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# Biogeochemical cycling of metals impacting by microbial mobilization and immobilization

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## ABSTRACT

Microbial mobilization and immobilization processes can affect the bioavailability and mobility of metals thereby influencing their toxicity and can therefore be utilized to treat solid and liquid wastes contaminated by metals. However, the microbial mobilization and immobilization of metals depends on the microbial metabolism, the environment conditions. In this review, mobilization and immobilization of metals are discussed with regard to the presence and function of involved microorganisms and in relation to applications such as bioleaching. Furthermore, the biosorption process is evaluated as a possible approach for microbial immobilization of metal on the basis of four mechanisms: (1) physical adsorption, (2) ion exchange, (3) complexation, and (4) microprecipitation. In addition, sulfide precipitation by sulfate reducing bacteria was included as an example of an application of microbial immobilization. Based on the evaluation and recommendations in this paper, bioremediation strategies for metals can be improved thus increasing the opportunity for field applications.


## Contents





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## Introduction

Human activities such as mining, metallurgy, industrial manufacturing and production, and domestic and agricultural use of metal containing compounds have affected the distribution of metals in the environment (Mohammed et al., 2011). As a result, a large amount of metals have been redistributed on the surface of the earth since the industrial revolution in the 18th century (Thevenon et al., 2011; Wuana and Okieimen, 2011). Therefore, there is a growing concern about the adverse effects of metals in the environment. The metals in terrestrial and aquatic environments have been shown to have toxicological effects on the environmental and human health due to toxicological effects and the ability to bioaccumulation in the food chain (Yi et al., 2011). There are 13 trace metals and metalloids in the environment: silver (Ag), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), thallium (Tl), and zinc (Zn), which are considered as the priority pollutants (Blais et al., 2008). These inorganic pollutants mainly originate from metallurgical processes, microelectronics manufacturing, energy production, mining, industrial waste discharge and natural sources such as metal liferous minerals (Voulvoulis et al., 2013). Sediments are the major contaminated phase for metals in aquatic systems. The concentration of metal contamination is controlled by atmospheric transport, precipitation and the weathering processes in addition to contamination from urban water systems such as storm water and wastewater (Harrison, 2012; Nagajyoti et al., 2010). Municipal and industrial wastewater as well as sewage overflows are the main contributors of toxic metal pollution to the aquatic systems (Stumm and Morgan, 2012).

Metals can be classified into two categories (A and B) on the basis of their chemical properties. Class A metal cations easily react with oxygen, while class B metal cations prefer nitrogen or sulfur as reactants (Ho, 2012). Class A metals can form stable products with hard acids or hard bases based on ionic bonds. The most common class A metal cations such as $K^+$, $Na^+$, and $Mg^{2+}$ are important components of biological cells. They exist in essential molecules for biological processes such as phospholipids and nucleic acids (Mao et al., 2013). For example, $Mg^{2+}$ is important to the living organisms because it can stabilize the soft structure of macromolecules such as RNA and DNA (Stumm and Morgan, 2012). Class B metals can react with soft acids to form stable products with covalent bonds. Some of these metals can also bind with methyl- and alkyl- to form metal complexes in biological systems (Fallah and Cundari, 2015). The "class B metals" discussed above was referred to as "metals" in the following chapter of this paper.

Many of the class B metals (*e.g.*, $Pb^{2+}$, $Hg^{2+}$, $Cr^{2+}$) are toxic and can accumulate into biological systems due to adverse effects on proteins and enzymes. For example, copper is an essential nutrient at low concentrations, however, excess copper is toxic to fish and is highly toxic to many invertebrate species such as crab, shrimp and oysters (Ezeonyejiaku et al., 2011). Studies indicated that chronic copper in aquatic environment can cause gill, kidneys and spleens damages (Yanong, 2010). In addition, excess copper can be a powerful reactive toxin to human's body causing many symptoms including immune diseases, fatigue, adrenal burnout, depression, and Alzheimer's (Govind and Madhuri, 2014). The toxic copper species include $Cu(OH)^+$, $Cu_2(OH)_2^{2+}$ and $CuCO_3$ (Okocha and Adedeji, 2012). On the other hand, $Cu^{2+}$ as an ion is widely present in aquatic environment and it is considered as the most toxic of dissolved copper species. Some class B metals (*e.g.*, Hg, Ag, and Cd) can cause organ dysfunction such as disturbance of vision, brain damage, lung and kidney failure and fragile bones, affects calcium regulation in biological systems (Gulati et al., 2010). Lead (Pb) can cause short-term memory loss and enhance the risk of cardiovascular diseases (Padmavathiamma and Li, 2007). Other class B metals such as As can impair natural cells activity and affect essential cellular processes such as oxidative phosphorylation and ATP synthesis (Tripathi et al., 2007). In addition, studies indicated that some of the class B metals can also lead to psychiatric disorders. For instance, Hg exposure can result in insomnia, loss of memory, and restlessness.

Microorganisms have been applied for the recovery of metals in polluted water and lands as an appropriate technology for soil bioremediation (Akpor and Muchie, 2010; Wuana and Okieimen, 2011). Two detoxifying mechanisms: microbial mobilization and immobilization have been exploited for *in-situ* or *ex-situ* bioremediation purpose. Microorganisms are capable of interacting with metals and change their oxidation state or organic complex thereby affecting the speciation and mobility of the metal elements (Olaniran et al., 2013). However, the mechanisms associated with metal bioremediation by microorganisms are still not well understood. Thus, this review focused on the role of microorganisms in the biogeochemical cycling of metals. In addition, the processes of mobilization and immobilization by the microorganisms under physic-chemical conditions of the environment were discussed.

## 1. Microbial mobilization

In natural environments, metals can exist in soil and sediments in different physical forms such as dissolved, colloidal, or as precipitates. They cannot be destroyed or biodegraded by microorganisms unlike biodegradation of organic pollutants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and organochloride pesticides (Marco-Urrea et al., 2015). Microorganisms can increase the bioavailability of metals by bioleaching, rock and mineral bioweathering and biodeterioration, and methylation (Gadd et al., 2012). These microbial processes play a significant role in the mobility of metals. Bioleaching is a process of using bacteria to dissolve metals and it is widely used to extract valuable metals such as copper and gold (Wang et al., 2009). While the metals of rock aggregates can be decomposed and redistributed by microorganisms through bioweathering process (Liu et al., 2011). Like bioleaching and bioweathering, methylation can also increase bioavailability and toxicity of metals. Some methylated metals such as methylmercury are lipophilic. As a result, microorganisms can facilitate volatilization of metals from the environment (Hsu-Kim et al., 2013). In addition, the impact of biological processes on metal is dependent on the metal forms and the



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