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Copper and pH Effects on Soil Nitrogen Mineralization after Compost Application

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ABSTRACT

The study looked to evaluate the effects of two levels of copper in a sandy clay loam soil (of the order Aridisol), and of five levels of pH, on the velocity of nitrogen mineralization after incorporating compost. The experiment underwent 10 treatments: five pH levels, and two copper levels (251 mg kg^{-1} and 345 mg kg^{-1}) with five replications. Planter pots were set as the experimental unit, and were maintained in a greenhouse for 108 days at a temperature of 25 °C. They were watered to maintain field capacity. The nitrate (NO_3^-) and ammonium (NH_4^+) contents were measured five times at 0, 27, 54, 81, and 108 days after compost application. Analysis of variance of data and Tukey test (p≤0.05), showed that the factors copper concentration and time affected ammonium and nitrate concentrations. It can be concluded that time is the factor of greatest importance in the process of organic-N mineralization in soils with medium to moderately high total levels of copper. Time factor weakly interact with the soil copper content, and is independent of the pH in a range from moderately acid to moderately alkaline.

Keywords: Nitrate; ammoniacal nitrogen; net effect of nitrogen; organic agriculture.

RESUMO

O estudo buscou avaliar os efeitos de dois níveis de cobre em um solo franco-argiloso (da ordem Aridisol), e de cinco níveis de pH, na velocidade de mineralização do nitrogênio após a incorporação do composto. O experimento foi submetido a 10 tratamentos: cinco níveis de pH e dois níveis de cobre (251 mg kg^{-1} e 345 mg kg^{-1}) com cinco repetições. Os vasos de plantio foram constituídos como unidade experimental e mantidos em casa de vegetação por 108 dias à temperatura de 25 °C. Eles foram regados para manter a capacidade de campo. Os teores de nitrato (NO_3^-) e amônio (NH_4^+) foram medidos cinco vezes aos 0, 27, 54, 81 e 108 dias após a aplicação do composto. A análise de variância dos dados e o teste de Tukey (p≤0,05), mostraram que os fatores concentração de cobre e tempo afetaram as concentrações de amônio e nitrato. Pode-se concluir que o tempo é o fator de maior importância no processo de mineralização do N orgânico em solos com teores totais de cobre médios a moderadamente altos. O fator tempo interage fracamente com o teor de cobre do solo e é independente do pH em uma faixa de moderadamente ácido a moderadamente alcalino.

Palavras-chave: Nitrato; nitrogênio amoniacal; efeito líquido do nitrogênio; agricultura orgânica.

INTRODUCTION

Some soils may have high or moderate contents of heavy metals, which can be harmful to health, safety, and wellbeing of the population, as well as to the life of the soil itself, the plants and animals that inhabit it. These contents limit the normal usage of soil and unfavorably alter the natural conditions of it (BEGUM, 2010).

Mining, agriculture, and the chemical industry are the greatest sources of no natural increased copper concentrations in the soil (SHARAFF et al., 2017). International soil quality norms for protecting the environment and human health do provide reference values, from up to 63 mg Cu kg^{-1} in Canada, 100 mg Cu kg^{-1} in Australia, and up to 200 mg Cu kg^{-1} in Germany, for agricultural soils (CCME, 2007). For any concentration over these, only a few plants can survive. In addition, higher Cu levels may influence or condition the productive capacity of some agricultural soils, depending on their acidity and their organic matter content, since they tend to form very stable compounds like chelates (copper – organic material) (DIAS, 2016; GROHSKOPF, 2016). These Cu levels may also interrupt some soil processes, due to the negative influence on micro and meso flora and fauna activity in the soil, and diminished decomposition of organic matter (CHRISTOU, 2017). The harmful effects of copper in particular deteriorate soil health and its use.

Copper, in high intracellular concentrations, generates oxidative stress, which provokes lipid peroxidation of the cellular membrane, increasing its permeability and leading to apoptosis. Through this mechanism, copper has an adverse effect on microbiology biomass in soils (Anderson et al., 2009; Li, 2017). Nevertheless, some soil bacteria have developed resistances to otherwise toxic copper concentrations, which allows for mineralization of organic forms of nitrogen (N) (MAGNANI and SOLIOZ, 2007).

Chemical equilibrium for copper, both in solution and in the soil colloids, depends on the pH of the solution and the quantity and type of clay present. Therefore, in soils with more alkaline pH conditions and sandy and loamy-sandy textures, the level of equilibrium and, thus, copper concentrations, are lower. Said another way, high pH values immobilize copper activity (DIAS, 2016; RIGBY, 2016). At the same time, reduced pH increases copper solubility, which, in turn, reduces mineralization of organic nitrogen.

In recent years, there has been an ever-growing environmental conscientiousness, for which clean production norms with some restrictions, mainly using the Good Agricultural Practices (GAP) as a basis, have been adopted. Additionally, the usage of organic fertilizers improves the physical and chemical characteristics of the soil. Organic compost is currently a substitute for inorganic nitrogen-contributing sources. Organic compost aggregates soil particulates, increases meso and macropores, favors air circulation (oxygen), increases available moisture retention, maintains more stable soil temperatures, and, as a result, improves productive capacity for plants (CAMPOS and SPERBERG, 2011). That said, the misuse of these residues, due to applications in high doses, is associated with harmful effects against health, plant and animal life within the soil, the meso- and microflora and fauna, and is a source of pollution for surface and ground waters (SHARAFF et al., 2017; LI et al., 2017). According to the above it is possible to postulate that after compost incorporation the soil pH level influence the velocity of organic nitrogen mineralization in a sandy clay loam soil with two copper concentrations. Therefore, the objective of this study was to evaluate the effect of five levels of pH in a sandy clay loam soil with two levels of copper after incorporating compost on nitrogen mineralization.

MATERIAL AND METHODS

The experiment was conducted at the Estación Experimental La Palma at the School of Agronomy of the Pontificia Universidad Católica de Valparaíso, located 5 km from the city of Quillota, Chile. Two Aridisol-order soils were used, both with a sandy clay loam texture (Tables 1 and 2), with different total copper concentrations (251 mg kg^{-1} and 345 mg kg^{-1}, respectively), and natural pH levels (7.37 and 6.37, respectively).

Compost Class A was applied, according to Chilean Norm 2880, vegetable in origin (Table 2), in a proportion of 1% (w/w). Soil pH was reduced with phosphoric acid, and increased with potassium hydroxide, in order to reach pH levels of 6.5, 7.0, 7.5, 8.0, and 8.5 in both soils. The amounts of acid and hydroxide applied were calibrated beforehand in the laboratory. The experiment underwent 10 treatments, with five pH levels and two copper levels (Soil $_{Cu}$ 345 and Soil $_{Cu\ 251}$), with five replications. Planter pots of 3 kg were set as the experimental unit, and were maintained in a greenhouse for 108 days at a temperature of 25°C.

Table 1 – Granulometry of the soils used, obtained at 0-15 cm depth

	$Soil_{Cu\ 345}$	$Soil_{Cu\ 251}$
Sand, %	42	51
Clay, %	26	23
Silt, %	31	26
Texture	SCL	SCL

The execution of the experiment included the following activities:

Compost application – soil was mechanically mixed in a proportion of 1% (w/w) compost, and later placed into 3 kg pots.

pH modification – to increase the pH levels, an aqueous solution of 4.48 g L^{-1} of potassium hydroxide was used; to reduce pH, a solution of 1.55 ml L-1 of phosphoric acid was applied.

Watering – soil was watered to maintain sufficient soil moisture, close to field capacity, in order to ensure microorganism activity. Field capacity of the soil in the pots was determined

by a mass balance. The pots were weighed weekly to determine the water lost in that period.
Weed control – at intervals of every four days, a manual weeding was performed in each pot, in order to avoid interference.

Chemical Analyses

At 0, 27, 54, 81, and 108 days after the start of the experiment (equivalent to 0, 25, 50, 75, and 100% of the total experiment time), soil samples were taken from each pot, and were sent to the Soil and Foliage Analysis Laboratory at the School of Agronomy to determine pH, NH_4^+, and NO_3^- present.
The NH_4^+ and NO_3^- were extracted with KCl 2M and determined by water vapor distillation, in the presence of MgO for NH_4^+ , and MgO and Devarda´s alloy, for NO_3^-. The pH was determined in the soil saturation extract.

Table 2 - Chemical characterization of soils and compost used

Determination	Unit	Soil$_{Cu\ 345}$	Soil$_{Cu\ 251}$	Compost
Organic matter	%	4.70	3.61	≥ 20.00
Electrical conductivity 25ºC	ds m^{-1}	1.20	1.26	3.00
pH		6.69	7.37	5.00
Total copper	mg kg^{-1}	345.00	251.00	___ Available
copper	mg kg^{-1}	109.00	66.80	___
Total nitrogen	%	0.38	0.33	0.67
Ammonium	mmol L^{-1}	41.80	26.10	30.90
Nitrate	mmol L^{-1}	4.52	5.29	29.20

Data Analysis

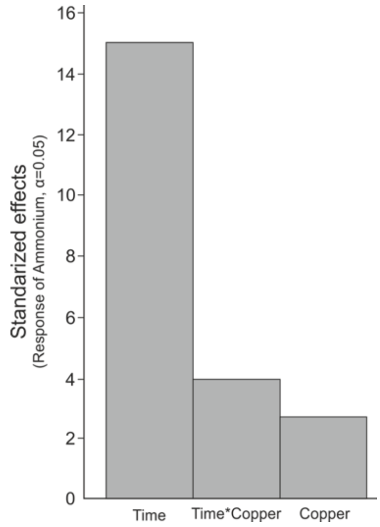
Data analysis was performed using the MINITAB 17 program for analysis of variance and Tukey test ($p \leq 0.05$). Ammonium and nitrate availability were analyzed as a function of pH levels, time, and copper. Afterwards, N-total was defined as the sum of all N contents contributed from NH_4^+ and NO_3^-.

RESULTS AND DISCUSSIONS

Effect of copper and pH on the production of ammonium as a function of time

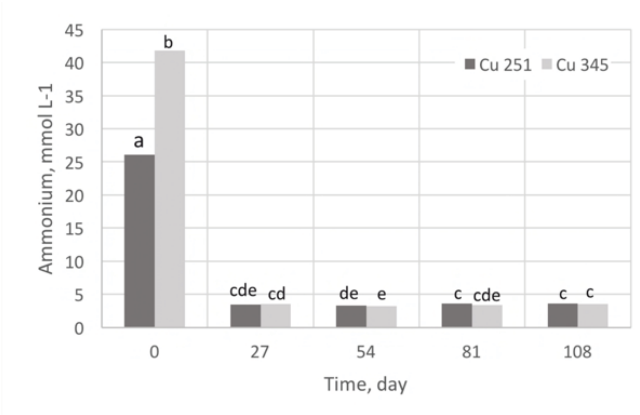
The analysis showed that only copper concentration and time affect ammonium concentration. As for pH, there were no significant effects, for which a second-order analysis was undertaken. Even though interactions for copper and time do exist, the greatest contributing factor clearly corresponds to time, since the effects of partial copper or copper-time interaction are quite weak (Figure 1).

Figure 1 - Standardized effects of interaction of copper soil concentration vs time on ammonium concentration after compost application.



Initially high ammonium concentration, though different throughout the soils, decayed rapidly in the first month. Afterward, values for both soils kept approximately constant up to three months, the time duration of the experiment. At 27 days after compost application, ammonium concentration showed no differences between the soils with high (Soil $_{Cu}$ 345) and low (Soil $_{Cu}$ 251) copper contents. This effect is most likely due, first, to a lesser content of organic matter in Soil $_{Cu}$ 251 (Table 2); and second, to the fact that this soil has better conditions for nitrification (Figure 2) than that of the greater copper concentration Soil $_{Cu}$ 345. The microorganisms responsible for the ammonium – nitrite – nitrate cycle probably acted in greater quantities and/or velocity in the soil with less copper content, which provoked an almost immediate reduction in the ammonium content. Furthermore, the following measurements detected practically no differences between the soils, not even over time. Thus, the concentration of this ion was reduced by approximately 90% by the time the measurement at 27 days after compost application was taken (Figure 2).

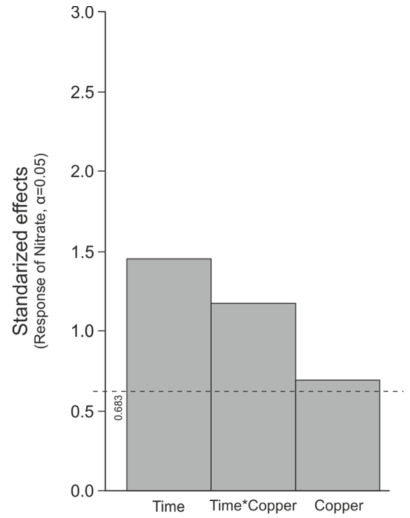
Figure 2 - Time variation of ammonium concentration after compost application to two soils with different copper content



Effect of copper and pH on the production of nitrate as a function of time

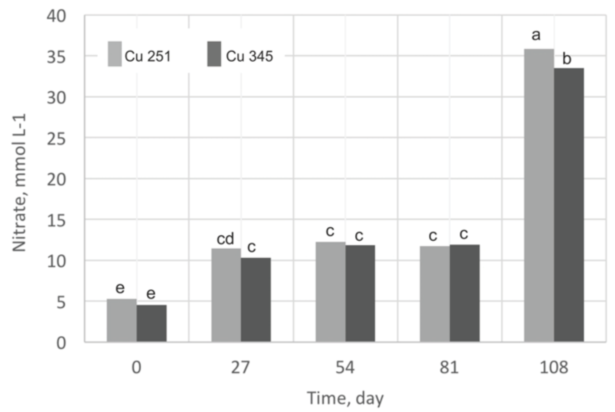
In the case of nitrate concentration in soils with high and low copper contents, soil copper concentration and time were shown to be the only factors with significant interaction, even though the time factor was far the greatest contributor. The pH effect in the range studied had no significant effect on nitrification (Figure 3).

Figure 3 – Standardized effects of interaction of copper soil concentration vs time on nitrate concentration after compost application.



During the experimentation period, nitrate concentration varied mainly as a function of time, and slightly between the soils studied (Figure 4). At the end of the experiment, there was a slightly greater nitrification in the soil with less copper content. In the intermediate period, between 27 and 81 days, nitrate concentration was maintained relatively constant, but higher than the value at the beginning of the experiment (Figure 4).

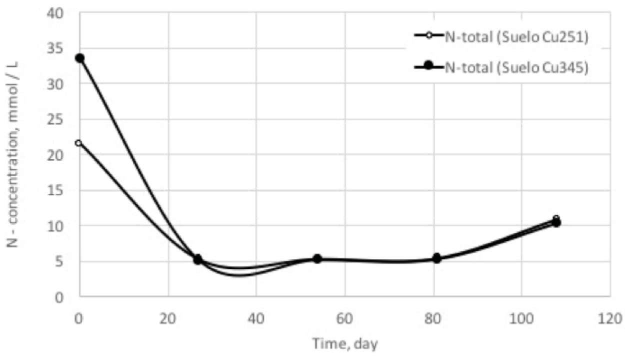
Figure 4 – Time variation of nitrate concentration after compost application to two soils with different copper content. (Similar letters in the column of same chemical means there is not difference, Tukey p ≤ 0.05)



Net effect (availability of N-total) in the two soils as a function of time

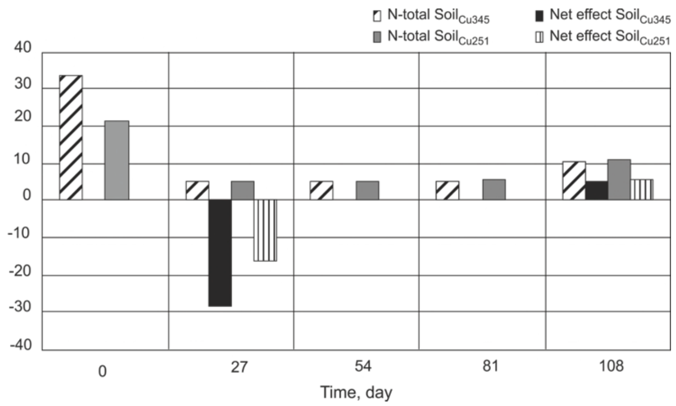
In order to compare the N contributions from ammonium and nitrate, N-total was defined as the sum of both types of N contents. In the experimental period, the availability of tN-total, initially different between the soils due to the effects of NH_4^+, showed no difference between soils after day 27, although it did increase as a function of time (Figure 5). Up to 27 days, the two soils recorded a loss of nitrogen (net immobilization), which was greater in Soil $_{Cu}$ 345 (Figure 6). This Figure also shows that, on measurements from days 54 and 81, net mineralization was much reduced, and at 108 days, a greater amount of nitrogen was recorded as compared to previous values.

Figure 5 – N-total concentration after compost application to two soils with different copper content.



Espinoza and Mozaffari (2012) affirm that, when organic matter decomposes, nitrogen is liberated into the soil solution through a sequence of chemical and biochemical reactions. As a consequence of this sequence of reactions, the concentration of this element varies with time, environmental conditions, and soil depth. In the case of this study, the results indicate that nitrate concentration (NO_3^-), which is one of the forms of nitrogen used by plants, changes mainly as a function of time.

Figure 6 – Net effect concentration N-total after compost application to two soils with different copper content.



Effect of soil pH on nitrification

Various studies have demonstrated that an increase in soil pH increases the rate of N mineralization in soil after compost application (HANAN and SCHIME, 2016). Nevertheless, there has been no significant effect found for pH between 5.3 and 7.5 on the velocity of decomposition of compost in soils with silty-clay and silty textures. Additionally, the optimal pH range for many oxidizing soil microbes is from pH 7 to 9, while, below pH 4.5, nitrification is nonexistent. In the pH range of 5 to 6, compost nitrification is inhibited in sandy soil. The range of soil acidity in which organic nitrogen transforms to nitrate is from pH 5.5 to around pH 10, with an optimal point at around pH 8.5 (HANAN and SCHIME, 2016; XIAO et al, 2013). The above is corroborated by Xiao et al. (2014), who indicates that the minimum and maximum tolerance limits oscillate between 5.5 to 6.7 and 9.6 and 10.4, respectively. Thus, it is improbable that soil pH is an important factor that regulates N mineralization in soils with typical soil pH as found in normal agricultural soils (RIGBY, 2016). The pH ranges applied in the experiment are within the minimum and maximum tolerance limits, which justifies the fact that no statistically significant differences were found in this study. This contradicts the hypothesis that different pH levels may directly influence nitrification through microbial activity, or indirectly, through copper solubility.

Effect of copper on nitrification

The sample taken on day 108 showed an important increase in soil nitrate concentration, with a slight difference between the soils with high and low copper contents. On the one hand, the slow increase of nitrate may be due to the fact that nitrobacteria were inhibited by the copper content, which, in turn and over time, were adapted by their defense mechanisms to be resistant to the inhibiting action. Copper does have an inhibitory effect on nitrifying bacteria, which significantly reduces nitrate availability (MOYA et al., 2017, GONZÁLEZ and ALVAREZ, 2014). On the other hand, non-inhibitory concentrations of copper and mercury deactivate the effect of nitrification inhib-
itors, such as thiourea and mercaptobenzothiazole (MEIER, et al., 2017). In the same study, MEIER et al. (2017) concluded that compost diminishes the bioavailability and absorption of Cu but improves the habitat of microorganisms and increases the growth of plants in soils with high copper content. Thus, the velocity of nitrogen mineralization or the rate of mineralization could possibly be used as an indicator for soil microbial activity.

Effect of time on nitrification

The organic-N mineralization process begins with ammonification. This process is a consequence of microbial activity in both aerobic and anaerobic conditions, and whose velocity is affected by temperature and multiple chemical and biochemical reactions within a certain pH range (DIAS, 2016). Mineralization occurs in two stages: first, bacteria of the genus Nitrosomonas intervene to pass NH_4^+ to NO_2^-. Next, the NO_2^- is converted to NO_3^- by genus Nitrobacter. The second stage reaction is quicker than stage 1, and both reactions are much quicker than the reaction of organic-N to $NH4^+$ (GONZÁLEZ, 2004). The time required for organic-N mineralization depends on the climate, the rate of application of organic matter, lignin content, the degree of contact between the material and the microorganisms, and the level of microflora activity in the soil. It is reasonable to estimate that, under favorable conditions for microbial activity, net mineralization could occur after four to eight weeks of active decomposition (HANAN and SCHIME, 2016). The present study recorded that the ammonification process occurs very quickly after the application of compost, and after 27 days, the ammonium concentration is significantly reduced, and remains mostly constant through the end of the experiment (day 108) (Figure 2). Sharaff et al. (2017) point out that ammonium may be immobilized by microorganisms and fixed by inorganic colloids in the soil. Nitrification, nevertheless, occurs more slowly, and can be conditioned by the presence or concentration of copper in the soil. The inhibitory effect of copper on microbiological reactions causes the nitrate concentration, for the period between days 27 and 81 in the experiment, to basically remain constant; this may be due to a period necessary for the nitrifying microbiological system to adapt. The greatest nitrate availability was observed on day 108 for the soil with less copper content (Figure 3). Thus, the greater the copper concentration, the greater amount of time needed to achieve maximum nitrate availability.

CONCLUSIONS

Time is the factor of greatest importance in the organic-N mineralization process in soils with moderate to moderately high amounts of total copper. This factor weakly interacts with copper content in the soils studied and is independent of the pH in a range from moderately acid to moderately alkaline.

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