



ICOBTE2011

11th International Conference on the Biogeochemistry of Trace Elements  
CONGRESS CENTER, FLORENCE, ITALY - JULY 3-7, 2011

July 8<sup>th</sup>, 2011

To whom it may concern,

This is to certify that following paper:

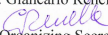
Redistribution of Ag in Two Calcareous and Noncalcareous Spiked Soils

*M. Esfahani Moghaddam, A. Fotovat, and G.H. Haghnia*

from the Ferdowsi University of Mashhad was presented at the 11<sup>th</sup> International Conference on the Biogeochemistry of Trace Elements (ICOBTE2011) held in Florence-Italy, 3-7 July 2011 and **published in CD of the conference proceedings**.

With best regards,

Prof. Giancarlo Renella, Conference chair of the 11<sup>th</sup> ICOBTE

  
The Organizing Secretariat:

Enic srl

Meetings & Events

50123 Firenze - Piazza Adua 1/d

Tel. +39 055 2608941 - Fax +39 055 2608948

[www.enic.it](http://www.enic.it)



# Redistribution of Ag in two calcareous and noncalcareous spiked soils

Moghaddam, M.E., A. Fotovat, and G.H. Haghnia

Department of Soil Science, Faculty of Agriculture, Ferdowsi University of Mashhad, PO Box 91775-1163, Mashhad, Iran.

Key words: Ag, contamination, fractionation, soil.

## Abstract

Review of literature clearly shows that environmental data are scarce on the behavior of silver (Ag) in soils. Ag toxicity and its fate in the environment are currently being debated and are important as challenging research topics. Even though there are several studies on its total content in soils, fractionation of Ag, especially in calcareous soils has not been investigated. Therefore, we utilized an eight-step chemical extraction procedure to determine the chemical fractions of Ag (i.e., EXCH, CARB, Me-Org, re-MeOx, H<sub>2</sub>O<sub>2</sub>-Org, am-MeOx, cr-FeOx, and RES) following 30 and 60 days incubation in a calcareous and noncalcareous soil amended with Ag (0 and 15 mg kg<sup>-1</sup>). Experimental results showed that Ag in nonamended soils was predominantly in the forms H<sub>2</sub>O<sub>2</sub>-Org > Me-Org > RES > CARB. These four fractions contributed more than 5% of total Ag concentration in noncalcareous soil. Redistribution of Ag in spiked noncalcareous soil was EXCH (34%), H<sub>2</sub>O<sub>2</sub>-Org (33%) and RES (17%). After 30 days incubation in contaminated noncalcareous soil, EXCH-Ag increased whereas CARB- and H<sub>2</sub>O<sub>2</sub>-Org-Ag decreased. However EXCH-Ag decreased and H<sub>2</sub>O<sub>2</sub>-Org-Ag increased after 60 days incubation ( $P < 0.05$ ). In calcareous soil after 30 days, EXCH- and RES-Ag increased but at the end of 60 days H<sub>2</sub>O<sub>2</sub>-Org-Ag increased. From our data we may conclude that addition of Ag results in increase of Ag mobility in soils but incubation may have adverse effect on its mobility. In general, chemical behavior of Ag, in terms of its redistribution into labile fractions in calcareous soil differed from noncalcareous soil.

## Introduction

Ag<sup>+</sup> as one of the most toxic forms of silver, has been categorized to the highest toxicity class (Ratte, 1999) and mainly is released into the aquatic environment from domestic, agricultural, and industrial sources (Wood et al, 1996.). Ag<sup>+</sup> has harmful effects on the soil microbial population and biochemical processes. In general, the Ag content of surface soils ranges from 0.01 to 5 mg kg<sup>-1</sup>, with most reported values being 1 mg kg<sup>-1</sup> (Alloway, 1995). Nowadays, soil pollution with Ag is a matter of concern as silver contamination and reported in several cases, such as Thailand from radiographic film wastes (Khunprasert et al, 2008), silver contamination in San Francisco Bay (Flegala et al, 2007), and also current applications of nanosilver containing materials in human life (Blaser et al, 2008). Even though there are many studies on the total content of Ag in soils, fractionation of Ag especially in calcareous soils has not been investigated. Therefore, our objectives were to provide fundamental information on the chemical behavior and the fate of Ag in polluted soils, and to quantify redistribution processes of Ag in contaminated soils.

## Materials and methods

We studied 8-step chemical fractions (Krishnamurti, 1995) of Ag (i.e., EXCH, CARB, Me-Org, re-MeOx, H<sub>2</sub>O<sub>2</sub>-Org, am-MeOx, cr-FeOx, and RES) after 30 and 60 days incubation in two calcareous and noncalcareous soils amended with Ag (0 and 15 mg kg<sup>-1</sup>). After fractionation, Ag concentration in samples was analyzed by atomic absorption spectrophotometer (AAS) and graphite furnace atomic absorption spectrometry (GFAAS) (Shimadzu AA-670). Statistical calculations were carried out with Minitab and MSTATC.

## Results and discussion

Selected chemical and physical properties of the soils are given in Table 1.

Table 1 Some physical and chemical properties of soils.

Soil	noncalcareous	calcareous
Depth (cm)	0-30	0-30
Clay (g kg <sup>-1</sup> )	220	250
Silt (g kg <sup>-1</sup> )	280	230
Sand (g kg <sup>-1</sup> )	500	520
EC (dS m <sup>-1</sup> )	3.6	2.5
pH	7.1	7.6
OC (g kg <sup>-1</sup> )	5.5	4.7
CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	13.91	11.09
CaCO <sub>3</sub> (g kg <sup>-1</sup> )	29.8	208.0
Total Ag (mg kg <sup>-1</sup> )	0.2	0.6

Ag in nonamended noncalcareous soil occurred predominantly in the forms H<sub>2</sub>O<sub>2</sub>-Org > Me-Org > RES > CARB and other fractions were negligible (<5%) (Fig.1.a). Experimental results showed that addition of Ag to noncalcareous soil resulted in increase of EXCH-Ag whereas, CARB- and Me-Org-Ag decreased ( $P < 0.05$ ). After 30 days incubation, relative distribution of Ag in H<sub>2</sub>O<sub>2</sub>-Org fractions decreased but after 60 days incubation increased. In noncalcareous soil, RES-Ag did not change significantly. After incubation, Me-Org-Ag in nonamended soil increased. In contrast, H<sub>2</sub>O<sub>2</sub>-Org-Ag decreased after 60 days ( $P < 0.05$ ). Distribution of Ag in other fractions among control and spiked soils did not significantly alter. In amended noncalcareous soil, EXCH-Ag decreased with time while H<sub>2</sub>O<sub>2</sub>-Org increased ( $P < 0.05$ ). Incubation did not influence Ag distribution in other fractions.

Although there are several studies on silver total content in soils, fractionation of Ag in soils has not been extensively studied. Hou et al. (2005) found average distribution of Ag in H<sub>2</sub>O<sub>2</sub>-Org > Me-Org > RES fractions in Fluvisol loaded with Ag. However our results showed that Ag in spiked soil was found in the following fractions EXCH > H<sub>2</sub>O<sub>2</sub>-Org > RES fractions. This may be due to the variation of incubation time in two studies. Jones et al (1986) reported that in contaminated soils, nearly half of the total Ag was in

residual fraction. Time redistributed Ag to OM fractions which have high affinity for Ag (Ratte, 1999). This behavior was similar to Cu, as Ma and Uren (1998) observed that EXCH- and CARB-Cu transformed to OM and FeOx fractions with time.

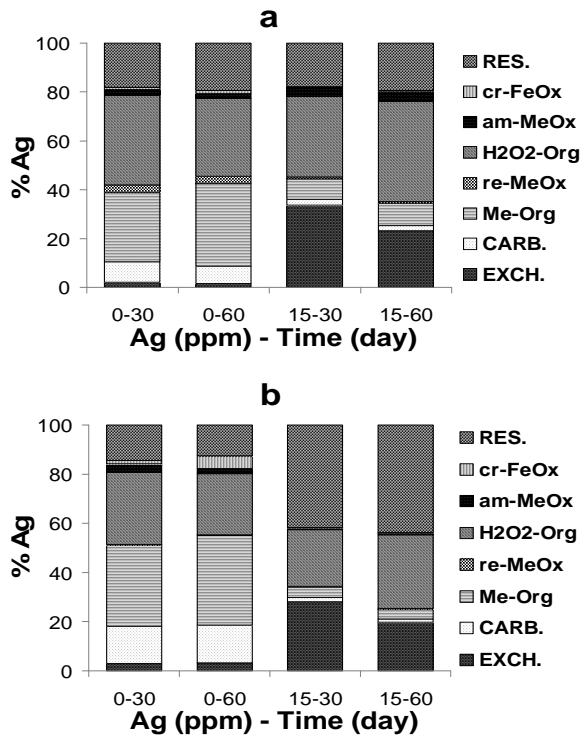


Figure 1. Percent distribution of Ag among various fractions in natural and metal loaded soils as affected by time in (a) noncalcareous soil, (b) calcareous soil.

Fig.1.b shows relative distribution of Ag in calcareous soil fractions. Ag behavior in calcareous soil was in order of Me-Org > H<sub>2</sub>O<sub>2</sub>-Org > CARB > RES. In spiked calcareous soil, the major chemical forms of Ag were RES (42%), EXCH (28%) and H<sub>2</sub>O<sub>2</sub>-Org (23%). Our review of the literature showed that there was not any research on the chemical behavior of Ag in calcareous soils. Renella et al. (2004) found Cd in native calcareous soil was slowly available and bound to CARB and RES forms. In the spiked soils, applied Cd mainly occurred in the CARB and EXCH fractions. Our results showed that after the 60-day incubation EXCH-Ag decreased while H<sub>2</sub>O<sub>2</sub>-Org-Ag increased. Jalali and Khanlari (2008) studied chemical fractions of Cd in several calcareous soils within 3 h to 4 weeks. They reported that EXCH- and CARB-Cd decreased during incubation time, whereas OM-, FEO- and MNO-Cd increased. It seems that Ag behavior with time in the current investigation was similar to Cd. In calcareous soil, our results are consistent with those of Jones et al (1986) examined chemical distribution of Ag in Welsh soils.

### Conclusions

Loading Ag into noncalcareous soil resulted in its distribution from less to more mobile fractions. In spiked

calcareous soil with Ag, EXCH- and RES-Ag increased but bulk of RES- was more than EXCH-Ag. Therefore, Ag mobility in calcareous soil was less than noncalcareous soil. Moreover, incubation time redistributed Ag to less mobile fractions.

### References

- Alloway, B.J., 1995. Heavy Metals in Soils. Blackie Academic and Professional, London, United Kingdom.
- Blaser, S.A., M. Scheringer, M. MacLeod, and K. Hungerbühler. 2008. Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. *Sci. Tot. Env.* 390: 396–409.
- Flegala, A.R., C.L. Brown, S. Squirea, J.R.M. Ross, G.M. Scelfo, and S. Hibdon. 2007. Spatial and temporal variations in silver contamination and toxicity in San Francisco Bay. *Env. Res.* 105: 34–52.
- Hou, H., T. Takamatsu, M.K. Koshikawa, and M. Hosomi. 2005. Migration of silver, Indium, Tin, Antimony and Bismuth and variations in their chemical fractions on addition to uncontaminated soils. *Soil Sci.* 170. 624–639.
- Jalali, M., and Z.V. Khanlari. 2008. Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran. *Geoderma* 143: 26–40.
- Jones, K.C., B.E. Davies, and P.J. Peterson. 1986. Silver in Welsh soils: physical and chemical distribution studies. *Geoderma* 37: 157–174.
- Khunprasert, P., N. Grisdanurak, J. Thaveesri, V. Danutra, and W. Puttitavorn. 2008. Radiographic film waste management in Thailand and cleaner technology for silver leaching. *J. Clean. Product.* 16: 28–36.
- Krishnamurti, G.S.R., P.M. Huang, K.C.J. Van Rees, L.M. Kozak, and H.P.W. Rostad, 1995. Speciation of particulate-bound cadmium of soils and its bioavailability. *Analyst* 120: 659–665
- Ma Y.B., and N.C. Uren. 1998. Transformations of heavy metals added to soil: application of a new sequential extraction procedure. *Geoderma* 84: 157–168.
- Ratte, H.T. 1999. Bioaccumulation and toxicity of silver compounds: a review. *Env. Toxicol. Chem.* 18: 89–108.
- Renella, G., P. Adamo, M.R. Bianco, L. Landi, P. Violante, and P. Nannipieri. 2004. Availability and speciation of cadmium added to a calcareous soil under various management. *Eur. J. Soil Sci.* 55: 123–133.
- Wood, C.M., C. Hogdtrand, and F. Galvez. 1996. The physiology of waterborne silver toxicity in freshwater rainbow trout (*Oncorhynchus mykiss*). *Aquat. Toxicol.* 35: 93–109.