CHEMICAL AND MICROBIAL PROPERTIES IN CONTAMINATED SOILS AROUND A MAGNESITE MINE IN NORTHEAST CHINA

D. YANG1,2, D.-H. ZENG1*, J. ZHANG3, L.-J. LI1,2 AND R. MAO1,2

1Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China
2Graduate University of Chinese Academy of Sciences, Beijing 100049, China
3USDA Forest Service, Pacific Southwest Research Station, 3644 Avech Parkway, Redding, CA 96002, USA

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ABSTRACT

We measured soil chemical and microbial properties at a depth of 0–20 cm among mine tailings, abandoned mined land, contaminated cropland, and uncontaminated cropland around a magnesite mine near Haicheng City, Liaoning Province, China. The objective was to clarify the impact of Mg on the soils. We found that soluble Mg2+ concentration and pH were significantly higher in contaminated soils (266–345 mg kg⁻¹ and 9.9–10.3, respectively) than in uncontaminated soils (140 mg kg⁻¹ and 7.1, respectively). Soil nutrients (total N, total P, mineral N, available P and soluble Ca) and microbial biomass C and N decreased as pH and soluble Mg2+ concentration increased. In addition, an increase of microbial metabolic quotient and a decrease of N mineralization rate were found in contaminated soils. Soluble Mg2+/Ca2+ ratios in contaminated soils were 3.5–8.9-times higher than in uncontaminated soils. Our results indicate that soil contamination in such magnesite mine regions is characterized by high pH, Mg2+ concentration and soluble Mg2+/Ca2+ ratio, and low microbial activity and N and P availability. Future soil amelioration in the magnesite regions should consider applying acid ameliorants to neutralize high pH and applying calcareous ameliorants to increase Ca2+ concentration. Copyright © 2011 John Wiley & Sons, Ltd.

KEY WORDS: magnesium dust; soil contamination; soil microbial activity; soil microbial biomass; Northeast China; soil chemistry

INTRODUCTION

Mining is one of the most land-degrading industries. Mining operations not only destroy original soils and vegetation cover but often leave some waste materials that contaminate air, water, and soils (Singh, 2005). Magnesite mining is a good example; the dusts from the mining and magnesite calcination have been reported to severely damage native vegetation and soils (Bradshaw, 1997; Machin and Navas, 2000). The current remediation actions are insufficient to prevent the spreading of dust with high concentrations of magnesium (mainly MgO and MgCO3) to surrounding forestlands and crop fields, so soil pollution and vegetation destruction are widespread in the regions. Machin and Navas (2000) found a significant pH increase in soils polluted by magnesite dusts in the Pamplona Valley in Spain. Kautz et al. (2001) reported that soil microbial biomass and activities decreased around a magnesite factory in the Slovak Republic compared with soils far from the factory. Joshi (1997) also found that the magnesite mining reduced soil organic matter and nitrogen content. Moreover, studies from a pot experiment showed that the high ratio of soluble Mg2+/Ca2+ caused by Mg-contaminants affects absorption of Ca2+ during plant growth, and is an important factor limiting plant colonization and survival (Li et al., 1990; Li and Yu, 1997). The causticity of the magnesium oxides in the mining dust burns leaves and broad-leaved species are especially vulnerable (Machin and Navas, 2000). Raman et al. (1993) reported that vegetation in a magnesite mining region of the Eastern Ghats, southern India, consisted only of scrub jungle. A successful rehabilitation of contaminated lands requires a full understanding of the mechanisms of soil development influenced by the mining spoils (Singh et al., 2006); however, more adequate information on the characteristics and underlying mechanisms of soil contamination in magnesite mine regions has been rarely reported in the literature.

China is the largest producer of magnesite in the world; the proven reserves of magnesite amount to about 3 billion metric tons in 28 mining areas (Wilson, 2008). About 86 per cent of these resources are concentrated in southeastern Liaoning Province, which has suffered extensive land degradation from dust depositions. Hardly any vegetation can survive near the mining sites and the calcination factory there. Land reclamation in such mining areas has become a great challenge for environmental management and ecological restoration. Remediation measures have not been successful. The survival rates of tree plantations is poor, and
the yield of the few crops that do survive is very low. The main reason for these failures is most likely a lack of understanding of the soil processes of the contaminated lands. In this study, we measured soil chemical and microbial properties in four sites which represent different degrees of pollution by Mg-contaminants around a magnesite mine near Haicheng, Liaoning, China. The objectives were (1) to quantify the magnitude of Mg-contamination in topsoils and (2) to determine the subsequent effects on key nutrient mineralization and biological processes of soils. The results are expected to provide specific recommendations for soil amendments that can be applied for the future acclamation of Mg-contaminated lands surrounding the magnesite mines in the region.

MATERIALS AND METHODS

Site Description
The study was conducted in the magnesite mining area near/ in Haicheng City (122°18′–123°08′E, 40°29′–41°11′N, with an elevation of 171 m asl), Liaoning Province, China. The Qingshan Mining Incorporated Company has been operating a large magnesite mining site and a calcination factory since 1990. A large area of mined land was abandoned by the Company after 10 years of mining. Only a few grasses grow on land adjacent to the mine, and corn yields on adjacent croplands are less than 20 per cent of the yields realized before the mining and factory began operation 18 years ago. The main source of pollution in the soil was the spreading and settling of dusts from the mining and calcination activities, which mainly contains MgCO₃ and MgO. The region receives about 700 mm precipitation annually. Mean annual temperature is 8.9°C and the mean potential evaporation is approximately 1760 mm per year. Before the mine was established, brown soil covered this area to a depth of approximately 50 cm and some relatively flat shrub lands were reclaimed to croplands (according to local oral traditions). A magnesite calcination factory is about 300 m distance from the present mining site. Sampling was conducted in four contaminated areas: a mine tailings site, an abandoned mined land area where mining ceased 8 years ago, a cropland contaminated by dusts (in which corn had been planted but most seedlings were dead during our investigation), and a distant cropland which was assumed to be less contaminated. The sketch of sampling sites relative to the present magnesite mine and calculation factory is shown in Figure 1. We chose these four sites instead of ones in a straight line from the emission source because the mine region is surrounded by mountains in the east, south and west, and there is a large reservoir in the north. The wind directions are mainly from the northeast. Therefore, we regarded this distant cropland site to be uncontaminated based on the normal corn yields in this region. The four selected sampling sites shared the same soil type and flat topography, and had similar vegetation which was dominated by Malus baccata and Ulmus pumila before mining.

Soil Collection
Soil sampling was conducted in June, 2008. Except for the uncontaminated cropland, all the sampling sites were covered by a varying thicknesses of hard but fragile compact crust [hydromagnesite 4MgCO₃·Mg(OH)₂·4H₂O, which was formed by dust accumulation and precipitation; Kautz et al., 2001]. Nine soil samples were randomly taken within an area of approximately 1500 m² at each site and each sample was comprised of five cores taken from the 0–20 cm soil layer after removing the crusts on the surface. Pieces of crust and visible plant materials were removed. All samples were sieved through a 2-mm mesh screen. Each soil sample was then divided into two subsamples. Of each pair of subsamples was air-dried at room temperature around 20°C for chemical analysis. The other subsample were stored at 4°C for less than 24 h before analyzing soil NH₄⁺–N, NO₃⁻–N concentrations, soil microbial respiration and potential net N mineralization rate (N₀), and microbial biomass C (MBC) and N (MBN).

Soil Analyses
Soil pH was determined in 1:2.5 soil/water suspension using a digital pH meter (Systronic Scientific Equipments Ltd., India). Soil moisture was measured gravimetrically by oven-drying at 105°C for 12 h. For determination of soil chemical properties, air-dried soil samples were ground and passed through a 0.2-mm sieve. Soil organic C (SOC) was determined by dichromate oxidation and titration with ferrous ammonium sulfate (Allen et al., 1986). Total N and total P were obtained from a complete digestion for 10 h.
CHEMICAL AND MICROBIAL PROPERTIES OF SOILS

with an H2SO4–HClO4 mixture and then determined by a continuous-flow autoanalyzer (AutoAnalyzer III®; Bran + Luebbe GmbH, Germany) using the indophenol blue method (Keeney and Nelson, 1982) for N and phosphomolybdic acid blue color method (Keeney and Nelson, 1982) for P. Available P was extracted with 0.5 mol L⁻¹ NaHCO3 (pH = 8.5) as reported by Olsen and Sommer (1982) and determined colorimetrically by the molybdate–ascorbic acid procedure (Murphy and Riley, 1962). Soil mineral N (NH4⁺–N + NO3⁻–N) concentrations were determined using the method described by Robertson et al. (1999). Soluble Ca and Mg concentrations were determined according to the method described by Thomas (1982) by atomic absorption spectrophotometry (AAS) after water extraction.

Soil MBC was determined with the chloroform fumigation extraction procedure (Vance et al., 1987). Soil MBN was determined by the fumigation extraction method of Joergensen and Brookes (1990). Three-replicate 25 g (fresh weight) portions of soils were weighed into 100 ml beakers and fumigated with ethanol-free chloroform in the dark at 20°C for 24 h. After the fumigant was removed, the soil was extracted with 100 ml 0.5 mol L⁻¹ K2SO4 for 30 min. Similarly, the unfumigated soil was extracted to determine the background soluble C and N level. The organic C concentration in the soil extracts was measured by dichromate oxidation, and MBC was calculated by:

\[
\text{MBC} = \frac{\text{EC}}{\text{B}_{\text{EC}}}, \quad \text{where} \quad \text{EC} = \text{difference in soluble organic C concentration between the fumigated and unfumigated soil, and the} \quad \text{B}_{\text{EC}} \text{used was 0.38 to account for the extraction efficiency (Lu, 1999). Ninhydrin N released on fumigation was converted to MBN using a conversion factor of 3:1 (Amato and Ladd, 1988).}
\]

Microbial respiration rate was measured by the method of Ross et al. (1999). Field-moist samples equivalent to 20 g oven-dried soil were aerobically incubated in 500 ml flasks at 25°C and 75 per cent water-holding capacity for 30 days. The air in the flasks was renewed with CO2-free air before the CO2 traps were placed inside the flasks. At days 3, 6, 11, 16, 24, and 30 of incubation, the evolved CO2 trapped in 10 ml of 0.1 mol L⁻¹ NaOH was measured by titration with 0.05 mol L⁻¹ HCl after adding 2 ml of 0.25 mol L⁻¹ BaCl2. The microbial metabolic quotient (qCO2) was calculated by dividing the mean daily value of soil respiration (across 30 days incubation) by the corresponding MBC.

Soil N0 was measured by the method described by Robertson et al. (1999). Briefly, a 25-g fresh soil sample was extracted with 100 ml 2 mol L⁻¹ KCl for 60 min to determine the initial mineral N concentration. Another 25 g fresh soil was weighed out and its moisture content was adjusted to water-holding capacity with distilled water and incubated aerobically at 25°C for 30 days. Soil moisture content was maintained at field capacity throughout the incubation. At the end of the incubation, the soil sample was extracted with 100 ml 2 mol L⁻¹ KCl for determining the final mineral N concentration. Mineral N concentrations were analyzed on an autoanalyzer (AutoAnalyzer III®; Bran + Luebbe GmbH, Germany). Soil N0 was obtained by the difference between the initial and final mineral N concentrations over 30 days incubation.

Statistical Analyses

One-way analysis of variance (ANOVA) was used to compare soil properties among four different sites. Mean values of MBC, MBN, qCO2, N0, SOC, total N, total P, and available nutrient (N, P, Ca and Mg) were tested for differences among sites with Tukey’s honestly significant difference (HSD) test. Repeated measures ANOVA was used to test the effects of different sites on soil basal respiration across whole incubation time. The Pearson’s correlation coefficients between variables were calculated by the Bivariate Correlations procedure. Significance is reported at α = 0.05. All statistical analyses were conducted using SPSS 13.0® for Windows software package.

RESULTS

Soil Chemical Properties

The mine tailings site had the highest soluble Mg²⁺ (345 mg kg⁻¹), while the uncontaminated cropland had the lowest value (140 mg kg⁻¹) as expected (Table I). In contrast, the uncontaminated cropland had the highest soluble Ca²⁺ concentration (87 mg kg⁻¹), whereas the mine tailings showed the lowest (22 mg kg⁻¹). The differences in soluble Mg²⁺ and Ca²⁺ concentrations were significant among four sites (p < 0.05). The soluble Mg²⁺/Ca²⁺ ratio was the lowest (1:6) in the uncontaminated cropland and the highest (16:0) in the mine tailings site. The Mg²⁺/Ca²⁺ ratios in the three contaminated sites were 3.5–8.9 times higher than the uncontaminated cropland.

Soil pH significantly differed among four sampling sites (Table I). It was the highest (10.3) in the mine tailings site, followed by the abandoned mined land (10.1) and the contaminated cropland (9.9), and the lowest value (7.1) was in the uncontaminated cropland, essentially neutral soil. Soil pH was increased by 2.8–3.2 units in the three contaminated sites compared with the uncontaminated cropland.

The SOC differed significantly among sites (p < 0.05). Both abandoned mined land and the uncontaminated cropland contained the similar SOC with 12.9 and 12.5 g kg⁻¹, respectively; there was no significant difference (p > 0.05) between the two sites (Table I). The mine tailings site had the lowest SOC (6.6 g kg⁻¹), while the contaminated cropland had 7.5 g kg⁻¹. The highest total N (1.31 g kg⁻¹) and total P (0.94 g kg⁻¹) were found in the uncontaminated cropland,
Table I. Mean (±1 standard error, n = 9) of soil soluble magnesium (Mg$^{2+}$), calcium (Ca$^{2+}$), pH, soil organic carbon (SOC), total nitrogen (TN), total phosphorus (TP), mineral nitrogen (MN), and available phosphorus (AP) in mine tailings (MT), abandoned mined land (AM), contaminated cropland (CC), and uncontaminated cropland (UC) at Haicheng, Liaoning, China.

<table>
<thead>
<tr>
<th>Site</th>
<th>Mg$^{2+}$ (mg kg$^{-1}$)</th>
<th>Ca$^{2+}$ (mg kg$^{-1}$)</th>
<th>pH</th>
<th>SOC (g kg$^{-1}$)</th>
<th>TN (g kg$^{-1}$)</th>
<th>TP (g kg$^{-1}$)</th>
<th>MN (mg kg$^{-1}$)</th>
<th>AP (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT</td>
<td>345 ± 16a</td>
<td>22 ± 1d</td>
<td>10.3 ± 0.0a</td>
<td>6.6 ± 0.2c</td>
<td>0.30 ± 0.01d</td>
<td>0.37 ± 0.01d</td>
<td>1.4 ± 0.2c</td>
<td>1.1 ± 0.1d</td>
</tr>
<tr>
<td>AM</td>
<td>292 ± 14b</td>
<td>40 ± 2b</td>
<td>10.1 ± 0.1b</td>
<td>12.9 ± 0.3a</td>
<td>0.72 ± 0.01b</td>
<td>0.43 ± 0.01b</td>
<td>5.9 ± 0.4b</td>
<td>11.4 ± 0.1c</td>
</tr>
<tr>
<td>CC</td>
<td>266 ± 14c</td>
<td>34 ± 2c</td>
<td>9.9 ± 0.0c</td>
<td>7.5 ± 0.1b</td>
<td>0.56 ± 0.01c</td>
<td>0.40 ± 0.01c</td>
<td>4.7 ± 0.4b</td>
<td>38.8 ± 1.2b</td>
</tr>
<tr>
<td>UC</td>
<td>140 ± 9d</td>
<td>87 ± 3a</td>
<td>7.1 ± 0.0d</td>
<td>12.5 ± 0.3a</td>
<td>1.31 ± 0.02a</td>
<td>0.94 ± 0.01a</td>
<td>2.49 ± 1.1a</td>
<td>14.4 ± 2.6a</td>
</tr>
</tbody>
</table>

Different letters in the same column indicate significant site difference (p < 0.05).

followed by the abandoned mined land (0.72 and 0.43 g kg$^{-1}$, respectively) and the contaminated cropland (0.56 and 0.40 g kg$^{-1}$, respectively). The lowest total N and total P (0.30 and 0.37 g kg$^{-1}$, respectively) were in the mine tailings site. Soil mineral N concentrations differed remarkably among four different sites. The highest mineral N concentration (24.9 mg kg$^{-1}$) was found in the uncontaminated cropland, while the lowest value (1.4 mg kg$^{-1}$) was found in the mine tailings site, and no significant difference in mineral N concentration was detected between the abandoned mined land and the contaminated cropland (p > 0.05). Available P showed the highest value (144.9 mg kg$^{-1}$) in the uncontaminated cropland, which was 3.7 folds more than that (38.8 mg kg$^{-1}$) in the contaminated cropland, 12.8 folds more than that in the abandoned mined land (11.4 mg kg$^{-1}$), and 134.2 folds more than that in the mine tailings site (1.1 mg kg$^{-1}$).

**Microbial Biomass C and N**

Soil MBC and MBN were significantly higher in the uncontaminated cropland than in the contaminated sites (Figure 2). The lowest MBC and MBN appeared in the mine tailings site. The difference in MBC was significant across all sites, but no significant difference in MBN was found between the abandoned mined land and the contaminated cropland.

**Microbial Respiration**

Soil respiration rate peaked in the first 3 days and generally declined throughout the 30 days incubation in the contaminated soils (Figure 3). However, soil respiration rate in the uncontaminated cropland showed a different pattern, with a decline before day 11 and then a slight increase. The abandoned mined land had the highest respiration rate although it did not differ from contaminated cropland; both soils had very similar respiration trend. The soil respiration rates of the mine tailings site and the uncontaminated cropland were lower than those of abandoned mined land and contaminated cropland. There was a significant difference in soil respiration rate between the mine tailings site and the uncontaminated cropland in the first 3 days, but no significant difference (p > 0.05) was found in days 4-11 of incubation (Figure 3).

Soil qCO$_2$ was significantly different among different sites (p < 0.05). The trend of qCO$_2$ was in order of uncontaminated cropland < contaminated cropland < abandoned mined
Chemical and Microbial Properties of Soils

Soil N Mineralization

The uncontaminated cropland had significantly higher \( \text{N}_0 \) (11.2 mg kg\(^{-1} \) 30 d\(^{-1} \)) than the contaminated cropland (4.8 mg kg\(^{-1} \) 30 d\(^{-1} \)) and the abandoned mined land (4.5 mg kg\(^{-1} \) 30 d\(^{-1} \)) \((p < 0.05, \text{Figure 5})\). The mine tailings site had the lowest \( \text{N}_0 \) (0.4 mg kg\(^{-1} \) 30 d\(^{-1} \)), which was significantly lower than any of the other sites. There was no significant difference in \( \text{N}_0 \) between the abandoned mined land and the contaminated cropland.

Correlation Among Measured Variables

Correlation analysis (Table II) revealed that the relationship between soluble Mg\(^{2+} \) and pH was positive. Total P, available P, mineral N, soluble Ca\(^{2+} \), and microbial biomass C and N were negatively correlated with pH. Soluble Mg\(^{2+} \) had a significant negative correlation with total N, mineral N, available P, soluble Ca\(^{2+} \), MBC, MBN and \( \text{N}_0 \). Soluble Mg\(^{2+} \)/Ca\(^{2+} \) ratio was negatively correlated with \( \text{N}_0 \) but positively correlated with \( q\text{CO}_2 \).

Discussion

Our investigation indicates that all the contaminated soils are characterized by alkalization and high soluble Mg\(^{2+} \) concentration, while the soil in uncontaminated cropland has neutral pH and low soluble Mg\(^{2+} \) concentration. High soluble Mg\(^{2+} \) concentration is caused by hydrolysis of MgCO\(_3\), whereas the high MgO in the dusts is responsible for a general increase in soil pH (Machin and Navas, 2000).

Soil pH plays an important role in nutrient cycling (Marion and Babcock, 1977; Mengel and Kirkby, 1982). Although soil pH does not directly control N availability, it does affect soil microbial activity. High pH can result in significant loss of N by volatilization, because NH\(_4^+\) tends to convert to NH\(_3\) gas that then diffuses from alkaline soil to the atmosphere (Mengel and Kirkby, 1982). Soil pH controls the availability of P. In acid soil, available P concentration increases as pH increases, while in alkaline soil, available P concentration decreases as pH increasing (Holford and Mattingly, 1975; Parfitt, 1978). Basic soil conditions (pH > 7.5) can cause excessive calcium to be present in soil solution which can precipitate with P, decreasing P availability (Marion and Babcock, 1977). In addition, soluble Mg\(^{2+} \) can directly affect available P by decreasing consolidation of phosphorus by calcium carbonate (Ferguson and McCarty, 1971; Marion and Babcock, 1977). Therefore, low available P and \( \text{N}_0 \) in the contaminated soils are apparently caused by high soil pH and Mg\(^{2+} \) concentration.

Soil microbes are very sensitive to changes of soil environment including fluctuations in temperature, extremes of water potential, extremes of pH, physical disturbances, as well as pollution (Domsch, 1980; Domsch \textit{et al.}, 1983; Killham and Firestone, 1984). Consistent with previously reported patterns (Brookes and McGrath, 1984; Chander and Brookes, 1991a), we found that soil MBC and MBN were significantly lower in the contaminated sites than in the uncontaminated cropland (Figure 2), suggesting that soluble Mg\(^{2+} \) and soil pH influence microbial biomass significantly.

Soil microbes mediate biogeochemical processes such as transformation of litter to soil organic matter and mineralization of organic matter (Ross \textit{et al.}, 1999; Chen...
The positive correlations between soil microbial biomass and nutrients (mineral N, and available P) (Table II) indicate that soil microbial biomass plays an important role in soil nutrient cycling (Araújo et al., 2008). Microbial biomass can reflect soil quality (Brookes, 2001); there are generally larger microbial biomass and available nutrients in healthy soils than in stressed soils (Liao and Xie, 2007; Li et al., 2010). Liao and Xie (2007) found an inhibitory effect of heavy metals on soil microbial biomass, and there was a consistent decrease in MBC and MBN with increase in heavy metal contamination. The decreases in MBC and MBN may be due to microorganisms in soil under heavy metal stress diverting energy from growth to cell maintenance functioning (Killham, 1985). On the other side, because more substrate is diverted toward catabolic processes at the expense of anabolic processes, the substrate utilization efficiency of microorganisms is low under stress conditions, and consequently microbial biomass reduces in the long run (Sparling, 1992). The lower mineral N and N0 in the contaminated sites are probably related to lower microbial activity on conditions of higher pH and Mg2+ concentration in this study.

The qCO2 (respiration-to-biomass ratio) has been applied as a sensitive indicator for investigating soil quality and is closely related to soil pollution and other environmental changes (Anderson and Domsch, 1993; Brookes, 1995; Li et al., 2010). In this study, all the contaminated sites had significantly higher qCO2 than did the uncontaminated cropland, which is consistent with the result of Brookes and McGrath (1984), who reported that qCO2 in the metal-contaminated soils was twice as great as that in the uncontaminated soils, although soil respiration rate was indistinguishable between uncontaminated and metal-contaminated soils on a Woburn Market Garden Experiment in England. Moreover, Chander and Brookes (1991b) reported that, compared to normal soils, there were less biomass formation from labeled substrate and higher qCO2 values in heavy metal-contaminated soils. We expected that higher qCO2 in the contaminated soils might be caused by higher pH and soluble Mg2+ concentration; however, neither pH nor soluble Mg2+ concentration was significantly correlated with qCO2. We did find that qCO2 was positively correlated with soluble Mg2+/Ca2+ ratio (Table II). Moreover, a negative correlation between soluble Mg2+/Ca2+ ratio and N0 (Table II) also imply that Mg2+/Ca2+ ratio would be the important factor influencing soil microbial activities. Clearly, the mechanisms underlying these relationships should be further studied.

In conclusion, the main effect on soils exposed to Mg-dusts was a great increase in Mg2+ concentration, pH, and soluble Mg2+/Ca2+ ratio, and a decrease in microbial activity and N, P, and Ca availability. All these would affect plant’s colonization and growth. Thus, the future soil amelioration in the magnesite regions may consider applying acid ameliorants to neutralize high pH and applying calcareous ameliorants to increase Ca2+ concentration.

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