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# Evaluations of the DMPP on organic and inorganic nitrogen mineralization and plant heavy metals absorption

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ABSTRACT

The use of biochemical technologies to regulate soil nitrogen (N) transformations is an important strategy to improve plant nutrient uptake and its quality. Effect of organic and inorganic N fertilizers combined application supplemented with the nitrification inhibitor 3,4-dimethyl pyrazole phosphate (DMPP) on N transformations in the soil and heavy metal uptake of pakchoi cabbage (*Brassica campestris* L. ssp. *chinensis*) was studied in three different kinds of soils (purplish clayey soil, red soil, and sandy loam soil). The results demonstrated that DMPP addition in the organic and inorganic N combined fertilization extended ammonium N retention, and greatly reduced nitrate and nitrite N concentrations in three soils. Compared to the regular organic and inorganic-N combined fertilizers, DMPP addition in this fertilization increased the pakchoi biomass by 9.8% to 15.8% and reduced its nitrate concentrations by 15.7% to 40.8%. Furthermore, DMPP addition in the combined organic and inorganic fertilization decreased the heavy metal content of Cu (7.8% to 25.6%), Zn (10.4% to 20.3%), and Cd (12.8% to 22.2%) in the plant. The addition of DMPP to the organic and inorganic-N combined fertilizers could decrease the heavy metal counterion nitrate uptake in the plant, alter soil pH and decrease the activity of Cu, Zn and Cd in the soil, and weaken the plant heavy metal uptake of Cd and Zn in the three soils. It is proposed that DMPP could be used to regulate N transformation in the soil and decrease the heavy metal content in the plant in the organic and inorganic N combined fertilization, thus improving plant quality and yields.

## 1. Introduction

In general, the Copper (Cu) and Zinc (Zn) are important micronutrients for plants, animals and humans at a very low-level concentration. But too much of these metals may exert negative effects on plant growth and crop yield, and also indirectly enter the food chain with a potentially harmful impact on human body (Wuana and Okieimen, 2011). Some feed additives, including trace elements and veterinary antibiotics have been widely used in the intensive cultivation of livestock and poultry, in order to promote animal growth or control diseases. As a result, it may result in serious pollution for continuously applying such manure in agricultural soil (Nicholson et al., 2003). Zhao et al. (2005) found that some organic manure largely application may increase the content of Cu, Zn and Cd (Cadmium) in the field. The accumulation of these heavy metals in agriculture fields can affect soil fertility and crop quality, and may also migrate from agricultural soil to human body (Zhao et al., 2005; Kumar et al., 2013). On the other hand, application of single chemical fertilizer resulted in agricultural field malnutrition, excessive nitrate, and poor quality of crops (Song et al., 2009). Manure has traditionally been widely used for improving soil fertility and ensuring sustainable land use and agricultural production development. Therefore, it is significantly important to eliminate or decrease the heavy metal pollution in the agricultural products for the manure application by using some technologies.

Nitrification inhibitors can reduce the amount of nitrogen loss and effectively increase the nitrogen uptake by plant in the soil (Hauck, 1980; Trenkel, 1997; Irigoyen et al., 2003; Di and Cameron, 2011; Kleineidam et al., 2011; Tan et al., 2013). 3,4-Dimethyl pyrazole phosphate (DMPP) has been tried as nitrification inhibitors in agriculture crops (Zerulla et al., 2001; Pasda, 2001). Effect of DMPP addition in inorganic $NH_4^+$-N form fertilizers or urea has been previously investigated (Zerulla et al., 2001; Li et al., 2008; Yu et al., 2007; Irigoyen et al., 2003). The application of organic and inorganic nitrogen fertilizers in combination is an important way to increase soil fertility and productivity (Gilly and Eghball, 2002; Azeez and Van Averbeke, 2010; Soumare et al., 2003; Gilly and Risse, 2000), and is also beneficial for the comprehensive disposal of livestock and poultry manure. Traditionally, soil pH and redox potential are the critical factors that

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affect the heavy metal mobilization and bioavailability in the soil (Uchimiya et al., 2010). In general, the transformation and cycling of carbon and nitrogen in soil can release the protons and cause the soil pH variation. The ammonification process may result in the release of hydroxide ions, while nitrification process may result in the release of hydrogen ions. In theory, combined ammonification and nitrification process of organic nitrogen compounds, including urea, one net mole of hydrogen ions was generated for every mole of nitrogen transformed. The nitrification inhibitor addition in the fertilizers could delay ammonium oxidization process and alter the soil pH and CEC, which might have the indirectly function to affect the heavy metals activity and mobility (Zerulla et al., 2001; Bolan et al., 2003). The plant uptake of nitrogen nutrient can influence the uptake of another cations and anions to maintain charge balance (Marschner, 2012). Heavy metal cations as a counterion for nitrate may be influenced by the nitrogen forms uptake between the plant and soil. Furthermore, the nitrogen forms in the soil may influence the heavy metal adsorption and desorption, which has the large function on its transformation and ecological environment (Bradl, 2004; Zhao et al., 2005). Therefore, it might be necessary to study the effects of organic and inorganic nitrogen combined fertilization with DMPP addition on nitrogen transformation in the soil and heavy metal absorption for the plant. The heavy metal and nitrate contents are the primary food quality parameters for the fresh pakchoi cabbage (*Brassica campestris* L. ssp. *chinensis*) which is almost entire consumed by the people (Chang et al., 2014; Zhou et al., 2016). In this study, the effects of the combined application of organic and inorganic nitrogen fertilizers supplemented with DMPP, on soil nitrogen transformations, heavy metal absorption and plant quality of nitrate content were studied by cultivating the pakchoi cabbage in three soils.

## 2. Materials and methods

### 2.1. Experimental soil

The soils, including a purplish clayey soil (Typic Gleyi-Stagnic Anthrosol), a red soil (Typic Agri-Udic Ferrosol), and a sandy loam soil (Typic Fe-Leachi-Stagnic Anthrosol), were acquired from three agriculture areas in Zhejiang Province, Donghu Town, Shaoxing City (120.2 E, 30.3 N), Jiangtang Town, Jinhua City (119.5 E, 29.1 N), and Yangdu Town, Jiaxing City (120.4 E, 30.4 N), respectively. The soil samples were collected from the 0–20 cm layer of the three farmlands. After removing debris and filtering through a 2-mm sieve, the samples were air-dried for future use. The basic characters of the soils were given in Table 1.

### 2.2. Experimental design

Each cement container with a size of 2 m × 0.9 m × 0.5 m (L × W × D) which had a layer of permeable sand in the bottom was used for the experiments. Purplish clayey soil, red soil, and sandy loam soil were added into the cement containers with the soil layer thickness of 35 cm, respectively. Water was then added to the soil to achieve a water holding capacity of 60% of the maximum field capacity. Then the soils were equilibrated for one month in the cement container in order to achieve a homogenous distribution of water. Each cement container was cultivated with a common regional crop of Chinese pakchoi cabbage (*Brassica campestris* L. ssp. *chinensis*) which was transplanted with seedling. Each cement container had the seedlings with the roughly same size before the fertilizers application. The average distance between plants in each cement container was approximately 10 cm. After seedlings were transplanted, fertilizers were applied to the upper 3 cm surface soil and then well mixed between plants. The soil in the 0–3 cm upper part of the container was also from the original field layer, and then was subjected to one of the following treatments: (1) no fertilization (CK), (2) regular organic and inorganic nitrogen combined

**Table 1**
The basic characters of the soils.

| Soil | pH | Organic matter ($g\ kg^{-1}$) | Total N ($g\ kg^{-1}$) | Ammonium-N ($mg\ kg^{-1}$) | Nitrate-N ($mg\ kg^{-1}$) | Available P ($mg\ kg^{-1}$) | Available K ($mg\ kg^{-1}$) | CEC ($cmol\ kg^{-1}$) | Total Cu ($mg\ kg^{-1}$) | Total Zn ($mg\ kg^{-1}$) | Total Cd ($mg\ kg^{-1}$) | Clay (%) | Silt (%) | Sand (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Purplish clayey soil | 5.85 ± 0.02 | 24.7 ± 0.3 | 1.61 ± 0.03 | 11.9 ± 0.4 | 21.4 ± 0.6 | 26.3 ± 0.2 | 73.8 ± 1.2 | 17.9 ± 0.8 | 46.7 ± 0.9 | 149.7 ± 1.9 | 0.23 ± 0.01 | 46.1 ± 0.5 | 43.8 ± 0.4 | 10.1 ± 0.1 |
| Red soil | 4.48 ± 0.01 | 16.8 ± 0.2 | 1.03 ± 0.02 | 9.7 ± 0.3 | 13.6 ± 0.3 | 25.1 ± 0.3 | 72.1 ± 1.0 | 7.8 ± 0.5 | 36.5 ± 0.8 | 186.7 ± 2.3 | 0.22 ± 0.00 | 23.7 ± 0.3 | 47.7 ± 0.2 | 29.1 ± 0.3 |
| Sandy loam soil | 7.15 ± 0.02 | 10.6 ± 0.2 | 0.85 ± 0.01 | 8.8 ± 0.3 | 12.2 ± 0.2 | 44.8 ± 0.4 | 64.0 ± 1.1 | 10.2 ± 0.6 | 52.6 ± 1.1 | 165.2 ± 1.8 | 0.25 ± 0.01 | 27.8 ± 0.2 | 63.0 ± 0.4 | 9.2 ± 0.2 |

Note: CEC, cation exchange capacity. Values are means ± S.E. pH was determined at soil to water ratios of 1:2.5 by using a pH electrode (Lu, 2000). The organic matter was determined by the method of Walkey and Black (1934). Total nitrogen was determined by the Kjeldahl distillation method (Bremner, 1965). Ammonium nitrogen and nitrate nitrogen were measured by the indophenol-blue absorption and Ultraviolet Spectrophotometry (Lu, 2000). Available potassium was determined by the method of Jones (1973). Soil CEC and particle analysis were detected by the method of Chapman (1965) and Lu (2000). Total Cu, Zn and Cd in the soil were digested by HF-$HNO_3$-$HClO_4$, and then the concentrations in the digested solution were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Fisher Scientific, USA) (Lu, 2000).