-P, 80.26 mg kg^{-1} exchangeable K [0–30 cm]) that examined the effect of banded-placement of N-P-K fertilizer had shown that 10–15 cm subsurface placement of urea (180 kg N ha^{-1}), calcium superphosphate (92 kg P_2O_5 ha^{-1}) and KCl (120 kg K_2O ha^{-1}) produced greatest taproot length and dry weight [78]. A long-term study (1970–2015) compared banded and broadcast P applications where banding increased with yield potential; for example, a P placement rate of ≤44 kg P_2O_5 ha^{-1} had a 0.49 t ha^{-1} maize grain yield advantage over broadcasting P. In a 5 cm × 5 cm P placement, three Illinois soils had much greater P use efficiency under low STP whilst broadcast had the maximum P use efficiency at high subsoil test P soils [79–81].

Borges and Mallarino [82] studied the deep-K band placement method for maize, where they observed maximum grain K uptake on the subsurface band on 14 out of 15 experimental sites over the broadcast K. Such comparative advantages could be attributed to the facts that subsurface starter fertilizer placement saturates the soil solution with nutrients especially slowly mobile nutrients such as P within the rhizosphere [83]. This can reduce the fixation and adsorption of P by soil particles, thereby increasing P availability [84,85]. When starter fertilizer is deep-placed, relatively greater water availability in the soil subsurface will enhance P solution and P transport, which also favours higher P availability [64,78]. Localized N and P nutrient concentrations resulting from banding fertilizer can stimulate root development and establishment of virtually ideal root architecture, thus increasing crop nutrient uptake and yield [11,78,86]. Regarding the maximum seed germination, early nutrient use efficiency, and crop productivity, a compromise must be reached between soil volume fertilized and root distribution to optimize chances for root–fertilizer contact and minimize P fixation [22,87–89]. These findings generally demand the understanding of fertilizer salt injury and NH_3 toxicity implications of crop productivity, which has become a human issue. Socio-economically, very few studies revealed the income generation from starter NPK placement in relation to crop productivity. It is worth mentioning that the response of grain sorghum (*Sorghum bicolor* L.) to starter NP liquid fertilizer placed 5 cm × 5 cm at 34 or 100 kg N ha^{-1} (1:1 and 3:1 N: P_20_5 ratios) resulted in 22% sorghum grain yield gain with over US$82 ha^{-1} profit [89–91].

Table 1. Summary of the crop response to different starter fertilization placement.

Crop	Fertilizer Salt Concentration and Its Application Rates	Mode of Placement	Crop Response
Cotton (*Gossypium hirsutum* L.)	calcium nitrate [$Ca(NO_3)_2$]: 0 17, 34, 68, and 102 L ha^{-1}	In-furrow; and broadcast	17, 34, or 68 L of $Ca(NO_3)_2$ ha^{-1} increased total yields on the two soils and can be applied in-furrow without reducing yields [92].
	APP solution (10-34-0; 10-34-0 + 32-0-0): 85 and 85 + 63 L ha^{-1}; urea ammonium nitrate (UAN) solution: (32-0-0; 28-0-0–5 (S)) 91; 103 L ha^{-1} respectively; CAN solution (9-0-0-11 (Ca): 85 L ha^{-1}	5 cm × 5 cm	Increased total shoot N and Ca, leaf area index, and shoot dry weight with starter fertilization from UAN compared to APP with no yield differences between fertilizers [93].
Soyabeans	Urea (34 kg N ha^{-1}), TSP (45 kg P_2O_5 ha^{-1}), Urea + TSP, DAP (45 kg P_2O_5 ha^{-1} and 18 kg N ha^{-1})	5 cm × 5 cm	Maximum seed establishment with minimal effect of starter fertilizer on soybean nodulation, biomass, canopy closure, and grain quality because soil with P > 15 ppm did not respond to starter fertilization on soybean yields, whilst DAP and urea reduced the number of nodules/roots [94].
	Urea (46-0-0): 0, 30, 60, and 90 kg N ha^{-1}; 137 kg P_2O_5 ha^{-1} and 72 kg K_2O ha^{-1}	Subsurface	60 kg N ha^{-1} increased plant height, first pod height, number of nodes, number of pods per plant, and seed yield) whilst 90 kg N ha^{-1} increased protein content [95].
	Research fields: P and K broadcast: 275 kg P_2O_5 ha^{-1} and 337 kg K_2O ha^{-1} (all applied ones). Banded: 32 and 64 kg P_2O_5 ha^{-1}; and 40 and 72 kg K_2O ha^{-1}; Farmer's fields: P and K broadcast: 275 kg P_2O_5 ha^{-1} and 337 kg K ha^{-1} (all applied ones). Banded: 32 or 128 kg P_2O_5 ha^{-1} and 40 or 159 kg K_2O ha^{-1}	broadcast; banded (15–20 cm deep); 5 cm × 5 cm	P fertilization increased yield on STP < 12 ppm (Bray-P1) at 0–15 cm depth and 0–7.5 cm. Banded K placements produced a slightly higher yield than the broadcast but were unrelated to STK. The P or K placement had little influence on early establishment but increased early P and K uptake whilst P-K banded increased plant dry weight but was site-specific [96].
	Urea: 0, 25, 50, and 75 kg N ha^{-1}; 40 kg P ha^{-1} (TSP) and (20 kg K ha^{-1} KCl	5 cm × 5 cm	Starter N fertilizer benefited root activity, leaf photosynthesis, and consequently, its yield where 25–75 kg N ha^{-1} increased grain yield by 1.28 and 0.62%, 2.47 and 2.77%, and 1.58 and 2.06% in 2 seasons, respectively, but 50 kg N ha^{-1} had the maximum grain yield of 3238.91 kg ha^{-1} and 3086.87 kg ha^{-1} over two seasons [97].
	Starter N: AN and Urea: 0, 8, 16, and 24 kg N ha^{-1}). P and K: 17 kg P ha^{-1} (TSP) and 12 kg K ha^{-1} (KCl)	5 cm × 5 cm	Starter N increased grain yield, early (V3–V4 and R1) plant biomass (6% increase), and plant N uptake, especially at 16 kg N ha^{-1} rate, compared to the no N treatment, but no difference in grain N or oil concentration [71].
	P rate: 0, 12, 24, and 36 kg P ha^{-1} yr^{-1}; K rate: 0, 42, 84, and 168 kg K ha^{-1} yr^{-1}	15 cm deep placement	Banding in strip-till produced 3100 kg seed ha^{-1}, 10, and 7% more yield than no-till broadcast and banding, respectively. Also, seed yield, the number of pods plant^{-1}, and trifoliate P concentration and accumulation increased with P fertilization and placement, whilst K fertilization decreased seed yield in no-till systems but not in the strip-till system [85].

Table 1. *Cont.*

Crop	Fertilizer Salt Concentration and Its Application Rates	Mode of Placement	Crop Response
Canola (*Brassica napus* L.)	DAP (18-46-0): 0, 17, 34, 51, 67, and 84 kg DAP ha^{-1})	In-furrow; no-tillage	71% stand count reduction with seed-placed DAP, but it did not impair grain yield due to canola's ability to compensate for open areas via branching, and up to 84 kg ha^{-1} with seed may be possible [98].
	DAP (18-46-0): 25 and 34 kg ha^{-1}	In-furrow; no-tillage	Soils with low STP and low soil pH generally had higher yield responses (201.75–403.5 kg ha^{-1}), but oil (39.9–42.8%) and protein (20.43%) content were similar under DAP and check [98].
Pea (*Pisum sativum* L.)	Urea; slow-release polymer-coated N fertilizer (ESN): 0, 22, 44 and 88 kg ha^{-1}	In-furrow	The positive effect of starter N was only pronounced when initial soil N was low ($\leq$10 kg ha^{-1} NO_3-N) and increased net return by up to USD 42 ha^{-1}, but urea hurt pea establishment, vigour, and seed yield when soil initial N was high ($\geq$44 kg ha^{-1} NO_3-N) and ESN outperformed urea [99].
Maize	Conventional urea (NCU); Polymer coated urea (PCU); anhydrous ammonia (AA) for140 kg N ha^{-1}	deep banding; broadcast; injected AA	Injecting AA into a no-till soil at pre-plant produced at $\geq$2 Mg ha^{-1} maize yields whilst broadcast was not a viable management system for maize production. Also, PCU over NCU is maximized due to minimum NH_3 production potential [70].
	Starter P placement: TSP (0-45-0) (broadcast); liquid APP (10-34-0)-subsurface: 46 kg P_2O_5 ha^{-1} and 89 kg P_2O_5 ha^{-1}	both broadcast and 5 cm × 5 cm	Starter P fertilizer increased crop plant P uptake, ear leaf P, grain P concentration, and yield under low STP. However, combining broadcast and deep-band P fertilizer had a more significant crop response [99].
	Compound fertilizer (100 kg N ha^{-1}, 70 kg P_2O_5 ha^{-1} and 130 kg K_2O ha^{-1})	broadcast vs. subsurface (5, 10, and 15 cm)	Plant emergence and stand (average of 7.687 plant m^{-2}) decreased with the depth of NP fertilization in the soil profile, whilst a 10 cm deep place stabilized the number of plants after emergence [100].
	UAN (28-0-0): 140 kg N ha^{-1} + 30 kg P ha^{-1} TSP (0-46-0) and 58 kg K ha^{-1} KCl (0-0-60)	broadcast UAN; dribble UAN; 10 cm deep placement	N fertilization at any placement method increased maize yield components (kernels per ear, grain yield), but maize yield increase to subsurface band (knife) N applications was about 10% higher than broadcast [101].
	Cattle Slurry (CS) spiked with $(^{15}NH_4)_2SO_4$	subsurface: 2, 5, or 8 cm below the seed	Higher maize biomass and P uptake at the 5-leaf stage were recorded after placing CS in a thick-centred layer 2, or 5 cm below the seed than at 8 cm, whilst 21% maize biomass increased when slurry was placed in a thinner layer covering the whole pot area [77].
	Liquid Starter mixtures: 65 kg ha^{-1} (7-9.1-5.8; 6-10.5-20; 10-14.8-0; 7-9.1-5.8; 7-7.9-5; 6-7.9-5); 10-14.8-0 (74; 86; 91; 163 kg ha^{-1}); 170 (16-10-2.5-1) kg ha^{-1}	Uniform P and K broadcast; in-furrow; 5 cm × 5 cm	Starter fertilization increased yield (200–671 kg ha^{-1}) and often increased early growth in low STP soils. Also, yield responses in high STP were small (80–194 kg ha^{-1}) when the starter was applied in the furrow and larger (165–465 kg ha^{-1}) when it was applied at 5 cm × 5 cm at higher N rates (16.3–27.2 kg N ha^{-1}) [42].

Table 1. *Cont.*

Crop	Fertilizer Salt Concentration and Its Application Rates	Mode of Placement	Crop Response
	Starter N (Urea): 30 kg N ha^{-1}. Starter P (TSP) and manure P rates: 0, 5, 10, 15, and 20 kg P ha^{-1}; Manure P: 0, 35, 30, 25, 20, and 15 kg ha^{-1}	5 cm × 5 cm	Starter P fertilizer increased silage maize dry matter yield at the 6-leaf stage when low starter P and high side-dressed manure P additions. Current starter P (30–40 kg ha^{-1}) recommended for maize can be reduced by up to 75% (5.0–7.5 kg ha^{-1}) without affecting yield, thus reducing annual P inputs and farmers' production costs [102].
	P fertilizer (10-34-0): 0 and 65 kg ha^{-1}. Broadcast supplements: 157 kg N ha^{-1} as $CO(NH_2)_2$ and 16.8 kg S ha^{-1} as $CaSO_4{\cdot}2H_2O$.	in-furrow	In-furrow fertilization increased early-season plant height and kernel mass and decreased days to silking, grain moisture at harvest, and kernel m^{-2} [59]
	DAP (18-46-0): 25 and 34 kg ha^{-1}	conventional band	Yield increased by 6–7% with the same fertilizer input with a yield-neutral savings potential of up to 50% of the current starter fertilizer application by the more precise fertilizer application [103].
	UAN: 0, 28, 56, and 84 kg ha^{-1}	5 cm × 5 cm	Yield was unaffected by starter N at two sites, whilst 56 or 84 kg N ha^{-1} increased yields at the third site. Starter N could increase early-season N uptake and early crop growth relative to no starter but had an inconsistent impact on maize yields [104].
	Starter N; for in-furrow and dribble: 11, 22, 45, and 56 kg N ha^{-1}; for 5 cm × 5 cm: 34, 67, 101, and 134 kg N ha^{-1}	In-furrow, dribble over-the-seed, 5 cm × 5 cm	Starter fertilizer increased early season dry matter production and grain yields; ≥22 kg N ha^{-1} in-furrow reduced stands and automatically reduced the yields; Plant stands were unaffected, with higher N rates in dribble over-the-row and subsurface [23].
	Initial N and K broadcast: 315 kg N and 270 kg K_2O ha^{-1}; Starter P fertilizer: 105 kg P_2O_5 ha^{-1} (TSP)	subsurface band (5, 10, 15, and 20 cm)	15 cm depth placement induced a larger root length density and rooting depth; higher number of root cortical aerenchyma, combined with larger cortical cell size, which reduces the metabolic cost required to establish them, which drives regulation processes and results in the allocation of more biomass to root proliferation; maximum biomass, N and P accumulation/assimilation, and 22% grain yield increase were established at 15cm depth; 74% P recovery efficiency, 150% P agronomic efficiency, and 21% for both the partial factor productivity of P and the partial factor productivity of N were at maximum at 15 cm depth [105].
	Starter N: AN and Urea: 0, 8, 16, and 24 kg N ha^{-1}). P and K: 17 kg P ha^{-1} (TSP) and 12 kg K ha^{-1} (KCl)	5 cm × 5 cm	High yield increases only with starter-N whilst starter P and K both increased yield, oil production, and N removal in all years [33].
	anhydrous ammonia (NH_3), UAN, urea, and AN: 0 and 165 kg N ha^{-1}	injected ammonia; broadcast; and 20 cm deep UAN	Injecting NH_3 or UAN below the surface resulted in consistently higher maize grain yields; %N in leaf and grain reflected an increase in N use efficiency with subsurface N placement, and %N in leaf was higher where N or UAN were injected than UAN or urea surface applied [106].

Table 1. *Cont.*

Crop	Fertilizer Salt Concentration and Its Application Rates	Mode of Placement	Crop Response
	Starter P-K and K fertilizers: 3-18-18: 5–7 kg P ha^{-1} and 10–14 kg K ha^{-1}, 0-0-30: 10–14 kg K ha^{-1}; broadcast fertilizer: 49–66 kg P ha^{-1} and 112–140 kg K ha^{-1}	in-furrow	Starter P-K applied in addition to broadcast P-K increased growth and P and K uptake compared with broadcast P–K but did not increase yield. K seldom had a starter effect on maize [107].
	Starter NP fertilizers: digestate (manure): 202 kg N ha^{-1} and 69 kg P_2O_5 ha^{-1}; DAP: 27 kg N ha^{-1} and 69 kg P_2O_5 ha^{-1}	deep-injection- digestate (DIG) subsurface placed	Starter fertilization with DAP recorded the best early vigour and canopy development. DIG and DAP led to earlier flowering, with similar and higher grain yields (+1.8 and +1.6 Mg ha^{-1}), but DIG application led to a higher grain protein content [16].
	Liquid Starter fertilizer: 3-18-18: 5–7 kg P ha^{-1} and 10–14 kg K ha^{-1}; Granulated P-K fertilizer broadcast: 49–66 kg P ha^{-1} and 112–140 kg K ha^{-1}	broadcast vs. in-furrow	Starter fertilizer increased grain yield at nine sites (800–2110 kg ha^{-1}) whilst starter fertilization, in addition to broadcast fertilization, did not increase yield at any site, but it increased maize early growth and P and K uptake more than broadcast [57].
	DAP: 27 kg N ha^{-1} and 30 kg P ha^{-1}; and AN	subsurface band (5 cm × 10 cm)	NP starter fertilization improved early maize growth assessed by LAI and biomass [17].
	Liquid NPK (10-40-10): 35, 50, 70, and 100 L ha^{-1}; conventional mineral starter fertilizers: 15-15-15 and KAN with 27% N (13.5% NH_4-N and 13.5% NO_3-N): 0 + 0 kg ha^{-1}; 150 + 100 kg ha^{-1} and 300 + 200 kg ha^{-1}	5 cm × 5 cm	Liquid starter fertilizer intensively increased plant growth in the initial stages of development and consequently 7.9–17.1% grain yield; the optimal choice of liquid starter fertilizer application technique can result in fertilizer savings by 30% without reducing yield [26].
	N (urea): 225 kg ha^{-1} and P_2O_5 (superphosphate): 120 kg ha^{-1}	subsurface band (5, 15, 25, and 35) cm	25 cm deep placement increased the maize yield by 13.8% and obtained the highest nitrogen use efficiency (43.6%), whilst 35 cm negatively affected the maize yield and N use [108].
Wheat	DAP, MAP, APP, and Nachurs (6-22-6-1S): all applied at 15 kg P ha^{-1}. MES-10 (12-40-0-10S) and MES-Z (12-40-0-10S-1Z): all applied at 14.7 kg P ha^{-1}. MOP (0-0-60) and Aspire (0-0-58-0.5B): all at 18.6 kg K ha^{-1}.	In-furrow	In-furrow fertilization did not improve yield over the control when STP or STK were above sufficiency. Still, it can potentially increase winter wheat grain yield and nutrient concentration when soil nutrients are limited [39].
	67 kg N ha^{-1} (broadcast) + 17 kg P ha^{-1} (TSP) (broadcast) + 33 kg K ha^{-1} KCl (broadcast) and 67 kg N ha^{-1} (subsurface)	broadcast UAN; surface band (dribble) UAN; subsurface band (knife) UAN (10 cm depth)	Wheat yields were more significant with knife application than with broadcast, but the yield differences were ≤0.5 Mg ha^{-1} in all cases [101].
	AN: 120 kg ha^{-1} (shallow-SP, deep-DP, and mixed-MP) placement	subsurface band: 7 cm (SP), 20 cm (DP), and 7–20 cm (MP) below the seed	MP and DP increased N content in harvested grain by 3.6% and 2.5%, respectively. DP increased grain yield by 11%, and expanding the fertilizer N placement depth potentially improved crop N content and yield, mitigated fertilizer-induced N_2O emissions, and to a smaller extent, increased methane oxidation [66].
	UAN (28 g kg^{-1}): 67 and 134 kg N ha^{-1}; plus, MOP: 62 kg K ha^{-1}	surface-broadcast and subsurface-knife	134 kg N ha^{-1} subsurface-knife treatment, averaging between 3500 and 4000 kg ha^{-1}.; subsurface N placement potentially increased grain yield [109].

Table 1. *Cont.*

Crop	Fertilizer Salt Concentration and Its Application Rates	Mode of Placement	Crop Response
	UAN: 34, 67, 100, and 134 kg N ha^{-1}	subsurface band (5 and 10 cm deep)	Subsurface applications resulted in higher rates of N uptake compared with surface treatments; No difference in grain N uptake was apparent between application depths of 5 and 10 cm; 10 cm depths had the most significant promise in benefiting yield in low N environments and increasing grain N [110].
Barley (*Hordeum vulgare* L.)	AN: 105 kg ha^{-1}	subsurface band-7 cm (shallow placement-SP), 20 cm (deep placement-DP), and 7–20 cm (mixed placement-MP) below the seed	Fertilization increased N concentrations mid-season in the plant biomass and in harvested straw and grain [66].

3. Mechanisms of Salt Injury and NH_3 Toxicity from Starter Fertilizer Placement

The lethal barrage of fertilizer toxicity occurs during seed germination and extends into seedlings' growth and development due to increased salt injury and NH_3 toxicity. Different chemical reactions were established to help elaborate saline–alkali injuries [111,112] and ammoniacal-N toxicity [13,24,113]. The osmotic pressure determination and simplified electrical conductance (EC) techniques have been developed as approaches to measuring fertilizer salt index (FSI) [30,32,37]. Fertilizer salt toxicity has resulted from the materials used in fertilizer formulation of mixtures that differ with the supply and pH levels and the mere statement of the grade, which is insufficient to guarantee the favourite quality of the soil solution across seasons. N and K fertilizers typically have greater salt index values than P fertilizers, and as the soil dries out, the salts will rise upward and injure seeds or early roots compared to phosphates [114]. Zörb et al. [115] highlight how these mechanisms that restrict plant growth and yield under salty circumstances might result in crop yield losses. For example, they discovered that soil extract salinity values of 2.5–7.2 dS m^{-1} of EC resulted in a 10% yield drop in wheat and maize and a 50% yield decrease at levels of 5.5–13 dS m^{-1} of EC. Simultaneously, ammoniacal-N (NH_4^+-N or NH_3-N) compounds that contain free NH_3 or decompose to form NH_3 are being used in substantial quantities. The principal valuable agent of toxicity to the seed and crops is NH_3 (aq or gas) concentration in soil solution [116]. When these concentrations arise, they passively spread into plant cells, which disturb cellular metabolism by interfering with the regulation of intracellular pH between the cytosol and vacuoles [117,118]. The question of how starter fertilizers produce salt injuries and NH_3 toxic symptoms (Table 2; Figure 3), which frequently result from their use, becomes a matter of both practical and theoretical interest. The details on the consequential effects of ammoniacal-N and/or salt toxicities on morpho-physiological and biochemical attributes at agronomic crop growth and development, as influenced by the different factors, are explained below.

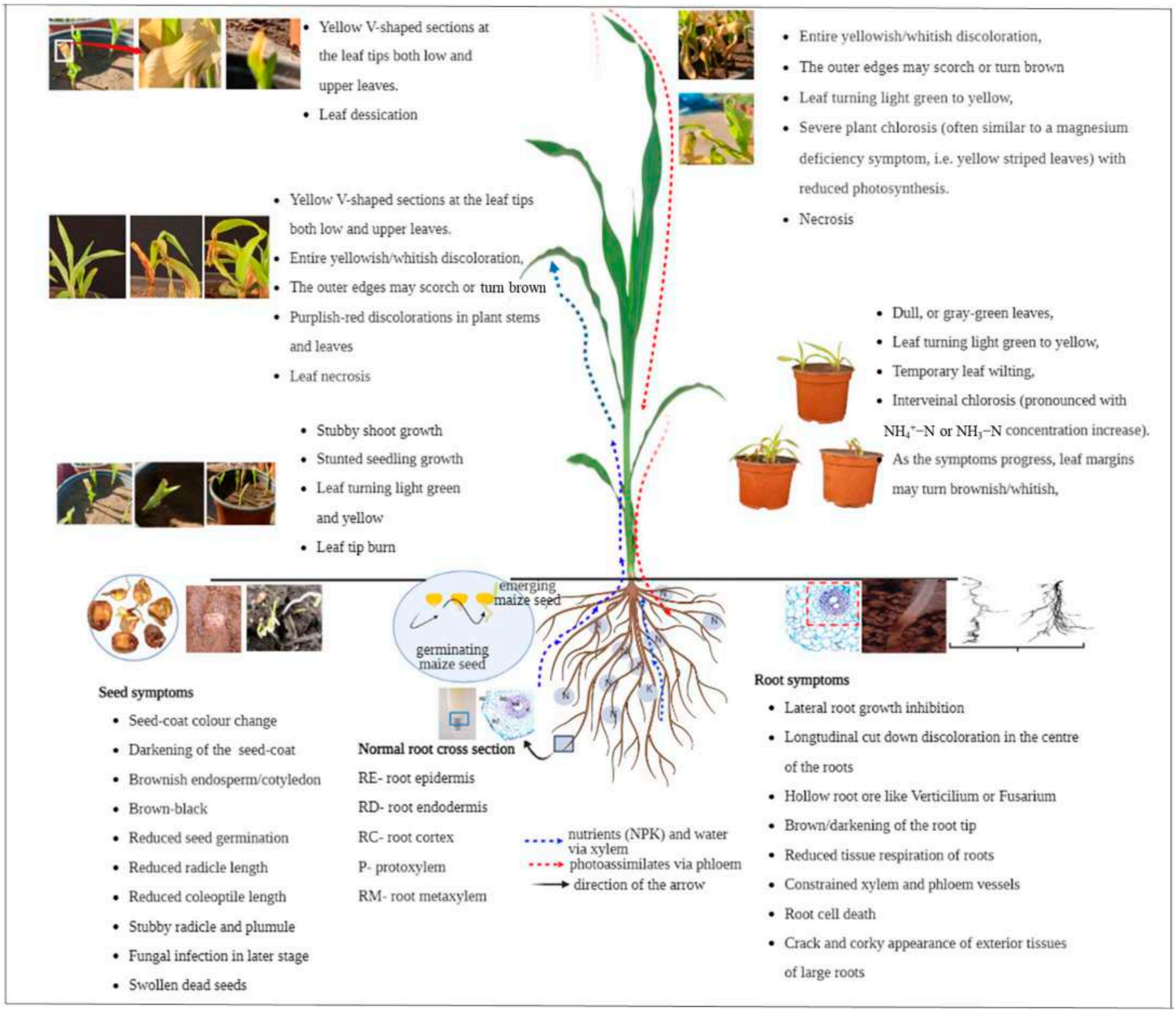

Figure 3. The schematic presentation for the signs and symptoms NH_3 toxicity.

3.1. Morpho-Physiological and Biochemical Crop Response to Fertilizer Salt Toxicity

High osmotic pressure from fertilizer salts around seeds or young seedlings causes plasmolysis, leading to tissue desiccation and potential cell death under irreversible conditions (Figures 3 and 4) [111,118–120]. Fertilizer salts that are beyond 100 times $NaNO_3$ osmotic potential deteriorate the plants' transpiring leaves, posing photoinhibition as well as directly weakening and reducing the plant water uptake from the rooting zone leading to seedling osmotic stress [119–121]. For example, neutral and alkaline salt on canola seed germination and seedling growth Na_2CO_3 (alkaline salt at 0–40 mM) and NaCl (0–200 mM) + pH (7–11) was evaluated. Wang et al. [120] revealed that the inhibition of canola seed germination and seedling growth was due to pH and the interaction between pH and salt ions. Khiari et al. [122] and Quinn et al. [9] supported that in the immediate vicinity of the DAP band, the temporal pH flux due to the fertilizer granules could result in a toxic zone that damages the seed, thus significantly affecting crop yield. Similarly, Barker et al. [123] directly placed cucumber seeds in the solution (KCl and K_2SO_4) of the order of 0.1 N K and observed severe injury of germinating cucumber seeds, which could be due to the effect of fertilizer formulation, where the same nutrient analysis may vary four- to five-fold in their impact on the osmotic pressure of the soil solution. This may not depend on the amount of plant nutrients in the fertilizer but rather on the carriers used to supply the plant nutrients [37].

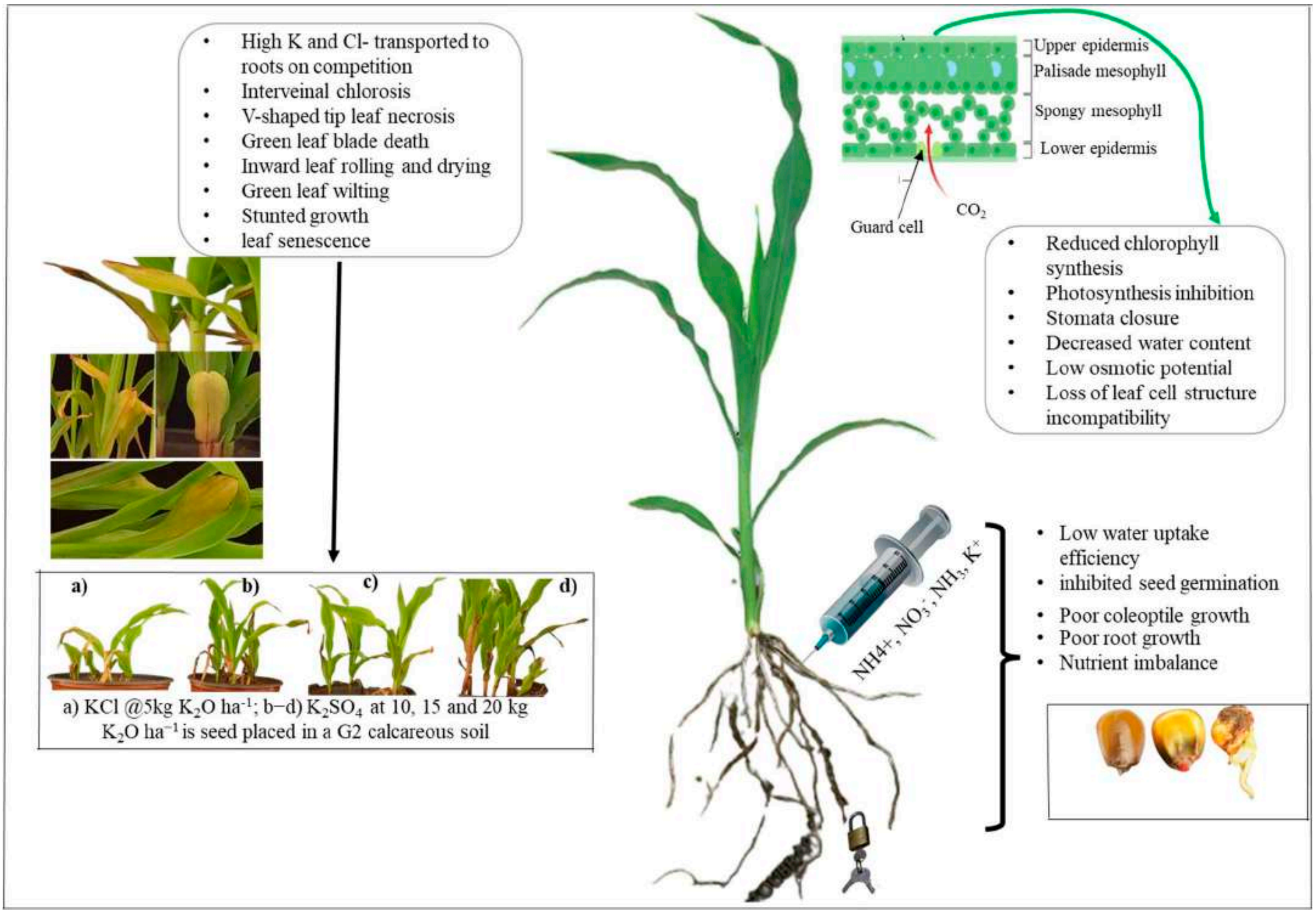

Figure 4. The schematic presentation for the signs and symptoms of fertilizer salt injury on crops.

3.2. Phenological and Biochemical Crop Response to Ammoniacal-N Toxicity of Starter Fertilizers

The detrimental effects of starter ammoniacal-N fertilizers on seed germination, seedling growth, and development (Figure 3) are irreversible and have been highly established in the 1960s with little current information in the 21st Century [11,124]. Detailed findings on the implications of ammoniacal-N toxicity are highlighted in Table 2. A no-seed–fertilizer contact laboratory experiment using urea containing 2.5, 5, and 10% biuret had equally increasing damage to germinating seeds that was assumed to be the effects of the NH_3 gas release from $\geq$0.02 g of urea [125,126]. In contrast, Bremner and Krogmeier [127] argue that the seed germination damage was due to the hydrolysis of urea by urease enzymes and neither by the fertilizer impurities formed during the manufacture of urea fertilizers. Other findings revealed that increasing urea fertilizer rates from 10 to 100 ppm on a loamy soil (pH 7) had little effect on seed germination compared to 1000 ppm with the highest (100%) seed death whilst NH_4NO_3, $(NH_4)_2SO_4$ and ammonium nitrate-limestone (ANL) fertilizers had a positive effect on seed germination and early growth of winter wheat and maize [128]. In cotton, canola, and canary (*Serinus canaria* L.) studies, severe darkening of the seedcoat, radicle, and coleoptile growth inhibition, discoloration on the filter paper, and residual moisture in the Petri dishes placed in the containers on racks containing NH_4OH solution of 102 $\times$ 10^{-4} M ammonium concentration [116]. This could be due to the accelerated leaching of electrolytes from the seed exposed to ammonia during imbibition [117,124]. An alternative flagged that anhydrous NH_3 posed a toxic environment, which was associated with strong retardation and inhibition of maize seed germination (>50% inhibition), early seedling growth, and plant stands when 994 ppm (pH 3) and 1628 ppm (pH 9) of (NH_3 + NH_4^+)-N was placed within the maize seeding zone [129]. Such effects could be explained by the protonation of NH_3 by surface acidity or by protons donated by carboxylic (-COOH), and phenolic (-C_6H_5OH) groups contained in soil organic matter. These reactions are endothermic and occur following injection of anhydrous ammonia at 10 atm leading to another exothermic reaction, the release of heat and rapid vaporization of NH_3 (gas) [25]. These results demonstrated that the same concentrations could inhibit weeds and potentially have herbicidal properties if incorporated via different proper agro-technics and fertilizations.

From the partial vapor pressure analysis of NH_3 (P_{NH3}) in soil air, 50% germination of maize was inhibited by P_{NH3} that ranges between 0.156- and 0.077-mm Hg when adding 2 *N* NH_4OH. Germination stopped when adding 26 meq NH_4OH per 100g of Elliot silt loam soil at 25% moisture [130]. Toxicity symptoms of NH_3 in cotton and sudangrass emerging radicles were registered at 0.17 mM and 0.23 mM, respectively, in sandy loam soil (pH 5.6) after the surface placement of $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, NH_4OH and $(NH_2)_2SO_4$ [113]. Research shows that the direct placement of cucumber seeds in 0.1 *N* and 0.01 *N* concentrations of both aqueous ammonium chloride (NH_4Cl) and sulphate [$(NH_4)_2SO_4$)] solution, respectively, inhibited its germination. However, germinated seeds had stubby radicles and plumules with no apparent difference between the two salts [123]. This may be due to the disruption of the electron transport chain in seedlings, especially when cell membranes are impermeable to NH_4^+ whilst NH_3 quickly passes the barriers.

DAP fertilizer placement on cereal crops resulted in seed germination and emergence inhibition due to its capacity to precipitate and inactivate Ca and Mg to relatively insoluble Ca-P and Mg-P complexes in crop seeds [117,131,132]. The same DAP fertilizer (120 kg N ha^{-1}) banded between 3–3.5 cm on Hagerstown silt loam soil (pH 6.8) inhibited the maize radicle growth due to increased concentration of NH_3 produced in the rhizosphere [133]. The finding on the determination of NH_3 volatilization caused by urea fertilizer applied at 0.58, 1.16, and 1.75 mg N g^{-1} soil and its damage to wheat seed germination, early seedling growth, and associated physiological mechanisms on wheat varieties unveiled that high concentrations of NH_3 from ammoniacal-N starter fertilizers had an apparent inhibition of wheat-root hair formation, root and shoot growth, leading to a 25% decline of the epidermal cell length and coleoptile inhibition (Figures 3 and 4) [11,118]. This could be due to high levels of residual NH_3 in or on the tissue that may have a growth stimulation compared to those grown in distilled water ([11,116,118]. Similarly, $(NH_4)_2SO_4$ solution that ranges from 1×10^{-3} to 3×10^{-3} M undissociated NH_3 in 0.01 M phosphate buffer (pH 7) had as high root respiration rate as 46–62% [134]. Ammoniacal-N fertilizer toxicity posed severe root damage with scorched brown tips and die-back necrotic and shrinking roots on wheat and canola [135,136]. Comparable observations indicated high fungal invasion associated with the shrinking of wheat and canola seeds within 5–7 days after planting following direct placement of 25 mg N cm^{-1} urea [11]. It is to be noted that high NH_4^+ (20–30 mol m^{-3}) inhibited the total root length, root volume, average root diameter, root tip diameter, and root surface area of low nitrogen use efficiency rice variety compared with regular N rate [137]. This may be due to competition for carbon skeletons between root growth and NH_4^+-N assimilation in NH_4^+-fed plants [138]. As correlated with the shoot biomass, when the N supply is highly abundant compared to the carbohydrate reserves, seedlings could face the danger of NH_3 toxicity due to depleted C reserves. This could be explained by the interaction between NH_3 and the oxygen-evolving complex (OEC) effect of NH_4^+ (1 mM) on chlorophyll fluorescence transients in *Medicago truncatula* [117,139]. Eventually, generic and simple models to estimate minimum input requirements of starter N, P, and K for target yields for agronomic crops for optimization and efficient management practices become critical.

Table 2. Fertilizer salts and their potential NH_3 toxicity implications in elucidating multiple responses to develop abiotic stress resilience in plants.

Crop	Fertilizer Salt Concentration	Placement Method	Stress Type and Its Condition	Response
Maize	NaCl + 50 mM/L KCl: (0, 20, 30, 40, 50) mM/L	direct seed-solvent	Salt injury (saline-neutral salts)	Increased germination inhibition; decreased photosynthetic pigments (chlorophyll-a, chlorophyll b, and carotenoids) and suppression of enzymes chlorophyll synthesis with increased NaCl + KCl concentration [140].
	Urea, biuret, $(NH_4)_2SO_4$, or NH_4OH, $NaNO_3$, NH_4NO_3 (all 17 kg N ha^{-1}), urea + 70 kg ha^{-1} $Ca(OH)_2$ (field)	banded	NH_3 toxicity	>32% NH_4-saturation from NH_4OH inhibited seed germination under a closed system and whilst no germination in the field; expect severe seedling injury at ≥1.7 kg of biuret-N ha^{-1}; ≥10% of biuret-N cause stunted and/or twisted and deformed whilst 5% biuret-N caused stunting but not a deformity [139].
	Urea: 1 and 2.5% biuret-N (greenhouse)			Decreased seed germination with higher percentages of biuret; stunted plants at 1% and 2.5% biuret-N with increased seedling deformation in the field [139].
Wheat	NaCl + 100 mM/L KCl	direct seed-solvent	Salt injury (saline-neutral salts)	The salts inhibited wheat seed-germination % and its rate; combining these salts had an antagonistic effect on seed germination; root and shoot lengths of wheat were drastically inhibited with the strong [141].
	$NaHCO_3$:Na_2CO_3: (0, 100, 200, . . ., 500) mM			Reductions of germination % and seedling growth; decreased K^+ concentrations of shoot and root with alkali conditions; root elongation decreased; proline and soluble sugar concentrations increased with the rising salinity [142].
	KCl and NaCl + KCl: (0, 100, 150 and 200) mM			Massive reduction of stem length, leaves length, stem breadth, number of tillers, number of leaves per plant, number of seeds per spike, spike length, the weight of the whole plant, and weight of 50 grains of wheat as the salinity levels increase [143,144].
Wheat, canola, and faba bean (*Vicia faba* L.)	Urea: 56, 112, and 168 kg N ha^{-1} for wheat; 34 kg N ha^{-1}, 67 kg N ha^{-1}, and 90 kg ha^{-1} for canola; Slow-release urea (SRU): 56, 112, and 168 kg N ha^{-1}-wheat/canola 11.4 cm layer of over 5.1-cm chicken manure, over 11.1 cm of unamended soil- faba bean 11.4 cm layer of over 5.1-cm natural compost- faba bean	In-furrow and deep placed (5 cm below the seed row)	NH_3 toxicity	Canola root apex and root hair die-back, discoloration symptoms, and accelerated lateral rooting; seed-placed urea stunted wheat shoot and root radicles growth, while SRU reduced these symptoms; toxicity-damage to a single tap root of the germinating canola and faba resulted in seedling mortality; urea and chicken manure elicited similar toxicity symptoms initiated at the root apex [11].

Table 2. *Cont.*

Crop	Fertilizer Salt Concentration	Placement Method	Stress Type and Its Condition	Response
Pumpkin (*Cucurbita pepo* L.)	KCl: (0, 1, 3, 5, 7 and 9) dS m^{-1}	direct seed-solvent	Salt injury (saline-neutral salts)	Pumpkin seed-germination rate, root length, shoot length, fresh root weight, and dry root weight, fresh shoot weight, and dry shoot weights decreased with increased EC of solution; seed hindrance in water uptake results in the inactivation of the enzymes responsible for seed germination and seed drying-out [145].
Oats (*Avena sativa* L.)	Na_2CO_3:$NaHCO_3$: (4–32) mM L^{-1}	direct seed-solvent	Salt injury (alkaline salts)	Reduced seed germination varied with genotypes; overall chlorophyll content reduction; disruption of water absorption by Na ions; stunted plant growth; reduced number of tillers and panicles on susceptible oats genotypes under alkali and salt application; many yellow leaves but no drying and lower chlorophyll content under alkaline and vice versa on salt stress; limited water absorption [146].
Quinoa (*Chenopodium quinoa* Willd)	KCl: (0, −0.1, −0.2 and −0.3) MPa	direct seed-solvent	Salt injury (saline-neutral salts)	Reduced germination %, first seed count, and seedling length at a low osmotic potential; inhibition of seed establishment; decreased early plant vigour; and severe shoot, root, and total length growth inhibition [147].
Cucumber (*Cucumis sativus* L.)	$(NH_4)_2SO_4$, KCl, and K_2SO_4: (0, 0.001, 0.01 and 0.1) *N*	Mixed media and solution (solution in contact with seed)	Salt injury and NH_3 toxicity	Total irreversible seed germination inhibition at high concentrations of K or NH_4^+ salts; Respiration inhibition of germinating seeds on both fertilizers; severe impairment of seedling development NH_4^+ salts, but not by K salts; inhibition of photosynthesis and greening of cotyledons; browning of the damaged root tips [123].
Sudangrass and cotton	$(NH_4)_2HPO_4$ (14.3 and 22.93); AS: $(NH_4)_2SO_4$ or $(NH)_2SO_4$—[(Aq NH_3 + AS: 40.68 and 65.55), NH_4OH (39.72) mM L^{-1} NH_4^+ + NH_3 (aq)	Soil–fertilizer–seed system (solution in contact with seed)	NH_3 toxicity	Flaccidity of sudangrass leaves; yellow discoloration of cotton roots; reduction in root growth rate at progressively higher solution pH levels [113].
Maize, cotton, wheat, barley, chickpea, sorghum, Canary, canola, and sunflower	NH_4OH (0–208 × 10^{-4} M): 0, 7, 12, 29, 54, and 102 NH_4^+ concentration	Soil–fertilizer–seed system (solution in contact with seed)	NH_3 toxicity	Chickpeas were unaffected at the highestconcentration (208 × 10^{-4} M); maize, wheat, barley, sorghum, panicum, and sunflowerhad intermediate tolerance; Radicle and coleoptile growth were more sensitive to NH_3 than germination; Coleoptile elongation of monocots was more sensitive to NH_3 than radicle elongation in half of the species [116].

Table 2. *Cont.*

Crop	Fertilizer Salt Concentration	Placement Method	Stress Type and Its Condition	Response
Lettuce, cauliflower, sugar beet, maize, and wheat	KNO_3, KCl, MAP and AN: [Cl (1.09), NO_3-N (1.98, 2.13), NH_4-H^+ (1.57, 2.13), P (0.7), K (1.09)] mmol/kg	Soil–fertilizer–seed system (solution in contact with seed)	Salt injury and NH_3 toxicity	Lettuce, cauliflower, and sugar beet seed germination were most sensitive to NPK nutrient mixtures, whilst wheat and maize were also sensitive at high rates; germination was never better with chloride-based than nitrate-based mixtures [148].
Barley, maize, rye, and wheat	Urea, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, $(NH_4)_2OH$, (KNO_2), (KNO_3): (0, 0.25, 0.5 and 1) mg g^{-1} soil	Soil–fertilizer placement (no seed contact)	NH_3 toxicity	NH_3 (g) from urea completely inhibited the germination of all crops; nitrite was more toxic to seeds than N in the form of urea merits attention because nitrite is produced during the nitrification of urea N in the soil, and nitrite accumulation has been observed in soils treated with urea [127].
Maize, wheat, and barley	Urea with 2.5, 5.0and 10.0% biuret: 45, 90 and 180 kg ha^{-1}; AN + 2.5% biuret: 45, 90 and 180 kg ha^{-1}	In-furrow	NH_3 toxicity	Urea with 2.5% biuret reduced stands of small grain by 30% at 23 kg N ha^{-1} rate whilst AN 10% stand reduction at 90 kg ha^{-1}; stands were 25 and 60% depressed after 45 and 90 kg ha^{-1} placement of urea; urea + 10% biuret broadcast at 180 kg ha^{-1} caused no damage to either maize or barley germination [126].
Rapeseed (*Brassica napus* L.)	KCl: 0, 13.4, and 26.8 mM	direct seed–salt solution	Salt injury	Seed germination, seedling growth, radicle, plumule lengths, and biomass decreased with increased KCl; salt ions and osmotic pressure limit seed-water absorption, cause nutritional imbalance and reduce photosynthetic efficiency and other physiological disorders [149].
Canola	$NaHCO_3$: (0, 50, 100. . ., 300) mM and Na_2CO_3: (0, 10, 20. . ., 50, 75. . ., 150) mM	direct seed–salt solution	Alkaline salt injury	Alkaline salts strongly inhibited canola seed germination, seedling growth, root growth, shoot length, and fresh weight. Canola had high K^+ concentration in leaves and increased Ca^{2+} and Mg^{2+} in roots under Na_2CO_3, but Mg^{2+} significantly declined whilst K^+ and Ca^{2+} concentration increased; excess Na^+ influx into the cytoplasm observed depolarizes the membrane potential and activates K^+ outward rectifier channels [120].

4. Effective Strategies to Neutralize Fertilizer Toxicity for Optimal Cropping Systems

Much attention is currently going towards improving the sustainable use of fertilizers, providing an innovative framework to deal with fertilizer toxicities (Table 3). To manage fertilizer salt injury and NH_3 toxicity, control-and-slow-release fertilizers (CRFs and SRFs)- e.g., urea–formaldehyde, isobutylenediurea, and sulphur, polymer, or both coatings, respectively, can inhibit NH_3 production and toxicity, as well minimizing fertilizer toxicity to improve crop production [150,151]. The novel waterborne and biodegradable coating nanocomposite formulations particularised from cellulose nanocrystals (CNC)-filled poly (vinyl alcohol) (PVA) for SRFs N-P-K potentially reduced salt distribution and NH_3 toxicity by improving nutrient use efficiency [152,153]. Nonetheless, blended methylcellulose/lignin biocomposite and lignin–sodium alginate biopolymeric SRFs, and biobased cellulosic biochar nanocomposite formulations of DAP did improve agronomic performance of wheat by promoting effective plant establishment with no NH_3 toxicity recorded; thus, promoting improved environmental health issues [154,155].

It is to be noted that a double-layer polymer-coated urea (DPCU), urease inhibitors (N-(n-butyl) thiophosphoric triamide (NBPT), N-(n-propyl) thiophosphoric triamide (NPPT) placed near the seed zone slowly released N for improved starter N fertilizer use efficiency and crop productivity with little/no toxicity implications [156,157]. Compaction of urea (0.5 g N kg^{-1}) and TSP (0.11, 0.22, and 0.33 g P kg^{-1}) provided an effective way to improve the efficiency of banded urea for maize production by delaying urea hydrolysis through the addition of acidic materials, which minimized seed-germination inhibition potentials [136]. This is due to a decline in estimated NH_3 concentration from 8.28–9.93 mmol kg^{-1} and 0.03–0.13 mmol kg^{-1} urea alone to 0.11–0.51 mmol kg^{-1} and 0.01–0.05 mmol kg^{-1} at 2 and 4 cm when TSP placed and led to the 97% seed germination promotion ([136,158]). Furthermore, banded organo-mineral fertilizers (OMFs) produced from MAP (2.87 mol/L $NH_4H_2PO_4$ (pH~3.5) or DAP-alkaline [3.82 mol/L $(NH_4)_2HPO_4$; pH ~8.0]) and mixed pig slurry led to reduced fertilizer toxicity due to the increased buffering capacity during OMFs production cycle that minimized the adverse effects of high acidic or alkaline mineral fertilizers. OMFs band placement reduced the risk of short-term pH toxicity effect either by neutralizing acid (H^+) generated from chemical fertilizers or converting H^+ into another non-acidic form of H^+ [122,159]. Other research findings indicated that increasing K^+ concentrations in the rhizosphere could alleviate ammoniacal-N toxicity because K^+ increased the incorporation of ammoniacal-N into organic N-compounds by activating enzymes such as glutamine, synthetase, and glutamate dehydrogenase; and/or inhibiting the acquisition of ammoniacal-N by low-affinity transporters [117]. Similar observations indicated that careful placement of recommended rates of KCl could temporarily decrease the microsite pH near fertilizer N fertilizers granules through the displacement of exchangeable acidity, delaying urea hydrolysis [160].

Numerous studies proved that blending and/or formulating urea-triple superphosphate (TSP)-zeolite (0.75 and 1 g kg^{-1} of soil) or clinoptilolite zeolite and acidic materials (acidic P fertilizer, TSP) results in the reduction of NH_3 production and toxicity effects by 34–49% and simultaneously increased soil-exchangeable Ca, K and Mg in acid altered soils [161,162]. These clinoptilolite zeolite materials contain negative charges that efficiently and judiciously retain and release nutrients to ensure optimum plant use and release of NH_4^+, thus reducing ammonia volatilization within the rhizosphere [163]. In addition, band placement of one-time multi-nutrient fertilizer briquettes (26.7% N, 11.3% P_2O_5, and 11.3% K_2O) manufactured from 2:1 proportion of NPK compound and urea fertilizers, respectively, result in an increased smallholder crop productivity and profitability with no fertilizer toxicity [156,164,165]. Two-year field experiments with wheat-maize rotations optimized 38% of biogas slurry plus chemical fertilizer (174 kg N ha^{-1} from urea and DAP) that reduced NH_3 production (from 18% to 32%) and have potential NH_3 toxicity effect by improving plant stand and crop yield [12]. Other suggestions recommended the purchase and use of enhanced efficiency fertilizers (EEFs) to reduce fertilizer injury and NH_3 toxicity, which may depend to a great extent on the farmer's cropping system management abilities, the agronomic and environmental knowledge of the agricultural retailer and professional crop adviser [166].

It is interesting to note the advances and high adoption of information technology and decision support systems that have developed dynamic computer simulation models and digital support tools for millions at the farm level [24,167]. These include Azofert®, N-Expert, CropManage, GesCoN, FertiliCalc, Nutrient-Expert, PLANET, and smartphone versions of RB209 to provide nutrient recommendations for numerous commercial farms [151]. Moreover, the use of Rice Crop Manager (https://phapps.irri.org/ph/rcm/; accessed on 23 January 2023) has generated 2.66 million fertilizer recommendations in the Philippines (2013 to early 2021) and 250,000 in India (http://webapps.irri.org/in/od/rcm/, http://webapps.irri.org/in/br/cmrs/; 2017 to early 2021), while RiceAdvice (https://

www.riceadvice.info/en/; accessed on 23 January 2023) generated 100,000 recommendations in West-African countries (2014–2020) will little/or no fertilizer toxicity was observed. South Dakota State University developed a Fertilizer Seed Decision Aid spreadsheet and web calculator that select the crop to be grown, fertilizer type, seed furrow width, row spacing, tolerated stand loss, soil texture, and soil moisture at planting based on field and greenhouse research, which potentially reduced fertilizer toxicity (http://www.ipni.net/article/IPNI-3268; accessed on 23 January 2023). Combining such information technology, technical support, and guidelines from agronomists and extensions advisory-based experiences on the safe rate of seed–fertilizer–soil placement could bring valuable outcomes. In terms of agricultural mechanization, There was an adopted method for the precise application system of liquid starter fertilizers to detect seed information in real-time and control the solenoid valve to open automatically [67], which meets the demands of precise liquid starter fertilization (LSF) application [168].

Table 3. The potential tech-savvy that can be employed to alleviate starter fertilizer toxicities: salt injury and NH_3 toxicity.

Technology	Source of the Materials	Composition and Placement Method	Outcomes
Acidification and the addition of a nitrification inhibitor (DMPP, 3,4-dimethyl pyrazole phosphate) to animal manure	Raw dairy slurry and solid fractions from dairy slurry and digestate from a biogas plant	48.8 g manure kg^{-1} for raw slurry, raw slurry solid fractions, acidified slurry, nitrification inhibitor slurry, acidified + nitrification inhibitor slurry	increased plant biomass and plant P uptake from solid particles of both slurry and digestate; the combination of acidification and DMPP had a 49% plant biomass increment in the digestate solids treatment [169].
One-Time Fertilizer Briquettes	NPK (15-15-15 or 17-17-17): 2 × 50 kg bags; one 50–kg bag of urea to reach 100 kg N, 42.5 kg P_2O_5, and 42.5 kg K_2O	250 kg NPK compound fertilizer and 125 kg urea thoroughly mixed and briquetted to give 26.7-11.3-11.3; NPK fertilizer: +100%-Briquette and 75%-Briquette; Modified farmer practice (MFP-subsurface band at ~7 to 10 cm deep) and NPK 100%-MFP), 75%-MFP	Maximum maize grain yield had the following order: 100%-Briquette > 100%-MFP = 75%-Briquette > 75%-MFP > FP > control; the greatest gross profit margin of 0.46 was obtained with the 75%-Briquette treatment, followed by the 100%-Briquette treatment (~0.43), 100%-MFP (~0.39), 75%-MFP (~0.24), and FP (0.03) [164].
Urea-chitosan nanohybrid	Chitosin-urea prepared from a mixture of chitosan solution and urea (1% *w*/*v*; 1 g urea/100 mL chitosan solution)	80% urea + exogenous urea-chitosan nanohybrid 500 mg N/L; 60% urea + exogenous urea-chitosan nanohybrid 250 mg N/L; 60% urea + exogenous urea-chitosan nanohybrid 500 mg N/L; 40% urea + exogenous urea-chitosan nanohybrid 250 mg N/L; 40% urea + exogenous urea-chitosan nanohybrid 500 mg N/L	Increased growth, and all yield-related traits were obtained when rice plants were fertilized with exogenous urea–chitosan nanohybrid (i.e., 500 mg N/L+ 60% classical urea) [170].
Granular soil bio-enhancer (SBE)	SBE was physically obtained by grinding phosphate rocks at a nanoscale level and mixing it with azotobacters.	Applied at sowing 150 kg ha^{-1} and 250 kg ha^{-1} for DAP and SBE, respectively	SBE application before wheat sowing resulted in a greater early vigour of wheat seedlings compared to commercial DAP; a 56% increase in aerial dry biomass; 48% increase in plant height; 8.5% increase in LAI, while moderate percentage increases were detected for crop and tiller density [19].

Table 3. *Cont.*

Technology	Source of the Materials	Composition and Placement Method	Outcomes
polymer coated DAP	Polycarbonyldiamide; 1% in distilled water was manually prepared and blended with the fertilizer and dried	surface and sub-surface-applied coated N fertilizer	Wheat NUE were at maximum ([44.57 (N), 44.56 (P) and 44.53% (K)]) with the subsurface application of coated N fertilizer; NH_3 production and toxicity were found to be the lowest with subsurface-applied coated N fertilizer [171].
Digestate and biogas slurry (BS)	226.5 kg N/ha was applied at different ratios (100%, 80%, and 50%) between BS and chemical fertilizers (CF)	subsurface placement	CF produced a maximum yield of 6250 kg/ha, resulting from the combined application of 38% BS mixed with CF; BS treatments significantly reduced emissions from 18% to 32% relative to CF [12].
Blending mined humus deposits with ammonium orthophosphate fertilizers	Orthophosphate concentrations with the corresponding organic additives were 3-9-0 + 1.0% organic material, 5-15-0 + 1.7% organic material, and 7-21-0 + 2.4% organic material	Each formulation was subsurface placed at 28, 56, and 84 L/ha	Root growth was more significant for the 3-9-0 + 1.0% organic material [172].
Precise Application System	The real-time seed–fertilizer placement monitoring tool detection sensors for LSF	precise LSF application system in terms of operation quality at forward speeds of 4, 6, and 8 km/h and pressures of 0.10, 0.15, 0.20, 0.25, and 0.30 MPa	The quality index of the length of LSF was 96.4%, the range of FA was 1.34 to 13.86 mL, and QID was 82.6%, which signifies the developed system meets the demands of precise LSF application [67].
Organo-mineral fertilizers (OMF)	Solid fraction of pig slurry; MAP, DAP: MAP (2.87 mol/L of $NH_4H_2PO_4$) and DAP [3.82 mol/L of $(NH_4)_2HPO_4$] were prepared separately at 25 °C; Treated SPS were added to a mineral fertilizer mixture (1:1 MAP: DAP, *w*/*w*, pH: 5.8)	Different MAP amounts were mixed with DAP to obtain 0–60% MAP in the mineral fertilizer mixture matrix; different amounts of the solid fraction of pig slurry (SPS) were mixed with two mineral fertilizers (1: 1 MAP: DAP, *w*/*w*) to obtain 0. 20, 40, 60, 80, and 100% SPS in the final fertilizer mixture (i.e., OMF) then granulation process	Increasing MAP decreased the pH of the mineral fertilizer mixture (MF) from 8.0 (100% MAP) to <5.5; the target pH values of 5.8 and 7.0 were obtained, respectively, with 50% and 12.6% MAP in the MF; the pH values of the OMF (SPS + MF) varied from 5.8 (MF without SPS) to 6.0–6.9 (80% SPS + 20% MF), depending on the type of SPS. Therefore, SPS could be used in increasing proportions (up to 80%) in the OMF as an alternative to ammonium phosphate as a starter fertilizer [122].

5. Future Perspectives and Conclusions

5.1. Future Perspectives

From the review's findings, the authors would like to highlight some essential future requirements for the starter fertilizers with respective to fertilizer toxicities. With significant efforts in different fertilizer formulations and a shift in crop production technologies, the entire fertilizer research community needs to update the misleading and inconsistent fertilizer salt indices tables and develop the unknown ammoniacal-NH_3 production toxicity. The proposed complete system design of the updated fertilizer salt toxicities must be viable, open, and interpretable for both industrial and agronomic use. This information will become the groundbreaking that governs how sectors and companies manufacture and market their fertilizer products for specific uses today. Furthermore, future research should focus on developing comprehensive information perception standards and designing multi-protocol compatible gateways to mitigate fertilizer toxicity. Fertilizer companies should take great pride in producing high-analysis but low-salt-index fertilizer products with many uses and placement opportunities. In addition, fully utilizing the high throughput and precise technology developed through agricultural mechanization for starter fertilizer placement could potentially scale up global crop establishment, growth, and development toward achieving maximum attainable crop yields. Learning from the soil–fertilizer–seed crop interactions, exploiting the mechanisms underlying starter fertilizer salt injury and ammoniacal-N (NH_4^+-N or NH_3-N) could help to establish the fertilizer safe rate and placement techniques. Ammonia toxicity and osmotic effects on germination should be separately evaluated for fertilizer used on potentially important food crop species. Understanding the interactive impact of liming materials' role in accentuating the amount and rate of NH_3 synthesis from ammonium phosphate fertilizers is pivotal for the proper time of liming application. Making full exploration and discovering the fertility benefits and convenience of placing starter fertilizer as close to the seed as possible to maximize efficiency in relation to fertilizer toxicity is yet to be updated. To facilitate such initiatives in the above fields, the availability of funding is crucial.

5.2. Conclusions

This comprehensive analysis revealed the increment in global attention towards starter fertilizer placement and uses, but little is known about their salt injuries and potential NH_3 toxicity implications. Seeds and/or crops behave significantly differently in response to fertilizer toxicities, and this is determined by the genetic makeup of the species. In their early growth stages, some are more susceptible to fertilizer salt and ammoniacal-N stresses than plants in later growth stages. So, it is critical to understand the right salt concentration of the starter fertilizer and its placement. Renewed interest in placing fertilizer in or close to the seed row makes it essential to remember that an increase in salt concentration in the fertilizer band can cause seed and seedling injury. Improving fertilizer placement techniques through different technologies with the knowledge of the updated salt indices and potential NH_3 toxicities in different soils with different STP and STK levels could improve crop seed germination, emergence, growth, and development of crop species under varied agro-systems. Starter fertilization has considerable potential for the sustainability of agricultural systems, food, and nutritional security. This is a wake-up call regarding the need for a rapid increase in crop production and the promotion of soil health through proper and efficient use of starter fertilizers, which is currently high in most countries. We conclude that starter fertilizer recommendations and placement based on soil type, fertilizer type, and crop species could indeed be a holy grail that will remain elusive. Nevertheless, producers should discuss with dealers the exact sources being used, the salt index, and the potential NH_3 toxicity to prepare the starter fertilizers and the correct placement.

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