Dynamics of metal-humate complexation equilibria as revealed by isotope exchange studies – a matter of concentration and time

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Abstract

Complexation with dissolved humic matter can be crucial in controlling the mobility of toxic or radioactive contaminant metals. For speciation and transport modelling, a dynamic equilibrium process is commonly assumed, where association and dissociation run permanently. This is, however, questionable in view of reported observations of a growing resistance to dissociation over time. In this study, the isotope exchange principle was employed to gain direct insight into the dynamics of the complexation equilibrium, including kinetic inertisation phenomena.

Terbium(III), an analogue of trivalent actinides, was used as a representative of higher-valent metals. Isotherms of binding to (flocculated) humic acid, determined by means of ^{160}Tb as a radiotracer, were found to be identical regardless of whether the radioisotope was introduced together with the bulk of stable ^{159}Tb or subsequently after pre-equilibration for up to 3 months. Consequently, there is a permanent exchange of free and humic-bound Tb since all available binding sites are occupied in the plateau region of the isotherm. The existence of a dynamic equilibrium was thus evidenced. There was no indication of an inertisation under these experimental conditions.

If the small amount of ^{160}Tb was introduced prior to saturation with ^{159}Tb, the expected partial desorption of ^{160}Tb occurred at much lower rates than observed for the equilibration process in the reverse procedure. In addition, the rates decreased with time of pre-equilibration. Inertisation phenomena are thus confined to the stronger sites of humic molecules (occupied at low metal concentrations). Analysing the time-dependent course of isotope exchange according to first-order kinetics indicated that up to 3 years are needed to attain equilibrium. Since, however, metal–humic interaction remains reversible, exchange of metals between humic carriers and mineral surfaces cannot be neglected on the long time scale to be considered in predictive transport models.
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1. INTRODUCTION

Migration of multivalent toxic or radiotoxic metals, which are strongly adsorbed to mineral surfaces at moderate pH, is essentially governed by colloid-borne transport processes. Besides inorganic colloids, humic substances have been recognised to be important as carriers. Their complexing properties can dominate the aqueous species distribution of contaminant metals (Dearlove et al., 1991; Choppin, 1992; Kim et al., 1992). Collecting data on metal–humic complexation as a function of geochemical parameters has been a task for decades (e.g., Town and Filella, 2000; Milne et al., 2003), quantified in the form of conditional or semi-conditional stability constants (e.g., according to the charge neutralisation model (Kim and Czerwinski, 1996)) and of intrinsic equilibrium constants

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based on mechanistic approaches such as the NICA-Donnan model (Kinniburgh et al., 1996) or Tipping's models (Tipping, 2002), using continuous or discrete site affinity distributions, respectively.

For modelling humic-bound transport of metals, their solid–liquid distribution is considered to be the result of a competitive partitioning process between solid surface and humic colloids. Using equilibrium constants for adsorption and complexation implies that a steady local equilibrium exists under flow conditions. A dynamic exchange of free and adsorbed/complexed state is presumed. A number of models have been proposed (Knabner et al., 1996; Lührmann et al., 1998; Warwick et al., 2000; Schuessler et al., 2001; Schmitt et al., 2003; Bryan et al., 2005; Kim and Kim, 2007), part of them taking adsorption of the humic carriers into account (Knabner et al., 1996; Lührmann et al., 1998; Bryan et al., 2005; Kim and Kim, 2007). Most of these models allow for non-equilibrium conditions in case of slow kinetics compared to flow velocity, using rate constants instead of equilibrium constants (see Lippold and Lippmann-Pipke (2009) for an overview). However, it remains a basic prerequisite that interactions are reversible and dynamic in nature, i.e., association and dissociation are expected to run permanently.

The validity of this assumption is affected by a phenomenon that appears to be characteristic of higher-valent metals: Their ability to dissociate from humic complexants diminishes with increasing time of contact. Such rise in complex inertness (i.e., decrease in the rate of dissociation) was found in batch experiments with competing ligands (Cacheris and Choppin, 1987; Choppin and Clark, 1991) as well as with cation exchange resins (King et al., 2001; Geckeis et al., 2002). Implications on metal transport became manifest in column experiments (Rao et al., 1994; Artinger et al., 1998), showing that retardation is more and more reduced the longer the complex has been pre-equilibrated prior to injection, i.e., interaction of the metal with the stationary phase is increasingly prevented. These inertisation processes were observed for humate or fulvate complexes of Eu(III) (Rao et al., 1994; King et al., 2001; Geckeis et al., 2002), Am(III) (Artinger et al., 1998), Th (IV) (Cacheris and Choppin, 1987) and U(VI) (Choppin and Clark, 1991; Rao et al., 1994), within time frames ranging from 2 days to 6 months.

Most authors supposed some kind of diffusion process where bound metals move from surface sites to deeper sites inside the humic molecule. However, it was found that competition effects of Al(III) and Fe(III), pre-equilibrated with humic acid before introducing a second metal, show an increase as well, i.e., complexation of the subsequently added metal is more and more suppressed with increasing time of pre-equilibration (Lippold et al., 2007, 2012). Diffusion of the first metal away from the initial sites should, on the contrary, facilitate complexation of the second metal. An on-site inertisation, e.g., in consequence of induced conformational changes, seems more probable, even though spectroscopic evidence of structural rearrangements could not be provided so far.

Irrespectively of the mechanistic background, the question arises as to whether reversibility is impaired in this process. If, in the end, humic-bound metals are to be regarded as "fixed", this will entail completely different predictions of their migration behaviour than in the case of a dynamic partitioning process. Results from column experiments were successfully described by assuming such transition from an exchangeable state to a non-exchangeable state (KICAM approach and K1D transport code) (Schuessler et al., 2000, 2001; Warwick et al., 2000; Bryan et al., 2005).

The objective of this work was to obtain an improved understanding of the equilibrium characteristics of metal-humate complexation, particularly with regard to possible inertisation processes and their consequences in respect of reversibility. For "looking into" the dynamics of an equilibrium, radiotracer experiments are uniquely suited. A radioactive probe, introduced as a reactant into pre-equilibrated systems, will represent the overall equilibrium if there is a dynamic exchange. In case of a static equilibrium, however, the tracer will not get involved because the reaction has stopped, also on a molecular level. Adsorption or binding processes are then a simple "sticking". In a previous paper, the tracer exchange principle was applied to elucidate the dynamics of adsorption equilibria of humic substances (Lippold and Lippmann-Pipke, 2014). Several isotope exchange studies on metal-humate complexation can be found in the literature (Colston et al., 1997; Marx and Heumann, 1999; Mizera et al., 2001), all of which using separation methods like ultrafiltration, dialysis or size exclusion chromatography. Implications of inertisation effects were not considered so far.

The present study was performed with terbium(III) and the radioisotope ^{160}Tb (half-life: 72.3 days), contacted with humic acids for time periods up to 3 months corresponding to the time frame reported for inertisation phenomena. Flocculation was employed as a separation mechanism, avoiding techniques that are potentially invasive. Tb(III) was chosen as a representative of higher-valent metals. It is widely accepted that trivalent lanthanides are, to some extent, suitable as analogues of trivalent actinides such as Am(III), Cm(III) or Pu(III) (Choppin, 1995), which are in the focus of safety analyses for final repositories because of their long half-lives.

2. MATERIALS AND METHODS

2.1. Materials

Non-radioactive chemicals and humic acid (HA) were supplied by Sigma–Aldrich (Germany). Another humic acid was isolated from surface water collected on the raised bog "Kleiner Kranichsee" (near Carlsfeld, Germany). Separation was carried out according to the recommendations of the International Humic Substances Society (Aiken, 1985). Both humic materials were purified by repeated precipitation and redissolution with 0.1 M HCl and 0.1 M NaOH/0.01 M NaF, respectively, followed by dialysis and lyophilisation. Characteristics of these substances are given elsewhere (Lippold et al., 2005a,b). [^{160}Tb]TbCl$_3$ (activated up to 1 GBq per mg Tb) was purchased from Radioisotope Centre Polatom (Poland).