



# Changes in the chemical composition of an acidic soil treated with marble quarry and marble cutting wastes



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## HIGHLIGHTS

- Marble wastes at different rates were applied to an acidic soil.
- The effects of marble wastes on altering chemical composition of soil were evaluated at the end of 75 incubation period.
- The MQW and MCW applications significantly increased soil pH, CaCO<sub>3</sub> content, exchangeable Ca and Na contents.
- The MQW and MCW applications decreased exchangeable K, plant-available P and extractable Fe, Cu, Mn and Zn contents.
- Heavy metal (Cd, Ni and Pb) concentrations also decreased with marble waste applications.

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## ABSTRACT

Soil acidity greatly affects the availability of plant nutrients. The level of soil acidity can be adjusted by treating the soil with certain additives. The objective of this study was to determine the effect of marble quarry waste (MQW) and marble cutting waste (MCW) on the chemical composition and the acidity of a soil. Marble wastes at different rates were applied to an acid soil. Their effectiveness in neutralizing the soil pH was compared with that of agricultural lime. The changes in the chemical composition of the soil were also evaluated with column test at the end of a 75-day incubation period. The results indicated that the MQW and MCW applications significantly increased the soil pH (from 4.71 up to 6.54), the CaCO<sub>3</sub> content (from 0.33% up to 0.75%), and the exchangeable Ca (from 14.79 cmol kg<sup>-1</sup> up to 21.18 cmol kg<sup>-1</sup>) and Na (from 0.57 cmol kg<sup>-1</sup> up to 1.07 cmol kg<sup>-1</sup>) contents, but decreased the exchangeable K (from 0.46 cmol kg<sup>-1</sup> down to 0.28 cmol kg<sup>-1</sup>), the plant-available P (from 25.56 mg L<sup>-1</sup> down to 16.62 mg L<sup>-1</sup>), and the extractable Fe (from 259.43 mg L<sup>-1</sup> down to 55.4 mg L<sup>-1</sup>), Cu (from 1.97 mg L<sup>-1</sup> down to 1.42 mg L<sup>-1</sup>), Mn (from 17.89 mg L<sup>-1</sup> down to 4.61 mg L<sup>-1</sup>) and Zn (from 7.88 mg L<sup>-1</sup> down to 1.56 mg L<sup>-1</sup>) contents. In addition, the Cd (from 0.060 mg L<sup>-1</sup> down to 0.046 mg L<sup>-1</sup>), Ni (from 0.337 mg L<sup>-1</sup> down to 0.092 mg L<sup>-1</sup>) and Pb (from 28.00 mg L<sup>-1</sup> down to 20.08 mg L<sup>-1</sup>) concentrations decreased upon the treatment of the soil with marble wastes.

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## 1. Introduction

Soil acidification is a global problem and is proved by aluminum toxicity, low levels of pH and cation exchange capacity (CEC), and increase in exchangeable acidity (Zhao et al., 2015). Soil acidity is very important in terms of plant growth and nutrient availability. It produces complex interactions of plant growth limiting factors involving physical, chemical and biological properties of soil

(Fageria and Baligar, 2008). For many plant nutrients, the maximum availability is provided at neutral pH conditions. Soils with low pH are deficient in the plant available Ca, Mg, Mo and B, whereas, the Al, Fe and Mn concentrations increase and become toxic to plants in these soils (McLean, 1982). Therefore, maintenance of an appropriate pH of soil promotes plant growth because of better nutrient use.

Liming is a common practice used to control soil acidity. Lime applications to acidic soils increase the adsorption and precipitation of toxic metals, increase the nutrient availability and enhance biological activity (Voeller et al., 1998). Different types of calcium-containing materials are used for liming. Murata et al.

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(2002) studied the effects of calcitic limestone, dolomitic limestone, gypsum and single superphosphate on the soil pH and the nutrient availability of acid soils. They found that dolomitic or calcitic limestone significantly increased the soil pH and the exchangeable Ca and Mg levels. Kowalenko and Ihnat (2010) reported that the soil pH and the extractable Ca increased, but the amounts of the extractable Mn, Zn, K, Mg, Na, Al and Fe decreased with increased limestone rates. The phosphorus extractability also increased with agricultural lime application (Lemme et al., 2014). The application rate of liming materials is also important for the effectiveness of liming on pH neutralization and chemical composition changes in acidic soils. Muthukrishnan and Oleske (2008) emphasized that the samples having greater quantities of lime additions reached a desirable pH faster than those with smaller amendments.

In recent years, studies on the use of wastes for liming, especially marble wastes, as an alternative to agricultural lime has become of increasing interest (Melgar-Ramirez et al., 2012; Raymundo et al., 2013; Tozsin et al., 2014a, 2014b). Marble, a metamorphic limestone, basically contains calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) (Segadães et al., 2005). Marble wastes generated by quarries (marble quarry waste-MQW) and processing plants (marble cutting waste-MCW) pose serious economic, social and environmental problems (Noor et al., 2015). Tozsin et al. (2014a) suggested that marble wastes could be used as soil amendments for acidic soil remediation, and emphasized that the afore-mentioned negative impacts of marble wastes could be reduced. Although studies on the use of Ca-containing wastes for liming are well documented in literature, effects of marble waste applications on chemical composition of neutralized soil and liming effectiveness over agricultural lime are still need to be studied in different soil types. Therefore, the objectives of this study were to determine the effect of marble quarry waste (MQW) and marble cutting waste (MCW) on the chemical composition and the pH of an acidic soil, and to determine relative effectiveness of marble wastes over agricultural lime as a liming material.

## 2. Materials and methods

The experimental soil, classified as Typic Hapludults (Soil Survey Staff, 1992) was taken from the 0–20 cm depth of the Kelali garden, Inece village, Bulancak–Giresun–Turkey ( $38^\circ14'60''\text{E}$ ,  $40^\circ51'54''\text{N}$ ). The soil was air-dried and passed through a 2-mm sieve prior to the analyses. The soil pH was measured in soil suspensions with a soil to water ratio of 1:2.5 (v/v). The calcium carbonate concentrations were determined according to McLean (1982). The exchangeable cations were determined according to Rhoades (1982). The Fe, Cu, Mn, Zn, Cd, Ni and Pb contents were determined using an Inductively Coupled Plasma spectrometer (Perkin–Elmer Sciex Elan 6100 model) (Farmer and Gibson, 1981).

A column test was conducted for evaluating the effectiveness of the liming materials on the properties of the acidic soil after neutralization under laboratory conditions. The experimental procedures were described by Tozsin et al. (2014a). The materials used as soil amendment, marble quarry wastes (MQW) and marble cutting wastes (MCW), were obtained from the Afyonkarahisar region of Turkey, and agricultural lime (AL) was obtained from Niksar AS.

The treatments [4 liming materials (control, AL, MCW and MQW) and 3 application rates (1:1, 1.5:1 and 2:1)] were designed and implemented with three replicates in a factorial arrangement. Analysis of variance (ANOVA) was performed for determining the treatment effects, and Duncan's multiple comparison test procedure was used for mean comparisons (SAS Institute Inc., 1989).

## 3. Results and discussion

The experimental soil was loamy-textured with a pH of  $4.71 \pm 0.18$ . The chemical compositions of the liming materials used as soil amendment in this study, that is, agricultural lime (AL), marble quarry wastes (MQW) and marble cutting wastes (MCW), were presented in the previous work of Tozsin et al. (2014a). The CaO contents of AL, MQW and MCW were 55.86%, 55.04% and 50.80%, respectively.

For determining the effects of liming materials (LM) and the application rates (AR), the data were subjected to variance analysis (ANOVA). The ANOVA results indicated that the LM and AR had different effects on the pH and the chemical composition of the soil (Table 1). There were statistically significant differences among the liming materials, the soil pH, the exchangeable Ca and Mg, and the extractable P, Fe, Cu, Mn, Zn and Ni were affected significantly at  $p < 0.01$ , and the exchangeable Na and P were affected at  $p < 0.05$  significance levels. However, no differences were found among the liming materials on the  $\text{CaCO}_3$  content, and the exchangeable K and Cd contents. In addition, the soil pH, the  $\text{CaCO}_3$  content, the extractable Fe, and exchangeable Ca were significantly affected by the application rates at  $p < 0.05$  significant levels. The LM  $\times$  AR interaction was only significant for Ca and Zn contents of soil at  $p < 0.05$  significance levels.

Duncan's multiple comparison test results are presented in Table 2. At the end of a 75-day incubation period, the soil pH was 4.71 for the untreated soil, on average. The pH increased from 4.71 to 6.09, 6.33 and 6.54 with applications of MCW, AL, and MQW, respectively. The highest rate increase in soil pH was obtained with MQW application. The initial soil pH was very strongly acidic (Soil Survey Division Staff, 1993), but the pH was altered to slightly acidic after liming material applications. Although the application rates had a significant effect on soil pH, there was no significant effect of MQW and MCW applied at higher rates (1.5:1 and 2:1 rates). These results indicated that all three types of liming materials produced similar effects on the soil pH; therefore, marble wastes are effective as an alternative amendment to agricultural lime for use in neutralizing soil acidity. Consequently, even MCW applied at a rate of 1.5:1 might successfully be used for pH neutralization. The effectiveness of marble wastes on the neutralization of soil pH was discussed in detail in the previous work of the authors (Tozsin et al., 2014a). The findings of this study are in good agreement with those of Melgar-Ramirez et al. (2012), who determined that marble sludge was the most effective amendment for pH neutralization among the organic and inorganic wastes they applied.

The  $\text{CaCO}_3$  content of the soil increased from 0.33% up to as high as 0.75% after the liming material applications (Table 2). The highest  $\text{CaCO}_3$  content (0.75%) was obtained with MQW application, followed by MCW (0.61%) and AL (0.43%). These values corresponded to increases of 127%, 85% and 30% in the  $\text{CaCO}_3$  content with applications of MQW, MCW, and AL, respectively. The increase in the  $\text{CaCO}_3$  content increased as the application rates of the liming material increased. While the  $\text{CaCO}_3$  content of soil was 0.38% for the 1:1 application rate (1 equivalent weight per lime requirement weight), it reached 0.71% and 0.94% with 1.5:1 and 2:1 application rates, respectively.

The effects of liming materials and the application rates on the exchangeable cations (Ca, Mg, Na and K) were not all identical (Table 2). The exchangeable Ca content of soil increased with liming, but there were no significant differences between the control, AL and MCW. However, MQW application increased the exchangeable Ca content up to  $21.18 \text{ cmol kg}^{-1}$  with an increasing rate of 43% compared with the control, on average. The exchangeable Mg content was almost stable with the AL and MQW applications, but it decreased with the MCW application. Although there were

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