CHAPTER 11

The Role of Aquatic Ecosystems in the Elimination of Pollutants

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Abstract: Contamination of aquatic ecosystems is always of concern to environmental scientists; however, these systems also possess unique capabilities allowing them to eliminate or remediate certain levels of pollutants. Primarily through the presence of vegetation, aquatic ecosystems are known to be capable of removing or at least decreasing pollutant loads travelling through the aqueous phase. In addition to vegetation, soil/sediment and microbes play a significant role in transferring or transforming pollutants to acceptable levels in aquatic ecosystems. This chapter focuses on some of the primary literature describing phytoremediation of organic pollutants (e.g. hydrocarbons and pesticides) and inorganic pollutants (e.g. metals and nutrients). Research indicates the popularity and success of phytoremediation techniques used to clean up both organic and inorganic pollutants from the water column. While certain caution should always be exercised, phytoremediation continues to serve as a successful means of pollutant remediation in aquatic ecosystems.

INTRODUCTION

Aquatic ecosystems are often receptacles of point- and non-point source pollutants from spills, sprays, or runoff events. While much emphasis is placed on aquatic ecosystem damage from pollutants, research has demonstrated these unique systems have resilience and assimilative capacity in the mitigation of such pollutants. This chapter will focus on aquatic ecosystem responses to metal, nutrient, and pesticide inputs, primarily discussing the concept of pollutant remediation *via* plants (phytoremediation) and microbes. Because various review articles have been published regarding specific phytoremediation techniques [1, 2], this chapter is not meant as an exhaustive literature review. Instead, it provides a broad understanding of some of the principle concepts involved in aquatic system remediation (through plants) of common pollutants.

PHYTOREMEDIATION

Phytoremediation is generally defined as the use of plants and associated microbes to remove, contain or render harmless environmental pollutants [2, 3]. The nature of pollutants will affect their ability to successfully undergo phytoremediation. For example, while organic pollutants can be degraded, inorganic pollutants such as nutrients are unable to be degraded. Instead, through processes of phytoremediation, inorganic pollutants can be stabilized or sequestered. According to Susarla *et al.* [4], three general factors affect pollutant uptake and distribution within plants used in phytoremediation efforts: physicochemical properties of the pollutant (e.g. octanol water partition coefficient, vapor pressure, water solubility); environmental conditions (e.g. pH, temperature, soil moisture, organic matter); and plant characteristics (e.g. available enzymes and root systems). In addition to the factors affecting pollutant uptake, phytoremediation itself has five major mechanisms by which the process may operate [2, 4, 5, 6].

1. Phytoextraction/Phytoaccumulation: The pollutant is taken up by the plants, but not completely or quickly degraded, resulting in accumulation within the plant.
2. Phytovolatilization: The pollutant is converted by plants into a volatile form and released.
3. Phytostabilization: Typically observed with metals, plant root exudates alter the soil environment allowing the pollutant to precipitate.
4. Phytotransformation/Phytodegradation: The pollutant is eliminated *via* plant enzymes or enzyme co-factors.
5. Rhizodegradation: The pollutant is treated *via* enhanced activity of bacteria or fungi associated with plant roots in the rhizosphere.

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Not all mechanisms are equally effective for remediation of all pollutants. Phytoextraction, phytoaccumulation, and phytostabilization are efficient mechanisms for remediation of many metals, including cadmium, chromium, lead, nickel, and zinc. Mercury, selenium, and various chlorinated solvents are effectively remediated through phytovolatilization. Pollutants such as munitions, chlorinated solvents, and certain pesticides are best remediated through phytotransformation and phytodegradation. Rhizodegradation is an effective mechanism for remediation of radionuclides, certain organic chemicals, and metals.

AQUATIC SYSTEM REMEDIATION OF ORGANIC POLLUTANTS

Studies of organic pollutant remediation in aquatic systems tend to focus on structures such as oxbow lakes, detention ponds, riparian buffer zones, vegetated drainage ditches and constructed wetlands. As with inorganic pollutants, remediation occurs not only in and around vegetation, but also within sediment and aqueous phases *via* chemical and microbial processes. Polarity and lipophilicity of pollutants give reliable indications on their ability to be remediated *via* vegetation. Limited plant-pollutant uptake will be achieved with chemicals which are extremely polar due to difficulty in crossing biomembranes [7]. On the other hand, extremely lipophilic pollutants quickly penetrate biomembranes, only to be sorbed to root material. It is the pollutants with intermediate lipophilicity which are best remediated by vegetation. These pollutants can be translocated to upper plant parts, rather than become concentrated in root material [7]. According to Chaudhry *et al.* [8], by reducing plant wax viscosity, uptake of non-polar compounds will be enhanced. Additionally, factors which increase leaf cuticle hydration increase the permeability of hydrophilic compounds.

Once pesticides are absorbed in plant material, three main reactions are responsible for pollutant transformation [8]:

1. Degradative (e.g. hydrolysis and oxidation)
2. Synthetic (e.g. conjugation)
3. Rearrangement (e.g. epoxide formation)

Specific Examples of Organic Pollutant Phytoremediation

Euliss *et al.* [9] compared reduction of petroleum hydrocarbons found in sediments with sedge (*Carex stricta*), switchgrass (*Panicum virgatum*), and gamagrass (*Tripsacum dactyloides*) versus sediments under willow (*Salix exigua*), poplar (*Populus* spp.) or no vegetation. Significantly fewer residues of petroleum hydrocarbons (70%) were in sediments with sedge or grass; whereas only 20% fewer residual hydrocarbons were noted in the sediments containing trees or no vegetation. Two aquatic plants, *Juncus fontanesii* and *Lemna minor* have reportedly removed phenol concentrations ranging from 8 to 48 mg/L [10]. Polychlorinated biphenyls, another common organic pollutant, has been shown capable of being transferred from an aqueous spiked solution into plant material from the common reed (*Phragmites australis*) and rice (*Oryza sativa*) [11].

A great deal of phytoremediation literature addresses the ability to reduce pesticides. Many studies examine remediation capabilities within stream mesocosms, constructed wetlands, or vegetated drainage ditches. Several studies have examined the influence of vegetation on the reduction of pyrethroid insecticide concentrations in aqueous solution. In a mesocosm experiment, Moore *et al.* [12] reported *cis*-permethrin reduction ranging from 67 ± 6% in common cattails (*Typha latifolia*) to 71 ± 2% in cutgrass (*Leersia oryzoides*). Another study conducted by Moore *et al.* [13] examined permethrin mitigation in constructed ditches in Yolo County, California. The ditch distance needed to reduce permethrin concentrations to half of their original inflow concentration ($D_{1/2}$) in non-vegetated ditches (50-55 m) was basically twice that of vegetated ditches (21-22 m). Bennett *et al.* [14] determined that in order for initial bifenthrin and lambda-cyhalothrin aqueous inflow concentrations to be reduced to 0.1% of their initial value, a vegetated ditch 280 m would be necessary. Other vegetated ditch studies have reported 87% of the mean measured lambda-cyhalothrin was associated with plant material [15]. In a constructed wetland experiment, 49% of measured lambda-cyhalothrin was associated with vegetation, while 76% of cyfluthrin was found in vegetation [16].

Various studies have also examined the remediation of organophosphate insecticides and different herbicides with vegetation. After dosing a field-scale constructed wetland in the Mississippi Delta, USA, Moore *et al.* [17] reported

43% of the measured mass of the insecticide diazinon was associated with wetland plant material. In a California study, diazinon was amended into two constructed ditches, one vegetated and one non-vegetated. Ditch half-distances ($D_{1/2}$) were calculated (see previous paragraph for description) and results indicated a non-vegetated ditch would need three times the distance (158 m) of a vegetated ditch (55 m) to remediate the same diazinon concentration [13]. Comparing methyl parathion transport in vegetated versus non-vegetated constructed wetlands, Moore *et al.* [18] reported pesticide concentrations were detected in outflow samples of the non-vegetated wetland 30 min after initial dosing. During the same time sequence, methyl parathion concentrations in the vegetated wetland were only measured at 20 m (slightly less than half way through the system). Semi-permeable membrane devices deployed in both wetlands confirmed that, although methyl parathion concentrations reached the non-vegetated wetland outflow, no pesticide was detected in the vegetated wetland outflow [18]. Experimental constructed wetland mesocosms at the University of Mississippi Field Station were utilized for specific pesticide phytoremediation studies in the late 1990s. Results from those studies indicated that 25% and 10% of measured chlorpyrifos and metolachlor (herbicide), respectively, were associated with wetland plant material [19, 20]. A study examining atrazine mitigation in a vegetated drainage ditch populated with *Polygonum* spp., *Leersia oryzoides*, and *Sporobolus* spp. reported 61% of measured herbicide concentrations were associated with plant material [15]. Rice *et al.* [21] examined radiolabelled pesticide concentrations in aqueous solution in vegetated versus non-vegetated systems. In different systems vegetated with *Ceratophyllum demersum*, *Elodea canadensis,*and *Lemna minor*, 1%, 4%, and 23% of ^{14}C-metolachlor, respectively, remained in aqueous solution, while 61% of the pesticide was present in non-vegetated system aqueous solutions. Likewise, ^{14}C-atrazine was amended into identical systems. Percentage of pesticide remaining in aqueous solution was 41%, 63%, and 85% for *C. demersum*, *E. canadensis*, and *L. minor*, respectively. In non-vegetated systems, 85% of ^{14}C-atrazine remained in aqueous solution [21]. Rose *et al.* [22] monitored reduction of the herbicide fluometuron in open and vegetated ponds for consecutive growing seasons. Significant differences (58% reduction in vegetated pond versus 41% reduction in open pond) was noted during the second incubation of the second season.

Microbial Remediation of Organic Pollutants

Organic pollutants represent a vast range of chemicals with diverse properties and varying degrees of toxicity and recalcitrance to microbial remediation. Common pollutants include petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), nitroaromatics, polychlorinated biphenyls, industrial solvents and various pesticides [23]. The biodegradation of these materials has received a substantial amount of interest over the last two decades and interactions between various organic pollutants and microorganisms have been examined from physiological, molecular, and even evolutionary perspectives [24, 25, 26, 27]. At a basic level organic materials can be separated into those that are biodegradable (*i.e.* are transformed by microorganisms into more innocuous products, ultimately into carbon dioxide and water), those that are persistent (materials which are not biodegradable in certain environments), and those that are recalcitrant (materials which are resistant to biodegradation in most situations). While individual microorganisms are capable of degrading simple organics, typically the complete biodegradation of organic pollutants may involve the metabolic activity of several microbial populations acting as a consortium [28].

As well as the fundamental capability of natural bacterial populations to degrade an organic pollutant, a number of other considerations are important and may impact the effectiveness of microbial remediation [28]. Organic pollutants typically occur as mixtures of different groups of chemicals and even within specific groups (e.g. PAHs) there is a great deal of variability on degradability [28, 29]. Different organic substrates (or their degradation byproducts) may interfere with the microbial pathways used to degrade other substrates, impairing effective remediation. As well as substrate variability, certain microorganisms might also require electron acceptors other than oxygen; for example, sulfate reducing bacteria may be particularly effective in the reductive dehalogenation of highly substituted materials such as organochlorine compounds [30]. Even if metabolically suitable microbial populations and electron acceptors are present, interactions between the microorganisms and pollutant may be limited. Organic compounds can become associated with polymers in the soil matrix limiting their accessibility to microbial populations [31], and the same could occur in aquatic sediments. At a more fundamental level, many organics are also insoluble in water, and this is likely to be a limiting factor in the degradation of materials such as polychlorinated biphenyls in aquatic ecosystems, although the microbial production of surfactants may overcome this to some extent [23]. Limited accessibility of microbial populations to organic pollutants also means that the concentration of pollutant that the microorganisms are exposed to may be substantially lower than the actual

concentration in the system, and these lower concentrations may be below the threshold needed for induction of degradative enzyme systems even if the natural microbial populations contain them [32, 33]. The movement of microorganisms towards increasing concentrations of pollutants (*i.e.* positive chemotaxis) may be just as important as actual degradative ability in the microbial remediation of some organic contaminants [29].

Populations of the bacterium *Pseudomonas putida* can show both chemotaxis towards and the ability to degrade the two-ring PAH naphthalene if they possess the appropriate plasmid [34], and natural microbial populations are likely to show the same capabilities. Naphthalene is a common organic micropollutant in water and many bacteria capable of degrading naphthalene have been isolated [29]. Similarly a large number of bacteria appear to be capable of degrading three-rings PAHs such as phenanthrene, and as with naphthalene degraders, these bacteria represent a diverse range of bacterial taxa [35, 36, 37]. The capability of microorganisms to degrade higher molecular weight PAHs such as benzo[*a*]pyrene, a five-ring carcinogenic compound that is a commonly formed from combustion of organic material, is much more limited [37]. Those bacteria that can oxidize benzo[*a*]pyrene generally do so through cometabolism, requiring the presence of other organic substrates either for metabolism or to stimulate PAH degradation [38, 39]. Various fungi have been shown to be potential degraders of benzo[*a*]pyrene and other high molecular weight PAHs in terrestrial environments [37, 40], but the importance of fungi as degraders of PAHs in aquatic ecosystems is not known.

Nitroaromatic organic compounds released from incomplete fossil fuel combustion and as feedstock in the manufacture of materials such as pesticides are generally regarded as being fairly recalcitrant to bioremediation, especially through oxidative reactions [27, 41]. Few microorganisms are capable of using nitroaromatics substrates as their sole source of carbon and/or nitrogen, although many more appear to be capable of reducing nitroaromatics to corresponding aminoaromatics through the action of various nitroreductases [27]. This typically occurs under anaerobic conditions, and may be the major method by which poly-nitroaromatic compounds can be degraded [42]. Intermediate products, however, may be more toxic than the original pollutant, and effective mineralization in aquatic sediments is likely to require consortia of many different interacting microbial populations. Simpler mono- and di-nitroaromatics are mineralized aerobically by some bacteria that potentially use them as a source of carbon, energy, and nitrogen [27]. Various actinomycetes and pseudomonads can hydroxylate the nitro groups in 2-nitrophenol and 4-nitrophenol, releasing nitrite and forming dihydroxybenzene which is subsequently mineralized [43, 44, 45]. These reactions are important in the microbial degradation of the pesticides parathion and methyl parathion which are first hydrolyzed to yield 4-nitrophenol, which is subsequently hydroxylated [46]. Monoxygenases and dioxygenases are involved in the hydroxylation of mono- and di-nitroaromatics, respectively, but other aerobic degradation mechanisms exist in some bacteria [27]. However, compared to many non-nitrogen containing organic pollutants, nitroaromatics are more resistant to microbial mineralization and the majority of studies have been at the bench- or laboratory-scale rather than in natural environments.

As with nitroaromatics, most organic molecules that contain substituted groups are more recalcitrant to microbial remediation than simpler hydrocarbons. This is especially true of halogenated organic pollutants, even those with relatively simple modifications of aromatic hydrocarbons such as chloro- and fluoro-benzene. However, while most bacteria in natural environments have no ability to degrade these compounds, continued exposure to simple halogenated aromatics encourages genetic exchange between bacterial populations and has been shown to result in the evolution of new degradative pathways [47, 48]. Organics with more extensive substitutions such as the pesticide 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) or polychlorinated biphenyls (PCBs) are more difficult to degrade. Microorganisms that degrade these materials do so through either an oxidative process, in which they use the pollutant as the main substrate for metabolism, or through reductive dehalogenation, in which the halogen groups are replaced with hydrogen [42]. Reductive dechlorination of PCBs appears to be common in contaminated aquatic sediments and typically involves populations of anaerobic microorganisms such as the sulfate reducing bacteria [30, 42]. However, while microbial consortia may process chlorinated organic compounds completely, most of the isolated bacteria that are capable of reductive dehalogenation do not do so completely so that end products of remediation may still contain chlorine groups. A notable exception is *Dehalococcoides ethenogenes* which can reductively dechlorinate the solvent tetrachloroethene to ethene, using perchloroethene as an electron acceptor for metabolism [49, 50]. *D. ethenogenes* is also interesting in that while most bacteria that have been studied from the perspective of pollutant remediation belong to well studied microbial groups such as the Proteobacteria or Firmicutes, *D. ethenogenes* is related to the Chloroflexi [51], a poorly studied group of unusual

photosynthetic organisms. This illustrates the importance of considering the possible role of all microorganisms in natural ecosystems for bioremediation, not just those that have been previously studied. It suggests that other poorly studied groups of bacteria may have novel metabolic pathways for pollutant removal that are as yet undiscovered.

AQUATIC SYSTEM REMEDIATION OF INORGANIC POLLUTANTS: METALS

Aquatic systems ranging from lotic (*i.e.*, rivers, streams) to lentic ecosystems (*i.e.*, wetlands, lakes, oxbows) have the ability to transform heavy metal pollutants from the water column through various ecological processes. Plants, sediments and microbes actively participate through biological and chemical processes to transform, remediate, and stabilize toxic metal pollutants. Marshes or constructed treatment wetlands are most often used for phytoremediation of metals [52]. However, the remediation capabilities of the system are not limited to plants. Sediments actively participate in forming metal complexes, reducing certain metal forms, and binding elements to particulate matter. Lentic conditions create ideal circumstances for decreases in soil redox, habitat for aquatic plants, and reducing toxic, soluble valence forms of metals to insoluble, reduced non-toxic forms.

Phytostabilization is the most common form of phytoremediation whereby assimilation and transformation of elements are restricted to the roots and there is no translocation of elements to the shoot. Often these plants are called root accumulators [53]. Plants with a higher concentration of element within the plant tissue than in the surrounding substrate (*i.e.*, water or sediment) are often considered hyperaccumulators and often exhibit luxury uptake. Luxury uptake is the ability to increase elemental concentrations within the plant tissue beyond the needs of the plant for normal metabolic functions [54]. The optimal plant for phytoextraction should not only be able to tolerate and accumulate high levels of heavy metals in its harvestable parts, but also have a rapid growth rate and the potential to produce a high biomass in the field. An ideal plant for rhizodegradation should have rapidly growing roots with the ability to remove toxic metals from solution over extended periods of time [5].

Studies in plant response to heavy metals have suggested that plants have evolved two different physiological mechanisms which enable them to tolerate metal toxicity: accumulators and excluders [55]. Accumulators concentrate sequestered metals in plant parts at low to high concentrations above background concentrations. Excluders have differential uptake and transport between root and shoot which result in constant low shoot/root levels over a wide range of external concentrations. In accumulators, root uptake and transport are more or less in balance, but metals can still accumulate in the roots. Excluders do not generally regulate metal uptake, with restriction of transport from root to shoot as the likely mechanism reducing metal toxicity. Studies have suggested that plants growing on metalliferous soils cannot prevent metal uptake, but can only restrict it and hence accumulate metals in root and shoot tissues at varying concentrations. Different plant species globally have shown considerable differences in their uptake ability for various metal species. Baker [55] highlighted 12 different wetland and upland species that had 18-fold variation for zinc, 240-fold difference for lead, and 273-fold for cadmium.

Phytoremediation of metals has several advantages:

- Metals can be selectively removed at low concentrations (*i.e.* a polishing step)
- It can occur on site with through flow, or biomass can be transported to a specific site
- There is an initial low capital investment and low operating cost as compared to traditional methods of remediation

Specific Examples of Metal Phytoremediation

Maine *et al.* [56] identified two strategies of metal remediation depending on the plant species used. Submerged non-rooted *Eichornia crassipes* retained the majority (97%) of metals in macrophytic biomass, while a community co-habitated or completely dominated with *Typha domingensis* had the majority of metals associated with the sediments. This example illustrates the varying degrees of assimilatory capacity between aquatic plants. Water hyacinth (*E. crassipes*) has also been used to phytoremediate iron-rich wastewaters in constructed wetlands [57]. Iron removal by water hyacinth was largely due to the process of rhizofiltration and phytostabilization, since chemical precipitation of iron oxides was followed by flocculation and sedimentation. In this study, phytoremediation seemed to not be very

substantial in iron accumulation in comparison to chemical precipitation. Rhizofiltration was the predominant mechanism of remediation of iron since a substantial portion was localized in the roots. Iron phytoextraction was possibly negligible due to the physiological barriers to iron transport to aerial tissues. Caution must be exercised with the use of *E. crassipes,* since it is considered a noxious weed in many countries.

Sharma and Gaur [58] examined the ability of *Lemna polyrhiza* to remediate zinc, lead, and nickel. It was noted that the plant had a rapid increase of metal assimilation within 12 hours, with subsequent assimilation reaching a plateau. It is hypothesized that within the initial 12 hours, rapid, passive uptake of metals occur, while thereafter the assimilation occurs at a slower rate due to metabolic control. A consequence of too great a concentration of heavy metals is the decline and inhibition of chlorophyll synthesis. Thus, most plants have an evolutionary and metabolic constraint to assimilation of certain elements.

Zazo *et al.* [59] examined two species, *Typha latifolia* and *Carex lurida* for their phytoremediation ability in reducing hexavalent chromium. Irrespective of the plant species, as there were no significant differences between species; hexavalent chromium removal was enhanced by plants, with a decrease in soil redox promoted by organic root exudates released by the plants. In low redox conditions, iron and sulfate reduction is increased. Additionally, concentrations of ferrous iron and sulfides increase in the sediment pore water which in turn reduces hexavalent chromium to Cr_{III}. Soils high in organic humic substances will also possess the ability to transform and sequester toxic metals ions. Humic acids constitute a large organic carbon fraction and represent a significant electron donor reservoir for metal reduction and amelioration [59].

Often plants will significantly phytostablize contaminants whereby metals are reduced in and around the roots [60, 61]. The aquatic plant rhizosphere provides a particularly effective, locally oxidized/reduced environment for metal precipitation and adsorption outside the root. *Phragmites australis* roots have been shown to accumulate Fe, Cu, Zn, Pb and Cd, with little to no translocation of metals within the plant to rhizomes and shoots. Iron plaque formation of Fe-oxyhydroxides formed by oxygen evolution by the roots and microbial metabolism is believe to be a mechanism of avoiding toxicity of reduced forms of Fe and Mn to roots under flooded conditions. Vesk *et al.* [62] identified where various element species occurred within the roots of aquatic plants. Iron was often present at highest concentrations at the root surface and decreased within the cell, while trace metals (Cu, Zn, Pb) had highest concentrations occurring within the plant cell, and decreasing towards the root surface. Meyers *et al.* [63] examined the uptake and distribution of lead sequestered by hydroponically grown *Brassica juncea.* The study showed lead uptake was restricted to the root tissue suggested rhizofiltration, where the concentration of lead was always two to three orders of magnitude greater in roots than in shoots. Electron microscopy work revealed substantial and predominantly intracellular uptake at the root tip, while endocytosis of lead within the plasma membrane was not observed. Further experiments demonstrated uptake of lead increase as concentration of lead in solution increased.

In some instances an interaction occurs between metals. Studies have shown [64] that manganese absorption by plant tissue will be suppressed or depressed by high levels of iron precipitate or assimilation. For example *Juncus effusus* showed reduced concentrations of manganese in shoots as a result of high iron concentrations. Thus, phytostabilization of one element could result in deficiencies in other elements important to metabolic functions such as growth.

Plants can accelerate and promote bioremediation of metals and other contaminants by stimulating the growth and metabolism of microorganisms through the release of nutrients and oxygen. There is a significant amount of information concerning the influence of aquatic plants on metal fluxes at larger scales. There is also a substantial amount of information concerning small scale laboratory research addressing kinetics of metal uptake in aquatic plants. There is still a very relevant need for research understanding processes of metal accumulation and transformation in the field and how it affects larger scales.

Microbial Remediation of Metals and Metalloids

The microbial remediation of metals differs from that of organic pollutants as metals are not degraded into what are ultimately innocuous products [65]. Rather, interactions between microorganisms and metals may change the redox state of the metal or alter its mobility in the environment. At a basic level, interactions between microorganisms and metal contaminants in aquatic ecosystems can be separated into four broad types: (1) microbial redox transformations that

change the metals mobility; (2) volatilization or precipitation from the water column; (3) absorption of metals to microbial cells or cellular products (biosorption); and (4) microbial transformations of other chemicals that indirectly influence metal behavior [66]. Commonly, a number of these processes will be involved in the microbial remediation of metals and metalloids; for example, dissimilatory metal reduction as part of anaerobic respiration (a redox transformation) can result in a metals precipitation or biosorption. Aquatic ecosystems harbor appreciable numbers and diversity of bacteria that metabolize or are resistant to toxic metals and many of these organisms are capable of biotransforming elements into forms of different mobility and toxicity. Fig. (1) illustrates some of the microbial processes that can be involved in transforming metals in oxic and anoxic layers of aquatic environments.

Microbial interactions with arsenic are an example of naturally occurring metal-microbe processes that may have remediation potential. Studies suggest that arsenic resistant bacteria are a common component of both aquatic and terrestrial ecosystems, even those not suffering from arsenic pollution [67, 68]. Bacteria possess a number of genetic and physiological systems for dealing with arsenic toxicity including redox transformations and its incorporation into organic forms [69]. The metabolic process of arsenite (As_{III}) oxidation converts arsenic to the less toxic arsenate (As_V) and has been shown to occur in a number of bacteria, either as a resistance mechanism or as a form of energy generating metabolism [70, 71, 72, 73]. The microbial oxidation of arsenite has been proposed as a bioremediation strategy for aquatic environments [70], as the resulting arsenate is much less soluble and can be more easily removed through steps such as alkaline precipitation with lime [74].

While inorganic arsenic becomes less mobile and toxic following oxidation, the opposite is true for other metals. The oxidized forms of chromium and the radioactive metals uranium and technetium are much more water soluble than their reduced forms [65, 75] so that, in contrast to arsenic, it is the microbial reduction of these metals which may be more beneficial to the remediation of aquatic environments. Differences in the mobility of various metals in different redox states also highlight a fundamental difference in remediation strategies for aquatic and terrestrial environments. In solid phase systems (soils) it is typically beneficial to increase metal mobility so they are removed from the system; however, in aquatic phases the opposite approach (to encourage microbial redox processes that decrease metals mobility and increase their precipitation or adsorption) is often more desirable [75].

The reduction of chromium from the toxic and highly soluble Cr_{VI} to relatively insoluble Cr_{III} has been demonstrated in a wide range of microorganisms including bacteria, fungi, and algae [76, 77]. Chromate reducing enzyme systems vary greatly between bacteria and include both soluble enzymes, those associated with the cell membrane, and enzymes capable of reducing Cr_{VI} either aerobically or anaerobically [78, 79]. Such diversity suggests that bacterial chromate reductases may be useful in the bioremediation of chromium contaminated sites in a wide range of environments [80]. As is the case with arsenic, chromium resistant bacteria appear to be ubiquitous, having been recovered from both chromium impacted and non-polluted environments [81].

Toxic metals can also be removed from aquatic environments *via* their precipitation with the products of other microbial redox processes. Dissimilatory sulfate reducing bacteria, a common group of bacteria in aquatic sediments that utilize sulfate as the terminal electron acceptor in anaerobic respiration, produce hydrogen sulfide as a waste product. The sulfide produced can precipitate and immobilize arsenic [82] and abiotically reduce Cr_{VI} to Cr_{III} [83]. Sulfate reducing bacteria have also been shown to reduce aqueous concentrations of cadmium, copper, iron, nickel and zinc through the formation of insoluble metal sulfides in model systems [84, 85] and similar processes are possible in natural environments. Dissimilatory iron-reducing bacteria convert Fe^{3+} to Fe^{2+} during their anaerobic respiration, and Fe^{2+} can also abiotically reduce and immobilize toxic metals such as chromium [83]. Some iron-reducing bacteria such as species of *Geobacter* and *Shewanella* are also capable of directly reducing other metals as part of their metabolism, and may be useful in the reductive remediation of technetium, cobalt, and uranium [86, 87, 88].

While sulfate and iron-reducing bacteria are typically found in anoxic aquatic sediments, they can also be important components of aquatic biofilms [89, 90]. Biofilms are naturally occurring communities of attached microorganisms found on any submerged surface, and they are characterized by a complex architectural structure often with both aerobic and anaerobic layers [91, 92]. They often support a diverse range of microbial populations in close proximity to each other, which can be important in bioremediation [93]. Furthermore, the cells within biofilms are enclosed within a matrix of extracellular polysaccharides or slime, which itself can remove metal contaminants from the surrounding water through the process of biosorption [94, 95, 96]. The combination of sulfate reduction and

potential biosorption/precipitation of metal sulfides within the biofilm structure can be a particular effective method of remediation and has been shown to be effective for metals such as chromium, copper, and lead [97, 98, 99].

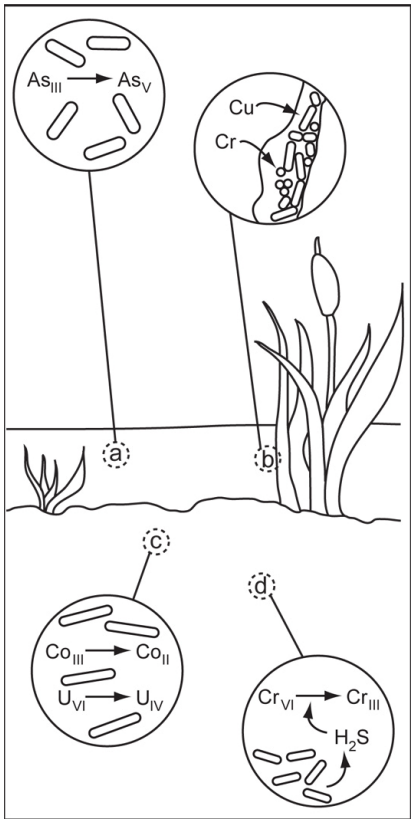

Figure 1. Microbial processes that can remediate metal pollution in aquatic ecosystems include: (a) the aerobic oxidation of metals such as arsenic which can reduce their mobility and toxicity; (b) the absorption of metals such as chromium and copper to biofilms associated with sediments and aquatic plants; (c) the microbial reduction of metals such as cobalt and uranium to less toxic forms by iron-reducing bacteria such as *Shewanella*; (d) indirect transformations resulting from microbial metabolism that result in metal precipitation, such as the reduction of chromium following the production of hydrogen sulfide by sulfate-reducing bacteria in anoxic sediments.

Sulfate-reducing bacteria in anoxic sediments and biofilms are important mediators of mercury methylation [100, 101, 102], which can have negative impacts on human activities because methylmercury is highly toxic and subject to biomagnification through aquatic food webs [103]. However, sulfate-bacteria may also play some role in the removal of aqueous mercury (Hg^{2+}) *via* the production of hydrogen sulfide as a waste product which can react with Hg^{2+} to form the much less soluble mercuric sulfide [104]. Of more importance from a remediation aspect is the enzymatic reduction of Hg^{2+} to elemental mercury (Hg^0) which is common and widespread throughout bacteria [105, 106]. Elemental mercury is insoluble and much less toxic than other forms. It is also volatile so that the microbial reduction of Hg^{2+} to Hg^0 is a significant mechanism that can contribute to the removal of mercury from natural waters to the atmosphere [106]. Mercury contaminated environments select for microorganisms capable of carrying out this transformation [107], which is encoded for by a number of mercury resistance (*mer*) genes [105, 106].

Bacterial mercury resistance genes are usually located on plasmids and are often components of transposons [105, 106, 108, 109]. These mobile genetic elements can be passed between bacterial species *via* the process of horizontal gene transfer and the evolutionary history of *mer* genes suggest that this has been a relatively frequent occurrence in the past [110]. The same phenomenon has been shown for arsenic resistance genes, which are also often borne on plasmids [111].

Mobile resistance genes demonstrate the capability of natural microbial communities to respond and adapt to environmental pollution both from metals and organic pollutants [112]. From an applied perspective they present an

excellent opportunity to incorporate biotechnology into bioremediation in that the genes can be transferred into specific bacterial species that may be suitable for a particular environment. Such an approach is likely to be particularly beneficial in environments where there are multiple contaminants, in that traits such as metal resistance may be passed onto to organic-degrading bacterial populations [23].

AQUATIC SYSTEM REMEDIATION OF INORGANIC POLLUTANTS: NUTRIENTS

Unlike previously described organic pollutants and metals, nutrients are a vital component in aquatic systems. Productivity and trophic status of aquatic systems impart information on not only the stability, but also the relative ecological health of aquatic systems. Problems arise however, when nutrients in aquatic systems reach levels in excess of the natural system's capacity to utilize them. Nutrient concentrations must strike a fine balance between the needs of the aquatic system and excessive levels which will lead to ecological problems such as hypoxia or harmful algal blooms.

Several studies have examined abilities of aquatic plants to remediate excessive nutrient concentrations. Cronk and Fennessy [113] warn that nitrogen and phosphorus removal from water by vegetation is not the major pathway for nutrient remediation where concentrations are high. More success can be achieved with plants in a nutrient phytoremediation scenario when overall nitrogen and phosphorus concentrations have lower loads. Nutrient uptake by plants is also dependent on several factors including season, plant growth rate, plant biomass, and latitude [113]. In a two year study in northwest Mississippi, USA, Kröger *et al.* [114, 115] reported that vegetated drainage ditches reduced 53% and 43% of the dissolved inorganic nitrogen and maximum inorganic effluent phosphorus loads, respectively. Mesocosm scale studies reported $83 \pm 3\%$ and $40 \pm 8\%$ decrease in aqueous ammonia and nitrate concentrations, respectively, in systems vegetated with *Ludwigia peploides* [116]. Although it was least effective in decreasing ammonia and nitrate concentrations, the aquatic plant *Leersia oryzoides* was more effective than *L. peploides* at removing organophosphorus ($29 \pm 7\%$) [116]. Two separate studies examined the use of *Eichhornia crassipes* in remediating excessive nutrients from water. In a system with a 21 day hydraulic retention time, 100% removal of total nitrogen and phosphorus was achieved after nine weeks of treatment through *E. crassipes* [117]. Using a 31-day batch growth experiment with *E. crassipes*, reductions of total Kjeldahl nitrogen, ammonium, and total phosphorus were 92%, 99%, and 99%, respectively [118].

CONCLUSIONS

Aquatic systems are resilient habitats which receive many point and non-point-source pollutants. Rather than focus on their contamination, this chapter was devoted to the abundance of literature demonstrating remediation capabilities – primarily phytoremediation – of these aquatic systems. Although the literature presented within this chapter is not an exhaustive review of all the research conducted in these specific areas, it provides a solid foundation for those interested in the ability of vegetation to clean waters receiving pollutants. Cautions exist, of course, when using phytoremediation for any pollutant. While benefits certainly exist, there are also drawbacks to using phytoremediation tools. For example, harvested biomass from metal phytoextraction may be a hazardous waste. Improper initial planning may lead to a potential food chain effect due to consumption of contaminated plants. Just as a mechanic cannot fix every problem with a wrench, phytoremediation should be considered as a valuable tool in practitioners' environmental toolbox. Remediation of aquatic systems is equivalent to an "ecological tag-team" of physical, chemical, and biological processes conducted in plants, sediment, and water.

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