FEB

INFLUENCE OF CaCO$_3$ ON THE

ALUMINIUM TOXICITY IN LEACHATES OF

SOILS CONTAMINATED BY ACIDIC MINE DRAINAGE

Inés García[1], María Diez[2], Francisco Martín[2],
Mariano Simón[1], Juan Antonio Sánchez[1] and Fernando del Moral[1].

[1] Departamento de Edafología y Química Agrícola. Universidad de Almería, Almería, Spain
[2] Departamento de Edafología y Química Agrícola. Universidad de Granada, Granada, Spain.

ABSTRACT

The Ap horizon of a Typic Haploxerept was mixed with increasing amounts of CaCO$_3$ (20, 40, 60, 80, and 100 g kg^{-1}). A pollutant solution coming from acidic mine drainage (AMD) was added both to the original soil as well as to the five soil-CaCO$_3$ mixtures, and the leachates were collected and analyzed. The results indicate that the CaCO$_3$ in soil reduces the aluminium toxicity in the leachates, by raising the pH, lowering the Al concentration, and reducing the activity of the Al species. An equation is calculated to determine, from the pH of the AMD and the CaCO$_3$ content in soil, the amount of pollutant solution that can be added to a soil without adversely affecting the Al toxicity of the leachate.

KEYWORDS: Soil, acidic mine drainage, calcium carbonate, aluminium toxicity.

INTRODUCTION

The sulphide oxidation in mine spoils is a complex bio-geochemical process that releases sulphate ions, intensifies acidity, and solubilizes different elements associated with sulphides [1]. In the case of pyrite, the most abundant sulphide in these spoils, the oxidation can be represented by the reaction:

$$4FeS_2 + 15O_2 + 14H_2O \longrightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \quad (1)$$

When the acidic solution generated by the oxidation of the pyrite infiltrates the soil, the protons may act as weathering agents, promoting the dissolution of other soil components and increasing the ionic concentration in the soil solution and drainage waters [2]. The release of large amounts of aluminium is of particular concern because of the risk of phytotoxicity [3-7]. The activity of total Al in solution is not a suitable indicator of Al toxicity, whereas the soil pH and the Al species present in the soil solution are more important [8]. Al^{3+} and monomeric hydroxylates of Al are generally considered to be the most toxic species, while the Al-SO4 complex is less toxic [9-11]. On the other hand, cations such as Ca and Mg have been shown to reduce Al toxicity [12-13].

When the acidic mine drainage (AMD) infiltrates soils with CaCO$_3$, the acidity is neutralized, Ca^{2+} is released, and the dissolved aluminium reacts with the sulphate ions forming Al-SO4 complexes and precipitating as basaluminite [14]. The aim of the present work is to determine the liming rates necessary to mitigate the Al toxicity in leachates of soils affected by AMD.

MATERIALS AND METHODS

The experiment used the Ap horizon of a Typic Haploxerept [15] with intermediate buffering capacity (pH = 7.6, sandy-loam texture, cation-exchange capacity (CEC) of 16.3 cmol$_{(+)}$ kg^{-1}, base saturation about 70%, and organic-carbon content lower than 3 g kg^{-1}). The element concentration (%) was: 36.5 Si, 5.17 Al, 2.39 Fe, 0.85 Ca, 0.37 Mg, 0.63 Na, and 1.21 K. The soil sample was air-dried and sieved through 2 mm mesh size. Five samples were prepared by the addition of increasing amounts of CaCO$_3$ to the original soil sample (20, 40, 60, 80, and 100 g kg^{-1}). Each sample was introduced in a glass column of inner diameter 3.5 cm and 10 cm length, narrowing towards the bottom to inner diameter 0.4 cm. The bottoms of the columns were refilled with fiberglass to retain the

soil within the columns. Each column was hand-packed with 50 g of the original soil sampled and with the five soil-$CaCO_3$ mixtures. In all cases, the height of the soil column was 5 cm. The pollutant solution from the acid mine drainage (AMD) used had a pH of 1.8 and the element concentration (mg dm^{-3}) was: SO_4 15078, Fe 4360, Al 290, Ca 9.6, Mg 222, Na 45, and K 1.8. The top of the soil column was covered with a 2 cm layer of fibreglass to facilitate a uniform flow. Afterwards, in darkness, to inhibit algal growth [16], 50 cm^3 of AMD with a 10 cm^3 h^{-1} flow were added to each column. This addition was repeated three times every 5 days. The pH of the leachates collected in each addition was measured, and the solutions were immediately filtered through cellulose filters (0.45 μm pore) by vacuum suction into Pyrex™ flasks previously washed with acid, and stored at < 4ºC before analysis. The pH of the soil was measured in a 1:2.5 soil:water suspension and the total element concentration determined by X-Ray fluorescence. Organic carbon was analyzed by dry combustion with a LECO instrument. Fe, Al, Ca, and Mg concentration in the AMD and leachates were measured by atomic absorption spectroscopy; Na and K by flame photometry; and SO_4^{2-} by ion chromatography in a Dionex DX-120 instrument. The amount of each element precipitated was calculated by the difference between the concentrations in AMD and in leachates. The Al species present in leachates were processed using the computer program Solmineq [17]. The Al toxicity indexes of the leachates were estimated from Ca+Mg/Al molar ratio [18] and from the activity of Al species [19]. Values lower than 1 in the first index, and higher than 1 in the second, indicate Al toxicity.

RESULTS AND DISCUSSION

Precipitated aluminium in soil

Precipitated aluminium in soil (PAl) was found to be linearly and significantly ($P<0.001$) related to the Al added with the AMD (AMDAl) and with the $CaCO_3$ content in soil ($SCaCO_3$) by the multiple regression:

$$PAl \ (mg/kg) = -318.1 + 0.149 \ AMDAl \ (mg/kg) + 11.21 \ SCaCO_3 \ (g/kg) \quad r^2 = 0.562 \tag{2}$$

This indicates that, in decarbonate soil, Al does not precipitate; even in soils with 20 g $CaCO_3$ kg^{-1} Al precipitates only when the pollution is relatively low (≤ 2 dm^3 AMD kg^{-1} dry soil); on the contrary, in the soils with $CaCO_3$ content ≥ 40 g kg^{-1} some of the Al present in the AMD invariably precipitates.

On the other hand, PAl was significantly ($P<0.001$) and directly related to precipitated sulphates (PSO_4^{2-}) but inversely to precipitated iron (PFe), by the multiple regression:

$$PAl \ (mg/kg) = -131.6 + 0.088 \ PSO_4^{2-} \ (mg/kg) - 0.066 PFe \ (mg/kg) \quad r^2 = 0.773 \tag{3}$$

Consequently, the sulphate ions dissolved in the AMD increased the precipitation of aluminium in soil, probably as basaluminite, while the dissolved iron reduced this precipitation. This reduction could be related to the significant ($P<0.001$) linear relationship between PSO_4^{2-} and PFe, by the equation:

$$PSO_4^{2-} \ (mg/kg) = 2477.9 + 1.761 \ PFe \ (mg/kg) \quad r^2 = 0.879 \tag{4}$$

This indicates that iron and sulphate in the AMD tended to precipitate in soil, probably as Fe-hydroxysulphate [14], which would reduce the concentration of SO_4^{2-} ions in the soil solution and, consequently, PAl (Eq. 3).

Aluminium in the leachates

Aluminium concentration (LAl) was inversely and significantly ($P<0.001$) related to the pH of the leachate (LpH) by the equation:

$$LAl \ (mmol \ dm^{-3}) = -13.11 + 73.03 \ LpH^{-1} \quad r^2 = 0.959 \tag{5}$$

This indicates that the leachates had only Al when the pH was lower than 5.5. On the other hand, LpH was significantly ($P<0.001$) and directly related to the $SCaCO_3$ but inversely to H^+ added from AMD ($AMDH^+$) by the multiple regression:

$$LpH = 3.99 + 3.45 \ SCaCO_3 \ (mol \ kg^{-1}) - 39.79 \ AMDH^+ \ (mol \ kg^{-1}) \quad r^2 = 0.878 \tag{6}$$

This equation allows an estimation, depending on the $CaCO_3$ content, of the acidity that each soil can neutralize when the pH of the leachate remains below 5.5 and, consequently, can contain dissolved Al. Therefore, the pH of the leachate of soils with a $CaCO_3$ content < 0.4 mol kg^{-1} was consistently below 5.5, regardless of the AMD added; whereas soils with 0.6 mol $CaCO_3$ kg^{-1} needed the addition of 0.013 mol H^+ kg^{-1} to reach LpH < 5.5, 0.031 mol H^+ kg^{-1} in soils with 0.8 mol $CaCO_3$ kg^{-1}, and 0.049 mol H^+ kg^{-1} in soils with 1.0 mol $CaCO_3$ kg^{-1}.

In addition, with Eqs. 5 and 6 considered together, LAl was significantly ($P<0.001$) and directly related to $AMDH^+$ but inversely to $SCaCO_3$ by the multiple regression:

$$LAl \ (mg \ dm^{-3}) = 208.5 + 6396.6 \ AMDH^+ \ (mol \ kg^{-1}) - 530.3 \ SCaCO_3 \ (mol \ kg^{-1}) \quad r^2 = 0.789 \tag{7}$$

This indicates that in the soil without $CaCO_3$ the Al concentration in leachate was higher than the Al concentration in AMD and, therefore, the added H^+ in the AMD causes the weathering of the primary minerals in soils, promoting the dissolution of Al and increasing its concentration in the leachates.

On the other hand, the activity of the Al species in the leachates (L[Al]) was significantly ($P<0.001$) and directly related to LAl but inversely to LpH by the multiple regression:

$$L[Al](\mu mol \ dm^{-3}) = 1207.9 + 564.3 \ LAl \ (mmol \ dm^{-3}) - 220.2 \ LpH \quad r^2 = 0.999 \tag{8}$$

This indicates that, for a certain Al concentration in the leachate, the activity of the species of Al decreases when pH increases.

Consequently (Eqs. 6 to 8), $L_{[Al]}$ was significantly ($P<0.001$) and directly related to $AMDH^+$ but inversely to $SCaCO_3$ by the multiple regression:

$$L_{[Al]}(\mu mol\ dm^{-3}) = 4795.8 + 140.0\ AMDH^+\ (mmol\ kg^{-1}) - 11.86\ SCaCO_3\ (mmol\ kg^{-1})\ r^2 = 0.793 \quad (9)$$

Aluminium toxicity of the leachates

The Al toxicity index (ATI) of the leachates was calculated according to [19]:

$$ATI = [9\{Al^{3+}\} + 4\{AlOH^{2+}\} + \{Al(OH)_2^+\} + 9\{Al(OH)_4^-\} + \{Al(SO_4^+)\}] / [\ 4\{Ca^{2+}\} + 4\{Mg^{2+}\} + 0.02\{K^+\} + 0.02\{Na^+\}]$$

In this expression, brackets denote molar activities and each element is weighted by a coefficient intended to reflect its relative effect. ATI values higher than 1 denotes Al toxicity.

Because the ATI was significantly ($P<0.001$) and directly related to $L_{[Al]}$ (Fig. 1), ATI was significantly ($P<0.001$) and directly related to $AMDH^+$ but inversely to $SCaCO_3$ by the multiple regression:

$$ATI = 0.296 + 1.102\ 10^{-2}\ AMDH^+\ (mmol\ kg^{-1}) - 8.804\ 10^{-4}\ SCaCO_3\ (mmol\ kg^{-1})\ r^2 = 0.790 \quad (10)$$

This equation allowing to calculate, from the pH of the AMD and the $CaCO_3$ content of the soil, the amount of AMD that can be added to the soil to obtain drainage water without the risk of Al toxicity.

On the other hand, the toxicity index estimated from the molar ratio between the divalent basic cations and the aluminium (Ca+Mg/Al) in the leachates, was significantly related ($P<0.001$) to ATI by the potential regression:

$$Ca+Mg/Al = 0.5535\ ATI^{-1.0911}\ r^2 = 0.986 \quad (11)$$

This indicates that when ATI = 1 the value of Ca+Mg/Al is 0.55, in this case, the authors [18] estimate toxicity by the mean of a decrease in root growth and in the mycorrhiza development. When Ca+Mg/Al $\leq$ 0.15, the toxicity is extreme because the root growth stops, the thinner roots die, and the tree undergoes severe stress, this corresponding with ATI > 3.5.
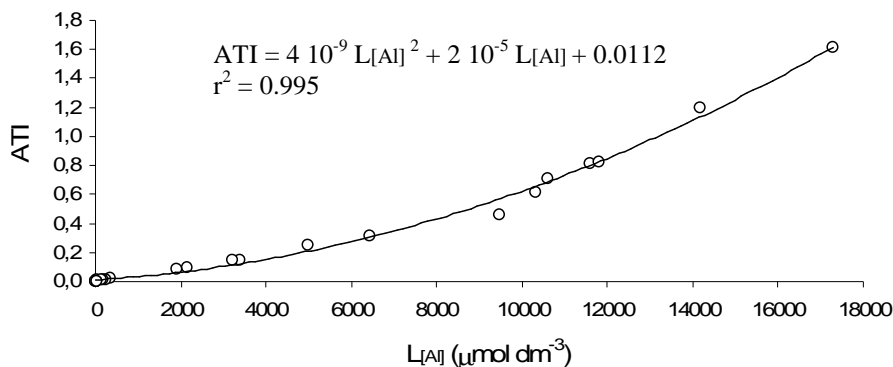

$$ATI = 4\ 10^{-9}\ L_{[Al]}^2 + 2\ 10^{-5}\ L_{[Al]} + 0.0112$$
$$r^2 = 0.995$$

FIGURE 1 - ATI values versus L[Al] values.

CONCLUSION

The influence of the AMD in soil causes the weathering of the primary minerals and increases the aluminium concentration in the drainage waters. Both the Al concentration in the drainage waters, as well as the activity of the Al species and the toxicity indexes of Al were significantly and directly related to the added H^+ coming from AMD, but inversely to the $CaCO_3$ content in the soil. Consequently, measuring the pH of the AMD and the $CaCO_3$ content of the soil, the amount of AMD that can be added to the soil without adverse effects of Al toxicity in the leachates can be estimated.

ACKNOWLEDGEMENTS

REFERENCES

[1] Stumm, W. and Morgan, J.J. (1981). Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters. New York: John Wiley & Sons, 218.

[2] Nordstrom, D.K.(1982). Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In: Acid

FEB

sulphate weathering. Soil Science Society of America. J.A. Kitrick, D.S. Fanning and Hossner (Ed-s), Madison WI, 37-56.

[3] Adams, F. and Lund, Z. F. (1966). Effects of solution of chemical activity of soil solution aluminum of cotton root penetration of acid subsoils. Soil Science 101, 193-198.

[4] Pavan, M.A. and Bingham, F.T. (1982). Toxicity of aluminum to coffee seedlings grown in nutrient solution. Soil Science Society of American Journal 46, 993-997.

[5] Blamey, F.P.C., Edwards, D.G. and Asher, C.J. (1983). Effects of aluminum, OH:Al and P:Al molar rations, and ionic strength on soybean root elongation in solution culture. Soil Science 136, 197-207.

[6] Alva, A.K., Blamey, F.P.C. and Edwards, D.G. (1986). An evaluation of aluminum indices to predict aluminum toxicity to plants grown in nutrient solutions. Soil Science Plant Analysis 17, 1271-1280.

[7] Sucoff, E., Thornton, F.C. and Joslin, J.D. (1990). Sensitivity of tree seedlings to aluminum: I. Honeylocust. Journal of Environmental Quality 19, 163-171.

[8] Adams, F. and Moore, B.L. (1983). Chemical factors affecting root growth in subsoil horizons of coastal plain soils. Soil Science Society of America Journal 47, 99-102.

[9] Alva, A.K., Edwards, D.G., Asher, C.J. and Blamey, F.P.C. (1986). Relationships between root length of soybean and calculated activities of aluminum monomers in nutrient solution. Soil Science Society America Journal 50, 959-962.

[10] Kinraide,T.B. (1997). Reconsidering the rhizotoxicity of hydroxyl, sulphate, and fluoride complexes of aluminium. Journal of Experimental Botany 48, 1115-1124.

[11] Stevens, D.P., McLaughlin, M.J. and Alston, A.M. (1997). Phytotoxicity of aluminium-fluoride complexes and their uptake from solution culture by *Avena sativa* and *Lycopersicon esculentum*. Plant Soil 192, 81-93.

[12] Rhue, R.D.G. and Grogan, C.O. (1977). Screening corn for Al tolerance using different Ca an Mg concentrations. Agronomy Journal 69, 755-760.

[13] Kinraide, T.B. and Parker, D.R. (1987). Cation amelioration of aluminum toxicity in wheat. Plant Physiology 83, 546-551.

[14] Simón, M., Martín, F., García, I., Bouza, P., Dorronsoro, C. and Aguilar, J. (2005). Interaction of limestone grains and acidic solutions from the oxidation of pyrite tailings. Environmental Pollution 135, 65-72.

[15] Soil Survey Staff (1990). Keys to Soil Taxonomy, 8th edition. Pocahontas Press, Inc. Blacksburg, Virginia, USA, 422.

[16] Sneddon, I.R., Orueetxebarria, M., Hodson, M.E., Schofield, P.F. and Valsami-Jones, E. (2006). Use of bone meal amendments to immobilise Pb, Zn and Cd in soil: A leaching column study. Environmental Pollution 144, 816-825.

[17] Kharaka, Y.; Gunter, W., Aggarwal, P, Perkins, E. and Debraal, J. (1989). Solmineq 88: A computer program for Geochemical Modelling of Water- Rock interactions. U. S. Geological Survey. Menlo Park, California, 420.

[18] Sverdrup, H. and Warfringe, P. (1992). A model for impact of soil solution Ca:Al ratio, soil moisture and temperature on tree base cation uptake. Water, Air and Soil Pollution 61, 365-383.

[19] Boudot, J.P., Maitat, O., Merlet, D. and Rouiller, J. (2000). Soil solutions and surface water analysis in two contrasted watersheds by acid deposition, Vosges mountains, N.E. France: interpretation in terms of Al impact and nutrient imbalance. Chemosphere 41, 1419-1429.

CORRESPONDING AUTHOR

Inés García Fernández
Dpto. Edafología y Química Agrícola
Escuela Politécnica Superior.
Universidad de Almería.
CITE IIB. La Cañada de San Urbano.
4120. Almería
SPAIN

Phone: +34 950 015117
Fax. +34 950015319
E-mail: inesgar@ual.es