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## **Metal dissociation from humic colloids: Kinetics with time-dependent rate constants**

Holger Lippold <sup>a,\*</sup>, Lukáš Zedek <sup>b</sup>

<sup>a</sup> *Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology  
(Research Site Leipzig), Permoserstr. 15, 04318 Leipzig, Germany*

<sup>b</sup> *Technical University of Liberec, Faculty of Mechatronics, Informatics and  
Interdisciplinary Studies, Studentská 1402/2, 461 17 Liberec 1, Czech Republic*

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\* Corresponding author.

*E-mail address:* [h.lippold@hzdr.de](mailto:h.lippold@hzdr.de) (H. Lippold).

## Abstract

The mobility of contaminant metals in aqueous subsurface environments is largely controlled by their interaction with humic substances as colloidal constituents of Dissolved Organic Matter. Transport models for predicting carrier-bound migration are based on a competitive partitioning process between solid surface and colloids. However, it has been observed that dissociation of multivalent metals from humic complexes is a slow kinetic process, which is even more impeded with increasing time of contact. Based on findings obtained in isotope exchange experiments, the convoluted time dependence of dissociation was fully described by a complex two-site approach, integrating rate “constants” that are in turn time-dependent. Thus, this study presents the treatment of a particular phenomenon: kinetics within kinetics. The analysis showed that the inertization process does not lead to irreversible binding. Consequently, thermodynamic concepts using equilibrium constants remain applicable in speciation and transport modeling if long time frames are appropriate.

*Keywords:* Colloids; Desorption; Humic complexes; Kinetic model; Metal binding; Natural organic matter

## 1. Introduction

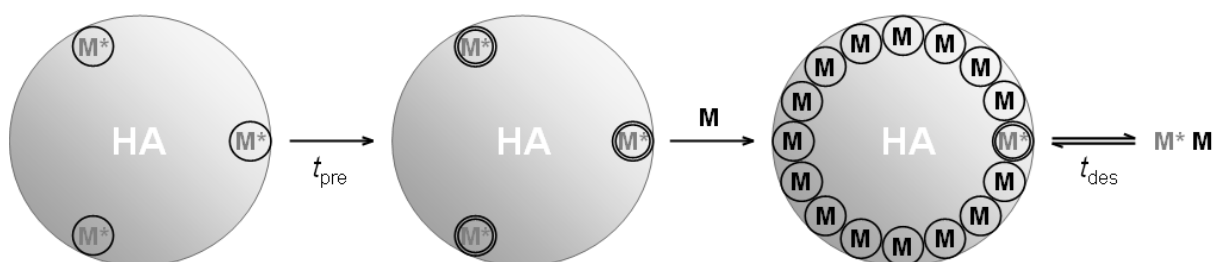
Migration of toxic or radiotoxic metals at higher valence states is limited by their strong adsorption to mineral surfaces. However, mobility can be considerably enhanced by interaction with humic colloids acting as carriers. The complexing properties of their functional groups (carboxyl and phenolic hydroxyl) can dominate the speciation of multivalent metals (Dearlove et al., 1991; Choppin, 1992; Kim et al., 1992). A large database of stability constants exists, based on conditional approaches like the Charge Neutralization Model (Kim and Czerwinski, 1996) or mechanistic concepts such as the NICA-Donnan model (Kinniburgh et al., 1996) and Tipping’s models (Tipping, 2002). Efforts have been taken to predict humic-bound migration by transport codes, integrating various conceptual models (with or without carrier adsorption) into the advection-dispersion equation (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).

Reviewing the fundamentals of chemical kinetics is beyond the scope of this paper. Elementary and complex rate laws describe reaction rates as a function of concentrations raised to the power of (partial) orders depending on the reaction mechanism. The linking parameter is the reaction rate constant, which is dependent on external conditions like temperature or ionic strength, but – as a matter of principle – independent of time.

However, the interaction of higher-valent metals with humic substances is characterized by a peculiar feature: dissociation is more and more hindered the longer both components are in contact. Such growing inertness was observed for humic complexes with 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 different

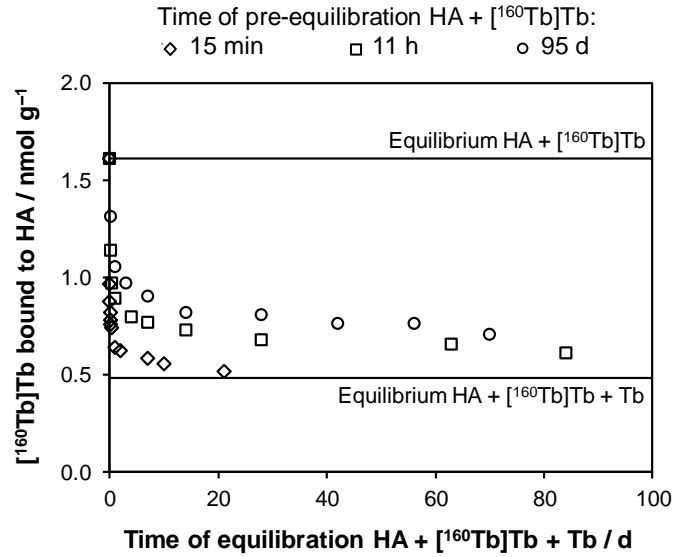
time frames, both in batch experiments with competing ligands or resins and in column experiments, where retardation of the metal was found to be reduced for increasing times of pre-equilibration with humic colloids prior to injection. These studies focused on the mobility of actinides at former nuclear test sites or in the far field of final radwaste repositories. Certainly, the importance of kinetic aspects in the complexation of multivalent metals with humic material is not confined to radiotoxic elements. The bioavailability and/or toxicity of Al(III) and Fe(III) is essentially determined by their association with Dissolved Organic Matter (Dobranskyte et al., 2006; Hasegawa et al., 2017), and humic colloids contribute a significant part to REE patterns used for tracing distribution processes in the hydrogeosphere (Pourret et al., 2007).

Since it was an open question as to what extent the reversibility of metal-humate complexation is affected by the inertization process, we used the principle of isotope exchange for probing the inner dynamics of the complexation equilibrium (Lippold et al., 2017). The REE terbium, with its radioisotope  $^{160}\text{Tb}$ , was employed as a chemical analog of trivalent actinides. For humic acid saturated with Tb(III) (natural stable isotope  $^{159}\text{Tb}$ ), exchange for  $^{160}\text{Tb}$  was found to be rapid, regardless of whether the complex had been pre-equilibrated for time periods up to 3 months. Thus, a dynamic equilibrium was evidenced, with no indications of an inertization over time. However, different findings were obtained if the sequence of introducing the isotopes was reversed, as illustrated in Fig. 1.



**Fig. 1.** Schematic representation of isotope exchange experiments starting from a low metal load of humic acid (HA) with the radioisotope ( $M^*$ ) for variable times of pre-equilibration ( $t_{\text{pre}}$ ), followed by saturation with the stable isotope ( $M$ ), which initiates partial desorption observed over variable times ( $t_{\text{des}}$ ).

In these experiments, humic acid was first contacted with a small amount of the radiotracer  $[^{160}\text{Tb}]\text{Tb}$  and then saturated with the stable isotope  $^{159}\text{Tb}$ . To represent total Tb in a dynamic equilibrium, partial release of the radioisotope is provoked, since the humic-bound fraction of total Tb is lower in the plateau region of the binding isotherm. As shown in Fig. 2, this process turned out to be very slow, and moreover, the rate was dependent on the time of pre-equilibration between  $[^{160}\text{Tb}]\text{Tb}$  and humic acid. Obviously, the inertization phenomenon is confined to the strongest binding sites, which are occupied if the metal is present at trace concentrations.



**Fig. 2.** Release of  $[^{160}\text{Tb}]\text{Tb}$  from humic acid (HA) initiated by saturation with non-radioactive Tb after different times of pre-equilibration with the radiotracer ( $0.5 \text{ g L}^{-1}$  HA,  $1 \text{ nM } [^{160}\text{Tb}]\text{Tb}$ ,  $2 \text{ mM Tb}$ ,  $0.1 \text{ M NaClO}_4$ ,  $\text{pH } 4.0$ ; data taken from Lippold et al. (2017)).

The observed influence of the pre-equilibration time implies that each data series is in turn affected by the inertization, since it is also active during the slow liberation of  $[^{160}\text{Tb}]\text{Tb}$ . Thus, the present system is characterized by a particular situation: kinetics within kinetics. Such a convoluted time dependence requires an appropriate treatment where rate constants are no longer constants. Solving this kinetic problem was the objective of this work.

## 2. Kinetic model development

According to first-order kinetics, the rate of approach to equilibrium regarding the concentration of humic-bound  $[^{160}\text{Tb}]\text{Tb}$  ( $c_{\text{ads}}$ ) in the above experiments is

$$-\frac{dc_{\text{ads}}}{dt_{\text{des}}} = k(c_{\text{ads}} - c_{\text{ads}}^{\text{eq}}) \quad (1)$$

where  $k$  is the rate constant,  $t_{\text{des}}$  is the time elapsed after saturation with stable Tb, and the index eq refers to the equilibrium state. (Since humic colloids may be considered as a dispersed solid phase, the terms adsorption and desorption are employed here for metal binding and release, respectively.)

Giving consideration to the very fast desorption at the initial stage, a two-component approach was chosen where the total amount of sites occupied by  $[^{160}\text{Tb}]\text{Tb}$  was split into a fast desorbing and a slowly desorbing part (1 and 2) with the fractions  $x$  and  $(1 - x)$ , respectively. At any time, the mass balance

$$c_{\text{ads}} = c_{\text{ads},1} + c_{\text{ads},2} \quad (2)$$

holds. Only at the initial state and at the equilibrium state, the degree of occupancy by [ $^{160}\text{Tb}$ ]Tb is equal for both types of sites:

$$c_{\text{ads},1}^{\text{ini}} = x c_{\text{ads}}^{\text{ini}} \quad (3a)$$

$$c_{\text{ads},2}^{\text{ini}} = (1 - x) c_{\text{ads}}^{\text{ini}} \quad (3b)$$

$$c_{\text{ads},1}^{\text{eq}} = x c_{\text{ads}}^{\text{eq}} \quad (4a)$$

$$c_{\text{ads},2}^{\text{eq}} = (1 - x) c_{\text{ads}}^{\text{eq}} \quad (4b)$$

The index ini denotes the initial state prior to saturation. Integration of Eq. (1) is carried out separately for the sites of type 1 and 2 with the corresponding rate constants  $k_1$  and  $k_2$ . For the case under study, however, these parameters are not constant but exhibit a time dependence themselves, which must be included in the integration:

$$- \int_{c_{\text{ads},1}^{\text{ini}}}^{c_{\text{ads},1}} \frac{1}{c_{\text{ads},1} - c_{\text{ads},1}^{\text{eq}}} dc_{\text{ads},1} = \int_{t_{\text{des}}=0}^{t_{\text{des}}} k_1(t) dt_{\text{des}} \quad (5a)$$

$$- \int_{c_{\text{ads},2}^{\text{ini}}}^{c_{\text{ads},2}} \frac{1}{c_{\text{ads},2} - c_{\text{ads},2}^{\text{eq}}} dc_{\text{ads},2} = \int_{t_{\text{des}}=0}^{t_{\text{des}}} k_2(t) dt_{\text{des}} \quad (5b)$$

The time  $t$  controlling  $k_1$  and  $k_2$  is the total time including the period of pre-equilibration  $t_{\text{pre}}$  prior to desorption:

$$t = t_{\text{pre}} + t_{\text{des}} \quad (6)$$

For both  $k$  values, the process of inertization is described by an empirical function:

$$k_1(t) = a_1 (t_{\text{pre}} + t_{\text{des}})^{-b_1} + k_{\infty,1} \quad (7a)$$

$$k_2(t) = a_2 (t_{\text{pre}} + t_{\text{des}})^{-b_2} + k_{\infty,2} \quad (7b)$$

Beside the parameters  $a$  and  $b$ , an offset value  $k_{\infty}$  for infinite time is included because  $k$  does not necessarily decline to zero. Integration and rearrangement leads to the following time functions:

$$c_{\text{ads},1} = (c_{\text{ads},1}^{\text{ini}} - c_{\text{ads},1}^{\text{eq}}) \exp \left\{ \frac{a_1}{b_1 - 1} \left[ (t_{\text{pre}} + t_{\text{des}})^{1-b_1} - t_{\text{pre}}^{1-b_1} \right] \right\} \exp(-k_{\infty,1} t_{\text{des}}) + c_{\text{ads},1}^{\text{eq}} \quad (8a)$$

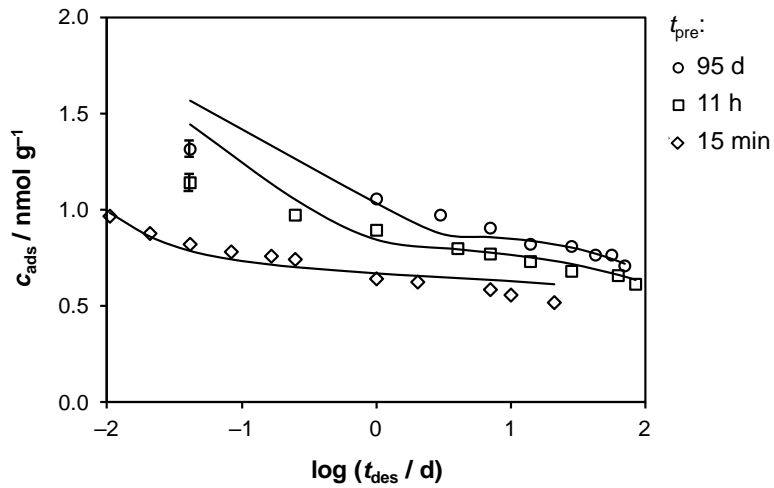
$$c_{\text{ads},2} = (c_{\text{ads},2}^{\text{ini}} - c_{\text{ads},2}^{\text{eq}}) \exp \left\{ \frac{a_2}{b_2 - 1} \left[ (t_{\text{pre}} + t_{\text{des}})^{1-b_2} - t_{\text{pre}}^{1-b_2} \right] \right\} \exp(-k_{\infty,2} t_{\text{des}}) + c_{\text{ads},2}^{\text{eq}} \quad (8b)$$

Summing up under consideration of the boundary conditions given by Eqs. (3a) - (4b) yields the temporal course of metal desorption in total:

$$c_{\text{ads}} = c_{\text{ads}}^{\text{eq}} + x(c_{\text{ads}}^{\text{ini}} - c_{\text{ads}}^{\text{eq}}) \exp\left\{\frac{a_1}{b_1 - 1} \left[(t_{\text{pre}} + t_{\text{des}})^{1-b_1} - t_{\text{pre}}^{1-b_1}\right]\right\} \exp(-k_{\infty,1} t_{\text{des}}) + \\ + (1 - x)(c_{\text{ads}}^{\text{ini}} - c_{\text{ads}}^{\text{eq}}) \exp\left\{\frac{a_2}{b_2 - 1} \left[(t_{\text{pre}} + t_{\text{des}})^{1-b_2} - t_{\text{pre}}^{1-b_2}\right]\right\} \exp(-k_{\infty,2} t_{\text{des}}) \quad (9)$$

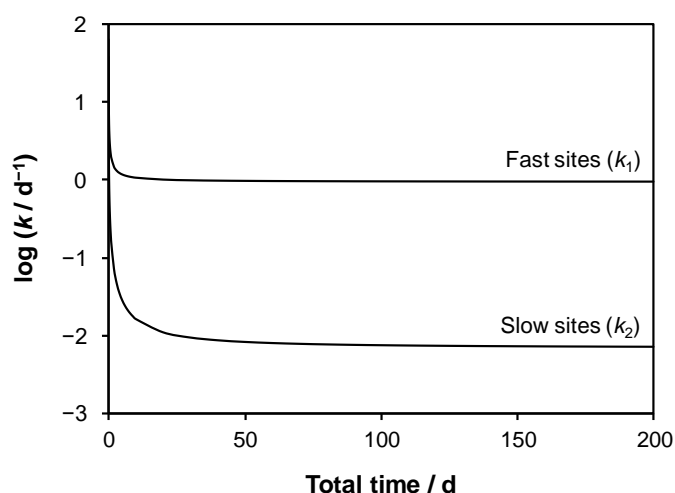
### 3. Results and discussion

The parameters of Eq. (9) were adjusted to the experimentally obtained data sets. In Fig. 3, the modeling results are presented on a semilogarithmic scale for better visibility of the initial phase. Apart from an overestimation for the shortest times in case of longer pre-equilibration, all data series can be reproduced on the basis of one set of parameter values, covering the superimposition of two time-dependent processes (dissociation and inertization) for two types of binding sites. Thus, a kinetic process was adequately described by rate “constants” with an inherent time dependence.



**Fig. 3.** Modeling results (lines) obtained with Eq. (9) using the parameter values  $x = 0.65$ ,  $a_1 = 2.2$ ,  $b_1 = 0.99$ ,  $k_{\infty,1} = 1.5 \text{ d}^{-1}$ ,  $a_2 = 0.1$ ,  $b_2 = 1.2$ ,  $k_{\infty,2} = 0.007 \text{ d}^{-1}$ .

With the adjusted parameter set, the values of  $k_1$  and  $k_2$  as a function of time can be calculated according to Eqs. (7a) and (7b), respectively. The results are shown in Fig. 4. Immediately after complex formation, inertization proceeds rapidly. However, this trend declines after several days, turning into a very slow decrease. Most notably, the  $k$  values do not strive toward zero, i.e., the inertization phenomenon is not a process that leads to irreversible binding. Regardless of the time of “aging”, humic metal complexes will always respond to a decrease in metal concentration in their aqueous environment and finally reach the equilibrium state.



**Fig. 4.** Inertization process reflected by decreasing rate constants as extracted from the model.

Nonetheless, the time periods can be considerable. In the present case, about 2 years of equilibration are required for complexes aged more than 1 month. Dissociation rates will, however, increase at higher pH, lower ionic strength and lower HA concentration because agglomeration is driven back and the colloidal structure is expanded (Rao et al., 1994; Simpson 2002; Monsallier et al. 2003). It must be noted that the HA concentration, used here for experimental reasons, exceeds natural aqueous concentrations by 1-2 orders of magnitude, and the pH value of 4 is situated at the acidic edge of environmental conditions. The isotope exchange technique provides direct insight into the dynamics of equilibria in a non-invasive way since no reagent is added, but the release rates are likely to be affected by the concentration shift initiating the process.

The mathematical structure of Eqs. (7a) and (7b) proved to be most suitable to reflect the time course of inertization, although a theoretical increase in  $k$  to infinity must be tolerated as time approaches zero. Attempts were made to use a (less empirical) first-order exponential approach with  $k$  declining from a start value to an end value, but the relative positions of the data series could not be reproduced on this basis.

The mechanism of the inertization process is still a matter of some controversy. In-diffusion of the metal into the interior of the humic colloids was favored as an explanation for a long time (Cacheris and Choppin, 1987; Choppin and Clark, 1991; Rao et al., 1994; Engebretson and von Wandruszka, 1998; King et al., 2001), but was disproven by analogous findings for systems with competing metals (Lippold et al., 2012). An on-site stabilization, possibly due to intra- or intermolecular bridging of humic structures (as suggested by Geckeis et al. (2002)), appears most probable, although spectroscopic evidence is missing so far. This is supported by the fact that our kinetic data are best described without assuming a transfer of the metal from fast sites to slow sites. Based on new insights obtained by mass-spectrometric techniques, state-of-the-art concepts consider humic colloids as aggregates of smaller entities rather than polyelectrolytes (Sutton and Sposito, 2005). The slow progress of structural rearrangements



causing inertization might be explained by a crucial role of (residual) naturally inherent metals, partly present as clusters, which are slowly disaggregated and/or desorbed over time.

#### 4. Conclusions

Breaking the rules of classical kinetics by introducing time-dependent rate “constants” proved to be a suitable way to describe slow reactions of humic metal complexes, which exhibit the peculiarity of convoluted rates. The increasing inertness must be considered in any attempt to deduce organically bound metal fractions from the composition of aquatic systems (and vice versa) if conditions change relatively fast. For modeling speciation or migration in nearly stagnant systems on a long time scale, however, thermodynamic methodologies using equilibrium constants remain fully applicable, since the inertization process is limited in time and extent. Regarding adsorbed humic material and high-molecular-weight components of clay organic matter, the possible importance of kinetic effects is still in need of investigation.

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