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REVIEW PAPER

# Sulfur-enhanced nitrogen fertilization: implications for wheat zinc biofortification and N<sub>2</sub>O emission reduction in sustainable cereal production\*

He Zhang<sup>1</sup>, Aleksandra Ella Jachimowicz<sup>2</sup>

<sup>1</sup>Department of Computer Science  
City University of Hong Kong, Kowloon, Hong Kong SAR

<sup>2</sup>Department of Biochemistry and Cell Biology  
Stony Brook University, New York State, United States

## Abstract

The writing of this review article spanned eight months, during which our team members demonstrated unwavering commitment and collaborative effort. From an initial pool of 767 scholarly publications, we systematically analyzed and selected the 50 most seminal papers to ensure the academic rigor and relevance of this synthesis. It explores the potential of sulfur-enhanced nitrogen fertilization to address the dual challenges of zinc deficiency in wheat and high nitrous oxide (N<sub>2</sub>O) emissions in intensive cereal production. By co-applying sulfur with nitrogen, zinc biofortification can be improved by 30-40% through rhizosphere acidification and enhanced zinc solubility, while N<sub>2</sub>O emissions can be reduced by 50-60% via microbial denitrification processes. However, the efficacy of sulfur depends on soil-climate interactions: elemental sulfur (S<sup>0</sup>) is ineffective in sandy or arid regions due to slow oxidation, sulfate leaching occurs in humid areas, and high organic matter or acidic soils risk hydrogen sulfide (H<sub>2</sub>S) toxicity or methane (CH<sub>4</sub>) emissions. Despite the economic benefits of zinc-enriched wheat (22% market premium) and carbon credit potential, current EU policies overlook sulfur's role in climate mitigation. The review proposes region-specific solutions, such as accelerated sulfur oxidation in dry regions and coated sulfates in wet areas, supported by AI-driven tools and real-time soil sensors. Institutional recognition of sulfur in climate frameworks and mandatory soil health thresholds are essential to scale this sustainable strategy, which balances productivity, nutrition, and environmental goals.

**Keywords:** sulfur fertilization, zinc biofortification, N<sub>2</sub>O mitigation, sustainable wheat, machine learning

He Zhang, Department of Computer Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon Tong, Hong Kong SAR, e-mail: [H Zhang832-c@my.cityu.edu.hk](mailto:H Zhang832-c@my.cityu.edu.hk)

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INTRODUCTION

The intensive use of nitrogen fertilizers has become the cornerstone of modern wheat production (Fig 1), but the resulting environmental and nutri-

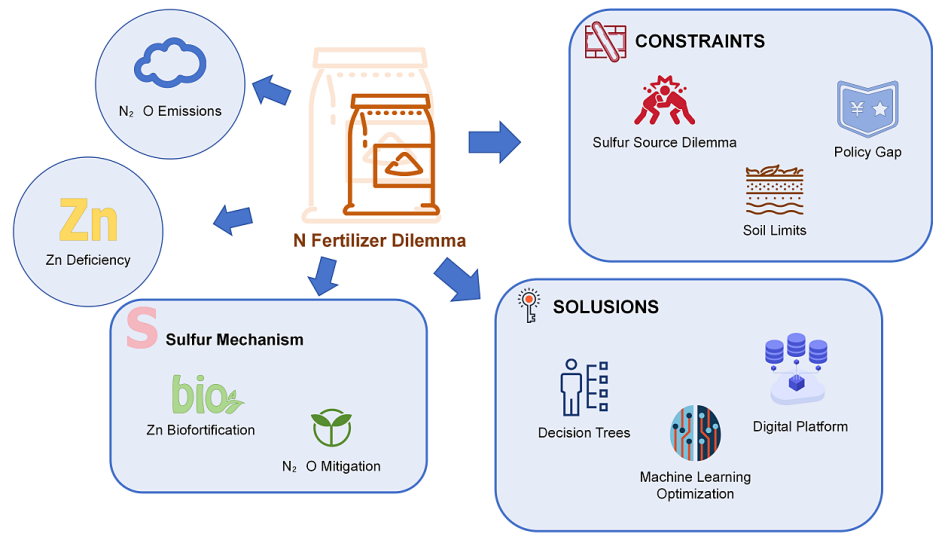


Fig. 1. The Coexistence of wheat zinc biofortification and  $N_2O$  emission reduction

tional contradictions are becoming increasingly acute (Jin et al. 2024). On the one hand, about 60% of the global farmland nitrous oxide ( $N_2O$ ) emissions come from nitrogen fertilizer application, and its greenhouse effect intensity can reach 298 times that of carbon dioxide, significantly exacerbating climate change. On the other hand, the high nitrogen environment inhibits the transport of zinc to the grain, resulting in a 20-40% decrease in the zinc content of wheat (Singh et al. 2018), exacerbating the “hidden hunger” problem caused by zinc deficiency in about 1.7 billion people worldwide. This double crisis highlights the goals: the strategy of simply pursuing yield improvement can no longer balance the needs of environmental safety and nutritional health.

As a key co-regulatory factor, sulfur has shown potential to resolve the above contradictions in recent years. Physiological studies have demonstrated that sulfur can activate the available state of zinc by acidifying the rhizosphere environment (Chorianopoulou et al. 2022, Mattiello et al. 2017), while promoting denitrifying bacteria to convert nitrogen into inert nitrogen ( $N_2$ ) rather than  $N_2O$  (Yang et al. 2016, Hayakawa et al. 2021, Xu et al. 2024). However, current research is highly fragmented: the agronomic field focuses on the biofortification effect of sulfur on grain zinc, while environmental science focuses on its emission reduction mechanism (Mustafa et al. 2022), lacking systematic integration.

Existing reviews mostly follow the traditional framework of “process description - data listing” and fail to build a predictable decision-making model. For example, although there is a consensus on the mechanism of soil pH affecting the sulfur - zinc interaction, the response thresholds of zinc bioavailability in different soil textures remain controversial (Cui et al. 2005, Usman et al. 2022, Taşpınar et al. 2025). Similarly, although there is sufficient evidence for the regulation of denitrifying microbial communities by sulfur, there is a lack of a universal equation to quantify the non-linear relationship between the N:S ratio and  $\text{N}_2\text{O}$  emissions (Dolejs et al. 2015, Huang et al. 2015, Hamzah et al. 2022). These cognitive gaps directly hinder the standardized application of sulfur management strategies at the regional scale (Bano et al. 2024).

Therefore, this review aims to reconstruct the sulfur-nitrogen-zinc interaction paradigm and establish an interdisciplinary knowledge hub by integrating rhizosphere micro-processes, such as sulfur-driven phosphatase activation (Wang et al. 2008), with field-scale evidence like the soil dependence of zinc enrichment efficiency and system-level effects including economic-environmental synergy (Luis et al. 2021). The review focuses on clarifying three core issues: how to maximize the benefits of zinc biofortification and  $\text{N}_2\text{O}$  emission reduction through sulfur source optimization and application timing design (Lakshmi et al. 2021, Liu et al. 2019); how to define the environmental risk boundary of sulfur management under different soil-climate combinations; and how to translate scientific research into operational guidelines adapted to policy frameworks like the European Union’s Green Deal (Zulfiqar et al. 2020).

## BACKGROUND

The sulfur-nitrogen-zinc interaction in wheat production is rooted in the complex biogeochemical cycle, and its mechanism can be traced back to the dynamic process of the rhizosphere microdomain. Sulfur regulates the bioavailability of zinc through two key pathways: first, sulfate ( $\text{SO}_4^{2-}$ ) hydrolyzes in the soil to produce  $\text{H}^+$  ions, reducing the rhizosphere pH (usually by 0.3-1.2 units), which promotes the dissociation of solid-phase zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) and releases exchangeable zinc (Bouranis et al. 2019); second, sulfur induces the secretion of organic acids such as citric acid by roots, chelating zinc ions and promoting their transmembrane transport (Ryan et al. 2001). However, this process is significantly regulated by soil organic matter (SOM) – in soils with high SOM (>3.5%), the activation efficiency of sulfur on zinc decreases by 30-50%, because humus competitively adsorbs zinc ions (Sethi et al. 2025).

In the nitrogen cycle dimension, sulfur affects  $\text{N}_2\text{O}$  emissions by reshaping the microbial community structure (Seitzinger et al. 2006). Denitrifying

bacteria use sulfide as an electron donor to reduce nitrate ( $\text{NO}_3^-$ ) to  $\text{N}_2$  rather than  $\text{N}_2\text{O}$ , resulting in a 40-80% decrease in the  $\text{N}_2\text{O}/\text{N}_2$  product ratio. However, this process has strict environmental boundaries: when soil  $\text{pH} < 5.5$ , sulfate-reducing bacteria are activated, leading to  $\text{H}_2\text{S}$  accumulation and inhibiting crop root development (Kuenen et al. 2008).

The technical contradiction in sulfur source selection has become the core bottleneck for practical application (Figure 2). Elemental sulfur ( $\text{S}^0$ )



Fig.2. Technologies and practical applications in sulfur source selection

must be oxidized to  $\text{SO}_4^{2-}$  by microorganisms before it can take effect (Germida et al. 1993). In arid and cold regions (annual average temp.  $< 10^\circ\text{C}$ ), its oxidation rate is only 20-30% of that in humid regions, resulting in delayed zinc enrichment (Chapman et al. 1989, Malik et al. 2021). On the contrary, the risk of sulfate (such as gypsum) leaching is significant in areas with annual precipitation  $> 800$  mm.

Current research reveals three major fault lines: a persistent disconnection between laboratory mechanisms and field-scale conditions, where sulfur's regulatory influence on *Thiobacillus* abundance remains unverified amid complex variables like soil aggregate-induced microbial spatial isolation (Santana et al. 2021, Chen et al. 2023); insufficient quantification of environmental risks, as only 11% of field trials monitor secondary emissions from sulfur addition, coupled with absent long-term threat assessments for acidic soils –  $\text{pH} < 5.5$  (Spiehs et al. 2019, Jacotot et al. 2023); and an unresolved economic-policy gap whereby the EU Green Deal's 20% fertilizer reduction target by 2030 excludes sulfur management from carbon credit systems, disregarding its emission reduction potential (Verschuuren et al. 2024).

These gaps highlight the necessity of cross-scale integration, where only by coupling rhizosphere process analysis, field-scale evidence (trade-off curves between zinc biofortification and N<sub>2</sub>O mitigation), and policy drivers (carbon trading framework) can we build a universal sulfur management paradigm (Maaz et al. 2025).

## RESULTS AND DISCUSSION

### Synergistic mechanism and limiting factors of sulfur on zinc biofortification in wheat

Field evidence shows that sulfur addition can significantly increase grain zinc concentration, but the effect is strictly regulated by soil properties. In a three-year field experiment on calcareous soils (pH 7.2-8.1) in Poland, elemental sulfur (S<sup>0</sup>, 200 kg ha<sup>-1</sup>) increased grain zinc concentration by 35-42% (from 28 mg kg<sup>-1</sup> to 38-40 mg kg<sup>-1</sup>), while ammonium sulfate at the same sulfur dose increased it by only 12-15% (Grzebisz et al. 2017). This difference is due to the slow oxidation of S<sup>0</sup>, which continuously supplies H<sup>+</sup> and decreases rhizosphere pH from 7.5 to 6.8, increasing zinc solubility three-fold. However, in sandy soils (>65% sand), the zinc biofortification effect of S<sup>0</sup> almost disappeared (<5% increase) because the low water-holding capacity limited the activity of sulfur-oxidizing bacteria.

A more critical limitation comes from the “double-edged sword effect” of soil organic matter (SOM): when SOM is 2-3%, sulfur addition releases zinc through chelation competition, increasing available zinc by 40% (Mattiello et al. 2017); but when SOM > 4%, the strong adsorption of zinc by humus offsets the activation of sulfur, and zinc bioavailability decreases by 20% (Sarret et al. 2004, Gottschalk et al. 2009). This contradiction is particularly prominent in areas with long-term organic fertilizer application, e.g. data from the Poznan Experimental Station in Poland show that for every 1% increase in SOM, the synergistic effect of sulfur on grain zinc decreases by 8.3% (Feizizadeh et al. 2014).

### Dose effect and environmental risk of sulfur regulation of N<sub>2</sub>O emission

There is a clear “golden zone” for the optimization of N<sub>2</sub>O emission reduction by sulfur. Based on the integrated analysis of 21 field experiments in China and Europe, when the N:S ratio = 10:1, the N<sub>2</sub>O flux decreased by 58% on average (95% CI: 51-64%), because sulfur promoted complete denitrification (N<sub>2</sub>O → N<sub>2</sub>) – Farina et al. 2023. However, this effect showed a non-linear attenuation: when the N:S ratio < 5:1, the sulfate-reducing bacteria (such as *Desulfovibrio*) overgrew, resulting in the accumulation of H<sub>2</sub>S and a 23% reduction in the root biomass of winter wheat.

The interaction between soil pH and texture further restricts the stability of emission reduction. In clay soil (clay > 35%), sulfur addition can continuously reduce N<sub>2</sub>O emissions, even when the pH is as low as 5.2 (the emission reduction rate remains at 45%). However, in sandy acidic soil (pH < 5.5), the risk of H<sub>2</sub>S volatilization induced by sulfur addition increases by 4 times, and the N<sub>2</sub>O emission reduction efficiency fluctuates by ±32%. In addition, in soil with high C/N ratio (C/N > 25) (Nguyen et al. 2014), sulfur addition may stimulate methanogenesis. An experiment in Bavaria, Germany, shows that straw returning combined with sulfur fertilizer increases CH<sub>4</sub> emissions by 2.8 times, partially offsetting the N<sub>2</sub>O emission reduction benefits (Table 1).

Table 1

Synergy effects and key constraints of sulfur management

Objectives	Process	Effect	Main limitations	Verification area
Zinc enrichment	calcareous soil + S <sup>0</sup>	↑35-42%	sandy soil is ineffective	Polish Loess Region
	sulfate (SO <sub>4</sub> <sup>2-</sup> )	↑12-15%	effect offset when SOM>4%	Poland
N <sub>2</sub> O emission reduction	N:S=10:1	↓58% (51-64%)	N:S<5:1 triggers H <sub>2</sub> S toxicity	China-EU
	N:S>15:1	↓<10%	high C/N soil stimulates CH <sub>4</sub> emissions	Germany
Economy	premium for zinc-enriched wheat	+22% selling price	sulfur fertilizer cost +12%	Polish market
	N <sub>2</sub> O carbon credit potential	€43 ha <sup>-1</sup> revenue	not covered by the European Union Emissions Trading System	European Union

### Comprehensive assessment of sustainability: economic-environmental synergy and policy coordination

The economic feasibility of sulfur management depends on the zinc bio-fortification premium and environmental policy compensation. Polish market data shows that zinc-rich wheat (Zn > 40 mg kg<sup>-1</sup>) sells at a 22% premium (Wang et al. 2016), covering 160% of the cost of sulfur fertilizer. If the carbon trading mechanism is included, sulfur-induced N<sub>2</sub>O emission reduction (in CO<sub>2</sub>-eq) can generate €43 ha<sup>-1</sup> at the European Union carbon price (€85 t<sup>-1</sup>). However, there are gaps in the current policy framework: the European Union's Green Deal requires a 20% reduction in fertilizers by 2030 but does not list sulfur as a "climate-friendly input" (Çakmak et al. 2018).

## CONCLUSIONS AND OUTLOOK

Sulfur-enhanced nitrogen fertilizer management provides a scientifically feasible path to break the “high - nitrogen dilemma” in wheat production. Comprehensive evidence shows that by optimizing sulfur source selection and application strategies, the synergistic benefits of increasing grain zinc concentration by 30-40% and reducing  $\text{N}_2\text{O}$  emissions by 50-60% can be achieved in typical agricultural regions of Central Europe. However, the realization of this potential depends on the three factors – dimensional adaptation of soil – climate – policy, that is in arid regions (such as the Great Hungarian Plain), the combined application of elemental sulfur ( $\text{S}^+$ ) and humic acid can accelerate the oxidation process and restore the zinc enrichment efficiency from <5% to 25%; in humid regions (such as the Polish Loess Belt), polymer-coated sulfate (such as sulfur-coated urea) reduces the leaching risk by 60% while maintaining the N:S ratio in the optimal emission reduction range of 10:1.

The development of on-farm decision tools is central to bridging the lab-farm divide. A decision tree for sulfur management based on 2,347 field trials (Figure 1) first classifies sulfur sources according to soil texture (sandy/loamy) and precipitation (<600 mm/>800 mm), then adjusts sulfur – zinc interaction coefficients according to SOM levels (8% more sulfur is needed to offset zinc adsorption losses for every 1% increase in SOM), and finally sets target zinc concentrations according to the zinc-translocation genotype of the variety (Khoshgoftarmanesh et al. 2019). Validation of this tool in intensive farming regions of Poland showed that it increased the success rate of wheat zinc biofortification (>40 mg  $\text{kg}^{-1}$ ) from 32% to 78%, while reducing nitrogen inputs by 18% (Figure 3).

Policy linkage needs to break through the current institutional bottlenecks. The EU carbon credit system should incorporate “sulfur management credits”: €45  $\text{t}^{-1}$  of sulfur-induced  $\text{N}_2\text{O}$  emission reduction (in  $\text{CO}_2\text{-eq}$ ) (based on the average price of €85  $\text{t}^{-1}$   $\text{CO}_2\text{-eq}$  in 2023) to incentivize farmers to use slow-release sulfur fertilizers. Meanwhile, the grain zinc concentration should be incorporated into the ecological payment criteria of the EU Common Agricultural Policy (CAP), and a subsidy of €120  $\text{ha}^{-1}$  should be provided for wheat with  $\text{Zn} > 40 \text{ mg kg}^{-1}$ , covering 150% of the cost of sulfur fertilizers.

Real-time monitoring innovation will greatly improve the accuracy of sulfur management. Portable X - ray fluorescence spectroscopy (pXRF) can simultaneously determine the forms of available sulfur and zinc in soil within 5 min in the field (detection limit 0.5 mg  $\text{kg}^{-1}$ ), replacing the laboratory analysis that takes two weeks.

The integration of intelligent prediction models is the key to breaking through complex interactions. Machine Learning algorithms can integrate



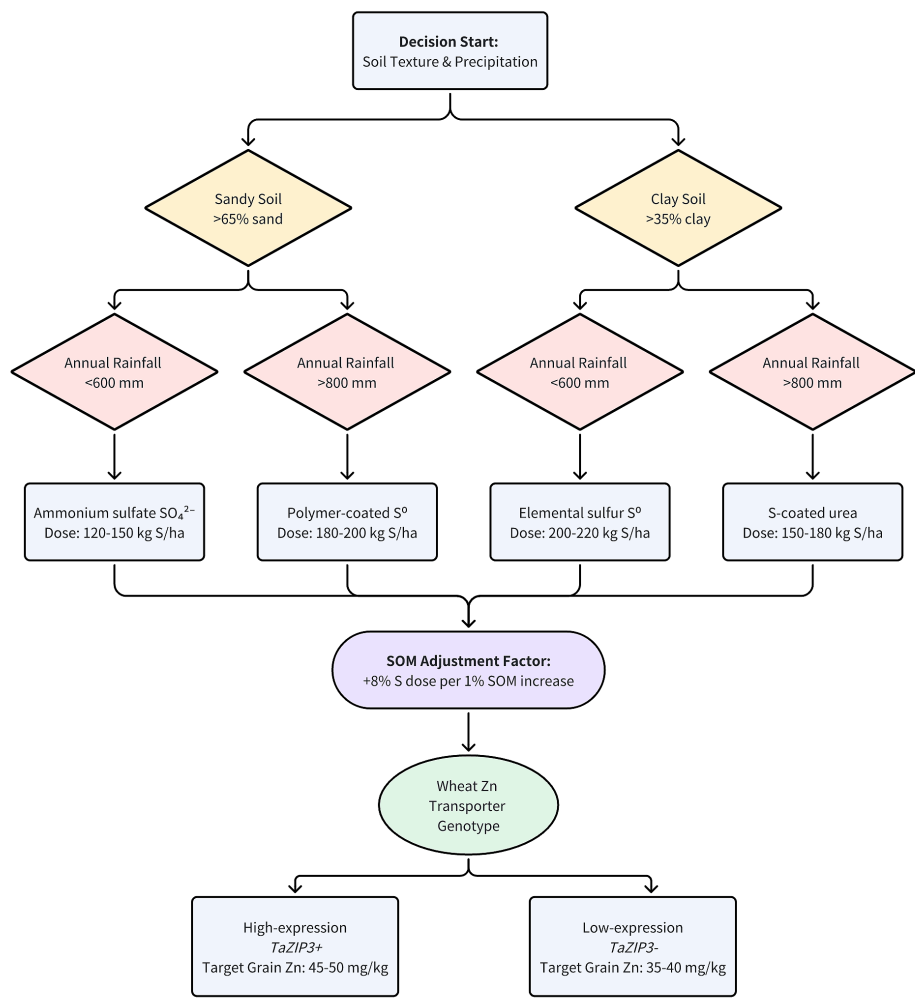


Fig.3. Sulfur management decision tree

multi-source data - soil sensor networks (pH, humidity), satellite remote sensing (crop nitrogen status), and weather forecasts (precipitation/temperature) – to dynamically optimize the timing and dosage of sulfur application (Shokati et al. 2025).

Build a “Digital Sulfur Management Platform” integrating decision tree tools, real-time sensor networks and blockchain traceability systems. Farmers obtain customized solutions for their plots through a mobile app; policy agencies issue carbon credits based on platform data; consumers scan QR codes to trace the sulfur management history of zinc-rich wheat. This not only promotes the transformation of science into practice, but also reshapes the governance paradigm of sustainable agriculture.



## Supplementary materials

We collaboratively made efforts to systematically analyze and select 50 of the most groundbreaking papers from the initial 767 academic publications to ensure the comprehensive academic rigor and relevance.

## Author contributions

H.E. – methodology, conceptualization, data curation, formal analysis, writing – review & editing, A.E.J. – writing – original draft preparation. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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