MANGANESE MOBILITY IN SOILS UNDER THE IMPACT OF ALKALINE DUST EMISSION

Halina Dąbkowska-Naskręt, Hanna Jaworska

Chair of Soil Science and Soil Protection
University of Technology and Life Sciences in Bydgoszcz

Abstract

Manganese is required by plants for photosynthesis. It is also is a key activator in a number of critical processes in plant tissues. Moreover, it has been proven that Mn is an essential element for animals and people.

Manganese deficiency may occur in soils that are sandy alkaline or calcareous. The objective of the study was to asses the long-term impact of alkaline cement dust, emitted by the Lafarge Cement Plant in Bielawy (Kujawy region) on manganese availability in soils in the vicinity of the source of emission.

The mobility of Mn was estimated by DTPA-extraction of soil samples. It was stated that DTPA-extractable Mn was in the range of 0.81-12.07 mg kg^{-1} i.e. below the recommended limits for the proper plant growth. The lowest content was detected in soils adjacent to the cement plant, with the highest pH due to the most intensive alkaline dust emission. Cement dust acts like a liming substance and affects manganese mobility.

Key words: manganese, mobility, cement dust, alkalization.

MOBILNOŚĆ MANGANU W GLEBACH BĘDĄCYCH POD WPŁYWEM PYŁÓW ALKALICZNYCH

Abstrakt

Mangan jest niezbędny dla roślin w procesie fotosyntezy oraz jako aktywator wielu procesów zachodzących w tkankach roślinnych. Stwierdzono także, że jest on istotnym pierwiastkiem dla zwierząt i człowieka.

prof. dr hab. Halina Dąbkowska-Naskręt, Chair of Soil Science and Soil Protection, University of Technology and Life Sciences, 85-029 Bydgoszcz, Bernardyńska 6, e-mail: dabkowska@utp.edu.pl

Niedobór manganu występuje w glebach piaszczystych, węglanowych lub o odczynie alkalicznym. Celem badań była ocena wieloletniego wpływu emisji pyłu cementowego o odczynie alkalicznym emitowanego przez Zakłady Cementowe Lafarge S.A. w Bielawach (Kujawy) na dostępność manganu w glebach w sąsiedztwie źródła emisji.

Mobilność manganu oznaczono przez ekstrakcję próbek gleby roztworem DTPA. Stwierdzono, że zawartość DTPA – ekstrahowanego Mn była w zakresie 0.81-12.07 mg kg^{-1}, tj. poniżej wartości deficytowych dla roślin. Pył cementowy działa na gleby jak materiał wapnujący i wpływa na mobilność manganu.

Słowa kluczowe: mangan, mobilność, pył cementowy, alkalizacja.

INTRODUCTION

Manganese is an essential trace element which occurs in varying amounts in all tissues. It is a constituent or activator of enzymes in plants and animals. This micronutrient is required for photosynthesis and is a key activator in a number of critical metabolic processes in plants (YU, RENGEL 1999). Moreover, Mn is important in the development of resistance in plants to root and foliar diseases of fungal origin, lowering the inoculum potential of soil-borne pathogens. Animals need Mn for neural development (FROSLIE 1990). It has also been proven that Mn is an essential element for humans (VAN CAMPEN 1991). It was reported that Mn^{+2} ions protect biological components and living cells from oxidative damage (VARANI et. al. 1991).

Manganese deficiency occurs in soils that are alkaline, calcerous, saline or sandy. The concentration of available Mn is also related to the cropping system or the way land is maintained (ŻARCZYŃSKI et al. 2011). Yields of crops grown on calcerous soils are frequently limited by Mn deficiency resulting from a low Mn availability rather than a low Mn content in the soil.

Antropogenically alkalized soils may suffer from a low or deficit level of this micronutrient in an available form. Long-term exposure to alkaline dust pollution from a cement plant has resulted in soil alkalization (CIEŚLA et al. 1994). The problem of pollution is caused by the production, handling and transportation of cement. Heavy metals are among the best-known substances emitted during the process of cement manufacture. Furthermore, alkaline dust has a harmful effect on the soil environment. Air pollutants generated during the cement manufacturing process consist primarily of particulates from raw and finished materials as well as by-products of fuel combustion. The raw material – a combination of calcareous rock (limestone) and aluminosilicate material is brought to temperatures up to 1450°C to decarbonate the calcareous material and to produce cement clinker. Portland cement is a fine powder comprised of calcium oxide (60 to 67%) silicon oxide (17 to 25%) aluminium trioxide (3 to 8%) and ferric oxide (0-5%). The cement and lime industry is among the industries generating most dust (FARMER 1993).

The objective of the present study has been to asses the long-term impact of alkaline cement dust on the mobility of manganese in soils adjacent to a cement plant. The Lafarge Cement S.A. plant, located in Bielawy (Kujawy region), has been chosen for the study. The plant is a serious source of environmental dust pollution.

The scarcity of published information about the Mn status in soils contaminated with cement dust encouraged the above study undertaken in an attempt to fill this gap in our knowledge.

MATERIAL AND METHODS

The analyzed location lies in the rural area of Kujawy region. The research material comprised samples of sandy soils, taken at different distances from the pollution emitter, i.e. the Lafarge Cement S.A. plant in Bielawy (Figure 1). Soils were sampled from two depths (0-20 cm and 20-40 cm) at six sites located in different distances from the source of dust emission. The soil material was sampled once a year for six years (2006-2011).
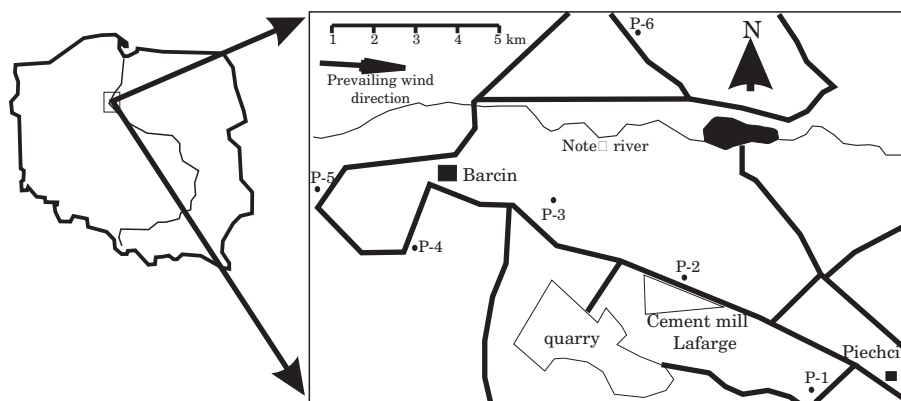

Fig. 1. Location of soil samples

The soil samples were air dried and crushed to pass through a 2 mm mesh sieve. The soil's pH was measured in a 1:2,5 (w:v) soil to water suspension using a glass electrode pH-meter.

The soil samples were digested in a mixture of HCl and HNO_3 concentrated acids for the determination of total amounts of manganese. Manganese availability to plants was estimated by extracting with DTPA-solution, according to LINDSAY and NORVELL (1978). The concentrations of Mn in solutions were measured by atomic absorption spectrometry on a PU 9100 X Philips instrument. All soil samples were analyzed in triplicate.

The statistical analysis of the results was performed with a Statistica 8.0 PL computer programme. The probability level of $\alpha = 0.05$ was selected to establish statistical significance.

RESULTS AND DISCUSSION

Table 1 provides information about some general characteristics of the soils examined in this study. The texture of the soils varied only a little and all the samples were classified as sandy soil. The content of soil organic carbon was generally low (less than 12.0 g kg^{-1}) ranging from 7.6 to 14.0 g kg^{-1}, except for sample P2.

The pH of the soils differed depending on the location and sampling period, varying from 5.49 to 8.83 (Table 2). The highest pH was detected in samples in the direct vicinity of the cement plant (site P2). The elevated alkaline pH occurred each year of the study (2006-2011) and was observed in surface and subsurface samples from site P2.

The natural soil pH is in the range 5.0-6.2 (CIEŚLA et. al. 1994). Thus, differences in the pH of these soils compared to their originally slightly acidic pH correspond to differences in the H^+ concentration equal $\sim$ 5.000 fold ($\sim$ 3.5 pH units).

Table 1

Selected properties of soils

Sample	Depth (cm)	Corg (g kg^{-1})	CaCO$_3$ (%)	Mn total (mg kg^{-1})
P1	0 - 20	11.9	0.33	272.2
	20 - 40	8.50	0.29	243.3
P2	0 - 20	14.1	6.80	319.1
	20 - 40	8.20	4.60	346.4
P3	0 - 20	11.5	-	261.0
	20 - 40	10.0	-	276.1
P4	0 - 20	10.7	-	218.1
	20 - 40	9.10	-	229.4
P5	0 - 20	11.7	1.80	168.9
	20 - 40	10.2	1.30	144.1
P6	0 - 20	8.50	-	163.1
	20 - 40	7.60	-	140.6

Table 2

Changes in DTPA extracted Mn and concentration of (H⁺) in soils during
the 6 years of observations

Sample	Depth (cm)	pH H$_2$O	SD	DTPA- Mn (mg kg^{-1})	SD**
P1	0 - 20	6.32 - 8.05 * 7.22	0.59	1.6 - 6.27 * 3.81	1.73
	20 - 40	6.51 - 7.34 8.18	0.56	1.27 - 4.52 3.02	1.18
P2	0 - 20	7.94 - 8.52 8.12	0.22	1.05 - 11.5 3.78	3.84
	20 - 40	8.10 - 8.83 8.30	0.26	1.02 - 10.9 3.26	3.79
P3	0 - 20	5.89 - 6.72 6.19	0.30	4.23 - 8.62 5.68	1.73
	20 - 40	5.90 - 6.72 6.30	0.36	2.60 - 7.10 4.81	1.73
P4	0 - 20	6.01 - 6.42 6.23	0.16	2.67 - 7.70 5.53	1.95
	20 - 40	5.98 - 6.58 6.27	0.26	1.08 - 12.0 6.22	4.07
P5	0 - 20	6.20 - 7.80 7.38	0.62	0.83 - 10.0 5.25	4.15
	20 - 40	6.08 - 7.78 7.42	0.61	0.81 - 6.40 2.66	2.03
P6	0 - 20	5.49 - 6.54 6.06	0.40	1.60 - 3.40 2.60	0.71
	20 - 40	5.76 - 6.96 6.22	0.47	1.07 - 6.10 3.01	1.94

*minimum – maximum
   mean value
**SD – standard deviation

Dust falling on the soil caused a shift in the soil pH to the alkaline side due to carbonates present in emitted particles. Calcium carbonate was detected in samples located in the direct vicinity of the emitter (Table 1). In soils adjacent to the cement plant, the content of CaCO$_3$ ranged between 0.33% to 6.8% in surface sample and from 0.29% to 4.6% in subsurface samples, typically increasing in the subsequent years. The soil sampled at site P-2 had the pH above 7.94 up to 8.52 (mean value 8.12) in the surface and 8.10 up to 8.33 (mean 8.30) in the subsurface horizon. In soils lying in the same region but unaffected by the cement plant, pH values were in the

range 5.0-6.2. Some previous research on soils near the Lafarge Plant in Bielawy showed that the parent material did not contain $CaCO_3$ (CIEŚLA et al. 1994).

Much smaller changes were observed in soils located further from the cement dust emission point (sites P2-P4 and P6). Calcium carbonate in acid soils being under the impact of industrial emission is described as the tracer of the pollution lead by the cement industry (ZERROUGI, SBAA 2008).

The total Mn concentrations in soils varied from 140.6 to 346.5 mg kg^{-1} and DTPA-extractable Mn was in the range 0.81-12.07 mg kg^{-1} (Table 2). The lowest content of DTPA-Mn was detected in site P2 with the highest pH. A simple linear correlation analysis showed few significant correlations between soil properties and DTPA extractable manganese. Significant correlation was obtained between organic matter and DTPA-extractable manganese (r = 0.4273, α = 0.05) in the studied soils. The soil organic matter content has been associated with an increased Mn availability in numerous experiments (MORAGHAN, MASCAGNI 1991, MC BRIDE 1989). The effect of organic matter has been attributed to formation of complexes.

Critical levels for DTPA-extractable Mn range from 2.5 to 5.0 mg kg^{-1} (MORAGHAN, MASCAGNI 1991). Extractable Mn showed no correlation with the pH (or exactly with the concentration of H$^+$ ions) in the examined soils. However, such a correlation was obtained for soil sampled in the direct vicinity of cement plant (site P2; Figure 1). A significant (r = 0.6211) statistical correlation was observed between [H+] concentration and DTPA extractable Mn in P2 soil (Figure 2). For this site, significant correlations between Corg and DTPA-Mn as well as between the $CaCO_3$ concentration and DTPA extractable Mn (r = 0.499, r = 0575, respectively). were obtained for six years of the observation period (Figures 3 and 4). Cement dust rich in $CaCO_3$ acts like a liming substance and affects the plant availability of manganese in soils from the site adjacent to the cement plant.

A negative trend in response to the alkaline contaminant was observed in almost all the soil samples and in all the years of the study. It was the most evident for site P2 (Figure 1).

The Mn deficit to plants arises from complex interactions of many factors and is related to soil properties, plant-specific factors and their interactions at the soil-root interface (TONG et al. 1997, THOMSON et al. 2005).

Manganese deficiency may occur as a primary condition, where the soil (and its parent material) is poor in manganese (like sandy soils), or in a secondary form, associated with an alkaline pH of the soil. Several authors (WEI et al. 2006, MC BRIDE 1989) have found that pH has the strongest effect on the availability of Mn. The mobility of amphoteric cations (Mn) decreases when soil undergoes an alkaline treatment.

The two main forms of Mn is soils are soluble Mn(II) and hardly soluble Mn(IV). In well-aerated soils, Mn occurs as Mn(II) ions in the soil solution,
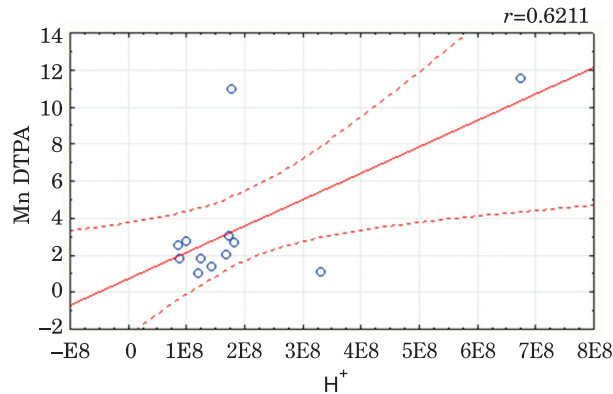
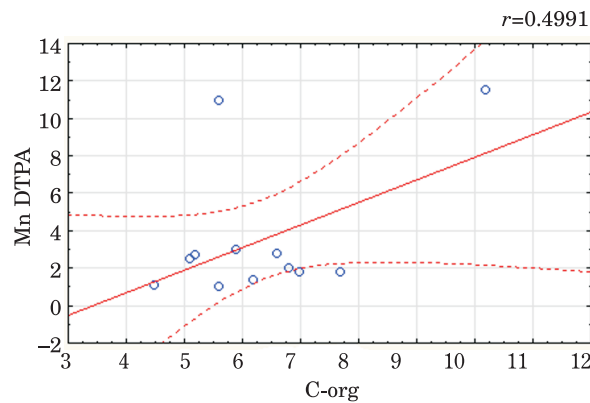Fig. 2. Corelation between (H$^+$) concentration and Mn-DTPA in P2 soil

Fig. 3. Corelation between C-org. concentration and Mn-DTPA in P2 soil

Mn(II) adsorbed by organic matter and clay minerals or co-precipitates (BARTLETT, JANES 1993). In calcerous soils with high soil pH, plant available Mn(II) is oxidized to Mn(IV) ions. Moreover, NORVELL (1988) stated that when soil pH > 8, auto-oxidation of Mn(II) took place. Manganese oxides are very strong oxididizing agents with oxidation potentials higher than O_2 itself. The high soil pH in site P2 could have initiated the auto-oxidation process and reduced the manganese mobility.

Mobility and bioavailability of manganese are largely governed by the pH and redox conditions. An increase in the soil's pH lowers the mobility of this micronutrient due to the oxidation of soluble Mn(II) to hardly soluble Mn(IV) which occurs at about neutral pH (NORVEL 1988). Other authors (PONNAMPERUNA 1986) reported that the amount of water-soluble manganese decreased to a tenth when the pH in soil increased from 7 to 8. The analyzed
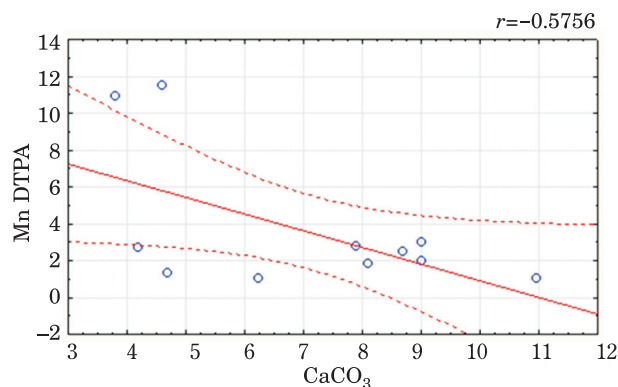
Fig. 4. Corelation between CaCO$_3$ content and Mn-DTPA in P2 soil

soils in the direct vicinity of the cement plant had a pH in these ranges, thus the impact of alkalization on the Mn mobility was the most profound there.

In such alkaline soil, nitrogen fertilization with some acid forming fertilizer like $(NH_4)_2SO_4$ is recommended, as it will acidify the soil solution, which in turn will enhance the mobility of Mn, B and Fe (DOMAGAŁA-ŚWIĄTKIEWICZ, SADY 2010). This is particularly important for crops sensitive to Mn deficiency.

CONCLUSIONS

1. The alkalization of the soil environment by cement dust complicates mineral nutrition due to disrupting good manganese availability in soils, particularly ones adjacent to the source of emission.

2. Cement dust rich in CaCO$_3$, acts like a liming substance and affects plant availability of manganese in soils in the vicinity of a cement plant.

3. Based on the metal extractability with DTPA, it was concluded that concentrations of plant-available manganese in cement dust affected soils were below the recommended limits due to alkalization of soils by cement particles.

REFERENCES

BARTLETT J., JANES B.A. 1993. *Redox chemistry of soils.* Adv. Agron., 50: 151-208.

CIEŚLA W., ZALEWSKI W., JAWORSKA H. 1994. *Acidity and related properties in arable soils in the midst of KCW – Kujawy lime and cement plant.* Zesz. Probl. Post. Nauk Rol., 413: 75-81. (in Polish)

Domagała-Świątkiewicz I., Sady W. 2010. *Effect of nitrogen fertilization on Cu, Mn, Zn, Fe, B and Mo availability in commercially grown white head cabbage.* J. Elementol., 15(3): 455-465.

Farmer A.M. 1993. *The effects of dust on vegetation – a review.* Environ. Pollut., 79: 63-75.

Froslie A. 1990. *Problems on deficiency and excess of minerals in animal nutrition.* In: *Geomedicine.* J. Lag (ed). Boca Raton, CRC Press, 37-60.

Lindsay W.L. Norvell W.A. 1978. *Development of a DTPA soil test for Zn, Fe, Mn and Cu.* Soil Sci. Soc. Am. J., 42: 421-428.

Mc Bride M.B. 1989. *Reactions controlling heavy metals solubility in soils.* Adv. Soil Sci., 10: 1-56.

Moraghan J. T., Mascagni H.J. 1991. *Environmental and soil factors affecting micronutrient deficiencies and toxicities.* In: *Micronutrients in agriculture.* J.J. Mortvedt (ed)., 371--411.

Norvell W.A. 1988. *Inorganic reactions of manganese in soils.* In: *Manganese in soils and plants.* Graham R.D. (ed). Kluwer Academic Publishers., 37-58 pp.

Ponnamperuna F.N. 1986. *Behavior of trace elements as affected by redox process.* Int. Soc. Soil Sci., 715-728.

Thomson J.A., Huber D.M., Guest C.A., Schultze D.G. 2005. *Fungal manganese oxidation in a reduced soil.* Environ. Microbiol., 7(9): 1480-1487.

Tong Y., Rengel Z., Graham R.D. 1997. *Interactions between nitrogen and manganese nutrition of barley genotypes differing in manganese efficiency.* Ann. Botany, 79: 53-58.

Van Campen D.R. 1991. *Trace elements in human nutrition.* In: *Micronutrients in agriculture.* J.J. Mortvedt (ed)., 663-693 pp.

Varani J., Ginsburg I., Gibbs D.E., Mukhopadhyay P., Sulavik C., Johnson K.J., Weinberg J.M., Ryan V.S., Ward P.A. 1991. *Hydrogen peroxide - induced cell and tissue injury: protective effects of Mn $^{+2}$.* Inflamm., 15: 291-301.

Wei X., Hao M., Gale W. 2006. *Changes in soil properties and availability of soil micronutrients after 18 years of cropping and fertilization.* Soil Tillage Res., 91: 120-130.

Yu P., Rengel Z. 1999. *Micronutrients deficiency influence plant growth and activities superoxide dismutases in narrow leaf lupine.* Aun. Bot., 83: 175-182.

Zerrougi Z., Sbaa M. 2008. *Assessment of cement dust impact on the soil using principal component analysis and GIS.* Int. J. Environ. Sci. Technol., 5(1): 125-134.

Żarczyński P. Sienkiewicz S. Krzebietke S. 2011. *Effect of the way set-aside land is maintained on the content of available forms of selected micronutrients in soils.* J. Elem., 16(4): 651-657.DOI:10.5601/jelem.2011 16.4:10