

Behaviour and fate of soluble silver added to soils

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ABSTRACT

Silver (Ag) and silver nanoparticles (AgNPs) are increasingly being used in solar energy production, water purification, medicine and applications of nanotechnology. The antibacterial properties of Ag and AgNPs are the key reason for their addition to a range of consumer products. But these properties also represent a potential risk when Ag and or AgNPs are released into the environment by loss during mining processes, disposal of consumer and industrial products to wastewater, the residues of which (biosolids) are directly applied to land, and through application of Ag containing pesticides. Once in the soil environment, Ag (including Ag released from AgNP) may partition itself between the solid and liquid phases. But only a fraction of the total Ag concentration in soil may be in a labile or available form. The speciation and fate of Ag in soils will also be important for understanding what influences the amount of labile metal available for uptake by soil dwelling organisms.

This thesis presents the partitioning and lability of Ag added to a wide range of soils by measurement of the partition coefficient (K_d value) and concentration of labile metal (E -value) using an isotope dilution method. This initial method development, which was optimised for Ag, provided the basis for further evaluation of the long term aging of Ag and its impact on the labile metal pool, speciation of Ag over time and the significant interactions between Ag and dissolved organic matter (DOM).

An isotopic dilution method to simultaneously measure the K_d -value and E -value of Ag in soils was developed using the ^{110m}Ag radioisotope. E -values were corrected for possible interferences from non-isotopically exchangeable Ag associated with soil colloids in suspension (E_r -value). Measurement of K_d values for Ag in a range of soils indicated strong partitioning to the solid phase is positively associated with soil cation-

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exchange capacity or total organic carbon and pH. Measurements of labile Ag after a two week incubation period indicated rapid conversion of soluble Ag into non-isotopically exchangeable forms, either irreversibly adsorbed or precipitated in the soil. This indicated that measurements of labile Ag will be important to estimate toxicity risks to soil organisms or to predict bioaccumulation through the food chain.

The fate and lability of added soluble Ag in soils over time was examined by isotopic dilution 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 six 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.

There remains uncertainty in important aspects of Ag speciation in soils. In particular, the complexation of Ag⁺ with dissolved organic matter (DOM) appears complicated. It is not known whether DOM quality or quantity is more important. Complexed Ag across a wide range of soil water extracts with natural varying concentrations of dissolved organic carbon (DOC) was measured and was normalized to DOC concentration in order to observe differences in DOM affinity or strength of complexation with Ag⁺. Characterization of the DOM in the soil water extracts, was also carried out by size fractionation and elemental analysis, and spectroscopic analysis

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using UV-Visible, fluorescence and mid infra-red. Then using statistical analysis these qualities of DOM were used to explain the amount of complexed Ag measured in the soil water extracts. Overall the results indicated that up to 70% of Ag was strongly complexed in solution. The variability in Ag⁺ binding by DOM across different soils was most closely related ($R^2= 0.8$) to the MIR spectra of the extracts. The normalised Ag complexation values indicated that humic content and overall aromaticity increased Ag's affinity to DOM. Spectroscopic information from UV-Visible, mid infra-red and fluorescence spectroscopy was also shown to potentially be more useful in measuring and characterizing DOM than only chemical measurements. Silver's demonstrated affinity and ability to complex with DOM could result in increased mobilization of this metal in the soil environment.

DECLARATION

This work contains no material which has previously been accepted for the award of any degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by any other person, except where due reference has been made in text.

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Date

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STRUCTURE OF THIS THESIS

This thesis is presented as a combination of papers that have been published or submitted for publication.

Chapter 1 provides an overview of the literature on environmental chemistry of silver, reactivity and behaviour in soils and methods for the determination of available silver. This chapter also includes the proposed objectives of the research presented in this thesis.

Chapter 2 comprises a paper published in *Environmental Chemistry*. It describes the development of an isotope dilution method for the measurement of partitioning and lability of silver in soils.

Chapter 3 comprises a paper published in *Environmental Pollution*. It describes an ageing experiment to determine the long term fate and availability of silver in soils. It combines chemical lability measurements with solid phase speciation data collected by X-ray absorption near edge structure spectroscopy.

Chapter 4 comprises a paper that has been submitted for publication in *Environmental Pollution*. It describes an isotope labelling and cation exchange resin experiment to examine the complexation between complexed silver ions and dissolved organic matter in soil solutions.

Chapter 5 provides a synthesis of the findings contained in this thesis and includes recommendations for future work.

PUBLICATIONS ARISING FROM THIS THESIS

Settimio, L., McLaughlin, M.J., Kirby, J.K., Langdon, K.A., 2014. A method to determine silver partitioning and lability in soils. *Environmental Chemistry* **11**, 63-71.

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