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Proton and metal adsorption onto bacterial consortia: Stability constants for metal–bacterial surface complexes

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Abstract

In this study, we conduct potentiometric titrations and metal adsorption experiments (Cd, Ca, Cu, Pb, Sr, and Zn) using bacterial consortia grown from three representative locations and sampled over the course of a year in order to determine whether bacterial diversity affects proton and metal uptake behaviors. We observe significant changes in bacterial diversity from one site to another, and from month to month during the study period. Despite these changes in diversity, all of the bacterial consortia studied exhibit similar proton and metal uptake, strongly suggesting universal adsorption behavior for the bacterial species present in these samples. We demonstrate that a single, metal-specific, averaged surface complexation model can be used to reasonably account for the acid/base and metal adsorption behaviors of each consortium. We use a four discrete site non-electrostatic model to describe the protonation of the consortia functional groups, with averaged pK_a values of $3.2+0.2/-0.4$, $4.8+0.2/-0.3$, $6.5+0.3/-0.8$, and $9.2+0.1/-0.3$, and site concentrations of $(1.0\pm0.28)\times10^{-4}$, $(1.2\pm0.23)\times10^{-4}$, $(6.12\pm1.1)\times10^{-5}$, and $(9.7\pm2.0)\times10^{-5}$ moles of sites per gram wet mass of bacteria, respectively. The metal adsorption data are used to constrain site-specific bacterial surface complexation models, and we determine the stability constants for the important metal–bacterial surface complexes. These calculated stability constants correlate well to known stability constants for metal–acetate complexes, yielding predictive relationships that enable the estimation of the extent of adsorption of other metals onto bacterial consortia. This study demonstrates that a wide range of bacteria exhibit similar proton and metal adsorption behaviors, and that a single set of averaged acidity constants, site concentrations, and stability constants for metal–bacterial surface complexes can be used to model the adsorption behavior.

Keywords: Consortia; Adsorption; Bacteria; Metal; Surface complexation

1. Introduction

Bacterial surfaces can adsorb a wide range of heavy metal contaminants (e.g., Beveridge and Murray, 1976; Beveridge and Koval, 1981; Mullen et al, 1989). To better constrain and mitigate contaminant transport in the environment, it is important to develop models that determine the influence of bacteria on the speciation and distribution of heavy metals in the sub-surface. Site-

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specific surface complexation models, originally developed to quantify cation adsorption to mineral surfaces, have been successfully used to account for proton and metal adsorption to bacterial surfaces (e.g., Plette et al., 1996; Fein et al., 1997; Haas et al., 2001; Martinez et al., 2002). However, if each bacterial species exhibits unique adsorption characteristics as mineral surfaces do, then it would be an overwhelming task to determine the stability constants, site concentrations and acidity constants necessary for modeling metal adsorption onto all of the bacteria of environmental and geologic interest. A single location in a natural system can contain many bacterial species, and bacterial diversity can change from one location to another. Consequently, if surface complexation models are to be applied to realistic systems, it is important to determine if proton and metal adsorption behavior is species-specific or if commonalities exist among bacterial species.

A number of studies have noted similar adsorption behavior among individual bacterial species (e.g., Daughney et al., 1998; Small et al., 1999; Kulczycki et al., 2002; Ngwenya et al., 2003) and among artificial mixtures of pure strains of bacteria (Yee and Fein, 2003). Yee and Fein (2001) hypothesized that similarities in adsorption mechanisms exist for a wide range of bacterial species, and they conducted potentiometric titrations and Cd-bacteria adsorption experiments using a range of Gram-positive and Gram-negative species. Yee and Fein (2001) observed similar adsorption behavior for the variety of bacteria studied, suggesting that the structures that give rise to metal and proton adsorption are common over a wide range of bacterial species.

The hypothesis of universal bacterial adsorption behavior has been supported by a number of subsequent experimental studies. For example, Jiang et al. (2004) demonstrated that the attenuated total reflectance Fourier-transform infrared spectra of both Gram-positive and Gram-negative bacteria are similar and exhibit similar variations as a function pH. These similarities suggest a similarity in binding environments for metals between species, supporting a universal adsorption behavior that arises from similar cell wall functional group chemistries. Borrok et al. (2004a) measured H^+ and Cd adsorption onto bacterial consortia from a range of natural environments, demonstrating that the consortia exhibit similar proton and Cd adsorption behaviors, and that the adsorption onto all of the consortia can be modeled using a single set of stability constants. In addition, Borrok et al. (2005) compiled all currently available potentiometric titration datasets for individual bacterial species and bacterial consortia, noting general similarities in the proton adsorption behaviors and presenting an internally-consistent averaged set of ‘universal’ thermodynamic proton binding and site density parameters for modeling bacterial adsorption reactions in geologic systems. Although a large number of bacterial species appear to exhibit broadly similar adsorption behavior, some studies suggest that at least some bacteria have significantly different adsorptive properties. For example, Borrok et al. (2004b) showed that some bacteria that thrive in hydrocarbon-contaminated environments exhibit significantly enhanced adsorptive behavior compared to those from uncontaminated systems.

In this study, we expand the study of natural consortia of Borrok et al. (2004a) to test whether we observe similarities in binding environments for a much wider range of bacterial species than was tested by Borrok et al. (2004a), and we measure the extent of adsorption of other metals onto bacterial consortia as well. We obtain our range of bacterial diversity by growing consortia from samples taken from three natural settings and sampling those settings over the course of a year. We conduct potentiometric titrations using these bacterial consortia, and we measure the extents of Ca, Cd, Cu, Pb, Sr, and Zn adsorption onto the consortia as well. The results suggest strong similarities in binding environments on the bacterial cell walls, and we use the measurements to determine average stability constants for the important metal–bacterial surface complexes. We use the stability constants to constrain relationships between these values and metal–acetate stability constants so that our results can be extrapolated to other metals of environmental interest.

2. Methods

2.1. Sampling and growth of bacteria

Sample locations were in northern Indiana and included a river, a forest, and a soybean field site. Samples were collected 7 times from all three sites over the course of a year (October 2004 through September 2005) for potentiometric titration and Cd adsorption experiments. River water samples were also collected from October 2005 through January 2006 for follow-up experiments involving other metal cations. Bottles and scoops used to collect samples were sterilized and sealed in plastic bags before use. Water samples were collected by dipping the sample jar directly into the river. Soil samples were collected by removing the top 5 to 10 cm of topsoil and debris, and then directly scooping the soil specimen using the glass sample jar. Lids were placed loosely over the jars to allow for aerobic conditions and to prevent contamination.