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Bacterial Surface Controls on Metal Adsorption and Bioavailability: The Role of 'Minor' Binding Sites

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Adsorption of metals onto bacterial cell surfaces not only can control the environmental mobility of metals, but also represents the controlling step in metal bioavailability. Therefore, it is crucial to determine the functional groups responsible for metal adsorption in order to understand metal cycling and to optimize bioremediation strategies. Much early work on metal adsorption onto bacterial cells focused on the role of cell surface carboxyl and phosphoryl binding sites, and these sites dominate adsorption under relatively high metal loading conditions. However, under more environmentally-relevant low metal loading conditions, lower abundance sites that exhibit higher affinities for binding metals can dominate metal adsorption onto bacteria. This talk will discuss our recent work quantifying the abundance, pKa values, and importance of two of these types of lower abundance sites on bacterial surfaces: sulfhydryl and amine sites. We have used a range of approaches, from potentiometric titration and X-ray absorption spectroscopy measurements to bulk adsorption experiments using sulfhydryl- and/or amine-specific blocking molecules. Our results demonstrate that both sulfhydryl and amine sites are widespread on bacterial surfaces, and can control adsorption reactions of specific metals and other compounds. Sulfhydryl sites represent only 5-15% of the total sites on bacterial cell surfaces, but they exhibit thermodynamic stability constants for chalcophile metal-bacterial surface complexes that are orders of magnitude greater than those for metal-non-sulfhydryl complexes, and hence sulfhydryl binding of chalcophile elements dominate the adsorption of these metals. Amine sites are more abundant than sulfhydryl sites, representing up to 35% of total bacterial surface sites. Because amine sites become positively charged when protonated, they play an important role in binding, and hence the bioavailability of, metalloids that are present in solution as anions, such as Se(IV) and Cr(VI), and likely are responsible for the bacterial adsorption and bioavailability of other anions such as sulfate and anionic PFAS molecules. In addition to highlighting the importance of these relatively low-abundance bacterial surface binding sites, this talk will also demonstrate the power of using site-specific blocking molecules in order to elucidate the role of specific site types in a wide range of bacterial metabolic processes of geologic interest.