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# Analysis of the inhibitory effects of chloropicrin fumigation on nitrification in various soil types



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Dongdong Yan, Qiuxia Wang, Yuan Li, Canbin Ouyang, Meixia Guo, Aocheng Cao<sup>\*</sup>

Key Laboratory of Integrated Pest Management in Crops, Ministry of Agriculture, Institute of Plant Protection, Chinese Academy of Agricultural Sciences, Beijing, 100193, People's Republic of China

# HIGHLIGHTS

• Chloropicrin caused inhibitory effects on nitrification in different soil types.

• Nitrification recovered faster in sandy loam soils after chloropicrin fumigation.

• Soil texture and pH were two important factors influencing the inhibitory effect.

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### ABSTRACT

Chloropicrin retards the conversion of ammonia to nitrite during the nitrification process in soil. In our study, the dynamic effect of chloropicrin fumigation on soil nitrification was evaluated in five different soil types to identify relationships between soil properties and the effect of fumigation on nitrification. Chloropicrin significantly inhibited nitrification in all soils; however, the recovery of nitrification varied greatly between the soils. Following chloropicrin fumigation, nitrification recovered to the control level in all soils, except in the acidic Guangxi soil. Nitrification recovered faster in fumigated sandy loam Beijing soil than in the other four fumigated soils. Soil texture and pH were two important factors that influenced chloropicrin's inhibitory effect on nitrification. An S-shaped function was fitted to soil NO<sub>3</sub>-N content to assess the nitrification recovery tendency in different soils. Results demonstrated that  $t_{max}$  was greater in all fumigated soils than in untreated soils. Correlation calculations showed that  $t_{max}$  was strongly correlated to soil texture. The correlation analysis results indicated that the recovery rate of nitrification after chloropicrin fumigation is much faster in sandy loam soil than silty loam soil.

# 1. Introduction

Preplant soil fumigation with methyl bromide (MeBr) was used extensively for about 50 years for controlling soil insects, nematodes, weeds, and pathogens before planting high value crops (Ruzo, 2006). However, MeBr was listed under the Montreal Protocol as a controlled ozone depleting substance in 1992. In 1997, the Protocol specified that the use of this fumigant in agriculture should be phased out by 2015 in developing countries, except for quarantine and pre-shipment (QPS) uses, and critical or emergency uses (MBTOC, 2014). Chloropicrin is one of the most effective MeBr alternatives, and is widely used as a soil fumigant in many countries (Gullino et al., 2003). Of the currently available soil fumigants, chloropicrin is the most efficacious against plant pathogenic fungi and bacteria (Duniway, 2002). Chloropicrin has also been widely used in China in recent years and is registered for preplant soil fumigation in various crops, such as strawberry (Yan et al., 2012; Li et al., 2014), ginger (Li et al., 2013; Mao et al., 2014), cucumber (Wang et al., 2013), tomato, cotton, ornamental and others.

Fumigants are known to have broad biocidal activity and negative or even detrimental effects on target pathogens, but also on non-target microorganisms and soil ecosystems (Ibekwe, 2004; Yin et al., 2014). Fumigation alters soil nutrient dynamics (Butler et al., 2014), especially the nitrogen cycle (Yan et al., 2013). Chloropicrin has been shown to stimulate soil nitrogen mineralization and increase short-term mineralization rates. The available soil



<sup>\*</sup> Corresponding author. Department of Pesticides, Institute of Plant Protection, Chinese Academy of Agricultural Sciences, Beijing, 100193, People's Republic of China.

*E-mail address:* caoac@vip.sina.com (A. Cao).

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nutrients increase significantly following fumigation, benefitting plant uptake. As a result, fumigants are not only expected to provide good control of specific diseases, but they are also regarded as having a 'fertilizer effect' (Ruzo, 2006). Soil fumigants have significant inhibitory effects on nitrification, and chloropicrin was found to have a stronger inhibitory effect on nitrification compared with other fumigants (Yan et al., 2013).

Fumigants or other chemicals can cause disturbances in soil nitrification, and several environmental factors are also thought to affect or control nitrification in soil. Soil pH, moisture, oxygen and temperature are the most important factors controlling nitrification (Sierra, 2002; Szukics et al., 2010; Zhang et al., 2015). However, the effects of these factors on nitrification are variable. The nitrification inhibitory effect also varies with different soil textural properties (Barth et al., 2001).

Although previous investigations have indicated that chloropicrin significantly inhibits soil nitrification, few studies have investigated how soil properties, such texture or pH, affect the recovery of nitrification following chloropicrin fumigation. Chloropicrinis widely used on different crops with different soil ecosystems. It is desirable to quantify the effects of chloropicrin fumigation on nitrification in different soil types, in case some adjustment may be needed in the fertilization regime. The overall objective of this study was to quantify the dynamic effects of chloropicrin fumigation on soil nitrification in different soil types and to identify relationships between soil properties and the effect of fumigation on nitrification.

# 2. Materials and methods

# 2.1. Soils

In total, five different soils were tested in this study. The soils were selected to represent major soil types from different geographical regions of China. All soils were sampled from the ploughing layer in greenhouses, because in practice the fumigant is injected at about 30 cm below the soil surface to fumigate this layer. Detailed soil analytical data are presented in Table 1. The soils were sieved through a 2 mm screen before any treatments were applied.

# 2.2. Soil fumigation and incubation

Laboratory incubations were carried out within 2 weeks of soil collection, to minimize any decreases in microbial activity due to storage. The fumigant used was chloropicrin supplied by Dalian Lvfeng Chemical Co. Ltd.(Dalian, China), which is mainly used for the control of soilborne diseases (Ruzo, 2006). In our previous study, chloropicrin showed a stronger inhibitory effect on nitrification compared to the other tested fumigants (Yan et al., 2013).

Table 1

Basic physical and chemical	properties of soils	used in the experiment.
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300 g soil samples were placed in 500 ml glass jars, treated with  $(NH_4)_2SO_4$  (equivalent to 100 mg N kg<sup>-1</sup> soil) and mixed thoroughly. Chloropicrin was added into the jars at typical field application rates (50 mg kg<sup>-1</sup>) (Spokas et al., 2007). The experimental design consisted of a fumigant treatment and an untreated control in three replicates. This resulted in a total of 10 treatments (one fumigated and one unfumigated treatment for each of the five soils). The jars were sealed with rubber stoppers and left for 7 days in the dark at 25 °C. After 7 days fumigation, all the jars were taken to a ventilation hood to remove the fumigant gas, and the soils were mixed thoroughly before sampling. During a further incubation period, the soils were stirred and aerated for 10–15 min every day and sprayed with deionized water (depending on the weight loss), in order to maintain aerobic conditions and constant moisture.

## 2.3. Soil sampling and analysis

Soil samples were collected at 0, 1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22 and 24 weeks after fumigation (WAF; 0 WAF was defined as before fumigation, and 1 WAF was defined as the date when the fumigants were removed). Soil mineral nitrogen (NH<sup>+</sup><sub>4</sub>-N and NO<sup>-</sup><sub>3</sub>-N) levels were measured with a continuous flow analytical system (Futura Continuous Flow Analytical System, Alliance instruments, France) after extraction with 2 *M* KCl. Microbial biomass nitrogen (MBN) was estimated by the chloroform fumigation method (Brookes et al., 1985). Potential nitrification (PN) rates were measured by adding ammonium sulfate to catalyze the nitrite formation (Kurola et al., 2005). Chloropicrin in soil was determined by a sequential extraction procedure and analyzed using an Agilent 7890A gas chromatograph (Agilent Technologies, USA) with a micro electron capture detector (Zhang et al., 2005).

# 2.4. Data analysis

The amount of NO<sub>3</sub><sup>-</sup>N produced in incubation was calculated from the results of analyses for NO<sub>3</sub><sup>-</sup>N before and after incubation, and the nitrification inhibition rate following fumigation was calculated from [(C-S)]/C × 100, where S = amount of NO<sub>3</sub><sup>-</sup>N produced in the soil sample treated with fumigants, and C = amount of NO<sub>3</sub><sup>-</sup>N produced in the control (no fumigant added).

To assess the effect of fumigation on nitrification, an S-shaped function was fitted to the  $NO_3^--N$  concentrations of treated soil samples (De Neve et al., 2004; Chaves et al., 2006) using the following equation:

$$NO_{3}^{-} - N(t) = NO_{3}^{-} - N(0) + N_{A}[1 + \beta \exp(-kt)]^{-1}$$
(1)

where  $N_A$  (mg N kg<sup>-1</sup> soil) is the potential amount of N nitrified,  $\beta$  is a dimensionless quantity that determines the position of the

Soils	Soil taxonomic name	Location (longitude and latitude)	Clay %	Silt %	Sand %	NH <sub>4</sub> <sup>+</sup> -N mg kg <sup>-1</sup>	NO <sub>3</sub> -N mg kg <sup>-1</sup>	OM g kg <sup>-1</sup>	CEC cmol kg <sup>-1</sup>	рН 1:2.5	Moisture %	Bulk density g cm <sup>-3</sup>
1	Lateritic red soil	Guangxi (108°13'E,22°52'N)	7.5	69.6	22.9	15.3	49.9	36.6	9.7	5.18	19.1	0.75
2	Meadow soil	Liaoning (128°38'E,41°46'N)	3.3	53.8	42.9	9.6	29.5	39.2	12.2	6.69	11.3	0.81
3	Fluvo-aquic soil	Beijing (116°24′E,36°29′N)	2.3	22.2	75.6	5.3	31.1	29.6	10.2	8.17	8.8	0.82
4	Cinnamon soil	Shanxi (108°4'E, 34°18'N)	9.1	64.0	26.9	10.0	97.4	23.7	11.2	8.05	15.0	0.89
5	Fluvo-aquic soil	Shandong (118°52′E,36°54′N)	7.1	64.5	28.5	10.7	32.3	23.4	14.3	7.36	22.6	0.70

OM: organic matter; CEC: cation exchange capacity. Soil taxonomic name was classified according to PRC 1:1,000,000 scale soil map, and data is provided by Data Center for Resources and Environmental Sciences, Chinese Academy of Sciences.

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