LETTER

Activation effect of soil available nitrogen, manganese and cobalt after addition of different fumigants

Dongdong Yan, Qing Wang, Zhaoxin Song, Wensheng Fang, Qiuxia Wang, Yuan Li and Aocheng Cao

Institute of Plant Protection, Chinese Academy of Agricultural Sciences, Beijing, People’s Republic of China

E-mail: caoac@vip.sina.com

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Abstract
Soil fumigation is a well-established method for controlling soil-borne diseases. Better quantification of soil available nitrogen and trace elements may provide recommendations on the safe and effective application of soil fumigants. The effects of four fumigants on the available soil nitrogen and trace elements (including Mn, Co, Ni, Cu, Zn and Cd) were investigated in the laboratory incubation with agricultural soil. The results showed that soil fumigation increased soil mineral nitrogen and available Mn, Co, Ni. A significant increase of soil NH₄⁺-N and available Mn was observed in all fumigation treatments. Chloropicrin treatments showed the largest increase of soil NH₄⁺-N. In addition, chloropicrin and dazomet increased Mn and Co to a greater extent than dimethyl disulfide and 1,3-dichloropropene in soil. Available Mn content after chloropicrin fumigation has increased by 2.2 times compared with control treatments, and available Co content in dazomet treatments is also 2.8 times more than untreated control. In fumigated soil, the steady increase of soil available elements is beneficial to nutrient uptake by plants. Soil fumigation created an activation effect on soil mineral nitrogen and available trace elements, which may increase their bioavailability to plants and promote plant growth.

1. Introduction
Soil fumigation—the application of fumigant pesticides to bare soil—is widely used in many countries to control soil-borne pathogens, nematodes and weeds, and increase crop yield (Duniway 2002, Ruzo 2006, Cao et al 2013). Methyl bromide, which was widely used for soil fumigation in the past, was banned the uses of soil fumigation worldwide by 2015 under the Montreal Protocol for substances that depletes the ozone layer (MBTOC 2019). It has been replaced by several other fumigants including chloropicrin (CP), dimethyl disulfide (DMDS), 1,3-dichloropropene (1,3D) and dazomet (DZ) (Mao et al 2017, Yan et al 2019, Zhang et al 2019, Wang et al 2022). Fumigants are known to have a broad biocidal activity on target and non-target microorganisms, and as a result they kill most soil organisms (Ibekwe 2004, Fang et al 2018). Previous studies have reported that fumigants are not only able to control soil-borne diseases, but also change soil nutrient cycles (Yan et al 2013, Sennett et al 2021).

Soil nitrogen and soil trace elements (STEs) are necessary components of the soil which determine ultimately how supportive the soil is to plants and soil environment. The speciation of elements that can be readily absorbed by plants and organisms in the soil is called available fractions. Available fractions of soil nitrogen and STEs including manganese (Mn), copper (Cu), nickel (Ni), copper (Cu), zinc (Zn) and cadmium (Cd), is essential for maintaining agricultural productivity and soil ecosystem (Bose and Bhattacharyya 2008). Nitrogen is an active nutrient in the soil and crop growth demands a large amount of nitrogen. Most of the agricultural soils in the world are deficient in nitrogen. Soil nitrogen enters the atmosphere and hydrosphere through a series of chemical and physical processes, which ultimately affects the local and the global environment (Hawkes et al...
2005). Meanwhile, STEs are essential nutrients for plant growth and are of high ecological importance in the environment (Grüter et al. 2017). Mn, Co, Ni, Cu and Zn elements are redox-active that makes them behave as catalytically active cofactors in enzymes. These elements also have enzyme-activating functions, and they can also fulfill a structural role in stabilizing proteins (Shahid et al. 2016). It is reported that the content of Mn, Co, Ni, Cu, Zn and Cd in plants greatly affects crop growth, yield and quality (Hansch and Mendel 2009, Shahid et al. 2016).

Many factors influence the availability of soil nitrogen and STEs, including the properties of the soil and the microbial community (Tebo et al. 2005, DI et al. 2010). Soil fumigation has a broad-spectrum activity that decreases in abundance of microbial communities or inhibits their growth (Hoshino and Matsumoto 2007). Therefore, the changes of soil microbial communities could also cause disturbance of soil nutrient content and fractions. Despite previous research reports suggesting that soil fumigation significantly increases some elements in the soil, none of them have comprehensively quantified on the available fraction changes of STEs after fumigation. The objective of this study was to quantify the effect of different soil fumigation treatments on available fraction of soil nitrogen and STEs.

2. Materials and methods

2.1. Soil sampling

Soil samples were collected at a typical depth of 0–20 cm from the top layer from agricultural field located in Beijing (40.5°N, 116.0°E). The soil samples were sieved through a 2 cm mesh, thoroughly mixed and then kept for 7 days at 20°C in a clean and dark environment before any treatments were applied. Fumigation treatments of the soil were carried out within 2 weeks of soil collection, to avoid reductions in microbial activity due to soil water evaporation during storage. Soil moisture was 14.8%, and pH was 7.19. The organic matter was 34.38 g kg⁻¹, and soil particles were characterized as 21.60% sand, 65.29% silt and 13.11% clay.

2.2. Soil fumigation and incubation

The experimental design consisted of four fumigant treatments and an untreated control treatment in three replicates. Each fumigant treatment was prepared with 500 g soil samples in a 2.5 L desiccator and individually fumigated with CP, DMDS, 1,3D, DZ. All the desiccators were sealed with preservative replicates. Each fumigant treatment was prepared with 500 g soil samples in a 2.5 L desiccator and individually fumigated with CP, DMDS, 1,3D, DZ. All the desiccators were sealed with preservative film and vaseline, and incubated in the dark at 25°C for 7 days. Fumigants were applied into the desiccators at typical laboratory dosages for each chemical (CP 53 mg kg⁻¹, DMDS 68 mg kg⁻¹, 1,3D mg kg⁻¹ and DZ 75 mg kg⁻¹) (Spokas et al. 2007, Yan et al. 2013). The untreated control treatment was maintained under the same conditions, except no fumigant was applied. At the end of the fumigation period, the desiccators were placed in fume hood to vent the fumigant.

2.3. Soil available nitrogen and trace elements analysis

After the fumigants were fully vented from the soil in the desiccators, soil samples were extracted by potassium chloride for soil mineral nitrogen analysis. Standard automated colorimetric techniques were used to determine the soil mineral nitrogen (defined as NH₄⁺ -N and NO₃⁻ -N available nitrogen species), based on the Berthelot reaction and cadmium reduction method for each species, respectively. A Futura Continuous Flow Analytical System (Alliance Instrument, France) was used to determine nitrogen content. Soil samples were used to extract the available trace elements by diethylenetriaminepentaacetic acid (DTPA) extraction method (Lindsay and Norvell 1978). An Agilent 7700× Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used to quantify the available trace elements. The ICP-MS was operated at RF power 1550 W; spray chamber temperature 2°C; sample depth 10 mm; carrier gas flow rate 1 L min⁻¹; and cooling gas flow rate 15 L min⁻¹.

2.4. Data analysis

Each treatment result was expressed as the mean of three replicates. Data were analyzed for one-way ANOVA with SPSS Statistics 17.0 to determine the effect of fumigation on soil nitrogen and trace elements. Duncan values were calculated to separate the differences of treatment means followed by Duncan’s new multiple range test at significance level of 0.05 (Carrascosa et al. 2014, Yan et al. 2017). Graphs were plotted using Origin 8.0.

3. Results and discussion

3.1. Mineral nitrogen in fumigated soil

A rapid increase in soil NH₄⁺ -N was observed in response to fumigation. Figure 1 shows the amounts of NH₄⁺ -N (figure 1(A)) and NO₃⁻ –N (figure 1(B)) in unfumigated and fumigated soils. CP and DZ increased NH₄⁺ -N to 89.64 and 78.22 mg N kg⁻¹. DMDS and 1,3D increased NH₄⁺ –N to a lesser extent and attained 70.47 and 69.23
mg N kg\(^{-1}\) respectively. The largest increase of soil NH\(_4^+\) - N was observed in CP treatment, and the lowest was in 1,3D treatment. Fumigation treatments had different effects at soil NO\(_3^-\) - N concentration (figure 1(B)). A small reduction in NO\(_3^-\) - N concentration was observed after CP treatment, which decreased to 101.89 mg N kg\(^{-1}\). A small increase in NO\(_3^-\) - N concentration was observed after DZ treatment, which increased to 121.15 mg N kg\(^{-1}\). Compared to the control, there were no significant changes observed in NO\(_3^-\) - N concentration after DMDS and 1,3D treatments. The total amounts of NH\(_4^+\) - N and NO\(_3^-\) - N were rapidly increased compared with untreated control after fumigation treatments in soil. The total amounts of NH\(_4^+\) - N and NO\(_3^-\) - N were 125.53, 191.53, 179.65, 187.31 and 199.37 mg N kg\(^{-1}\) with untreated control, CP, DZ, DMDS and 1,3D treatments, respectively.

The process of decomposing organic nitrogen to mineral nitrogen by soil microorganisms is called ‘mineralization’. Soil fumigation has been shown to increase soil mineral nitrogen due to the mineralization of the microbial biomass killed during fumigation (De Neve et al 2004). Many studies have shown the impacts of fumigation on soil microorganisms (Ibekwe 2004, Li et al 2017). Fumigation always causes a significant decrease in soil microbial biomass because of the broad biocidal activity of fumigants. In our study, all four fumigants significantly increased soil NH\(_4^+\) - N, but they had a differential effect on NO\(_3^-\) - N. Generally, soil fumigation significantly increased soil mineral nitrogen. Ammonia volatilization from soil NH\(_4^+\) - N is a major potential pathway of nitrogen loss. Soil NO\(_3^-\) - N is repelled from soil particles because of its negative charge and is prone to both leaching losses and gaseous emission to the atmosphere as N\(_2\)O via denitrification. And they are also the main forms of nitrogen directly taken up by most plants. Our results were consistent with other studies (De Neve et al 2004, Ruzo 2006) that soil fumigation acted like a fertilizer in encouraging the production of soil available nitrogen.

3.2. Effect of soil fumigation on available trace elements
Mn and Co content were increased significantly after fumigation treatments compared with the untreated control. Mn content increased to 21.39 and 20.38 mg kg\(^{-1}\) in CP and DZ fumigation treatments, respectively (figure 2). The Mn content after CP fumigation is 3.2 times that of untreated control treatments. The increments of Mn content were significantly lower after DMDS and 1,3D fumigation compared with untreated control. Similarly, a remarkable increase of Co content was observed after all fumigation treatments. Co content in DZ, CP and DMDS treatments was significantly higher than untreated control. The highest value of Co content was observed in DZ treatment, which was 2.8 times that of untreated control treatments. The Cu, Zn, Ni and Cd concentrations showed minor changes after fumigation (figures 2(B), (C), (E) and (F)). Compared to the untreated control, Cu content increased significantly after DMDS treatment. Zn content significantly increased to 4.92 and 4.92 mg kg\(^{-1}\) after DMDS and DZ treatments. Ni content significantly increased to 368.40, 368.47 and 381.29 \(\mu\)g kg\(^{-1}\) after CP, DMDS and DZ treatments, respectively. Cd content significantly increased to 33.73 and 34.20 after CP and DMDS fumigation, respectively. However, the increments of Cu, Zn, Ni and Cd were lower compared to Mn and Co after the four fumigant treatments.

DTPA extractant targets not only the free ions in soil pore water but also some of the carbonate-bound and organic-bound fractions of metal in the soil. This single extraction method is widely used to provide information on the potential mobility, bioavailability and toxicity of STEs (Méndez et al 2012, Jafarnejadi et al 2013). Generally, it is very clear that fumigated soils have a readily and rapidly increase of available Mn and Co (figure 2). Previous studies have reported that some fumigation and sterilization methods increased the available Mn and Co, such as chloroform fumigation and gamma sterilization (Mcnamara et al 2003), Suda et al 2009). These reports showed that neutral monosaccharides and organic matter derived from dead microbial cells and
cell lysis have dissolved Mn oxides and correspondingly increased the amounts of available forms of Mn and Co. Accordingly it is widely accepted that Mn oxidizing microorganisms are considered to be the primal agents for the occurrence of natural Mn oxide phases in soil environments (Tebo et al 2005, Mayanna et al 2015). In addition, soil microorganisms have been recognised as the main driving force for the transformation of different forms of soil elements (Hawkes et al 2005, Yi et al 2022). Under circumneutral conditions, the microbial oxidation of some trace elements especially Mn and Co, can proceed relatively fast compared with abiotic oxidation in soil, such as homogenous and mineral surface-catalytic reactions. Previous research has found that diverse bacteria and fungi oxidize Mn(II) enzymatically and produce insoluble Mn(III, IV) oxides. Tebo et al pointed out that Mn(II)-oxidizing bacteria and fungi are ubiquitous in nature, such as Firmicutes, Proteobacteria and Actinobacteria (Tebo et al 2005). Recently, researchers reported that soil fumigation greatly inhibits the growth of microorganism populations, including these Mn-oxidizing microbes (Ibekwe et al 2001, Zhu et al 2020). Mn oxides strongly adsorbed many bio-essential and toxic trace elements including Co, Cu, Zn, Ni, Cd and the reactions in Mn oxides are known to exert a strong control on bioavailability and toxicity of these elements (Mayanna et al 2015).

In our study, the dissolution of Mn oxides and inhibition of Mn-oxidizing microbes by fumigants would be the main reasons for the increase of available soil trace elements. Fraction changes of elements in soil would cause a series of redox reactions and affect the soil ecological environment (Mundus et al 2012). The changes of STEs after fumigation varied between the fumigants due to the different impact of fumigation on soil microorganisms. There are diverse Mn-oxidizing microorganisms with various metabolism and complicated regulation in soil eco-system (Zhou and Fu 2020). In addition, there are also differences in the adsorption capacity of Mn oxides to heavy metal ions (Jiang et al 2017). With the increase of available fraction of Mn, Co, Cu, Zn and Ni in soil, soil fumigation exhibited a fertilizer effect in soil elements for plant uptake. Moreover, these elements are necessary and useful for plant growth. In fumigated soil, the steady increase of soil available nitrogen and several trace elements is beneficial to nutrient uptake by plants. This may also be an important reason for the significant promotion of plant growth and crop yield after soil fumigation (Mao et al 2017, Wang et al 2022).

4. Conclusions

In conclusion, results showed soil fumigation significantly changed the available nitrogen and trace elements in soil. All four fumigants increased the amounts of mineral nitrogen in soil. CP and DZ showed much stronger stimulation of available Mn and Co compared to DMDS and 1,3D. Soil fumigation created an activation effect on soil mineral nitrogen and available trace elements, which may increase their bioavailability to plants and promote plant growth.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Dongdong Yan  https://orcid.org/0000-0002-8196-4615
Wensheng Fang  https://orcid.org/0000-0002-4621-1853
Aocheng Cao  https://orcid.org/0000-0002-4137-4282

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