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Fate and lability of silver in soils: Effect of ageing

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ABSTRACT

The fate and lability of added soluble Ag in soils over time was examined by measurement of labile metal (E-value) by isotopic dilution using the ^{110m}Ag radioactive isotope and the solid-phase speciation of Ag by X-ray absorption near edge structure (XANES) spectroscopy. After two weeks of ageing the E-values for Ag decreased by 20–90% with a further decrease of 10–40% after six months. The overall decrease in labile Ag for all soils after the 6 month ageing period was 50–100%. The ageing was more rapid and pronounced in the alkaline soils. XANES results for Ag in soils indicated that for the majority of soils the added Ag^+ was reduced to metallic Ag over time, and associations with Fe-oxohydroxides and reduced S groups in organic matter also decreased Ag lability. Strong positive correlations were found between metallic Ag and non-labile Ag and between organic carbon and Ag bonded with S species.

1. Introduction

The use of silver (Ag) and silver nanoparticles (AgNPs) in applications such as solar energy, water purification, medicine and nanotechnology is rapidly increasing (Elvers et al., 1993). Commonly exploited for their antibacterial properties, Ag and increasingly AgNPs are being used in a range of consumer products but this may also lead to environmental risks following their potential release into the environment (Morones et al., 2005; Benn et al., 2010).

Apart from mining processes, the exposure pathways for Ag into the environment from urban areas (e.g. consumer products and industry) will be from wastewater treatment plants (WWTPs), predominantly via land application of biosolids (Johnson et al., 2005; Oliver et al., 2005) and through agriculture by application of Ag containing pesticides such as Agress® (Marques et al., 2011; Innovotech Products ~ Agr). As a result of these exposure pathways, soil environments may be one of the major sinks for Ag in the environment. Elevated concentrations of Ag may pose a risk to soil environments due to the potential toxicity of Ag to a range of organisms such as plants, invertebrates, microbes and bacteria living in soil (Ratte, 1999; Roh et al., 2009; Blamey et al., 2010; Throback et al., 2007; Murata et al., 2005).

When soluble metals are added to soils there are initial fast reactions which remove metals from soil solution (adsorption and precipitation), followed by slower reactions that continue to remove metals from the labile (i.e. exchangeable) pool. The decrease in metal lability that occurs with time after metal addition to soil is thought to occur through the following general mechanisms: micropore diffusion, cavity entrapment, occlusion in solid phases by co-precipitation and co-flocculation and surface precipitation (Ma et al., 2006a; Fendorf et al., 2004; Kabata-Pendias and Pendias, 2000). These processes are generally referred to as “aging”. As a consequence the bioavailability and toxicity of the metal to soil organisms may decrease with time as the actual exposure concentration decreases. The ageing of other metals in soils has been studied (e.g. As, Cu, Mo, and Zn) by measuring metal lability after various periods of time up to 27 months (Ma et al., 2006a; Fendorf et al., 2004; Ma et al., 2006b; Crout et al., 2006; Kirby et al., 2012). These studies have shown that the extent of ageing is dependent on the soil type and chemical properties of the metal, as well as environmental conditions such as temperature (Barrow, 1998). To date, little is known of the extent of ageing of soluble Ag in soils and with the predicted increase in Ag concentrations in the environment (due to increased use of Ag- and AgNP-containing products), it is important to examine the fate and potential bioavailability (lability) of soluble Ag in soils over time.

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Table 1
Selected physical and chemical properties of the soils.

Soil location	pH_{water}	Total organic carbon	DOC[b]	CEC[c]	Oxalate extractable		Particle size analysis			Water-extractable Cl	Water holding capacity	Total added ag
					Al	Fe	Clay	Silt	Sand			
		%	mg L^{-1}	$cmol_c\ kg^{-1}$	mg kg^{-1}	mg kg^{-1}	%	%	%	mg L^{-1}	%	mg kg^{-1}
Kingaroy	6.1	0.9	3	13	2500	2300	60	17	19	0.6	37	100 ± 7
Charleston	6.0	6.9	65	12	410	2500	14	12	63	3.1	32	190 ± 1
Balaklava	8.5	1.9	21	27	1200	650	30	20	47	3.0	35	180 ± 9
Port Kenny[a]	8.8	1.8	36	13	480	300	12	4.2	21	2.3	26	200 ± 30
Millicent	6.9	11.8	75	42	2300	1500	19	5.2	48	8.1	39	390 ± 20
Inman Valley	6.0	5.3	110	25	1500	3700	42	22	26	5.0	48	770 ± 10

[a] Note that particle size distribution for Port Kenny is equal to 37.2% due to the high concentration of $CaCO_3$ that is present in this soil (60%).
[b] Dissolved organic carbon.
[c] Cation exchange capacity.

The total concentration of metals in soils is known to be a poor indicator of the potential bioavailable fraction (McLaughlin et al., 2000). Isotopic dilution (ID) is an established method used to measure the total labile metal fraction in soils (in soil solution and on solid phases in rapid exchange with soil solution) and it is determined by calculating an *E*-value (Young et al., 2005; Nolan et al., 2004; Wendling et al., 2009). An ID method for Ag was recently developed to measure *E*-values for soils with a range of chemical and physical properties and added Ag concentrations (Settimio et al., 2014). This initial study found that not all soluble Ag added to the soil remained in the labile pool and significant ageing occurred after a relatively short period of time (two weeks). A similar result was also observed when $AgNO_3$ was added to soils and analysed by sequential extraction whereby soluble Ag was found to be rapidly immobilised in soil (Coutris et al., 2012). Although the amount of labile metal can be determined at various ageing periods using the ID method, there is still a lack of understanding in the chemistry associated with the labile and non-labile metal pools within the soil solid phase.

X-ray absorption spectroscopy (XAS) and in particular X-ray absorption near edge structure (XANES) spectroscopy using synchrotron radiation can be used to provide information on the oxidation state and coordination environment (hereby referred to as solid phase speciation) of metal contaminants in complex matrices such as soil, generally by analyzing the resulting spectra using principle components analysis (PCA) and linear combination fitting (LCF) (Lombi and Susini, 2009). Many studies have already demonstrated the ability of this technique to provide solid phase speciation data for a range of metal contaminants in soils e.g. As, Co, Cr, Cu, Mn, Ni, Pb (Lombi and Susini, 2009; Nolan et al., 2003). Examples of XANES spectroscopy applied to Ag can be found for a variety of media but has most commonly been used to assess the fate of AgNPs in a WWTP scenario and subsequent speciation in biosolids (Kaegi et al., 2011; Lombi et al., 2013; Ma et al., 2014; Whitley et al., 2013). Many of these studies have shown that $AgNO_3$ and AgNPs are commonly converted to Ag_2S or other Ag—S species in WWTPs. Other examples involving XANES spectroscopy include Ag speciation in liver tissue of marine mammals (Nakazawa et al., 2011), ageing of AgNPs in kaolin suspensions (Scheckel et al., 2010), reduction of Ag^+ to metallic Ag in plants (Beattie et al., 2011) and speciation of AgNPs added to microcosms with freshwater sediments (Bone et al., 2012). Overall these studies have shown that there is a tendency for Ag^+ or AgNPs (following dissolution) to form Ag—S bonded species or to be converted to metallic Ag.

There is a lack of understanding regarding the solid phase speciation and lability of Ag and its ageing in natural soils. Therefore the aim of this study was to examine the fate and lability of added soluble Ag over time by measuring labile Ag (*E*-value) concentrations and the solid-phase speciation of Ag (XANES) in soils. This will provide an insight into the long-term fate of Ag^+ ion added to soils and the mechanisms or interactions with soil components that can affect its lability and bioavailability to soil organisms.

2. Materials and methods

2.1. Soil sampling and characterisation

This study used soils that were sourced from six locations in Queensland and South Australia, Australia: Kingaroy, Charleston, Balaklava, Port Kenny, Millicent and Inman Valley. The soils were collected from 0 to 10 cm depth, air-dried, homogenised and sieved to <2 mm. Selected physical and chemical properties for the experimental soils can be found in Table 1. Soil pH was measured using a soil:solution ratio of 1:5 (m/v), with ultrapure deionised water (Milli-Q, Millipore) and shaking for 1 h. Total organic carbon (TOC) content, cation exchange capacity (CEC), particle size and oxalate-extractable aluminium (Al_{ox}) and iron (Fe_{ox}) were determined according to standard methods (Gee and Bauder, 1986; Rayment and Higginson, 1992). Concentrations of dissolved organic carbon (DOC) (Shimadzu TOC-$V_{CSH/CSN}$ + TNM-1) and chloride (Cl^-) (Dionex ICS-2500) were determined