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Effect of long-term N fertilization on Ca saturation and soil quality in a calcareous soil in a semiarid to sub-humid region

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This objective of this study was to investigate the effect of long-term N fertilizer application on Calcium (Ca) saturation in a calcareous farmland soil located in a semiarid to subhumid region. The soil type was a Lou soil (Eum-Orthic Anthrosol). Results from this study provide important information about the relationship between fertilization and soil fatigue in farmland. The study also provides insight about soil factors that impact crop stress resistance and changes traditional concepts regarding the Ca balance in calcareous soils. The results showed that across the landscape there was moderate variation in the soil organic matter content of the 10 to 20 cm soil layer. The soil organic matter content was highest near to the village, reflecting the traditional use of organic manure on the Guanzhong Plain and confirming the principle of “village at the center”. This result also highlighted uneven soil quality across the landscape due to human activity. The soil organic matter content was less but the soil available N content was greater in the 0 to 10 cm layer than the 10 to 20 cm layer. This observation is probably due to the application of inorganic fertilizer in modern agriculture. Soil Ca saturation declined by 15.38 to 14.46% as the distance from the village increased. This observation is probably due to interaction between ancient and modern fertilization practices as well as recent land policies. The pattern of changes for soil Ca saturation across the landscape was similar to the pattern of changes for soil organic matter content but opposite to the pattern of changes for soil available N. This proved that application of large amounts of inorganic N fertilizer can increase inorganic soil N and decrease Ca saturation. This is one symptom of soil potential degradation or soil fatigue. In summary, the application of inorganic fertilizer resulted in a significant decrease in the percent of soil Ca saturation in this calcareous soil. This indicates that the application of inorganic N fertilizer can cause a considerable decline in soil health and reduce the effectiveness of modern fertilizers.

Key words: Calcareous soil, degree of Ca saturation, fertilization, semiarid inclined to humid area.

INTRODUCTION

Calcium (Ca) is an essential plant nutrient. Among other roles, Ca plays a crucial part in regulating plant tolerance to a variety of stresses. Calcium fertilizer can stabilize crop yields and assure the sustainable development of agriculture (Jiang et al., 2005). Most soils contain enough Ca to meet plant needs; therefore, Ca deficiency is rare in field crops (Men and Jia, 2006). For this reason, little research has been done about soil Ca.

In recent decades, increases in environmental pollution, acid rain, and N fertilizer use have contributed to soil acidification and a decline in soil Ca (Federer et al., 1989; Qiu et al., 2002). As a result, there has been an increase in Ca deficiency in plants and a decrease in plant resistance to stress. This has resulted in economic

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losses. The study of soil Ca, especially the effect of N fertilizer on Ca transformations in soil will have important scientific value in the future. Such studies will also provide important guidelines for the management of non-calcareous soils.

Many researchers have investigated the spatial variability of macro- and micronutrient concentrations in topsoil, especially the spatial variability of soil N (Wei and Shao, 2007; Jia et al., 2008; Lian et al., 2008) and P concentrations (Xia and Gao, 1992; Liu et al., 2002; Xiang et al., 2004). However, there are few reports about the spatial variability of soil Ca and Mg concentrations. The main reason is that soil Ca and Mg concentrations are generally sufficient to meet crop needs, especially in semi-arid to sub-humid areas where the soil developed from loess parent material. In the Guanzhong Plain, Shaanxi Province, the traditional practices of manure application and deep plowing have played a key role in soil “recalcification” and the maintenance of soil Ca concentrations. However, the use of inorganic fertilizer instead of manure has accelerated the loss of soil Ca due to the exchange of NH$_4^+$ for Ca on the surface of soil particles. In addition, rotary tillage instead of plowing has led to Ca leaching and the deposition of Ca deep in the soil profile. In these ways, the traditional means of maintaining soil Ca concentrations was disrupted. The uptake of Ca by crops and a lack of an effective method for supplying Ca to agricultural soils have also contributed to declines in exchangeable Ca and soil Ca saturation. This has led to soil fatigue. Despite these problems, few people have paid attention to soil Ca deficiency and its dangers. Among factors affecting the soil Ca balance, the effect of inorganic fertilizers is especially important. Information about this topic will not only correct the traditional concept that Ca deficiency is unlikely to occur in calcareous soil, but also provide a scientific basis for precision management and fertilization.

People discarded a lot of farm-rubbish such as straw, night soil, live sewage and so on, it resulted in increased soil organic matter and Ca saturation in the region near to the village. However, because of lacking farm manure, people applied nitrogen on the farmland which is far away from the village, and lots of N leaded to reduction of Ca saturation. So the objective of this study was to investigate the effect of inorganic N fertilizer on exchangeable Ca and the spatial variability of Ca saturation in a calcareous soil that developed from loess parent material in a semi-arid – humid region. Calcium saturation was used as an index to determine soil fatigue due to modern cultivation, soil utilization, and production levels.

**MATERIALS AND METHODS**

Site description and experimental design

There are relatively plentiful light, heat, and water resources on the Guanzhong Plain, Shaanxi Province. The average temperature is 12.9°C. The average annual rainfall is 545 mm. More than 50% of the precipitation is received between July and September. Average annual evaporation is 993 mm. The area has a drought-prone semi-humid climate. A winter wheat - summer maize double cropping system became important in the region after the implementation of the land contract system about 30 years ago.

The experiment site was in the western part of the Yangling Demonstration Zone, Shaanxi Province, China. According to the distance between the farm land and the village, collecting soil samples from the fields which were near to the villages as test area and soil samples from the fields which were far away from the villages as the blank reference. Both of the test area and the blank fields were only shallow rotary plowed before sowing. A mixed fertilizer containing 220 kg.ha$^{-1}$ urea (N 46%) + 230 kg.ha$^{-1}$ KH$_2$PO$_4$ (P$_2$O$_5$ 52%) was used before planting. None top dressing during wheat (Zhengmai-9203) growth, soil samples were collected after wheat harvest for analysis. Each site was 180 m long from north to south and 400 m wide from east to west. The cropping practices at the experiment site are typical for the region. Soil properties in the area have been affected by thousands of years of agricultural use. The soil type is a Lou soil (Eum-Orthic Anthrosol). Selected properties of the soil before planting are shown in Table 1 (Guo, 1992). Two parallel lines running from east to west were selected in the test area for sampling. There were eight sample points on each line. Soil samples were collected from 0 to 10 cm, 10 to 20 cm, and 20 to 40 cm. Soil organic matter, soil available N, exchangeable Ca and CaCO$_3$ content were measured as described below and the percent of Ca saturation was calculated.

<table>
<thead>
<tr>
<th>Soil layers (cm)</th>
<th>Bulk density (g.cm$^{-3}$)</th>
<th>O.M (g.kg$^{-1}$)</th>
<th>Available N (mg.kg$^{-1}$)</th>
<th>Available P (mg.kg$^{-1}$)</th>
<th>Available K (mg.kg$^{-1}$)</th>
<th>C.E.C (cmol.kg$^{-1}$)</th>
<th>Degree of Ca saturation (%)</th>
<th>CaCO$_3$ (g.kg$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>1.28</td>
<td>20.71</td>
<td>65.22</td>
<td>2.67</td>
<td>200.51</td>
<td>14.99</td>
<td>65.12</td>
<td>84.82</td>
<td>8.03</td>
</tr>
<tr>
<td>10-20</td>
<td>1.29</td>
<td>17.16</td>
<td>60.47</td>
<td>2.66</td>
<td>196.73</td>
<td>14.89</td>
<td>63.39</td>
<td>82.85</td>
<td>8.05</td>
</tr>
<tr>
<td>20-40</td>
<td>1.42</td>
<td>10.94</td>
<td>30.46</td>
<td>2.63</td>
<td>178.00</td>
<td>14.66</td>
<td>59.10</td>
<td>48.91</td>
<td>8.17</td>
</tr>
</tbody>
</table>

**Table 1.** Main physical and chemical characters of tested soil before plating.
RESULTS

The spatial variability of test farmland soil properties

The study of spatial variability of soil properties is urgently needed for the development of modern precision agriculture. It is also an important basis for analyzing the development of farmland soil quality. This article explored the spatial distribution of soil organic matter, available N, Ca saturation and calcium carbonate in farmland soil.

The spatial distribution of soil organic matter

Soil organic matter is a significant source of soil nutrients. Soil organic matter content is mainly influenced by human factors. Thus, cropping systems and fertilization practices significantly affect the spatial variability of soil organic matter. The spatial distribution of soil organic matter for each soil layer is shown in Figures 1 to 3. That data show that the soil organic matter content in each layer tended to increase from the western part of village to the eastern part. The soil organic matter content in all three soil layers increased as the distance to the village decreased. Although affected by fertilization practices and environmental factors, the soil organic matter content is relatively stable under natural conditions. Thus, soil organic matter content is an “alternative indicator” to record all kinds of environmental information (Liu, 2009). The soil organic matter content in the 10 to 20 cm layer declined significantly at distances greater than 100 m from the village (Figure 2). This reflects the spatial radius of human fertilization during the time when organic fertilizer was the primary source of nutrients for agricultural crops. As fertilization practices changed, organic fertilizer was gradually replaced by inorganic fertilizer. As a result, the spatial distribution of soil organic matter is different in the 0 to 10 cm layer than in the 10 to 20 cm layer. In modern times, the soil organic matter content decreases more gradually as the distance from
the village increases.

The spatial distribution of soil available N

In modern agricultural production, a large amount of inorganic N fertilizer is applied to soil in order to increase food production. This results in the significant accumulation of soil N. This not only causes environmental pollution, but also affects the absorption of secondary macronutrients and micronutrients by crops. Furthermore, the application of inorganic N fertilizer can lead to an imbalance among soil nutrients, thus putting the soil in a “sub-healthy state”. Under these conditions, physiological diseases may increase, resulting in a reduction in crop yields. The spatial distribution of soil available N in the 0 to 10, 10 to 20, and 20 to 40 cm layers is shown in Figures 4 to 6. The soil available N content in each layer gradually decreased from the western part of the village to the eastern part. In contrast to the soil organic matter content, soil available N decreased as the distance from the village decreased. In general, there was a positive correlation between the soil organic matter content and the available N content. However, available N is formed from inorganic mineral N and low molecular weight available organic N. This means that the soil inorganic N content increases as the application of inorganic fertilizer increases. Nitrogen is highly mobile; therefore the soil available N content in each layer from 0 to 40 cm exhibited the same trends across the entire sample area. This shows that the application of inorganic N fertilizer can lead to the serious consequence of N accumulation in the soil profile.

The spatial distribution of Ca saturation

The cation to total exchangeable cation ratio on soil colloids directly impacts many physical and chemical soil properties as well as crop growth. Soil exchangeable Ca and Ca saturation are important indicators of soil health and are affected by soil parent material, climate, and fertilization. In calcareous soils, exchangeable Ca content and Ca saturation are affected by fertilization. Many years
ago, Ca saturation was >50 to 60%, even low concentrations of essential plant nutrients would be sufficient for optimum plant growth. Kovda (1981) excogitated that the degree of Ca saturation in healthy soil should be 60 to 70%. However, fertilization affects ion exchange, exchangeable ion composition, and buffering capacity (acidification) in soil. Therefore, our research would prove that fertilization could result in a decline in Ca saturation, although calcareous soil is rich in Ca. In the past, farmers generally plowed the soil and applied manure and other kinds of organic fertilizer. These practices played a vital role in "recalcification" and maintained the basic balance of soil exchangeable Ca. In contrast, modern agricultural production practices include the application of large amounts of inorganic fertilizer without plowing. This will inevitably lead to changes in the exchangeable Ca content and the degree of Ca saturation in calcareous soil.

The degree of Ca saturation indicated good soil health (Figure 1). However, there was significant variation in the degree of Ca saturation across the sample area (Figures 7 to 9). The changes in Ca saturation were similar to those of soil organic matter content, but opposite to those soil with available N. The percent of Ca saturation decreased as the distance from the village increased. This meant that soil health was best near to the village. Differences in the percent of soil Ca saturation between various layers declined as soil depth increased. Differences between the layers were a reflection of changes in fertilization practices across time. To be more specific, the area near to the village had a long history of manure application which contributed to soil recalcification. Thus Ca saturation is relatively high near to the village. In contrast, less manure was applied in areas far from the village and the level of soil recalcification in these areas was relatively low. In addition, the application of inorganic fertilizer leads to soil decalcification due to the exchange of NH₄ for Ca on the surface of soil particles. This is probably the main reason for the rapid decline as the distance from the village increases in soil Ca saturation. The application of large amounts of inorganic fertilizer also increases NH₄ adsorption on soil colloids and creates the phenomenon, the soil available N content increase as the distance from the village increase, and the trend of soil organic matter content is contrary.
As the degree of soil Ca saturation decreases, soil structure deteriorates and soil compaction increases. This has an important effect on water and nutrient movement in the soil. The decline in Ca saturation can also cause a reduction in the yield from unfertilized soil or a diminished yield response from fertilized soil.
Further, the decline in Ca saturation is a hidden process of soil degradation, and it is a main symptom of soil fatigue, too.

**The spatial distribution of calcium carbonate**

In calcareous soils, calcium carbonate plays a very important roll to promote the formation of soil aggregates and soil structure. Especially in the Guanzhong area, leaching and deposition of soil calcium carbonate and re-accumulation process of calcium carbonate in surface soil are simultaneous. The relationship between the level and length of soil fertility by human plays a crucial part in the degree of re-accumulation of calcium carbonate.

In Figures 10 to 12, greater variability of soil calcium carbonate content was shown in 0 to 40 cm soil layers. Compared to the variation of soil organic matter content, calcium carbonate content increased with soil depth. In the horizontal space, the variation of soil calcium carbonate content in 0 to 40 cm layers showed the same mutation with that of soil organic matters, that was the closer from the village, the higher the soil calcium carbonate content, which showed the same variability with soil calcium saturation.

In conclusions, the variation primarily has a direct relationship with the local long-standing habit of fertilization. The long-standing habit has developed since ancient times that composting the dung as soil fertilizers. As the applications of manure were limited by the transport conditions and other factors, the application of manure and organic fertilizers take the principle of proximity, thus forming a phenomenon that soil has the higher the degree of maturation and the more thick cover in the closer villages, also soil organic matter content were higher. The distribution characteristics of soil calcium carbonate affects by the distribution of soil cover thickness. The soil feces was rich in the calcium carbonate.
content, so the calcium carbonate content was relatively high in thick covered soils, soil carbonate calcium concentration in the underlying soil by leaching. Additionally, soil manure can be added in time to the surface soil, thus making the soil calcium carbonate content remained relatively stable.

**The spatial variability of reference farmland soil properties**

Soil organic matter, available-N, exchangeable Ca and calcium carbonate content were measured and Ca saturation was calculated in 0 to 40 cm soil layers on reference farmland as the blank area. In Figures 13, 14, 15 and 16, the spatial distribution of organic matter, available-N, Ca saturation and calcium carbonate content were shown in 0 to 40 cm soil layers. Compared to soil samples on the test farmland, organic matter, available-N, Ca saturation and calcium carbonate content were uniform spatial distribution. And the variations of organic matter, available-N and Ca saturation were shown, their contents decreased as the soil layer depth from the ground increased. In contrast to the other soil properties, soil calcium carbonate content increased as the soil layer depth from the ground increased. The phenomenon showed that calcium carbonate leaching and sedimentary were significant, so the dissociative Ca content in 20 to 40 cm soil layer was less than which in 0 to 10 cm and 10 to 20 cm. This is one of reasons which Ca saturation in 20 to 40 cm soil layer was least in 0 to 40 cm soil layers. Compared to the test farmland, variations of organic matter, available-N, exchangeable Ca and calcium carbonate content were not shown as stepladder on the reference farmland. It was concluded that cropping systems and fertilization practices significantly affect the spatial variability of soil properties.

**DISCUSSION**

The spatial variability of soil characteristics is affected by natural and human factors. In general, the spatial variability reflects soil management practices, and especially the degree of homogenization due to tillage. The 0 to 40 cm soil layer is the major area for root growth in this soil. Based on this fact, as well as for pedological reasons, we chose the 0 to 40 cm layer as the focus of our research. The 0 to 40 cm layer, which includes an ancient plow horizon, developed from the combined action of year-round manure application and the natural deposition of loess. The pedo-genetic mechanisms for the formation of the 0 to 40 cm layer and the ancient plow horizon are the same. And there are many informations about soil quality variability in the 0 to 40 cm layer at different times in history. In dryland areas, plant roots must be established in the subsoil in order to provide the plants with enough water. In this way, the subsoil may determine that structure of the plant community at the soil surface. In our study, the soil texture in the 0 to 40 cm layer was a heavy loam. The CEC was 21.98 cmol kg⁻¹ in the 0 to 10 cm layer, 21.89 cmol/kg in the 10 to 20 cm layer, and 21.71 cmol/kg in the 20 to 40 cm soil layer. Information about the variation of soil chemical properties in the 0 to 40 cm soil layers can provide information about the development of soil quality as well as the current soil quality under modern cultivation practices. The organic matter content, the available nitrogen content, the percent Ca saturation and calcium carbonate of the test farmland soil are shown in Table 2.

The soil organic matter content varied greatly in 0 to 40 cm soil layer (Table 2). The soil organic matter content was much greater in the 0 to 10 cm layer compared with the 10 to 20 cm layer. Soil available N followed a pattern similar to soil organic matter. Specifically, the maximum soil available N content was 87.69 g kg⁻¹ in the 0 to 10 cm layer.
Figure 13. Spatial distribution map of organic matter (g.kg⁻¹) on reference farmland.

layer compared to 70.80 g kg⁻¹ in the 10 to 20 cm layer. The minimum soil available N content was 60.80 g.kg⁻¹ in the 0 to 10 cm layer compared to 56.86 g kg⁻¹ in the 10 to 20 cm layer. The average soil available N was 71.74 g kg⁻¹ in the 0 to 10 cm layer compared to 62.65 g kg⁻¹ in the 10 to 20 cm layer. The average available N in the 20 to 40 cm layer was 43.35 g kg⁻¹. The percent of Ca saturation increased with soil depth, reaching a maximum of 72.87% in the 20 to 40 cm soil layer. The average Ca saturation in the 20 to 40 cm was 62.83%. A parameter is considered to have weak variation if the coefficient of variation (C.V.) is <0.1, moderate variation if the C.V. is between 0.1 and 1.0, and strong variation if the C.V. is >1.0 (Jiang and Fu, 2007). Based on this classification system, the soil organic matter content in the 0 to 40 and 10-20 cm soil layers had medium variation, whilst that in the 0 to 10 and 20 to 40 cm layers had weak variation. In comparison, available N in the 0 to 40 and 0 to 10 cm soil
The degree of Ca saturation had weak variation in all soil layers. Soil quality variation in the soil layers showed the layers had medium variation, whilst available N in the other two layers had weak variation. The degree of Ca saturation had weak variation in all soil layers.

Figure 14. Spatial distribution map of available-N (mg.kg⁻¹) on reference farmland.
fertilization model at different times. Variation of soil organic matter content was greater in the 10 to 20 cm layer than in the 0 to 10 cm layer. This indicates that in the past the improvement of soil fertility in the Guanzhong Area was mainly through the application of organic fertilizer. This adheres to the “proximity principle”. Modern fertilization primarily uses inorganic fertilizers. Organic fertilizers are applied only secondarily. This contributes to a decline in the spatial variation of soil organic matter content and an increase in spatial variability of available organic matter.
N. The observation that there is little difference in the Ca saturation among layers can be attributed to the fact that the Ca storage capacity in this calcareous soil is large. However, it can be clearly seen that the degree of Ca saturation has increased in the 0 to 10 cm layer due to modern cultivation and fertilization practices. Simultaneously, after mathematical statistics analysis, the organic matter content, the available nitrogen content, the percent Ca saturation and calcium carbonate of the reference farmland 0 to 40 cm soil are shown in Table 3.
Contrary to Ca saturation, the maximum average Ca saturation in the 20 to 40 cm was 59.45%. The value was the maximum in 0 to 40 cm soil layer, the average available N was 76.04 g kg⁻¹ in the 0 to 10 cm layer. The average soil available N was 76.04 g kg⁻¹ in the 0 to 10 cm layer compared to 65.02 g kg⁻¹ in the 10 to 20 cm layer. The maximum soil available N content was 77.68 g kg⁻¹ in the 20 to 40 cm layer. In the 0 to 10 cm layer compared to 71.96 g kg⁻¹, the maximum percent of Ca saturation was 96.01 g kg⁻¹ in the 20 to 40 cm soil layer, and the average calcium carbonate in the 20 to 40 cm was 96.01 g kg⁻¹. A parameter is considered to have weak variation if the coefficient of variation (C.V.) is <0.1, it was concluded that the organic matter content, the available nitrogen content, the percent Ca saturation and calcium carbonate were weak variation. Compared to the test farmland, C.V. was lower, so it showed again that cropping systems and fertilization practices significantly affect the spatial variability of soil properties.

**Conclusion**

Poor soil management and modern agricultural practices can change soil physical and chemical properties. These
changes, which are not always obvious, can lead to soil fatigue, soil degradation, and loss of productivity. This study showed that a decline in Ca saturation is one symptom of soil fatigue. Variability in soil organic matter content, available N content, and the degree of Ca saturation in a calcareous soil on the Guanzhong Plain reflected a decline in soil quality due to the long-term application of inorganic fertilizer in modern agricultural production. In other words, the application of large amounts of inorganic fertilizer led to the exchange of NH$_4$ for Ca the surface of soil particles (decalcification). This caused a decrease in Ca saturation. These changes confirm that invisible degradation has taken place in the calcareous soil. Most people assume that calcareous soils are not Ca deficient, but this study shows that a decline in Ca saturation can cause soil fatigue in calcareous soil.

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