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Effects of Nitrogen Fertilizer Application on Soil Properties and Arsenic Mobilization in Paddy Soil

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Abstract: Anthropogenic nitrogen (N) fertilization may substantially alter arsenic (As) behavior in the soil. However, a comprehensive understanding of how the soil As cycle responds to external N addition remains elusive. This study investigates the effects of various N fertilizers on soil properties and As mobility in paddy soil. Regardless of N sources, the concentrations of soluble As and SPLP-extractable As decreased with all N applications. Similarly, soil acidification occurred and dissolved iron (Fe) increased in most treatments, except for KNO_3 addition. However, only the KNO_3 application could reduce As desorption from soil minerals based on phosphate extraction. Also, KNO_3 enhanced both soil catalase (S-CAT) and dehydrogenase (S-DEH) activities. Other N treatments decreased S-CAT activities, but increased S-DEH activities. Principal components analysis indicated that phosphate extractable As was associated with NH_4^+-N concentration and S-DEH activity, while the concentrations of soluble As and SPLP-extractable As were associated with pH, S-CAT activity, and dissolved Fe. These results demonstrated that the soil properties induced by the N application are the main drivers of As desorption in paddy soil and that KNO_3 application is more eco-friendly than other N sources in As-contaminated paddy soil. This study shed light on the reasonable application of N-bearing fertilizers and the importance of soil properties to assess As mobility in As-contaminated paddy soil.

Keywords: nitrogen fertilizer; arsenic; soil properties; redox reactions; soil enzymatic activities

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Citation: Han, B.; Chen, W.-Q.; Jiao, Y.-Q.; Yang, R.; Niu, L.-L.; Chen, X.-R.; Ji, C.-Y.; Yin, D.-X. Effects of Nitrogen Fertilizer Application on Soil Properties and Arsenic Mobilization in Paddy Soil. *Sustainability* **2024**, *16*, 5565. https://doi.org/10.3390/su16135565

Academic Editor: Luciano Cavani

Received: 12 May 2024
Revised: 26 June 2024
Accepted: 26 June 2024
Published: 28 June 2024

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1. Introduction

Arsenic (As) is a redox-sensitive element with toxic and carcinogenic properties to organisms [1–3]. It is predominantly present in inorganic forms (As(V) and As(III)) in soils, but As(III), and As(0) also naturally occur. In general, the mobility of As depends on the redox potential, and it can be mobilized under both oxic and anoxic environments. Under oxidizing conditions, As is present in arsenate oxyanions, which prefer to be adsorbed at mineral surfaces [4,5]. In reducing soils, As occurs as uncharged arsenious acid ($H_3As^{III}O_3{}^0$) and arsenite ($H_2As^{III}O_3{}^-$) [6]. Therefore, As is substantially more mobile in reducing conditions than oxidizing conditions. Paddy soil is submerged during rice cultivation, thus forming an anaerobic environment and inducing several chemical changes in the soil, including pH and oxidation-reduction potential/redox potential (ORP/Eh) [7]. When compared to other cereals, rice is more efficient in accumulating As as a consequence of anaerobic/flooding conditions [8]. Therefore, As contamination in paddy soil and its environmental risk have been a serious global concern in recent years.

The mobility of As is responsible for its uptake by rice and is primarily affected by the physical and chemical factors of the soil like ORP, pH, soil nutrients, and adsorption/desorption processes [9,10]. Changes in pH and ORP directly affect redox transformation and As mobilization. Generally, a high pH increases negative charges at the soil surface, which may enhance the desorption of As into the aqueous solution, while a low pH induces less negative charges and promotes As adsorption to soil minerals [11]. In flooding

paddy soil, ORP decreases due to the depletion of oxygen (as the electron acceptor) and the dissolution of Fe(oxy)hydroxides, promoting As desorption into the soil solution [12,13]. Microbial activities can also be regulated by physicochemical properties and play an important role in As mobility [14]. Soil enzymes are vital for biochemical processes and are often used to indicate microbial activities. In particular, Catalase (CAT) is one of the important enzymes that contributes to oxygen degradation, and dehydrogenase (DHA) acts on the biological oxidation of soil organic compounds [6]. These oxidoreductases are the catalysts of oxidation-reduction reactions and are dependent on redox fluctuation [10,15], thus affecting As mobility.

In addition, soil nutrients, such as N, P, S, and other elements, are reported to affect the mobility of As in soil. N is an essential nutrient element promoting plant growth and being widely applied to paddy fields [16]; N-contained fertilizer is predominantly present in the form of ammonia, nitrate, or urea in agriculture [17]. In the soil, N predominantly exists in inorganic forms, including nitrate-N (NO_3^--N) and ammonium-N (NH_4^+-N), which both can be utilized by rice plants. The former is prevalent under aerobic conditions and the latter often exists in anaerobic/flooding soils [18]. In flooded paddy, the main form of N is NH_4^+-N, while the NO_3^--N content is relatively low. The addition of NH_4^+-N decreases the soil pH and drives the process of ammonia oxidation coupled with Fe(III) reduction under anaerobic conditions, which may enhance As reduction [19]. However, nitrate can be used as a strong oxidant for improving the reducing environment in the paddy soil [20]. The coupled NO_3^--N reduction and Fe(II) oxidation could oxidize Fe(II) to Fe(III) in the soil solution, thus increasing As sorption and reducing its release [21]. Additionally, nitrate significantly enhanced the abundance of As oxidized microbial and stimulated anaerobic microbial arsenite oxidation, thus attenuating As mobility [22]. Therefore, fertilizing with N sources can affect the mobilization of As in paddy soil.

In recent years, fertilization with significant amounts of N is a common strategy to increase rice yields. Previous studies investigated the interactions between N fertilizers and metal(loid) fates in soils, often with a single type fertilizer [22–24]. Less attention has been paid to the effect of redox chemistry dynamics induced by various N-contained fertilizers on As' fate in paddy soil. Here, the soil pH, ORP, dissolved N, dissolved Fe, and oxidoreductase activities were measured to evaluate the soil properties and oxidation/reduction reactions. Soluble As, SPLP extractable As, and phosphate extractable As were used to assess As mobility. The objective of the present study was to investigate the variation of soil properties induced by the application of N and its effect on As mobility in paddy soil.

2. Materials and Methods

2.1. Soil Samples Collection and Pre-Treatment

The soil used in this study was collected from a paddy field in the vicinity of Shimen realgar mine in Changde City, Hunan Province, China (coordinates: 111°1′45″ E, 29°38′45″ N), with annual average temperatures between 16 and 19 °C and annual precipitation between 1200 and 1700 mm. The soil was described and classified as an Alic Umbrisol following the World Reference Base for Soil Resources [25]. After being air-dried, the soil samples were ground and sieved through a 2 mm sieve. The basic physiochemical parameters including the texture, pH, dissolved organic carbon (DOC), nutrient contents, and availability were determined (Table 1). Also, the soils were digested using the USEPA 3050B method, and the typical metals were determined via inductively coupled plasma mass spectrometry (ICP-MS, NexION 300, PerkinElmer, Shelton, USA). Their concentrations were ($mg \cdot kg^{-1}$) as follows: 32.78 ± 1.05 (As), 0.36 ± 0.05 (Cd), 10.41 ± 0.08 (Co), 27.62 ± 4.30 (Cr), 18.73 ± 0.61 (Cu), 801.1 ± 28.01 (Fe), 128.9 ± 5.21 (Mn), 19.87 ± 1.04 (Ni), 80.64 ± 7.13 (Zn).

Table 1. Main physical and chemical properties of the tested soils.

Soil physical-Chemical Factors	Unit	Value (Mean ± SD)
Texture		Clay loam
pH		4.69 ± 0.07
DOC	$g \cdot kg^{-1}$	9.19 ± 0.09
Total N	$g \cdot kg^{-1}$	1.26 ± 0.04
Total P	$g \cdot kg^{-1}$	0.55 ± 0.00
Total K	$g \cdot kg^{-1}$	12.0 ± 0.01
Available N	$mg \cdot kg^{-1}$	92.8 ± 2.29
Available P	$mg \cdot kg^{-1}$	5.91 ± 0.03
Available K	$mg \cdot kg^{-1}$	101 ± 0.36

2.2. Soil Incubation with Nitrogen Application

To simulate paddy conditions, a flooding soil incubation experiment was performed. Firstly, soil (230 g per pot) was weighed and pre-incubated with deionized water at a 100% water-holding capacity for 14 d. Following this, the N fertilizer was added to each pot to achieve 1, 5, and 10 mM N per kg soil, respectively. Four N fertilizer types were used in this experiment for each application rate, including KNO_3, $(NH_4)_2SO_4$, NH_4NO_3, and CH_4N_2O (urea). The soil without the N addition was referred to as the control (CK). There are 13 treatments in total, and every treatment was carried out in three replicates. The water level was maintained at ~3 cm above the soil surface via daily weighing and adding water to compensate for any losses. The experiment was conducted in a greenhouse at a controlled temperature (22/28 °C, night/day) with 60–70% relative humidity. All pots were randomly placed, and their positions were changed every week during the whole incubation.

The soil pH and ORP were measured at the end of the 30d incubation period. Deeper soil samples were collected in each pot and centrifuged to separate porewater from the soil. The separated soil was air-dried and ground to pass a 2 mm sieve for As extraction. A portion of the soil in each sample was further ground and passed through a 0.15 mm sieve for enzymatic activity analysis.

2.3. Determination of NO_3^--N, NH_4^+-N, and Fe Content in Soil Porewater

The porewater was sampled via soil centrifugation (4000 rpm for 20 min) and then passed through 0.45 μm filters. The filtrate was stored in a 4 °C refrigerator for subsequent analysis. The NO_3^--N, NH_4^+-N, and Fe content were analyzed using colorimetric techniques following previous studies [26,27]. A subsample of porewater was acidified to a pH < 2 with 0.5 M HCl immediately after being filtered, and was used to analyze the As concentration with an atomic fluorescence spectrometer (AFS, Puxi PF5, Beijing, China).

2.4. Analyses of Mobile As

The bioavailable As in each treatment was determined using the phosphate extraction method [28], which is effective in desorbing As from constituents through a ligand exchange and provides a mild extraction medium to predict the As availability to plants [29,30]. Briefly, 1 g of the air-dried sieved sample was mixed with 25 mL of 0.5 M KH_2PO_4 and placed in a 50 mL polycarbonate centrifuge tube. These tubes were shaken for 24 h at 200 rpm and then centrifuged at 4000 rpm for 20 min. The supernatants were filtered through 0.45 μm filters and acidified with 0.5 M HCl to a pH < 2. The concentrations of As in the extracts were analyzed using AFS.

To simulate an acid rain environment, the synthetic precipitation leaching procedure (SPLP, USEPA 1312, 1994a) was conducted to investigate the short-term leachability of As [31]. Briefly, the soils were extracted with a mixture of H_2SO_4 and HNO_3 with a volume ratio of 4:1, which was diluted to a pH of 4.20 ± 0.05 (the extraction was called a SPLP fluid). Furthermore, 1 g of the homogenized soil sample and 40 mL of the SPLP fluid were put into a 50 mL centrifuge tube. The tubes were capped and shaken for 18 h at 200 rpm,

then centrifuged for 20 min at 4000 rpm. The supernatant leachate solutions were passed through a 0.45 μm filter, acidified to pH < 2, and analyzed for As using AFS.

2.5. Enzymatic Activity Analysis

Enzymatic activity has been considered a good indicator for assessing microorganism activity [32]. Two important intracellular enzymes, S-CAT and S-DEH, have been used to indicate the life processes of soil microbes and nutrient cycling [33]. S-CAT and S-DEH in the soil were measured to evaluate microorganism activity according to Stepniewska et al. (2009) [34]. Briefly, S-CAT was determined based on its ability to hydrolyze H_2O_2 via titration with 0.1 M $KMnO_4$. S-DEH was expressed as microgram triphenyl formazan (TPF) per gram of dry soil. Firstly, fresh soil was mixed with 0.8% TTC (2,3,5-triphenyl tetrazolium chloride) in Tris buffer (pH, 7.6) for 24 h in darkness at 30 °C. Then, triphenylformazan (TPF) extraction was conducted with a 50 mL mixture of acetone (90%, v/v) and CCI_4 (10%, v/v), followed by filtering through a 0.45 μm filter. The colorimetric intensity in the solution was measured at 485 nm.

2.6. Quality Control and Statistical Analysis

Each treatment contained triplicate samples and a reagent blank was used. During analysis, an analytical blank and calibration verification were included. The relative standard deviation (RSD) was $\leq$ 0.82%, and the recovery rate was 90–110% for As with AFS. All data are presented as the mean value of triplicates with standard error.

The linear regression analysis (Pearson's linear correlation) ($p < 0.05$) between independent variables was performed using SPSS 22.0 (IBM SPSS Statistics). Significant differences between different N treatments were determined according to a one-way analysis of variance (ANOVA), and the mean values were separated using Fisher's LSD test at $\alpha < 0.05$. The principal components analysis (PCA) of the parameters of all treatments was performed on the correlation matrix, as proposed by Andrews et al. (2002) [35] and Govaerts et al. (2006) [36]. Prior to the ANOVA analysis and PCA, dependent soil variables were tested for normality and homogeneity of variance using the Kolmogorov–Smirnov test and Leven's test, respectively. After the PCA, we extracted the variance eigenvalues and respective loadings for the first three principle components (Table S1).

3. Results and Discussion

3.1. N Fertilizers Can Acidify the Soil except for KNO_3

The original value of the pH in the control was 4.69, decreasing to 4.14 after 30 d of flooding incubation (Tables 1 and 2). All N amendments uniformly declined the soil pH, regardless of the types of N (Table 2). The pH of the soil declined by 0.20–0.94, 0.13–0.47, and 0.43–0.61 units in the $(NH_4)_2SO_4$, NH_4NO_3, and CH_4N_2O treatments, respectively. The soil pH tended to decrease with increasing N application rates, while the effect varied with N types. Compared to the control, the $(NH_4)_2SO_4$ and CH_4N_2O treatments significantly decrease the soil pH, while low-dose (1 mM) KNO_3 and NH_4NO_3 have no evident effect. This result might be attributed to how the CH_4N_2O and NH_4NO_3 addition might mainly release protons through hydrolysis under a certain threshold [37]. However, when the dose of CH_4N_2O or NH_4NO_3 reached up to 10 mM, the release of protons could be partly derived from nitrification. Also, the massive overdose might promote NH_3 production and then volatilization [38], then part of the volatilized NH_3 would re-enter the soil to produce OH^-, thus increasing the pH. In our study, 5 mM treatments of NH_4NO_3 and CH_4N_2O could release the most protons during the soil cultivation, thus having the lower pH.

Table 2. The pH and ORP were under different treatments after 30 days of incubation.

	Soil-pH				Soil-ORP (mV)			
	KNO_3	$(NH_4)_2SO_4$	NH_4NO_3	CH_4N_2O	KNO_3	$(NH_4)_2SO_4$	NH_4NO_3	CH_4N_2O
CK	4.14 ± 0.02 a	4.14 ± 0.02 a	4.14 ± 0.02 a	4.14 ± 0.02 a	−143 ± 0.42 d	−143 ± 0.42 d	−143 ± 0.42 a	−143 ± 0.42 b
1 mM	4.12 ± 0.01 a	3.94 ± 0.01 b	4.01 ± 0.01 a	3.70 ± 0.00 b	−116 ± 2.32 c	−139 ± 0.69 c	−122 ± 4.69 a	−136 ± 5.20 b
5 mM	4.02 ± 0.00 b	3.41 ± 0.01 c	3.67 ± 0.07 c	3.53 ± 0.03 c	129 ± 5.74 b	−69 ± 4.57 b	−133 ± 4.22 a	−125 ± 2.62 b
10 mM	3.94 ± 0.01 c	3.20 ± 0.01 d	3.84 ± 0.01 b	3.71 ± 0.01 b	230 ± 4.28 a	199 ± 5.78 a	−144 ± 1.78 a	−99 ± 2.92 a

Notes: Data are expressed as mean ± SD (n = 3). For each N type, numbers marked with different letters indicate significant differences between different application rates at $p < 0.05$ (LSD's test at $\alpha = 0.05$).

Soil pH is considered one of the important factors of As mobility [9], while acidification problems of soils are associated with the application of N. Our results are consistent with previous studies [39,40], which also confirmed that N fertilizer causes soil acidification. As Pan et al. (2020) [41] reported, N fertilizer applications significantly reduced the soil pH. The input of NH_4^+ strongly enhanced the H^+ production induced by nitrification [42] (Equations (1) and (2)).

$$NH_4^+ + 2O_2 = 2H^+ + NO_3^- + H_2O \quad (1)$$

$$CH_4N_2O + 4O_2 = 2H^+ + 2NO_3^- + H_2O + CO_2 \quad (2)$$

$$NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O \quad (3)$$

Under flooding cultivation, the oxygen content depleted gradually over time, and then NO_3^- replaced it as an electron acceptor to participate in microbial oxidation through the denitrification process. Denitrification consumes proton and reduces NO_3^- to N^2 (Equation (3)). Therefore, the value of pH was minimally affected by KNO_3 amendment when compared with other N fertilizers (Table 2). Similarly, previous research also reported that NH_4^+-N amendment decreased the pH of a medium loam soil more than NO_3^--N amendment [43,44]. The results indicate that soil acidification induced by the application of N is a common phenomenon, except for the appropriate dose of NO_3^--N.

3.2. Nitrogen Fertilizers Change ORP in As-Contaminated Soil

ORP is an important indicator for evaluating the oxidation-reduction status in soil [45]. The ORP values in the control soil were below −140 mV after 30 d of cultivation (Table 2), indicating a highly reducing condition and oxygen depletion via organic matter mineralization or biological/microbiological activities under flooding conditions. When compared with the control, the amendments of NH_4NO_3 and CH_4N_2O had no obvious effect on the ORP values. However, KNO_3 and $(NH_4)_2SO_4$ applications significantly increased the ORP values by ~261% and ~200%, respectively ($p < 0.05$). This is because both nitrate and sulfate could be used as electron acceptors of anaerobic bacteria after being oxygen-depleted, while the ORP scales at the same N ratio were higher in KNO_3 than in $(NH_4)_2SO_4$ treatments, which might be attributed to bacteria's preference for nitrate over sulfate [45].

Some previous research reported that ORP showed a pH-dependent behavior in paddy soils, as a consequence of microbial activities and organic matter decomposition or protons consumption for the reduction in Mn and Fe [46–48]. However, no significant correlation was observed between the pH and ORP values in the test soils (Table 3). In flooding soils, the effect of protons on ORP depends on the oxidant concentration undergoing reduction [49]. Based on the various minerals of geological interest, the redox potential fluctuated from −200 mV to 1000 mV when the pH values were around 4 in aqueous environments, but the pH range was narrow in reduced soils [50].

Table 3. Correlation coefficients among all parameters.

	pH	ORP	NH_4^+-N	NO_3^--N	S-CAT	S-DEH	Fe(II)	Total Fe	Porewater-As	SPLP-As	KH_2PO_4-As
pH	1	−0.21	−0.38 *	−0.42 **	0.77 **	−0.25	−0.04	−0.05	0.61 **	0.11	−0.18
ORP		1	−0.10	0.92 **	−0.16	−0.21	−0.12	−0.15	0.18	−0.13	−0.39 *
NH_4^+-N			1	−0.17	−0.55 **	0.61 **	0.74**	0.76 **	−0.11	0.01	0.09
NO_3^--N				1	−0.33 *	−0.27	−0.25	−0.28	−0.04	−0.15	−0.32
S-CAT					1	−0.26	−0.19	−0.22	0.50 **	0.27	−0.28
S-DEH						1	0.48 **	0.51 **	−0.40 *	−0.03	0.22
Fe(II)							1	0.99 **	0.13	0.08	−0.20
Total Fe								1	0.10	0.07	−0.14
Porewater-As									1	0.33 *	−0.29
SPLP-As										1	−0.13
KH_2PO_4-As											1

Notes: The asterisks indicate the significance of correlation among the different parameters (LSD's test at $\alpha = 0.05$, *, $p < 0.05$, **, $p < 0.01$).

3.3. Nitrogen Fertilizers Change the Solubility of Nitrogen and Iron in the Soil

The dissolved inorganic N that occupied ~85.6% of the total inorganic N in the cultivated control soil was mainly NO_3^--N (Figure 1). Fertilization with N, including all types of fertilizers, enhanced the dissolution of NO_3^--N in the porewater, especially higher rates of KNO_3 and $(NH_4)_2SO_4$ (5 mM and 10 mM), which was a consequence of nitrification (Equations (1) and (2)). However, the dissolved NH_4^+-N contents declined with low-level N fertilization (1 mM), but increased with a high rate of $(NH_4)_2SO_4$, NH_4NO_3, and CH_4N_2O. The input of the corresponding types of N via N-bearing fertilizers was also the reason for the enhancement of NO_3^--N in the soil. The dissolved Fe was determined by the total soluble Fe in the porewater, and the results showed that N fertilization decreased Fe solubility (Figure 2). This phenomenon may be a consequence of Fe(II) oxidation coupled with nitrate reduction [51].

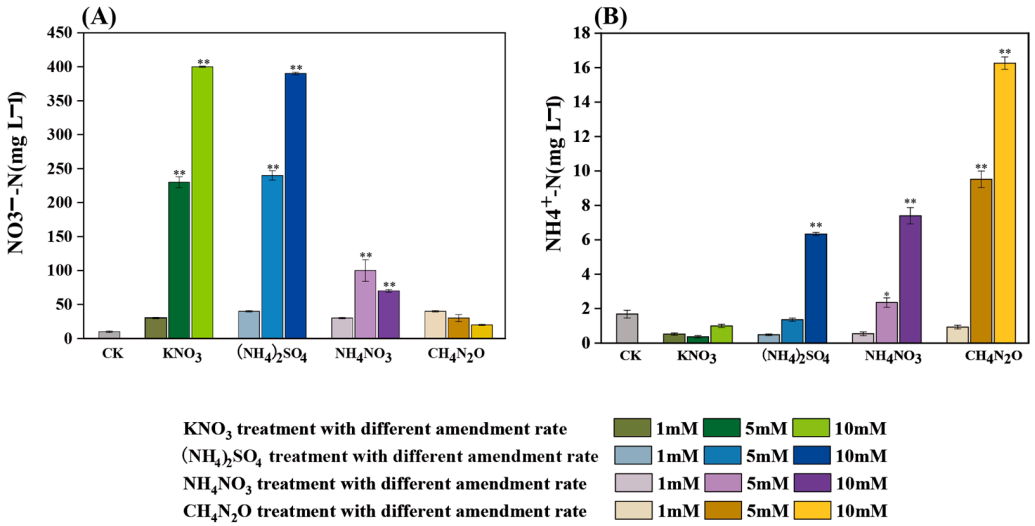


Figure 1. The contents of NO_3^--N (**A**) and NH_4^+-N (**B**) in soil porewater with different treatments. Notes: Data are expressed as mean ± SD (n = 3). The invisible error bar means that the standard deviation of the mean is small and close to zero. The asterisk indicates the significance of the difference between the control soil and different N treatments (LSD's test at $\alpha = 0.05$, *, $p < 0.05$; **, $p < 0.01$).

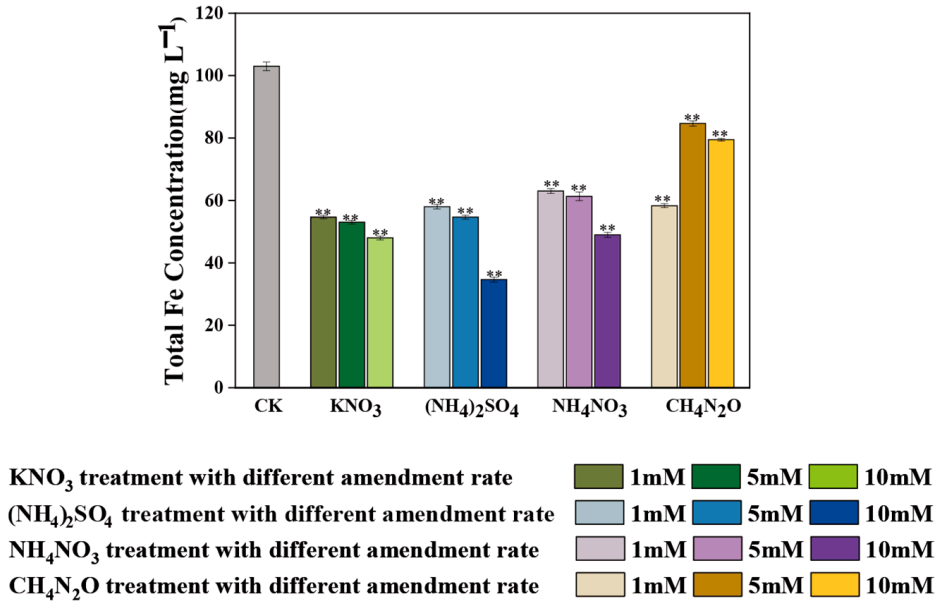


Figure 2. The contents of dissolved Fe in porewater. Notes: Data are expressed as mean ± SD (n = 3). The invisible error bar means that the standard deviation close to zero. The asterisks indicate the significance of the difference between the control soil and different N treatments (LSD's test at $\alpha = 0.05$, **, $p < 0.01$).

3.4. Nitrogen Fertilizers Inhibit S-CAT Activities While Enhancing S-DEH Activities in the Soil

Soil enzymes catalyze the main biochemical reactions involved in N cycles, and the enzymatic activity is sensitive to soil health [47]. S-CAT is an intracellular enzyme found in all aerobic bacteria and most facultative anaerobes, and it can split hydrogen peroxide into molecular oxygen and water, thus preventing cells from poisoning [34]. The activities of S-CAT were significantly influenced by N fertilizers, and the influences varied depending on N types and the application rates (Table 3 and Figure 3). After 30 d of cultivation, the S-CAT activities in the $(NH_4)_2SO_4$, NH_4NO_3, and CH_4N_2O treatments decreased by 18.4–71.0%, 10.3–40.1%, and 12.9–45.6%, respectively, and the mean S-CAT decreased with the increasing N fertilization rates. Dissimilarly, KNO_3 treatments increased the S-CAT activity under low and medium N additions (1 mM and 5 mM) and decreased it under high N conditions (10 mM). These results indicate that a limited dosage of KNO_3 could enhance S-CAT activities. Therefore, the application dosage of N-contained fertility needs to be addressed in paddy soil. As a previous study reported, KNO_3 amendment broke seed dormancy and improved seedling growth, while the activities of catalase and peroxidase enzymes showed an increase in concentrations of 0.2–0.4% and a strong decrease in high concentrations [52].

Correlation analysis shows a significant positive correlation between S-CAT and soil pH (Table 3, $p < 0.01$), which indicates that S-CAT activities decreased in most N fertilization treatments, which might be attributed to the reduction in the soil pH. This result is consistent with Quan et al.(2016) [53], who also found that the S-CAT activity and soil pH were significant positive correlation. However, there is no evident acidification in why the treatments with a low rate of KNO_3 obtained higher S-CAT than the control. The other reason is that medium KNO_3 applications could increase the number of aerobic microorganisms under flooding conditions [54].

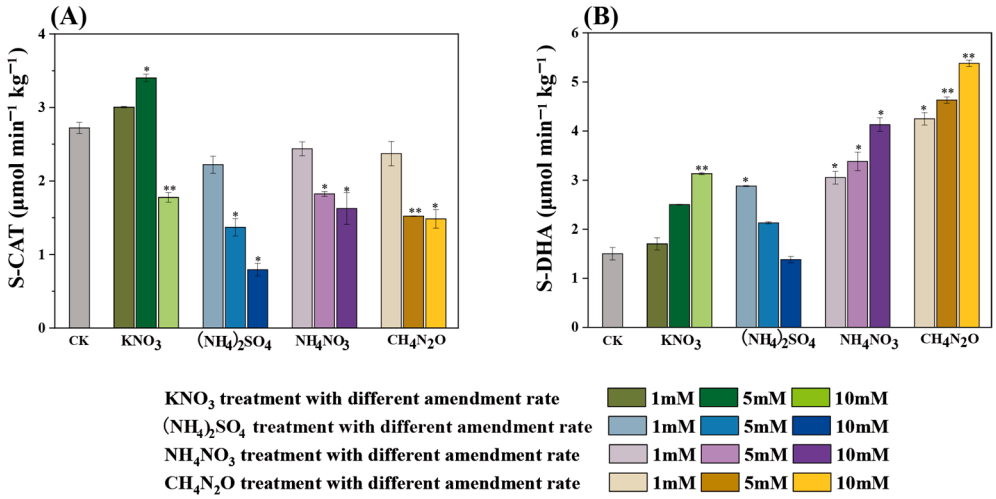


Figure 3. The activities (μmol min^{-1} kg^{-1}) of soil catalase (S-CAT) (**A**) and dehydrogenase (S-DEH) (**B**) under different treatments. Notes: Data are expressed as mean ± SD (n = 3). The invisible error bar means that the standard deviation of the mean is small and close to zero. The asterisks indicate the significance of the difference between the control soil and different N treatments (LSD's test at $\alpha = 0.05$, *, $p < 0.05$, **, $p < 0.01$).

The addition of the N fertilizer stimulated soil S-DEH activity, and it increased with the increase in the N application rate with KNO_3, NH_4NO_3, and CH_4N_2O. However, $(NH_4)_2SO_4$ application increased S-DEH activity at a low application rate (1 mM), while there was no evident effect at a higher application rate (5 mM and 10 mM). The S-DEH activity was enhanced significantly ($p < 0.05$) with the application of both NH_4NO_3 and CH_4N_2O when compared to the other treatments (Figure 3). This result indicated that N fertilization may trigger higher microbial metabolic activity than CK, except for the 10 mM $(NH_4)_2SO_4$ treatment [22]. One of the possible reasons is that the biochemical environment of the soil was less oxidative with a lower redox potential (Table 2) in the NH_4NO_3 and CH_4N_2O treatments [22,55].

3.5. The Effect of Nitrogen Amendments on As Mobility in the Soil

The concentrations of As in the porewater with KNO_3, $(NH_4)_2SO_4$, NH_4NO_3, and CH_4N_2O were 13.7–26.7%, 40.4–52.0%, 38.7–44.8%, and 30.5–50.5% lower than in the control, respectively (Figures 4A and S1A). All N applications, regardless of the applications rate, significantly decreased the dissolved As ($p < 0.05$). However, the application rate had no significant effect on the same N species, which was probably because the different nitrogen fertilizers contain different ions and have different effects on arsenic. The dissolution of As is one of the important indicators for available-As assessments. The soil pH and enzymatic activity may be the main factors as a result of the correlation analysis, demonstrating that the dissolved As was significantly positive/negative relative to the pH, S-CAT, and S-DEH activity (Table 3).

The concentrations of SPLP-extractable As were evidently reduced with 10 mM KNO_3 and 5 mM NH_4NO_3, while other treatments had no evident effect, though the concentration was reduced (Figures 4B and S1B). The water-soluble As may be the main factor of SPLP-extractable As according to the correlation analysis, which shows that the As concentration in the porewater and SPLP-extractable As were relatively significant ($p < 0.05$, Table 3). The concentrations of SPLP-extractable As were close to the water-soluble As in the control and KNO_3 treatments, but other N treatments seem to have increased acid rain leaching, demonstrated by the fact that As concentrations in SPLP extraction were evidently higher than in the porewater with $(NH_4)_2SO_4$, NH_4NO_3, and CH_4N_2O fertilization ($p < 0.05$). This result could be attributed to the acidification effect with these three N applications, while the soils were not acidified in the KNO_3 treatments (Table 2).

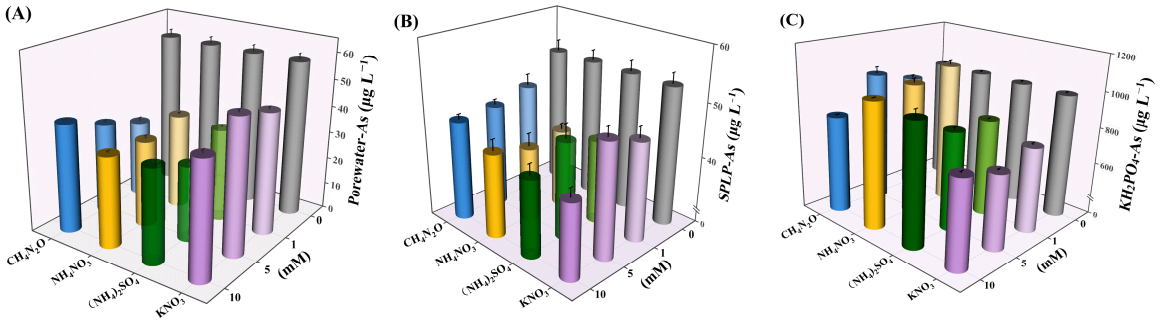


Figure 4. The porewater-As, SPLP-As, and KH_2PO_4-As concentrations under different treatments. ((**A**) Porewater-As concentration, (**B**) SPLP-As concentration, (**C**) KH_2PO_4-As concentration). Notes: Data are expressed as mean ± SD (n = 3). The invisible error bar means that the standard deviation of the mean is small and close to zero. The gray columns are the control without N application. The colors (blue, yellow, green, and purple) from light to dark represent the application rates from low to high.

The phosphate solution was found to be highly effective in extracting absorbed As from contaminated soil as a result of the ligand exchange of As and PO_4^{3-} [56]. The concentration of As in the KH_2PO_4 extraction was reduced by 20.8–27.7% in the KNO_3 treatments. Similarly, lower rates (1 mM and 5 mM) of $(NH_4)_2SO_4$ and 10 mM CH_4N_2O application also significantly decreased the KH_2PO_4 extractable As (Figures 4C and S1C). However, there was no evident decline in the extractable As in the NH_4NO_3 treatments. The results suggested that N fertilization with KNO_3 or proper application rates of $(NH_4)_2SO_4$ could significantly decrease the risk of As desorption from the contaminated soil, while the risk may be increased by NH_4NO_3 and $(NH_4)_2SO_4$ or CH_4N_2O with inappropriate application rates. The correlation analysis data revealed that KH_2PO_4 extractable As exhibited a negative correlation with the ORP in the soil, indicating that phosphate-extractable As may be dependent upon the variation of the oxidation-reduction reactions ($p < 0.01$, Table 3).

3.6. The Contribution of Soil Properties to As Mobility

For the different N treatments, PCA plots were used to visualize the key chemical parameters associated with pH, ORP, NO_3^--N, NH_4^+-N, S-CAT, S-DEH, dissolved Fe, water-soluble As, SPLP extractable As, and KH_2PO_4 extractable As (Figure 5 and Table S1). Clear associations among pH, S-CAT, and water-soluble As were found via the principal components analysis (PCA) of all N treatments. Similarly, KH_2PO_4 extractable As, NH_4^+-N, and S-DEH also presented clear associations. The PCA also highlights a clear differentiation in water-soluble As and KH_2PO_4 extractable As between the different N species. These parameters in the soil with KNO_3 applications were different from other N treatments (Figure 5B). The correlations between all parameters (Table 3) also highlight the important contribution of N fertilization on redox-sensitive changes in the soil, including the redox potential, oxidoreductase activity, and reductive dissolution of Fe, thus affecting the mobilization of As. The effects of the different parameters varied for both soluble As or extractable As.

Soil oxidation-reduction reactions play an important role in assessing As solubility, mobility, or bioavailability. Reducing soil conditions (ORP < 0 mV) greatly enhance the solubility and availability of As [57,58]. The application of KNO_3 significantly reduced water-soluble As and KH_2PO_4 extractable As, which could be attributed to the soil redox enhancement. The evident decline of ORP values with KNO_3 was observed, and the ORP values were negatively correlated with KH_2PO_4 extractable As ($p < 0.05$, Tables 2 and 3). In contrast, fertilization with other N species had fewer effects on the ORP values, especially NH_4NO_3. In addition, anaerobic microbial arsenite oxidation stimulated by nitrate also was the other reason. High rates (10 mM) of KNO_3 addition significantly decreased the S-CAT activity, but increased the S-DEH activity, demonstrating that microbe redox activities were

changed in the soil. Therefore, the dosage needs to be considered during the application of nitrogenous fertilizer, as shown in a previous study concerning KNO_3 amendment to break seed fertility and improve seeding growth, where the activities of catalase and peroxidase enzymes showed an increase in concentrations of 0.2–0.4% and decreased strongly in high concentrations of the seedling [52].

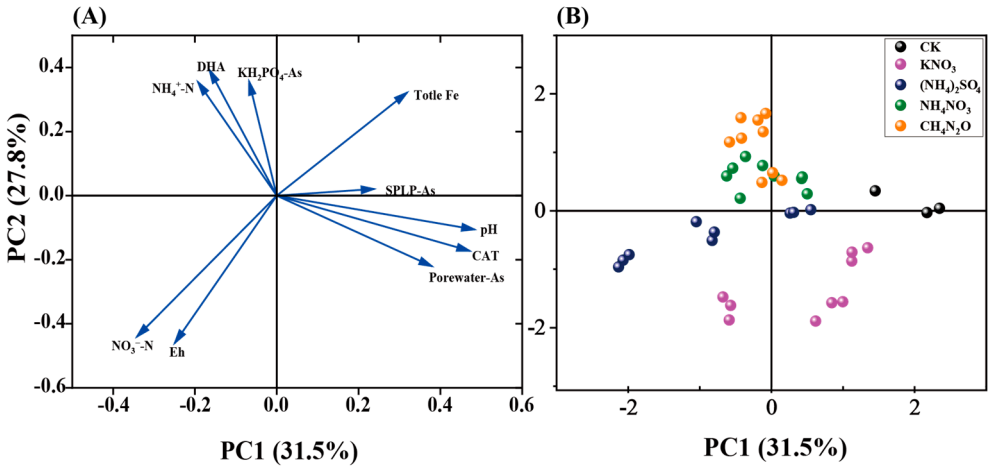


Figure 5. Factor load diagram (**A**) and score plot (**B**) of principal component analysis (the original analysis data shown in Table S1).

In paddy soil, As solubility is controlled not only by the redox potential, but also the amounts and types of the sorbent, such as Fe(III) hydroxides and As-combined minerals [39]. Soluble Fe in the porewater was also reduced with KNO_3 applications, suggesting that Fe oxidation occurred, which also adsorbed As on the mineral surface and thus decreased As mobility [59]. In general, oxidizing conditions and/or the presence of oxidants promote minerals immobilization, causing the precipitation of mobile As. Nitrate could be used as a powerful oxidant, which was responsible for oxidizing most Fe(II) under anoxic plus NO_3^--rich conditions [60]. Conversely, fertilization with NH_4^+-N ($(NH_4)_2SO_4$, NH_4NO_3, and CH_4N_2O) might increase the risks of soil acidification and As desorption from soil minerals (Table 2 and Figure 4C). This result was consistent with previous studies where NH_4^+-N could decrease the soil pH, as well as being used as a possible electron donor-induced reduction in Fe oxide minerals, thus increasing As mobility [61]. The link between NH_4^+-N and dissolved Fe ($R = 0.76$, $p < 0.01$) (Table 3) indicates the promoting effect of NH_4^+-N in Fe(III) reduction and As mobility [62,63].

4. Conclusions

In the present study, obvious changes in major redox-sensitive reactions in flooding paddy soil, such as redox potential, oxidoreductase activity, and the reductive dissolution of Fe, were caused by N fertilizers, thus affecting As mobilization. The observed phenomena suggested that N application had an important role in controlling As mobility, mainly by inducing redox-sensitive reactions in the soil. $(NH_4)_2SO_4$, NH_4NO_3, and CH_4N_2O were found to be risky for soil acidification and As desorption from soil. However, a suitable application rate of NO_3^--N fertilizer might be environmentally friendly in As-contaminated paddy soil. For example, medium rates of KNO_3 addition not only can increase soil enzymatic activities, but can also decrease As desorption with a low risk of soil acidification.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/su16135565/s1, Figure S1: The Porewater-As (A), SPLP-As (B) and KH_2PO_4-As (C) concentrations under different treatments; Table S1: Principal component analysis-Linear combination coefficient and weight results.

Author Contributions: Conceptualization, B.H. and R.Y.; methodology, L.-L.N.; validation, B.H., W.-Q.C. and D.-X.Y.; formal analysis, W.-Q.C.; investigation, X.-R.C. and C.-Y.J.; writing—original draft preparation, B.H. and R.Y.; writing—review and editing, B.H. and D.-X.Y.; visualization, W.-Q.C. and Y.-Q.J.; funding acquisition, D.-X.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 42107403.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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

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