

ORIGINAL PAPER

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Influence of iron pyrites and dicyandiamide on nitrification and ammonia volatilization from urea applied to loess brown earths (luvisols)

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Abstract Laboratory incubation study showed that iron pyrites retarded nitrification of urea-derived ammonium (NH_4^+), the effect being greatest at the highest level (10 000 mg kg^{-1} soil). Nitrification inhibition with 10 000 mg pyrite kg^{-1} soil, at the end of 30 days, was 40.3% compared to 55.9% for dicyandiamide (DCD). The inhibitory effect with lower rates of pyrite (100–500 mg kg^{-1}) lasted only up to 9 days. Urea+pyrite treatment was also found to have higher exchangeable $\text{NH}_4^+\text{-N}$ compared to urea alone. DCD-amended soils had the highest $\text{NH}_4^+\text{-N}$ content throughout. Pyrite-treated soils had about 7–86% lower ammonia volatilization losses than urea alone. Total NH_3 loss was the most with urea+DCD (7.9% of applied N), about 9% more than with urea alone.

Key words Ammonia volatilization · Denitrification · Dicyandiamide · Iron pyrites · Luvisols · Nitrification · Urea

Introduction

Nitrification inhibitors have been proposed as one of the management tools for the reduction of the potential hazards of fertilizer-derived nitrate pollution of surface and ground water and for the improvement of N use efficiency of crop plants (Prasad and Power 1995). At present, the most widespread and commercially used chemicals are dicyandiamide (DCD) and nitrapyrin. The high cost of these materials prevents their use in developing countries. Iron pyrites (FeS_2), occurring as sedimentary deposits in parts of northern India, have been found to inhibit nitrification (Blaise and Prasad 1993). However, their study has not

elucidated whether pyrite inhibits the conversions of NH_4^+ to NO_2^- or NO_2^- to NO_3^- . Moreover, the high NH_4^+ concentration resulting from the high N dose (500 mg kg^{-1}) used could have contributed to the inhibitory effect. The purpose of the present study was: (1) to assess the effect of iron pyrites vis-à-vis DCD on nitrification inhibition, (2) to establish which of the nitrification reactions are affected and (3) to find out the effect of iron pyrites on NH_3 volatilization from urea applied to loess brown earths (luvisols).

Materials and methods

The soil used in the study was a loess brown earth (luvisol) from cultivated fields at Dürnast, Freising, Germany, with a pH of 6.8 (1:2.5 soil:CaCl₂), organic C of 1.12% and total N of 0.12%.

Incubation technique

The experiment was set up by placing 100-g portions of air-dried soil directly in 300-ml polyethylene flasks (120 in nos.). The soils were moistened to 60% water-holding capacity. Then the flasks were pre-incubated for 2 weeks in an incubator maintained at $20^\circ\pm 1^\circ\text{C}$. Following pre-incubation the soil was treated with urea solution (100 mg N kg^{-1} soil) and different amounts of ground pyrite (100, 500, 1000, 5000 and 10 000 mg kg^{-1} soil designated as Py₁, Py₂, Py₃, Py₄ and Py₅, respectively). Agricultural grade pyrite was obtained from Pyrites and Phosphates Chemicals Limited, New Delhi, India, and it contained 20% and 22% total Fe and total S, respectively. The effect of pyrites was compared with DCD, obtained from SKW Trostberg AG, Germany, as a standard check. In the case of DCD treatment, 10% of the N was applied through DCD (approximately 15 mg DCD kg^{-1} soil) and the remainder through urea. Earlier workers in this laboratory found this dose to inhibit nitrification effectively. A no N control and urea alone treatments were also provided. Each treatment was replicated 3 times and separately for each date of sampling. The flasks were covered with parafilm provided with a few micropores for aeration, and placed in the incubator. Periodically the soil moisture was measured gravimetrically and replenished with distilled water.

Chemical analysis

After 3, 6, 9, 15 and 30 days, three flasks from each treatment were removed for extraction of mineral-N. Extraction was done by shaking

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for 1 hour on an end-over-end shaker with 0.1 N CaCl₂ (231–233 ml), taking into account the moisture content of the soil. After shaking, the flasks were left to stand for a few minutes and the pH was determined using combined electrodes. A small fraction was filtered (595 1/2 Schleicher and Schüll, Germany) and the filtrate was analysed for nitrite (NO₂⁻) and nitrate (NO₃⁻) by high-pressure liquid chromatography (Vilsmeyer 1984). Following filtration, ammonium-N (NH₄⁺) was determined using an Orion 95–12 NH₃-selective electrode (Germann-Bauer and Amberger 1989). None of the incubated soil samples contained more than 1 mg·kg⁻¹ NO₂⁻-N and for reasons of brevity it is referred to as NO₃⁻-N in the text. Percentage nitrification inhibition was calculated (1) using the formula of Bundy and Bremner (1973):

$$\frac{C - T}{C} \times 100 \quad (1)$$

where *C* is the amount of NO₃⁻ produced in the absence of inhibitor and *T* is the amount of NO₃⁻ produced in the soil treated with the test compound (pyrites and DCD).

Estimation of NH₃ volatilization

The incubation technique was similar to the one described above. Each treatment was replicated 3 times. The NH₃ evolved was trapped in 10 ml 4% boric acid-mixed indicator solution contained in the vials placed at the soil surface (Keeney and Nelson 1982). The vials were replaced daily during the first 3 days and later on the 7th and 15th days. Beyond 15 days no sizeable loss was observed. The trapped NH₃ was then titrated with standard 0.005 N H₂SO₄ and the amount of NH₃ evolved was calculated as percentage of N applied. At the end of 30 days, the amount of urea-N apparently immobilized and fixed in the clay fraction was calculated (2) by the formula:

$$100 - \{ \text{NH}_4^+ + \text{NO}_3^- - \text{N} + \text{NH}_3 \text{ lost (\% of applied N)} \} \quad (2)$$

with the assumption that denitrification losses are negligible.

The data for NH₄⁺, NO₃⁻ and NH₃ loss were statistically analysed using the procedures of Gomez and Gomez (1984) and differences between treatment means separated using least significant difference.

Results and discussion

Ammonium-N

Pyrite addition, in general, resulted in higher exchangeable NH₄⁺ compared to urea-N alone and slowed the disappearance of NH₄⁺-N (Fig. 1). The effect was most pronounced with urea+Py₅ followed by urea+Py₄, urea+Py₃ and urea+Py₂. The high NH₄⁺-N in pyrite-treated soils is attributed to nitrification inhibition (Blaise and Prasad 1993) and reduction in NH₃ volatilization (Blaise and Prasad 1995). DCD-treated soil samples had the highest NH₄⁺-N throughout the period of study, supporting earlier findings (Amberger 1986; Prakasa Rao and Puttana 1987).

Nitrate-N and nitrification inhibition

Addition of pyrite and DCD retarded the oxidation of urea-derived NH₄⁺, lowering the NO₃⁻ content compared to urea alone (Fig. 2). Pyrite at lower rates of application (100–500 mg kg⁻¹) had a marginal influence on nitrification compared to the higher rates (1000–10 000 mg kg⁻¹). Among the rates of addition, urea+Py₅ treatment had the

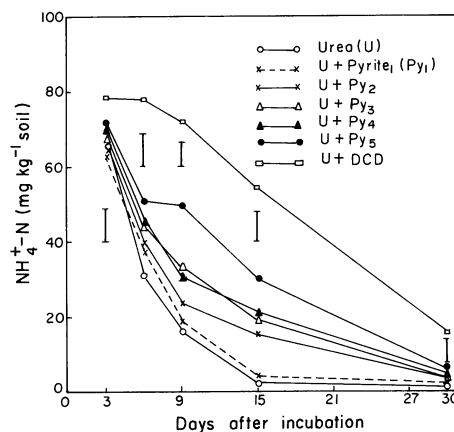


Fig. 1 Effect of pyrite and DCD on NH₄⁺ content following application of 100 mg urea-N kg⁻¹ soil (vertical bars indicate LSD *P* < 0.05)

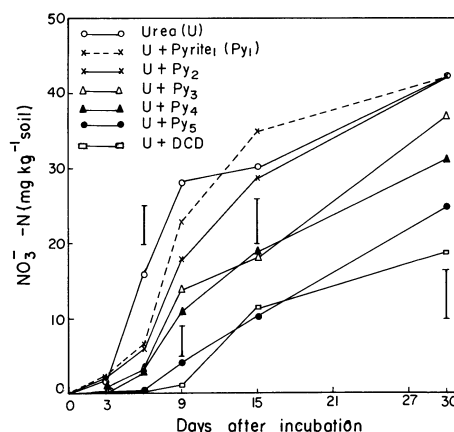


Fig. 2 Effect of pyrite and DCD on NO₃⁻ formation from urea-derived NH₄⁺

lowest NO₃⁻ content and did not differ significantly with urea+DCD. The inhibitory effect of pyrites increased with increasing level of application (Table 1). Soils treated with 10 000 mg pyrite kg⁻¹ soil had percentage inhibition comparable to DCD. Lower rates of pyrite application (100–500 mg kg⁻¹) retarded nitrification only up to 9 days. Non-accumulation of NO₂⁻ indicated that pyrite does not inhibit the second step of nitrification.

The exact mechanism by which pyrite inhibits nitrification is not known. It is therefore postulated that the effect of pyrite could be due to the toxic action of any one or a combination of the following: (1) sulphides (Prasad and Reddy 1977); (2) the oxidized forms of the sulphides, i.e. thiosulphates, tri- and tetrathionates; or (3) presence of Fe²⁺ ions (Goos and Ahrens 1992).

The decline in nitrification inhibition at the later stages was responsible for the drop in exchangeable NH₄⁺-N content. However, the decrease in NH₄⁺-N content did not correspond with the increase in NO₃⁻. This could be possibly due to NH₄⁺ fixation or immobilization by soil microorganisms and gaseous loss (NH₃ volatilization and denitrification). Total mineral-N at the end of 30 days was the least

Table 1 Effect (% nitrification inhibition) of pyrite and DCD on nitrification of urea-derived NH_4^+

	Days after incubation		
	9	15	30
Urea (U)+Py ₁	18.9	—	—
U+Py ₂	37.5	3.5	—
U+Py ₃	49.5	40.1	12.3
U+Py ₄	61.1	34.6	25.1
U+Py ₅	85.9	67.8	40.3
U+DCD	95.4	64.0	55.9

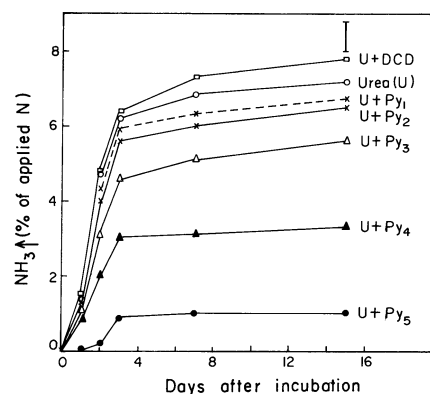
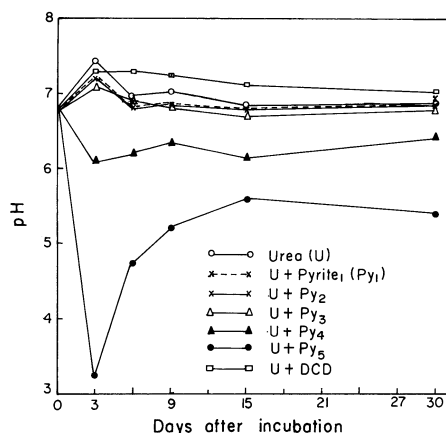
Table 2 Effect (% of applied N) of pyrite and DCD on mineral N, apparent immobilization and fixation and total NH_3 loss at the end of 30 days following application of 100 mg urea-N kg^{-1} soil

	Exchangeable NH_4^+ -N	NO_3^- -N	Immobilized +fixed-N	Total NH_3 volatilized (end of 15 days)
Urea (U)	1.1	42.2	49.5	7.2
U+Py ₁	1.9	42.1	49.3	6.7
U+Py ₂	2.9	41.9	48.7	6.5
U+Py ₃	2.8	37.0	54.6	5.6
U+Py ₄	4.1	31.6	60.9	3.4
U+Py ₅	5.6	25.2	68.2	1.0
U+DCD	14.8	18.6	58.7	7.9
LSD ($P=0.05$)	7.1	6.8	—	0.8

in the urea+Py₅ treatment followed by urea+Py₄ and urea+DCD (Table 2), whereas apparent immobilization and fixation was in the following order; urea+Py₅>urea+Py₄>urea+DCD>urea+Py₃>urea+urea+Py₁=urea+Py₂. Due to inhibition of nitrification and high exchangeable NH_4^+ content, NH_4^+ -N may have been fixed or immobilized. The increased microbial activity during pyrite oxidation could have been responsible for higher immobilization in the pyrite-treated samples. Rice and Tiedje (1989) suggested the preferential immobilization of NH_4^+ rather than NO_3^- , supporting the high immobilization of fertilizer-N with nitrification inhibitors. Fixation by the clay minerals could be another major factor. Loss of NO_3^- through denitrification can also be expected, even in aerobic soils, when O_2 depletion is greater than supply (Ottow 1992; Schwarz et al. 1994). Increased microbial activity (nitrification) and the temporarily reduced conditions created due to oxidation of pyrites (Fe^{2+} to Fe^{3+} and S^{2-} to SO_4^{2-}) may increase the demand of electron acceptors, resulting in available NO_3^- being denitrified. Ferrous (Fe^{2+}) iron-mediated chemodenitrification, in the pyrite-treated soils, is another possibility (Van Cleemput and Baert 1984).

NH_3 volatilization

Ammonia loss was the most during the first 3 days. Total NH_3 loss, at the end of 15 days, was 7.2% of applied N with urea (Fig. 3). Addition of pyrite significantly reduced

**Fig. 3** Cumulative ammonia volatilization losses from soils treated with urea, urea+pyrite and urea+DCD**Fig. 4** Effect of pyrite and DCD addition on soil pH

NH_3 volatilization losses. About 53% and 86% reduction in NH_3 loss was brought about by 5000 and 10000 mg pyrite kg^{-1} soil, respectively. With lower rates (100–1000 mg kg^{-1}) of pyrite, the reduction in NH_3 volatilization was only 7–22%. Acidity produced on oxidation of pyrites was responsible for reducing the NH_3 volatilization (Blaise and Prasad 1995), probably by neutralizing the NH_3 and HCO_3^- formed during hydrolysis of urea and buffering against pH increases (Ferguson et al. 1984). By the 3rd day a marked decline of about 3.55 (urea+Py₅) and 0.71 (urea+Py₄) pH units was observed (Fig. 4). Although the lower rates (100–1000 mg kg^{-1}) of pyrite did not result in an appreciable drop in pH, they maintained the pH lower than urea and urea+DCD treatments, which was responsible for the low NH_3 loss.

Urea+DCD treatment had about 9% more NH_3 loss than urea alone; however, the differences were not significant. The high NH_4^+ -N content (Fig. 1) and elevated pH (Fig. 4) maintained for a longer duration was the main cause for high NH_3 loss with urea-DCD. Our results further strengthen the findings of Prakasa Rao and Puttana (1987). To summarize, our results indicate that the dual advantage of pyrites, inhibiting nitrification and reducing NH_3 volatilization, can be achieved only with a high level of application.

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