Remediation Strategies for Mercury Contaminated Lakes and Reservoirs Within the State of California

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This Master’s Project

REMEDIATION STRATEGIES FOR MERCURY CONTAMINATED LAKES AND RESERVOIRS WITHIN THE STATE OF CALIFORNIA

by

Emily Chortek

is submitted in partial fulfillment of the requirements for the degree of:

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In

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Emily Chortek 

Date 

Gretchen Coffman, Ph. D. 

Date
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<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>Calcium Nitrate</td>
</tr>
<tr>
<td>CH$_3^-$</td>
<td>Methyl Group</td>
</tr>
<tr>
<td>CH$_3$Hg$^+$</td>
<td>Methylmercury</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Methane</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>Ferrous Iron</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>Ferric Iron</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>Hydrogen Sulfide</td>
</tr>
<tr>
<td>Hg$^0$</td>
<td>Elemental Mercury</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>Ionic Mercury</td>
</tr>
<tr>
<td>HgT</td>
<td>Total Mercury</td>
</tr>
<tr>
<td>HOS</td>
<td>Hypolimnetic Oxygenation</td>
</tr>
<tr>
<td>HS$^-$</td>
<td>Hydrogen Sulfide</td>
</tr>
<tr>
<td>MATS</td>
<td>Mercury and Air Toxics Standards</td>
</tr>
<tr>
<td>MeHg</td>
<td>Methylmercury</td>
</tr>
<tr>
<td>Mg/L</td>
<td>Milligram per liter</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>Manganese</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>Nitrate</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>Hydroxide</td>
</tr>
<tr>
<td>PPM</td>
<td>Parts per million</td>
</tr>
<tr>
<td>RCRA</td>
<td>Resource Conservation and Recovery Act</td>
</tr>
<tr>
<td>Redox</td>
<td>Reducing-Oxidizing</td>
</tr>
<tr>
<td>S$^{2-}$</td>
<td>Sulfide</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>Sulfate</td>
</tr>
<tr>
<td>SRB</td>
<td>Sulfate reducing bacteria</td>
</tr>
<tr>
<td>ug/g</td>
<td>Micrograms per gram</td>
</tr>
</tbody>
</table>
Abstract

Mercury is an environmental and public health concern due to its neurodegenerative effects and ubiquitous concentration within the environment. To mitigate these risks and reduce concentrations within the environment, remediation methods are necessary. The purpose of this paper is to investigate and evaluate the efficacy of a number of remediation options for mercury contaminated lakes and reservoirs in the State of California. This paper also identifies a number of challenges associated with the implementation of each method and provides recommendations for environmental managers to use when remediating mercury contaminated lakes. Hypolimnetic oxygenation (HOS) was found to be the least problematic remediation method and nitrate additions were found to be the most problematic. Remediation through dredging is only ideal for severely polluted sediments and can be cost prohibitive for many environmental managers. Phytoremediation is not an ideal method either due to lack of non-invasive mercury accumulating plants. Aqueous capping is a viable method, but only if the lake or reservoir is small in size. HOS is the least problematic remediation method investigated in this paper. HOS controls and prevents mercury from being methylated and entering the food web with the added benefit of increasing oxygen levels and cooling benthic temperatures. In order to decrease mercury deposition and mercury concentrations within California lakes, it is recommended that State and Federal legislation be passed to set mercury emission standards to reduce atmospheric deposition and emissions from coal fired power plants. In conjunction with legislative action, it is also recommended that both old and new coal fired power plants be fitted with advanced pollution control technologies to decrease mercury emissions in the United States. There is also the need to prioritize lakes for remediation efforts across the state due to limited environmental funding. Furthermore, it is also recommended to reduce risk of exposure in humans to eat fish lower on the food chain, or to eradicate animal proteins from their diet entirely.
Introduction

Mercury is a global pollutant and a neurotoxin that is both an environmental and public health concern. Increases in anthropogenic activity since the Industrial Revolution have increased the amount of mercury in the environment three-fold (Lamborg et al., 2014). Fossil fuel combustion, gold mining activities, and precious metal processing have released tremendous amounts of this element into the environment. Due to these activities in the State of California, exposures to mercury has increased in both wildlife and humans, causing neurodegenerative effects. In order to mitigate this issue, this research project posits a number of remediation techniques that may be able to alleviate the mercury pollution found in these freshwater lakes and reservoirs in the State of California.

Sources of Mercury

Mercury has both natural and anthropogenic sources. Natural sources of mercury exist in the Earth’s crust, volcanic eruptions, forest fires and emissions from the ocean (US EPA 2017). Global mercury emissions from both natural and anthropogenic sources are estimated to be between 2000 and 8000 metric tons annually, with the majority coming from anthropogenic sources (US EPA 2017) (USGS 2017). However, a disproportionate amount of anthropogenic activity contributes to global mercury emissions. The majority of these anthropogenic activities come from indirect sources. This includes: atmospheric emissions, surface deposition from industrial activities, like fossil fuel combustion, production of metals or coal burning for energy consumption (Michael et al. 2016) (US EPA 2017). Direct discharge of inorganic mercury also can come from mining practices, like chlor-alkali plants, or artisanal small-scale gold mining activities (ASGM) (Matthews et al. 2013).

Historic Mercury Pollution from Gold Mining Practices in California

Mining for precious metals, like gold, has contributed significantly to mercury pollution within California. While precious metal mining has generally ceased within the State, their effects upon the environment still remain. California is known for its’ rich history of gold mining, which has
led to one of the largest sources of direct mercury contamination to aquatic resources in California. Historically, mercury was used to increase the recovery of gold extraction. Miners would search for placer deposits, which are called alluvial or swath deposits, that are unconsolidated gravel that contains gold (Alpers et al. 2005). In order to extract the gold from these deposits, miners would spray water from high pressure hoses to break up these rock deposits into smaller pieces. Then, the slurry was funneled into a sluice where water and gravel would flow over the top of the screen, and gold pieces would fall through and be collected at the bottom. This extracted large pieces of gold, but was unsuccessful at collecting finer gold flakes. In order to increase gold recovery, hundreds of pounds of liquid mercury were added to the sluice and the mercury would bind to the gold, forming an amalgam. This solid was then collected and heated so the mercury would turn into vapor, leaving the solid gold behind (Gibb et al. 2014).

Unfortunately, this practice was extremely inefficient and mercury leached out into nearby soils, bedrock streams and mine tailings. Approximately 220 million pounds of mercury was produced in California from 1850 to 1981. From this total amount, mercury loss to the environment from hydraulic mining is estimated to be 10 million pounds (Alpers et al. 2005). On average, annual gold mining practices would lose approximately 25 percent of the mercury input into the system (Alpers et al. 2005). Today, hundreds of millions of pounds of mercury are still unaccounted for, and persist within aquatic systems throughout California.

**Mercury Speciation**

Mercury has many different species that partition into various areas of an ecosystem. (Table 1).

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical Formula</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgT</td>
<td>HgT</td>
<td>Total Mercury</td>
</tr>
<tr>
<td>Hg⁰</td>
<td>Hg(0)</td>
<td>Elemental Mercury</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>Hg(II)</td>
<td>Ionic Mercury</td>
</tr>
<tr>
<td>CH₃Hg⁺</td>
<td>MeHg⁺</td>
<td>Methylmercury</td>
</tr>
<tr>
<td>CH₃⁻</td>
<td>CH₃⁻</td>
<td>Methyl Group</td>
</tr>
</tbody>
</table>

Table 1. Mercury species found in the environment (Lamborg et al. 2014)
Each mercury species is considered an environmental pollutant, with organic mercury arguably the most damaging to the environment and biota. Total mercury, or HgT, is commonly used to describe all mercury species within a system. Hg\(^0\) is another species commonly known as elemental mercury (Center for Disease Control 2016). Elemental mercury exists as a liquid metal at room temperature. Elemental mercury can be found in dental amalgams, lightbulbs, and old thermometers (Fitzgerald and Lamborg 2007; Matthews et al. 2013). In the environment, elemental mercury exists in a gaseous form, where it has a long residence time, and globally transported (Fitzgerald and Lamborg 2007). Chronic, low-dose inhalation exposure can cause neurological damage, memory problems, and in high concentrations damage human lungs (CDC 2016).

Hg\(^{2+}\) is another form of mercury, commonly called ionic mercury. This is an inorganic form and is the most common species found in the environment (Lamborg et al. 2014). Often it complexes to other ions, forming a compound, like mercury chloride or mercury sulfide (Selin 2009) (Center for Disease Control 2016). These compounds can sometimes be found naturally or used in industrial processes.

Finally, there is the organic molecule CH\(_3\)Hg\(^+\), which is monomethylmercury, often shortened to methylmercury (MeHg\(^+\)). This species of mercury is arguably the most dangerous and potentially has the most significant adverse health effects of all mercury species. Methylmercury is a mercury atom that is bonds to a methyl group. Organic mercury compounds are formed when mercury bonds with carbon, or a carbon based chemical group. A methyl group consists of a carbon atom connected to three hydrogen atoms (CH\(_3\)) (Ullrich 2007). Methylmercury has the ability to bioaccumulate and biomagnify within food webs causing neurodegenerative effects in wildlife and humans when ingested over time (Bank et al. 2012).

**Mercury Cycling in Freshwater Systems**

Elemental mercury is emitted into the atmosphere from fossil fuel combustion or natural sources such as forest fires or volcanic eruptions. In the atmosphere, it can oxidize through a number of chemical reactions into ionic mercury (Krabbenhof and Rickert 2016). Once in its ionic form, it falls to the earth via wet or dry deposition (Selin 2009). It can either fall directly into a body of water, or land on terra firma and then washed into an aquatic system via runoff. Once ionic
mercury enters a body of water, it has three general transformation pathways (Figure 1). It can be reduced back into elemental mercury, and volatilize back into the atmosphere as a gas. The second pathway is its adsorption to sediments which collect at the bottom of lakes, rivers or reservoirs. Finally, ionic mercury can be methylated by sulfate reducing bacteria and converted into methylmercury (Fitzgerald and Lamborg 2007).

![AQUATIC MERCURY CYCLE](image)

Figure 1. Mercury Cycle in Aquatic Systems (Krabbenhoft and Rickert, 2016)

In order for methylmercury to be formed, certain conditions must be met. Sulfate or iron reducing bacteria that thrive in anaerobic or sub-oxic conditions must be present (Strickman and Mitchell 2017). Anaerobic conditions are commonly found at the bottom of a body of water, near the sediment-water interface. In addition to an oxygen poor environment, high levels of dissolved organic carbon, relatively warm temperatures and low pH levels are required for these microbes to metabolize mercury (Strickman and Mitchell 2017). Once the ionic mercury is
methylated, methylmercury can be ingested by phytoplankton and biomagnify up the food chain and throughout the aquatic food web (Bank et al. 2012).

Mercury transformations in aquatic systems go in both directions. Any of these processes can be reversed, given the right conditions. Thus, there may be multiple forms of mercury in one aquatic system at any given time.

**Why is Methylmercury an Environmental and Public Health Concern?**

Methylmercury exposure is an environmental concern and public health concern because it has the ability to bioaccumulate and biomagnify up the food chain (Bareket et al. 2016). Bioaccumulation is the process when an organism uptakes a toxin faster than it can be removed from the body; while biomagnification is the increase in concentration of a toxin with an increase in trophic level. Methylmercury enters the food web via direct uptake from phytoplankton in aquatic ecosystems. The methylmercury makes its way up the food chain to zooplankton, small fish, and then larger fish, resulting in fish tissue concentrations that are estimated to be $10^6$ times higher than surrounding water concentrations (Selin 2009; Matthews et al. 2013; Bareket et al. 2016). Tertiary predators in aquatic ecosystems, humans included, are at greatest risk for exposure and most likely to experience negative effects from methylmercury due to its biomagnification (Matulik et al. 2017). Ergo, the main exposure route of methylmercury in people is through consumption of fish high in mercury levels. Globally over 1.5 billion people consume seafood as their main source of animal protein (Driscoll et al. 2013). Pregnant women and children have higher risk of exposure because methylmercury can cross the blood-brain and placental barriers. This can cause developmental and neurological defects in fetuses and young children (Selin 2009; Hinwood et al. 2013).

Aside from women of child bearing age and infants, adult males are also potentially at risk for methylmercury exposure. Recent epidemiological studies surmise that consumption of contaminated seafood in adult males leads to an increased risk of cardiovascular disease (Selin 2009; Driscoll et al. 2013). Cardiovascular disease is one of the leading causes for mortality in developed countries (Driscoll et al. 2013). However, further research is necessary to bolster this finding.
Other disproportionately exposed groups include immigrant communities, indigenous peoples and recreational anglers. Immigrant communities may eat their own catch it its entirety, including tissues or organs other than just the fillets, thereby increasing their exposure to methylmercury (Driscoll et al. 2013). Indigenous peoples may depend more heavily on subsistence fishing and a more restricted diet either due to cultural practices or lack of economic means to afford other foods (Driscoll et al. 2013). While recreational anglers often enjoy eating what they can catch, even if they are not economically disadvantaged. California has a culturally and economically diverse populace, with millions of people potentially at risk for methylmercury exposure.

Not only is methylmercury a public health concern, it is also an environmental pollutant that has deleterious effects on wildlife, especially piscivorous fish. Sub-lethal and lethal effects occur at concentrations between 5-10 μg/g (wet weight) of methylmercury. However, even levels as low as 0.3 μg/g in the entire body of a fish demonstrate negative effects (Driscoll et al. 2013; Scheuhammer et al. 2015). Increased MeHg concentrations in the tissues of fish can compromise reproduction of pregnant females, retard embryonic development, alter biochemical processes and damage tissues or cells within the bodies of fish (Selin 2009; Lamborg et al. 2014; Cheng et al. 2016). The health of fisheries and aquatic ecosystems are threatened by mercury exposure at environmentally relevant concentrations.

**Research Objectives:**

This paper has a number of research objectives. The first objective is to determine available remediation techniques to reduce mercury, and methylmercury pollution within freshwater lakes and reservoirs within the State of California. I evaluated these techniques for their efficacy at controlling or removing mercury from a freshwater system. Finally, this paper aims to determine the challenges environmental managers and policy makers will need to overcome in order to reduce mercury pollution within lakes and reservoirs in the State of California. In addition to these objectives, I developed recommendations from the literature to control mercury in the future, both locally and globally.
Methods

In order to achieve my research objectives, I conducted a literature review. I focused my literature review on scientifically peer reviewed journal articles, government reports, and book chapters. I investigated remediation strategies for mercury-contaminated sediments, specifically in lakes and drinking water reservoirs within the State of California. I also evaluated and compared remediation strategies and their potentially efficacy to either prevent, or remove mercury from aquatic systems. In addition to my primary literature review, I developed management strategies and recommendations related to prevention and removal of methylmercury from aquatic resources in California.

The following criteria are used to analyze each remediation method:

1. Type of Treatment
2. Cost (If applicable)
3. Level of Contamination
4. Time Scale to Decontamination/Mercury Control
5. Appropriate for California
6. Advantages
7. Disadvantages

In Situ Aeration and Oxygenation

Lake Stratification

In order for methylation of mercury to occur, anaerobic conditions must be present. In both the summer and winter seasons, lakes and reservoirs are stratified by temperature, creating distinct layers. This stratification allows for oxygen to diffuse into the top layers of a lake, but oxygen cannot diffuse into the bottom of a lake. In situ aeration and oxygenation is a remediation method to deliver oxygen to the bottom of lakes or reservoirs to prevent the methylation of mercury by sulfate reducing bacteria.

In both the summer and winter months, lakes and reservoirs on the West Coast of the United States will stratify into distinct layers, with summer lake stratification the most
pronounced, assuming no strong winds are present. Warm air temperatures heat the surface of the lake, and prevent the warm water from sinking and mixing with deeper layers. The stratification of a lake however, depends on its depth, size and shape. Deeper lakes will show clear separation of layers and small lakes may never stratify due to warm temperatures throughout and constant wind movement.

There are three common layers within lakes and reservoirs: epilimnion, metalimnion, and hypolimnion (Figure 2, Queensland Government 2017). The epilimnion is the top layer of a lake that is influenced by solar radiation and wind. This layer is relatively warm due to the proximity to solar radiation and therefore a lower density than deeper, colder water, causing it to remain on the surface. The middle layer is called the metalimnion with a rapid change in temperature. This layer divides the epilimnion and hypolimnion and contains the thermocline. In the summer months, the thermocline acts like a barrier and prevents the two layers from mixing by wind action. The deepest layer is the hypolimnion. This layer is cold, dense, dark and usually undisturbed, relative to the other two layers.

![Diagram of stratification of lake zones](image)

Figure 2. Stratification of Lake Zones (Queensland Government 2017)

A lake can also be classified distribution and its assemblage of biota, not only changes in temperature. The near shore section of a lake is the littoral zone, which is shallow and light can easily penetrate the bottom sediments (Figure 3, Illinois EPA 2017). Vegetation is abundant in this zone. The limnetic zone is an area of open, offshore water, next to the littoral zone. This zone is exposed to sunlight near the surface resulting in a high abundance of phytoplankton. The
profundal zone is the deepest zone with little to no biological activity, or access to light. Many sportfish species, like bass or perch live here (Whittier et al. 2001). Aquatic sediments that comprise the bottom of a lake or reservoirs are often called the benthic zone. Bottom dwelling organisms, like small crustaceans, mollusks and invertebrates reside here (Whittier et al. 2001). Often this layer has minimal plant life, due to the lack of sunlight.

Figure 3. Biological stratification of lake layers (Illinois Environmental Protection Agency 2017)

**Oxygen Availability in Lakes and Reservoirs**

Oxygen concentrations within a lake are varied. This is due to the ability of gaseous oxygen to reach each distinct layer. Oxygen usually enters lakes in three ways, through atmospheric diffusion, photosynthetic action of plants and from inflow of streams depositing oxygen into the lake. The epilimnion has an abundance of oxygen from atmospheric diffusion, but the hypolimnion does not. The metalimnion acts like a barrier, preventing oxygen from diffusing into the hypolimnion. Since the hypolimnion is relatively deep, little solar radiation reaches this layer and oxygen production of photosynthesis does not occur. Any oxygen that reaches the hypolimnion is consumed by anaerobic bacteria and other microbes in the benthos until no oxygen remains.

High oxygen levels in lakes are imperative for the survival of cold water fish species and the prevention of eutrophication. Oxygen found in minimal levels (<2 mg/L) in a lake can be considered hypoxic, and depleted oxygen levels (0 mg/L) are considered anoxic (Beutel et al. 2017).
2014; McCord et al. 2016). The lack of oxygen in the hypolimnion creates conditions conducive for anaerobic, and sulfate reducing bacteria to convert inorganic mercury into methylmercury. The hypolimnion must be oxygenated to inhibit methylmercury production as will be discussed in the next section.

*What is Hypolimnetic Oxygenation?*

Hypolimnetic oxygenation (HOS) is an *in-situ* remediation method that increases oxygen levels found within the hypolimnion of lakes and reservoirs. Implementing this method increases dissolved oxygen (DO) levels in order to decrease methylmercury production in the hypolimnion and hopefully lower methylmercury bioaccumulation in fish. The process of HOS requires anoxic ambient water to be collected into a device, mixed with gaseous oxygen or ambient air, and then released back into the hypolimnion. HOS systems are often designed to meet the specific oxygen needs of the biota in each lake, however targeted DO levels are approximately 5 mg/L (McCord et al., 2016). HOS systems come in a variety of configurations, which can be suspended within the hypolimnion, or rest on the bottom of the lake at the sediment water interface (Beutel and Horne, 1999).

*How Does Hypolimnetic Oxygenation Inhibit Methylmercury Production?*

Oxygenation of benthic sediments and the hypolimnion may prevent the production of methylmercury through a variety of mechanisms. Sulfate reducing bacteria reduce sulfate (SO$_4^{2-}$) during their metabolic processes of breaking down carbon. This activity converts sulfate into sulfide (S$^{2-}$). Sulfate reducing bacteria (SRB) do not thrive in oxygenated waters. Therefore, the more oxygenated the water is, the fewer SRB’s present. The methylation zone moves deeper into benthic sediments where the hypolimnion is oxygenated and makes it difficult for methylmercury to diffuse upwards and become bioavailable. If conversion of methylmercury is reduced or prevented, less of it will enter the food web and become a threat to tertiary biota and people. Oxic conditions promote the growth of aerobic bacteria that do not rely on the uptake of mercury or methylation of mercury as part of their biological processes.
Hypolimnetic Oxygenation Devices and Systems

Multiple types of HOS systems exist, the most common of which are either aeration or oxygenation. Examples of these systems include: airlift aerators, speece cones, and bubble plume diffusers. Airlift aerator systems pipe in ambient air or oxygen gas and expose it to lake water in a contact chamber (Figure 4 Chowdhury et al. 2014). Compressed air is pumped into the bottom of a vertical contact chamber, where it is mixed with hypolimnetic waters. Due to its positive buoyancy, the mixture rises through the contact chamber allowing air to diffuse into the water. In the separator box, the air can be off gassed and released into the atmosphere, while the newly aerated water is piped back down past the thermocline and deposited into the hypolimnion (Singleton and Little 2006).

Figure 4. Simplified image of an airlift aerator (Chowdhury et al. 2014)

Another effective oxygenation method is to use a speece cone, originally known as a submerged down flow bubble contactor. This system consists of a conical holding tank, oxygen gas input, source of water and a diffuser, which releases oxygenated water into the hypolimnion (Singleton and Little 2006). Water is sucked into the device through an intake valve where it is pumped into the top of the cone. Here oxygen gas is pumped in and introduced at the neck of the
cone (Figure 5, Chortek 2017). The down flow of the water is stronger than that of the positively buoyant oxygen gas, preventing any gas from escaping and forcing mixing to occur. As the water flows down the sides of the cone, the flow rate slows, and the oxygen bubbles get smaller until they are fully diffused into the water. The oxygenated water is then released at the bottom of the cone through a diffuser back into the hypolimnion (Singleton and Little 2006).

![Diagram of conceptual speece cone](image)

Figure 5. Drawing of conceptual speece cone (Chortek 2017)

Bubble plume diffusers can also be used to oxygenate the hypolimnion. Bubble plume diffusers consists of tubing with small holes where gas can escape into surrounding waters (Figure 6, Singleton and Little 2006). Bubble plume diffusers can either be circular or linear and can use either ambient air or oxygen gas. Gas flows slowly through the bubble plume diffusers and are ideal for deep lakes where the majority of bubbles will dissolve in the hypolimnion. This method does not disrupt the thermocline because the oxygenated water will float up until it is neutrally buoyant in the hypolimnion, and then flow horizontally outwards (Singleton and Little 2006). Disruption of the thermocline is possible with the other two devices (speece cone and airlift aerator) if managed improperly.
Biological and Chemical Benefits of Maintaining an Aerobic Hypolimnion

The most favorable outcome of increasing oxygen within the hypolimnion is the fact that higher DO levels ($\geq 5$ mg/L) will limit the amount of mercury released into the reservoir. Oxic conditions do not favor the growth of sulfate-reducing bacteria. This means that other genera of bacteria, like denitrifying bacteria, will be dominant during these conditions. They do not methylate mercury as part of their biological processes.

There are a variety of biological and chemical benefits to maintaining an aerobic hypolimnion. Oxygenating the hypolimnion keeps all lake layers separated, and helps the profundal zone to remain cold. Keeping the hypolimnion layer cool provides necessary habitat for sportfish, like bass, and is also essential for other downstream biota, especially in the warm summer months. The cool profundal zone provides a refuge for zooplankton during the day in order to avoid predation (Beutel and Horne 1999).

In addition to biological benefits, maintaining an oxic hypolimnion also prevents the release of problematic chemical compounds that are usually adsorbed by sediments. Compounds can include iron ($Fe^{2+}$), manganese ($Mn^{2+}$), and sulfide ($S^{2-}$). These chemicals degrade the aesthetic quality and taste of drinking water. They also play a role in the methylation and release of mercury in an aquatic system (Beutel and Horne 1999). Maintaining an oxygenated hypolimnion also keeps iron and manganese oxides within surface sediments, slowing and sometimes preventing upward diffusion of methylmercury. These act as a sorption barrier to
upwardly diffusing methylmercury within benthic sediments (McCord et al. 2016). Most mercury is methylated within the upper most 10 centimeters of sediment, sometimes even within the top 3 centimeters (Ndungu et al 2016). A combination of an oxygenated hypolimnion and presence of iron and manganese ions further prevents methylmercury from entering ambient waters. The presence of iron and manganese and their compounds, in aquatic sediments may cause methylmercury to bind to these metals instead of being released into ambient waters.

Maintaining oxic conditions helps decrease the occurrence of eutrophication and decreases the release of ortho-P and ammonia from microorganisms. Orthophosphate (Ortho-P) and ammonia are unfavorable compounds that can be released during anoxic lake conditions (Beutel and Horne 1999). Ortho-P is a species of phosphate that is reactive within environmental systems, and when released can cause eutrophication since phosphorous is a limiting nutrient in California.

It is important to maintain oxic conditions in order to avoid this problem and avoid methylmercury conversion. Too much sulfide residing in hypolimnetic waters is problematic. During fall turnover, when lake layers completely mix, sulfide that was stored in the bottom of the lake is brought to the surface and the water column temperature mixes and becomes homogenous. This frees up the sulfide and hydrogen in the water and forms hydrogen sulfide (H₂S) due to the lack of oxygen and abundance of hydrogen. Hydrogen sulfide is a toxic gas that can cause fish kills. At moderate levels, sulfide can enhance the bioavailability of ionic mercury for methylation (McCord et al. 2016). Reducing sulfide concentrations in reservoirs will decrease mercury’s bioavailability which in turn will reduce the amount of mercury phytoplankton uptake and decrease the amount of mercury entering into the food web.

Benefits of Implementing Hypolimnnetic Oxygenation

Hypolimnetic oxygenation has been an effective method to control the release of methylmercury within four lakes in the Guadalupe River Watershed, San Jose. The four lakes are: Stevens Creek Reservoir, Guadalupe Reservoir, Calero Reservoir and Almaden Reservoir. The Guadalupe River Watershed is a complex hydrologic system that is contaminated by the New Almaden mercury mine, the largest mercury producer in North America (McCord et al. 2016). The installation and use of an HOS system in these lakes is to reduce hypolimnetic methylmercury
concentrations and thereby reduce mercury concentrations in biota. HOS systems delivered 5 mg/L of pure oxygen gas to the hypolimnion during the summer months of operation. With this system in place, Calero Reservoir mercury levels decreased to 1.5 ng/L (McCord et al. 2016). Results for the three other lakes are still being calculated.

Implementing HOS systems into a mercury contaminated lake yields some energy and monetary benefits. HOS systems are run during spring and summer months, when thermal stratification is most pronounced. During the cooler winter months, mercury methylation is not as prolific and lakes are not as biologically active. This means that HOS devices do not need to be run year-round, only 6-8 months out of the year. Thus, decreasing energy requirements, decreasing costs and potential emissions from energy use are all benefits of HOS installation.

The efficiency of an HOS system can be increased by substituting compressed air for pure oxygen gas. By using pure oxygen gas, rather than ambient air, profundal waters are better oxygenated. Injections of pure oxygen gas can deliver 60-80% more dissolved oxygen than ambient air (Beutel and Horne 1999) (Ashley et al. 2014). By using pure oxygen gas, rather than ambient air, profundal waters are better oxygenated. Using ambient air, which is comprised of about 70% nitrogen, may cause bottom waters to be supersaturated with nitrogen gas and further exacerbate anoxic conditions (Beutel and Horne 1999).

**Challenges of Implementing Hypolimnetic Oxygenation**

There are a number of challenges that need to be overcome when implementing hypolimnetic oxygenation systems in anoxic lakes and reservoirs, including timing and initial oxygen levels. HOS systems are designed to meet oxygen demand, not overcome a deficit. Thus, it is imperative that HOS systems are initiated before hypoxic conditions set in. HOS systems are designed to deliver a set amount of oxygen and keep ambient waters at a particular level, not to overcome excess biological or chemical oxygen demand within a reservoir (McCord et al. 2016). Ideally, these systems would be installed and running in the spring, but no later than the beginning of summer when thermal stratification begins and oxygen levels at the profundal zone begin to decline.

Ideally, HOS systems should be installed in the benthic zone or on the sediment-water interface. Installing HOS devices in the profundal zone allows for small hypoxic gaps to develop, even if the rest of the hypolimnion is well mixed due to the upward lift of bubble plumes.
Lateral diffusion should also be incorporated into future HOS designs of aeration devices, in order to minimize potential hypoxic gaps and areas for further mercury methylolation.

Another challenge with HOS is the potential for increased turbulence between lake layers. Excess turbulence and destratification of layers potentially releases methylmercury from the hypolimnion into the epilimnion, allowing it to become bioavailable. There should be a balance between oxygen delivery and induced turbulence. A high flow of gas, and higher rate of diffusion from an HOS device increases oxygen levels within the hypolimnion. This increased flow rate also increases turbulence between the hypolimnion and the rest of the layers in the lake (McCord et al. 2016). Too much turbulence may erode the thermocline mixing all layers within the lake. This mixing increase temperatures throughout the lake and may release mercury into upper layers of the lake where it is more accessible to biota. High diffusion rates may increase oxygen levels in the reservoir, but increase mercury exposure in biota, rendering this technique ineffective at mitigation of both aqueous mercury concentrations and mercury uptake in phytoplankton.

In Situ Aqueous Capping

Contaminated sediments can be immobilized and isolated via in situ aqueous capping (Figure 7 Chortek 2017; Randall and Chattopadhyay 2013). Capping is a well-tested method and can be an effective remediation option. Contaminants are covered from ambient waters by the cap, thereby decreasing the risk of release into upper waters. An aqueous cap provides a complete seal between the aquatic environment and contaminated sediment. A chemically active cap also provides sorption or chemical isolation of dissolved metals, like activated carbon (Randall and Chattopadhyay 2013). Physical, and sometimes chemically reactive barriers are placed on a site to contain contaminated soils in place (EPA 2017). Physical barriers prevent the movement of benthic organisms, namely invertebrates, and prevent predators from consuming these contaminated organisms, thereby preventing bioaccumulation of mercury in the food chain (Cassidy et al. 2002). Both chemical and physical caps can stabilize the benthic sediments and prevent erosion. Barriers that are used can be natural or man-made and they can be comprised of sand, gravel, clean sediment or man-made layers, like geotextiles (EPA 2017). Geotextiles are
permeable material used for soil stability commonly made from polypropylene or polyester (Mizkowska et al. 2017). They are included in caps to make them more effective.

![Diagram of in situ aqueous cap](財富.png)

Figure 7. Drawing of an in situ aqueous cap (Chortek 2017)

To evaluate the effectiveness of a physical cap and biointrusion prevention, researchers from Western Michigan University conducted a number of experiments in 2002 in the Great Lakes Drainage Basin. An in situ aqueous cap was placed in Gull Creek, Michigan, in order to control the bioaccumulation of mercury by stopping biointrusion and erosion (Cassidy et al. 2002). This method prevents the vertical movement of benthic organisms, and prevents fish from feeding in contaminated sediments, thereby decreasing erosion and bioaccumulation of mercury. A geotextile layer was placed on top of contaminated sediments with an additional 3 cm of sand and pea gravel to hold the cap in place (Cassidy et al. 2002). At the end of the seven-month experiment, approximately $4.26 \pm 2.47\%$ of benthic organisms were able to pass through the cap, demonstrating a successful means to control biointrusion and mercury bioaccumulation via aqueous capping (Cassidy et al. 2002).

**Benefits of Implementing In-Situ Aqueous Capping**

If the remediation site is small and shallow in depth, aqueous capping is much more cost effective than in situ dredging and disposal. In addition, in situ aqueous capping also has the added benefit of low environmental impacts. This method causes minimal disturbance to existing ecosystems, minimizes transport of contaminated sediments and lowers the risk of resuspension of contaminated sediments (Wang et al. 2004). Capping stabilizes sediment, decreases erosion
and transport of contaminated sediment and is most effective when movement of hydrologic flows are minimal (EPA 2017). In-situ aqueous capping would be ideal for a lake or reservoir that has minimal disturbances from human activities and low winds.

Capping and its materials, have the added benefit of passively sorbing other problematic heavy metals, besides mercury. Contaminated sites often have concentrations of heavy metals including but not limited to: lead, chromium, arsenic, zinc, cadmium and copper (Wuana & Okieimen 2011). Depending on the materials the cap is comprised of, heavy metals can be stabilized and removed from surrounding water. Common capping materials include clean sediment, clay, cement and zeolites (Wuana & Okieimen 2011). Each material used has a different immobilization mechanism, whether that is chemical adsorption, precipitation or formation of more stable complexes which prevent heavy metals from being released from beneath the cap.

Challenges to Implementing In-Situ Aqueous Capping

The main challenge of in situ aqueous capping is that it does not remove mercury species from the contaminated site. It is designed to isolate and immobilize mercury from coming into contact with ambient water and biota, not remove it from a system. Capping may reduce the amount of mercury that is available for uptake, but it does not remove mercury from an aquatic system.

The in situ aqueous capping method is appropriate for sites with low hydrodynamic flows, like lakes, reservoirs and bays (Wang et al. 2004). Sites with strong groundwater flow, tides, storms, wind, shipping etc. may scour the cap and rerelease the contaminated sediment (Wang et al. 2014) (Randall and Chattopadhyay 2013). Proper evaluation of environmental factors is critical before installing a cap, to insure the cap will be effective. Even with ideal site conditions and the ability to sorb additional problematic heavy metals, ongoing monitoring of in situ aqueous caps is necessary. This is to ensure the remediation activities are effective and further action is not needed.

One big drawback to in situ aqueous capping is that mercury may continue to be methylated under the cap if organic matter is available. Methylation occurs mostly in the upper 15 centimeters of benthic sediments. To be highly effective, the cap should be greater than 10 centimeters. This can physically prevent mercury from passing through the cap and potentially
allow methylmercury to sorb to materials within the cap, further preventing it from reaching ambient waters (Randall and Chattopadhyay 2013; Ndungu et al. 2016). High organic matter content in the cap can also provide conditions ideal for SRBs (Ndungu et al. 2016). To avoid this, the in-situ cap should be comprised of low organic matter to decrease the potential of methylmercury formation (Ngungu et al. 2016).

In addition to low organic content, the cap must be sufficiently thick and include sorptive materials. Puncturing of a cap is only an issue if the cap itself is thin. Caps can be compromised by hydrological flow or biologic activity. Benthic organisms also create holes in the cap due to their activities (Wang et al. 2014). Therefore, it is important to make sure the cap is sufficiently thick and includes sorptive materials to minimize the amount of mercury that may be released into the ambient water. Geotextiles with activated carbon in them are an ideal choice for capping due to their ability to sorb mercury to these materials (Ndungu et al. 2010).

In-situ aqueous caps may not be an effective remediation method in all cases. The cost to place an in-situ cap can be very expensive for large scale sites (greater than 1000 acres). Installation itself can cost $25/m². This does not include the cost of the materials themselves (Randall and Chattopadhyay 2013). Total capping costs on average are estimated to be $600,000 (Henry 2000).

**In Situ Dredging**

Dredging is an in-situ remediation method that removes contaminated sediments from a site. There are two types of dredging: mechanical and hydraulic. Mechanical dredging is the removal of sediment by scooping or digging with a clamshell bucket (Figure 7; Randall and Chattopadhyay 2013; EPA 2017). This method is ideal for sediments that are hard, dense, or clay like. Hydraulic dredging is the removal of a liquid slurry that is comprised of a mixture of water and sediment (EPA 2017). This method is ideal for sediments comprised of finely grained materials. The slurry is suctioned up and out of the site. Once on land, the water has to be removed from the collected sediments, also called dewatering. If contaminated, the water must be treated and then the disposed sediments are transported off site and then either decontaminated or buried.
Benefits Associated with In Situ Dredging

One of the greatest advantages of dredging compared to the other remediation methods is that it can remediate large amounts of contaminated sediments. Dredging might be ideal for contaminated sites that are large in size, or have high concentrations of a contaminant (Wang et
al. 2014). A site in Minamata Bay, Japan, used dredging as a remediation technique successfully. Inorganic and methylmercury were released directly into Minamata Bay as byproduct from the production of acetaldehyde from 1932 to 1968 in a nearby chlor-alkali plant (Akito et al. 2014). What ensued in years after were severe cases of mercury poisoning, and eventual diagnosis of Minamata disease in the mid 1950s due to the consumption of contaminated seafood. To minimize the risk of exposure to mercury, Minamata Bay and its bottom sediments were hydraulically dredged from 1977-1990. Mercury sediment concentrations ranged from 0.04 ppm to 553 ppm before dredging began (Akito et al. 2014). After dredging was completed, average mercury sediment concentrations were estimated to be 0.06-16 ppm (Akito et al. 2014). In this case, dredging was an effective way to quickly remove severely contaminated sediments and drastically improve both sediment and water quality within Minamata Bay. Dredging contaminated sediments within California lakes or reservoirs would be ideal if there is evidence of very high mercury concentrations, or if a large number of subsistence fishing populations were at risk of exposure.

There are also a number of other benefits associated with hydraulic and mechanical dredging. Hydraulic dredging is ideal for narrow water bodies and can be used in shallow waters ($\leq 9$ m), making this method versatile and can increase accessibility to contaminated sites (Ragnarsson et al. 2015). It also has the added benefit of easily removing sand, silt and fine pore sediments, which are often found as benthic media in lakes. In contrast to the removal of fine grain sediments, mechanical dredging is ideal to remove rocky or coarse debris from lakes (Randall and Chattopadhyay 2013). In addition to easy removal of sediments, hydraulic dredging is also less likely to suspend contaminated sediments. The strong pump and hose mechanisms act like a vacuum, efficiently removing sediments from the lake bottom. Both dredging methods are efficient at removing unwanted contaminated sediments from freshwater systems.

**Challenges Associated with In Situ Dredging**

The in-situ dredging poses many challenges as a remediation method for mercury. It is expensive and the disposal process can take a long time. Disposal sites may leak and release the contaminant, trading one cleanup site for another. This method removes contaminated sediment, cleans up one site, and then raises the issue of where to dispose or contain contaminated
sediments once removed. There is also the potential for leakage and contamination of the storage site if proper precautions are not taken.

There is also a high risk for resuspension of sediments when sediment is being dredged. Dredging causes high disturbances to the aquatic environment. This could release mercury in the upper layers of a lake, exposing biota to methylmercury. Mercury could be transported downstream through outlet streams or enter into groundwater (Want et al. 2004). Dredging activities should be slow to minimize the disturbance of sediment. If dredging activities are not slow, this remediation strategy may increase turbidity of the water, which can inhibit photosynthetic activity of plants and increase water temperatures if severe enough.

Dredging can also cause oxidation of anoxic sediments, releasing contaminants that were sorbed to sediments (Wang et al. 2014). This temporarily increases conditions that cause the release of sulfate and organic matter, which favors methylmercury production (Wang et al. 2014). Therefore, dredging activities should be monitored both during active dredging, and post dredging to prevent the release of problematic compounds.

Both mechanical and hydraulic dredging can be an expensive method of mercury remediation, as specialized equipment is required for both types of dredging operations (Wang et al. 2014). Mechanical dredging requires a trained operator, clamshell bucket and arm, and barge or platform for the machine to sit on while it is excavating sediments. Hydraulic dredging also requires a trained operator, suction arm to uptake sediments, pump and tubing to carry sediments to the dewatering site.

In addition to equipment costs, physical transport and removal of sediments can be costly. Excavation of sediments can cost up to $1409/m³ (Wang et al. 2014). This can be costly if there is a large volume to remove and clean. After dredging a site, future monitoring is necessary to verify an acceptable amount of the contaminant has been removed. Monitoring, while necessary, adds an additional cost to an already expensive project. In situ dredging removes mercury that is deposited via atmospheric deposition or point source pollution. It does not reduce the sources of atmospheric mercury and its exorbitant cost makes this remediation method cost-prohibitive if dealing with low contamination, or small-scale sites.
Phytoremediation

Phytoremediation is a method that uses plants to uptake heavy metals, like mercury, to reduce contamination of ecological sites (Henry 2000). Phytoremediation permanently removes mercury from the surrounding environment and stores it in adjacent plant biomass. Ideally, the plant species used would extract high concentrations of heavy metals into their roots and produce a large quantity of plant biomass (Henry 2000). The plant species used must have the ability to tolerate high levels of mercury in their system. The efficacy of this treatment method depends on the concentration of the contaminant, contaminant species of mercury, the dispersal of mercury within the environment and timeframe for a site to be cleaned up.

A pilot scale laboratory experiment conducted by Marrugo-Negrete et al. (2017) demonstrated the effectiveness of using yellow velvetleaf (*Limnocharis flava*) as a cost effective and easy way to remediate gold mine effluent and mercury contaminated water and sediments. Over a thirty-test day period it was recorded that the removal rate of mercury was based on exposure time. The longer the plants were exposed to contaminated media, the more mercury was removed, with up to 90% of the mercury present sequestered in the plant biomass (Marrugo-Negrete et al. 2017). The results from this study are indicative of the yellow velvet leaf as a mercury accumulator and species capable of remediation mercury contaminated water and sediments.

Benefits of Implementing Phytoremediation

There are a number of benefits to implementing in situ phytoremediation as a way to control the release of mercury in the environment. One major advantage to implementing phytoremediation is that it is a non-invasive strategy like nitrate additions or HOS. Unlike capping or dredging, phytoremediation does not cause sediment resuspension or disturbance of contaminated soils. This further minimizes the risk of mercury release into the water column, and subsequent uptake into phytoplankton and bioaccumulation. Sites that are ideal for phytoremediation include ecologically sensitive sites, with low mercury concentrations.

Phytoremediation is an easy method to implement. It does not require specialized heavy equipment or personnel, unlike capping or dredging activities. The average citizen is capable of
planting or transplanting the appropriate species on the site, however they must wear personal protective gear.

This ease of implementation also translates into a reduced cost compared to capping, dredging and off-site storage. One acre of contaminated sandy loam, (50 cm in depth) is estimated to cost between $60,000 and $100,000 to treat with phytoremediation versus $400,000 to dredge and dispose of the same quantity (Henry 2000). In addition to reduced monetary costs, in situ phytoremediation also decreases the amount of waste that has to be disposed of at hazardous waste landfills by ninety five percent (Henry 2000). This significantly reduces the cost of a phytoremediation project, especially since mercury contaminated soils are considered hazardous waste by RCRA (Henry 2000).

In situ phytoremediation may help sequester other heavy metals or problematic contaminants. This method can be used for a number of chemical compounds, including but not limited to chlorinated solvents, pesticides, cadmium, lead and chromium (Table 3 Henry 2000). *Juncus maritimus*, commonly known as a sea rush, has a high capacity to uptake mercury in sediments (Randall and Chattopadhyay 2013). More research is needed to see if multiple compounds can be sequestered by these species, and how quickly sequestration occurs.

Table 2. Chemical compounds that are amenable to phytoremediation (Henry 2000)

<table>
<thead>
<tr>
<th>Organics</th>
<th>Inorganics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorinated Solvents</td>
<td>Metals</td>
</tr>
<tr>
<td>TCE, PCE, MTBE, carbon, tetrachloride</td>
<td>B, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn</td>
</tr>
<tr>
<td>Explosives</td>
<td>Radionuclides</td>
</tr>
<tr>
<td>TNT, DNT, RDX, and other nitroaromatics</td>
<td>Cs, ³⁹H, Sr, U</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Others</td>
</tr>
<tr>
<td>atrazine, bentazon, and other chlorinated and nitroaromatic chemicals</td>
<td>As, Na, NO₃, NH₄, PO₄, perchlorate (ClO₄⁻)</td>
</tr>
<tr>
<td>Wood Preserving Chemicals</td>
<td></td>
</tr>
<tr>
<td>PCP and other PAH’s</td>
<td></td>
</tr>
</tbody>
</table>
Challenges of Implementing Phytoremediation

Phytoremediation has some serious challenges that must be overcome when considering this method for the decontamination of mercury. Phytoremediation is a slow process and can take years or decades to effectively remove mercury contamination from lakes. Furthermore, there are a limited number of plant species that can tolerate the uptake of mercury, like *Juncus maritimus* or hyacinth species, many of which are invasive (Skinner et al. 2007). More research is necessary to identify a larger number of plant species that tolerate mercury uptake, native to the region of California and that uptake mercury quickly.

There may be unintended consequences of the plant species affecting local biodiversity. Not all contaminated sites are suitable for the plants used in phytoremediation. The introduction of non-native or invasive plants may unfavorably alter local ecological community structure and food webs. There is also the concern that non-native plants may not have the appropriate adaptations to local climate. This may affect the production of plant biomass. The lower the biomass that is produced, the less mercury, or other heavy metals that will be removed from the contaminated lake (Henry 2000). Phytoremediation is also limited to the rooting depth of the plants. Mercury can only be removed as far as a plant’s rooting system extends. This is not ideal if a site has deep contamination.

There is a concern that if the plants successfully sequester mercury, herbivorous animals may ingest the toxic plant biomass and expose themselves to mercury. Further research is necessary to see if this phenomenon is of biological concern. This may accidentally introduce more mercury into the food web, rendering phytoremediation possibly counterproductive.

What happens to the mercury when the plants die off? Plants that sequester heavy metals, mercury included, have a limited life span. Once they die, they are then considered hazardous waste and need to be removed and contained properly by RCRA standards (Henry 2000). If phytoremediation is going to be an effective method of remediation, these plants must be harvested before they completely decompose and rerelease the sequestered mercury back into the environment.
**Chemical Additions**

Chemical additions to lakes are a fairly new approach to control mercury concentrations in contaminated sites. These additions of chemicals, like calcium nitrate solution, rely on manipulating reducing-oxidizing conditions within a lake to prevent the methylation of mercury. There are a number of hypothesis as to how this is exactly done. The three main hypothesis are that nitrate additions alter the methylation and demethylation rate in aquatic systems. The second posits the growth of denitrifying bacteria, that outcompete sulfate reducing bacteria. And the last mechanism suggests that the addition of nitrate increases methylmercury sorption to iron and manganese oxyhydroxides, rendering the mercury unavailable to uptake by phytoplankton due to the amalgams physical size.

**Environmentally Relevant Reducing-Oxidizing (Redox) Conditions**

Nitrate additions depend on manipulating aquatic redox reactions to prevent the methylation of mercury. Depending on abiotic conditions within an aquatic system, microorganisms will consume compounds during their metabolic processes (Figure 7 Baker et al. 2000). Redox reactions are a type of chemical reaction that involve the transfer of electrons. These reactions always occur in pairs, in which one substance is oxidized, and the other substance is simultaneously reduced. The process of oxidation is described as the loss of electrons (Baker et al. 2000), whereas the process of reduction is the gaining of electrons (Baker et al. 2000). Oxidized chemical forms are represented in a circle in Figure 7 while reduced chemical forms are represented in a diamond.

During metabolic processes, microbes will actively consume compounds that have a high free energy charge. Microbes will select the next most energetic oxidant in the sequence (if oxygen is depleted) to metabolize organic matter via aerobic respiration (Figure 7 Baker et al. 2000). Oxygen is the first compound to be consumed during a redox reaction because it has a high free energy change and is a strong oxidizing agent (Baker et al. 2000). Once oxygen is depleted in the benthic layer of a lake, anaerobic microbes outcompete aerobic microbes due to lack of oxygen. They first consume nitrate, then iron, then sulfate, and finally methane in that order (Figure 7 Baker et al. 2000).
Once the oxygen has been consumed at the sediment water interface, and becomes suboxic, other chemical compounds are oxidized for microbial metabolic processes. Each subsequent compound will produce less energy than the previous. In addition to oxygen, nitrate is the strongest available oxidizing agent. Nitrate (NO$_3^-$) is reduced, and converted into nitrogen (N$_2$) by anaerobic nitrogen fixing bacteria in the process of denitrification. Once both oxygen and nitrogen species are consumed, metals are then used for metabolic processes. Commonly reduced metals are both iron and manganese. Ferric iron (Fe$^{3+}$) is reduced to ferrous iron (Fe$^{2+}$). This process is facilitated by iron reducing bacteria that may also have the capacity to methylate mercury. After iron is reduced, then sulfate (SO$_4^{2-}$) is reduced into hydrogen sulfide (H$_2$S or HS$^-$) by sulfate reducing bacteria. These bacteria are responsible for the methylation of mercury in anaerobic conditions. Then lastly, methanogenesis occurs in a reaction that reduces CO$_2$ to CH$_4$. This reaction occurs under the most anaerobic conditions, if all other oxidants are in low quantities or are depleted. Methanogenesis occurs in swamps, rice paddies, and flooded areas that are frequently or permanently flooded. As each subsequent compound is used for respiration, less and less energy is produced (Figure 8 Baker et al. 2000).
Nitrate Addition as a Remediation Strategy

Understanding environmental redox conditions are essential in knowing how chemical additions, such as nitrate, control the methylation of mercury in an aquatic system. Using chemicals as an additive to prevent the conversion of mercury is a novel in situ remediation approach, with the most common additive being nitrate (NO$_3^-$), specifically calcium nitrate (Ca(NO$_3^-$)$_2$) (Matthews et al. 2015). This technique is currently being investigated on the East Coast of the United States within lakes and reservoirs contaminated by mercury.

There are a number of mechanisms for regulating the release of methylmercury through the use of chemicals additions. The addition of nitrate prevents an aquatic system from entering heavily reduced conditions, whereas additions of iron and sulfate are the main chemicals that facilitate metabolic activity of microbes. The addition of nitrate has been shown to prevent the production of methylmercury in aquatic systems (Matthews et al. 2013). Nitrate is a strong oxidizing agent, and ideal for the consumption of organic matter by microbes if oxygen is not

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reductive processes equation</th>
<th>Free energy $\Delta G^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic respiration</td>
<td>$\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$</td>
<td>$-120.0$</td>
</tr>
<tr>
<td>Denitrification</td>
<td>$\text{CH}_2\text{O} + (4/5)\text{NO}_3^- + (4/5)\text{H}^+ = (7/5)\text{H}_2\text{O}$ + $\text{(2/5)N}_2 + \text{CO}_2$</td>
<td>$-113.9$</td>
</tr>
<tr>
<td>Mn(IV) reduction</td>
<td>$\text{CH}_2\text{O} + 2\text{MnO}_2 + 4\text{H}^+ = 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$ + $\text{CO}_2$</td>
<td>$-81.3$</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>$\text{CH}_2\text{O} + 8\text{H}^+ + 4\text{Fe(OH)}_3 = 4\text{Fe}^{2+} + 11\text{H}_2\text{O}$ + $\text{CO}_2$</td>
<td>$-27.7$</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>$\text{CH}_2\text{O} + (\frac{1}{4})\text{SO}_4^{2-} + (\frac{1}{4})\text{H}^+ = (\frac{1}{4})\text{HS}^- + \text{H}_2\text{O}$ + $\text{CO}_2$</td>
<td>$-25.0$</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>$\text{CH}_2\text{O} + (\frac{1}{4})\text{CO}_2 = (\frac{1}{2})\text{CH}_4 + \text{CO}_2$</td>
<td>$-19.2$</td>
</tr>
<tr>
<td>Fermentation</td>
<td>$\text{CH}_3\text{O} + (1/3)\text{H}_2\text{O} = (2/3)\text{CH}_4\text{OH} + (1/3)\text{CO}_2$</td>
<td>$-8.6$</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Reaction</th>
<th>Oxidative processes equation</th>
<th>Free energy $\Delta G^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane oxidation</td>
<td>$\text{O}_2 + (\frac{3}{4})\text{CH}_4 = (\frac{3}{4})\text{CO}_2 + \text{H}_2\text{O}$</td>
<td>$-97.7$</td>
</tr>
<tr>
<td>Sulfur oxidation</td>
<td>$\text{O}_2 + (\frac{3}{4})\text{HS}^- = (\frac{3}{4})\text{SO}_4^{2-} + (\frac{3}{4})\text{H}^+$</td>
<td>$-85.0$</td>
</tr>
<tr>
<td>Fe(III) oxidation</td>
<td>$\text{O}_2 + 4\text{Fe}^{2+} + 10\text{H}_2\text{O} = 4\text{Fe(OH)}_3 + 8\text{H}^+$</td>
<td>$-92.3$</td>
</tr>
<tr>
<td>Nitrification</td>
<td>$\text{O}_2 + (\frac{1}{4})\text{NH}_4^+ = (\frac{1}{4})\text{NO}_3^- + \text{H}^+ + (\frac{1}{4})\text{H}_2\text{O}$</td>
<td>$-41.7$</td>
</tr>
<tr>
<td>Mn(III) oxidation</td>
<td>$\text{O}_2 + 2\text{Mn}^{2+} + 2\text{H}_2\text{O} = 2\text{MnO}_2 + 4\text{H}^+$</td>
<td>$-38.6$</td>
</tr>
</tbody>
</table>

Figure 10. The sequence of redox reactions in aqueous environments and their respective free energy (Baker et al. 2000)
readily available. Adding nitrate into a lake or reservoir promotes the growth of denitrifying bacteria as the dominant active microorganisms within an aquatic system and prevents dominance of SRB from becoming the dominant and active species (Matthews et al. 2013). Denitrifying bacteria are not capable of mercury methylation, unlike iron, or sulfate reducing bacteria (Cleckner et al. 1999). This suppresses the growth of SRB and little methylmercury is produced. In addition, this mechanism suppresses both iron and manganese reduction and inhibits anaerobic metabolic pathways.

Another posited mechanism for nitrate control on methylmercury accumulation in aquatic systems is the increased sorption of methylmercury to iron and manganese oxyhydroxides in benthic sediments. Under aerobic conditions, ferric iron (Fe$^{3+}$), the oxidized form, is the dominant iron species. Under anaerobic conditions, ferrous iron (Fe$^{2+}$), the reduced form of iron is dominant. Ferrous iron is commonly found in anoxic waters and is water soluble. In reduced conditions, it stays in solution and iron reducers will produce ferrous iron through their metabolic activities. For nitrate additions to be effective, it is important to ensure the aquatic system favors ferric iron as the predominant form of iron. This form is not water soluble and precipitates out of the dissolved phase as a particulate. Ferric iron is now available to bind with water molecules, hydroxides (OH$^-$), and organic matter. These clusters of compounds form flocculants, which attracts methylmercury and sticks to the flocculent. Oxyhydroxides have a large surface area, so many methylmercury atoms can stick to it. At this point, the flocculent is too big for phytoplankton to passively or actively take up into their cell walls, preventing methylmercury from entering the food web. Once sorbed to the iron or manganese oxyhydroxide, methylmercury is not biologically available for uptake.

**Benefits of Implementing Nitrate Addition**

The addition of nitrate into a mercury-contaminated body of water is a novel remediation method. This method relies on manipulating redox conditions within a lake to prevent the methylation of mercury, and subsequent release into the food web. Nitrate addition promotes the growth of denitrifying bacteria and their consumption of nitrate for their metabolic processes. Denitrifying bacteria are not known for their methylating properties. With appropriate redox conditions the methylation of mercury is prohibited. Conditions in these lakes are more likely to
be in an oxidized state and water quality improves. This also has the added benefit of preventing the release of iron and manganese that reduce the aesthetic quality of drinking water. The sorption of iron, manganese and sulfide stays bound to sediments or other compounds, which are not released into ambient drinking water, causing poor taste and smell.

Nitrate additions have been used to successfully control mercury methylation in the State of New York at Onondaga Lake in 2011. A local chlor-alkali plant discharged 75,00 kg of mercury into the lake contaminating aquatic biota and benthic sediments (Matthews et al. 2013). To remediate the lake, a liquid calcium nitrate solution was added to the hypolimnion three times per week from June 30 to October 10 to control the release of methylmercury. At the end of this pilot study methylmercury levels had decreased by 95% from previous levels recorded in 2009 (Matthews et al. 2013). It was also noted that during fall turnover, methylmercury concentrations were not apparent, demonstrating a successful control of methylmercury release in Onondaga Lake (Matthews et al. 2013).

Nitrate additions are not a cost prohibitive remediation method like dredging. Both solid and liquid calcium nitrate solutions can be easily purchased. Typical calcium nitrate solutions can approximately cost $2.00 to $20.00 per gallon (USP Technologies, 2017). However, total costs will depend on: the volume of lake water that needs to be treated, how often this lake water needs to be treated, the initial mass of calcium nitrate, tap water that is combined with calcium nitrate to form a calcium nitrate solution, and subsequent delivery method into the lake (hose or pump system).

*Challenges of Implementing Nitrate Addition*

There are a number of challenges when adding nitrate to a mercury contaminated lake or reservoir. Within the State of California, excess nitrogen is problematic. California is responsible for producing more than one third of the vegetables in the United States and two thirds of the country’s fruits and nuts (CDFA 2016). Vast amounts of farmland are required to produce such a large crop volume, which need a large amount of nitrate based fertilizers. Excess nitrate that is used to fertilize crops runs off into nearby waterways during heavy rainfall events. This runoff will eventually drain into larger rivers or waterways, causing eutrophiciation and hypoxic conditions downstream. This extra nitrogen can cause rapid growth of aquatic plants and algae in
California’s lakes. When plants and algae respire, and decompose, they consume oxygen in the water leading to hypoxia, fish kills and eutrophication. Such conditions are favorable for the methylation of mercury and growth of sulfate or iron reducing bacteria, thereby increasing methylmercury concentrations in lake water.

Excess nitrogen is also problematic if it enters groundwater aquifers or reservoirs used for drinking water and human consumption. If humans, especially infants, consume water with excess nitrogen, they can contract blue baby syndrome. Nitrate is consumed and then converted into nitrite in the stomach or digestive system (Knobeloch et al. 2000). Nitrite is responsible for oxidizing the hemoglobin in red blood cells, which is then transformed into methemoglobin (Knobeloch et al. 2000). Methemoglobin is unable to transport oxygen like hemoglobin. This condition prevents the blood from moving oxygen into the body’s cells, causing a blue coloration in babies. This is especially concerning because nitrate contamination and exposure mainly occurs through consumption of private well water, of which sixteen percent of the US population depends (Manassaram et al. 2006).

Nitrate addition for remediation of mercury is problematic for both environmental and human health reasons. The addition of excess nitrate in lakes and reservoirs causes eutrophication in the State of California, since nitrate is limiting. People who consume water with excess nitrogen can contract blue baby syndrome. These environmental and human health outcomes may not be worth the risk. Nitrate addition may suppress the production of methylmercury, but produces nitrogen, which is already a problematic surface and groundwater contaminant.

**Comparative Analysis of Remediation Methods**

Implementation of mercury control in lakes and reservoirs is a complex matter. Each method discussed previously has a number of advantages and disadvantages to its implementation remediation of mercury within lakes and reservoirs. Environmental managers and policy makers will have to critically analyze all benefits and drawbacks when choosing a remediation method. A number of important criteria have been chosen to compare benefits and challenges. They are equally weighted and are listed in no particular order. Table 3 presents a summary of results of the comparative analysis of remediation methods.

![Image](image_url)
Table 3. Summary of Comparative Analysis of Remediation Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Type of Treatment</th>
<th>Cost</th>
<th>Level of Contamination</th>
<th>Time Scale to Decontamination/Hg Control</th>
<th>Appropriate for CA</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Project Implementation Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capping</td>
<td>Containment</td>
<td>$5</td>
<td>Low-Medium</td>
<td>Fast</td>
<td>Yes</td>
<td>Effective, ideal for low hydrodynamic flows</td>
<td>Does not remove Hg, possible remobilization of sediments during installation</td>
<td>Almaden Lake, San Jose (CA)</td>
</tr>
<tr>
<td>Dredging</td>
<td>Removal</td>
<td>$$$</td>
<td>High</td>
<td>Fast</td>
<td>Yes</td>
<td>Ideal for highly contaminated sites</td>
<td>Invasive, possible remobilization, requires constant monitoring to ensure efficacy</td>
<td>Minamata Bay, Japan</td>
</tr>
<tr>
<td>Hypolimnetic Oxygenation</td>
<td>Prevents Methylation</td>
<td>$5</td>
<td>Low-Medium</td>
<td>Medium</td>
<td>Yes</td>
<td>Maintain cool water temperatures, high DO levels</td>
<td>Cannot overcome oxygen deficit, does not remove Hg from a system</td>
<td>Stevens Creek Reservoir, Guadalupe Reservoir, Almaden Reservoir, Calero Reservoir (CA)</td>
</tr>
<tr>
<td>Nitrate Addition</td>
<td>Prevents Methylation</td>
<td>$</td>
<td>Low-Medium</td>
<td>Medium</td>
<td>No</td>
<td>Favors growth of denitrifying bacteria, non-Hg methylators</td>
<td>Can cause eutrophication, pollutes drinking water</td>
<td>Onondaga Lake (NY)</td>
</tr>
<tr>
<td>Phytoremediation</td>
<td>Removal</td>
<td>$</td>
<td>Medium-High</td>
<td>Slow</td>
<td>Possibly</td>
<td>Non-invasive, removes metals other than Hg, garners public support, effective</td>
<td>Few species will sequester Hg, risk introducing invasive/non-native species into aquatic systems</td>
<td>Tapajos Lake, Negro Lake, Amazon River, Brazil</td>
</tr>
</tbody>
</table>

The following criteria were used to analyze each remediation method:

1. Type of Treatment
2. Cost (If applicable)
3. Level of Contamination
4. Time Scale to Decontamination/Mercury Control
5. Appropriate for California
6. Advantages
7. Disadvantages

Chemical additions, like calcium nitrate, have been a novel approach to control the methylation and release of mercury within aquatic systems on the East Coast. A number of pilot studies have been successful in New York and Virginia, but nitrate studies have not been conducted west of the Mississippi. Remediation by nitrate addition is done by controlling redox reactions and promoting the growth of denitrifying bacteria. Results of Matthews et al. (2013) study showed successful mercury control within one summer season. However, even with its inexpensive cost, nitrate additions are not a contaminant removal method. As a whole, nitrate additions would be problematic within California since the state already has issues with eutrophication, fish kills, hypoxia in rivers and lakes, and groundwater pollution. A significant percentage of Californians depend on well water, much of which is already contaminated with
nitrate. Excess nitrate in drinking water causes a serious risk to pregnant women and children for contracting blue baby syndrome. It would be counterproductive for an environmental manager to implement this method and would be trading one issue for another. Overall, there are too many disadvantages related to nitrate additions for this method to be effective for mercury control within the State of California.

In contrast to nitrate additions, dredging is a well-established and effective method for mercury removal within aquatic systems. Dredging was successfully used to restore Minamata Bay, Japan (1970s-1990s). The total mass of mercury found within benthic sediments of the Bay were estimated to be 3.4 tons, and an average concentration of mercury in surface sediments was 3.0 mg/kg (Akito et al. 2014). This project successfully decreased total mercury concentrations from 553 mg/kg to 16 mg/kg (Akito et al. 2014). Dredging is an excellent remediation method in case of an emergency spill, in a heavily contaminated area or if used in the excavation of point source pollution, but expensive costs may prohibit its use.

Dredging is a fairly invasive removal and remediation method that can disturb underlying sediment. This remobilizes sediments into upper waters, increases turbidity, and can make methylmercury available for uptake by phytoplankton, which makes this method ideal only for highly contaminated sites. Other methods, like hypolimnetic oxygenation, capping and phytoremediation can all control the release of mercury, but are much less disruptive. In addition, dredging is also cost prohibitive for sites that have low to medium mercury contamination. The removal of one cubic meter of sediment is estimated to cost approximately $1500 (Wang et al. 2014). The excavation and disposal of one acre of contaminated soil has been estimated to cost $400,000 (Henry 2000). Clearly, for large contaminated sites, removal of sediments can be extremely expensive and cost prohibitive for many environmental managers. For highly contaminated sites, or sites that have high risk of exposure to the public the cost may be justified. However, many lakes and reservoirs in California are either smaller in size, or have lower mercury concentrations, making dredging an inadequate remediation choice. Dredging does not seem like the optimal remediation choice in most of California’s lakes and reservoirs.

Like dredging, phytoremediation is a well-tested and effective remediation method, and garners broad public support. Phytoremediation uses plant biomass to remove heavy metals from contaminated sediments to decrease their concentrations within the environment. This method has been used locally, and globally, to control a number of heavy metals aside from mercury,
including but not limited to cadmium, zinc, and arsenic (Henry 2000). It can be used to decrease any concentration of a contaminant, but is often used to treat heavily contaminated sites due to its ease of implementation and cost effectiveness.

Phytoremediation is the most cost effective method out of all remediation methods discussed in this paper. Costs can range from $60,000 to $100,000 to treat one acre of contaminated soil (50 cm in depth) while implementing other methods, can cost hundreds of thousands, if not millions of dollars (Henry 2000). Costs come from propagating or purchasing and shipping the plants to the contaminated site. Installation can be done for a minimal cost, or even be completed by staff with only minimal training and proper protective equipment.

Even with public support and the low cost, there are some serious drawbacks that need to be considered before environmental managers implement this method to control or clean up large scale mercury concentration. Phytoremediation is a very slow process. The accumulation of a heavy metal like mercury will impede a plant’s natural growth. The timescale to decontaminate a site, or decrease concentrations to acceptable levels can take years if not decades to accomplish. Then, once the plant biomass has accumulated enough mercury to be deemed acceptable, the plant matter must be removed and treated as hazardous waste and stored properly. If it is not removed, the plants will decompose and the accumulated mercury will then be released back into the environment, rendering the process ineffective.

Phytoremediation may introduce non-native and invasive plant species into aquatic systems of California. There are a number of plant species that can accumulate mercury, like water hyacinths, sea rush and large leaf holly fern (Skinner et al. 2007) (Chattopadhyay et al. 2012). However, outside of their native habitat, these plants can be very invasive. This introduction can alter sensitive environments and change the ecological roles each species plays in a system. Non-native plants may grow uncontrollably, given the right conditions, out competing other species and changing ecological communities for the worse. If this method were employed in lakes and reservoirs in California, environmental managers would have to implement removal programs for the invasive plant species used for phytoremediation.

Another drawback to the implementation of phytoremediation is the fact that plants can only penetrate the first few meters of contaminated soils. Their uptake of mercury is limited to the physical reach of their root structure. Phytoremediation is not effective if there is a deep layer of contaminated sediment. Therefore, the removal of mercury would be incomplete and another
remediation method or species would have to be implemented to reach the deepest layer of contamination. Removal via phytoremediation is ideal for shallow lakes or contamination along the banks of a lake where the depth of contamination is shallow and sunlight can promote plant growth. Phytoremediation cannot be used when attempting to treat benthic soils, deep within lakes and reservoirs, since plants cannot grow at these depths.

Environmental managers will have to decide if the ecological risks associated with phytoremediation outweigh the need to decrease mercury concentrations within aquatic systems. If native plants can be used for remediation, then risks are low. Overall, phytoremediation is a low-cost method that can remove a variety of heavy metals from sediments but the benefits may end there. The method is slow and may only be effective in very shallow waters, and in most cases, would require a second method to remove mercury from deeper sediments. After the uptake of mercury, plant biomass must be treated as hazardous waste and properly disposed. Finally, further research is necessary to identify, or genetically modify mercury accumulators that are endemic to California to avoid the introduction of invasive plant species. Phytoremediation may be a remediation option in limited cases, but within the State of California it should be implemented with caution.

Like dredging and phytoremediation, aqueous capping is a well-tested and effective method for mercury control. Materials like sand, gravel or geotextile fabrics isolate contaminated sediments from ambient waters, preventing the release of mercury into the food web. Methylmercury can be sorbed to these materials, preventing their escape into ambient waters. Even with highly sorptive materials, methylmercury can still escape through the cap if it is punctured. This can occur through bioturbation and activity of benthic organisms or remobilization during high hydrodynamic flows, like strong groundwater currents, storms, tides or human activity. In this case, it is imperative that the cap be at least 20 cm thick to reduce the risk of puncture and remobilization (Ndungu et al. 2016). Capping is ideal for containing a range of low to medium mercury concentrations. Capping is also a viable method for lakes or reservoirs small in size. The materials, labor and installation expenses can become cumbersome and cost prohibitive, if large areas need to be capped (Henry 2000).

Implementing hypolimnetic oxygenation as a method to control the release of methylmercury in California lakes and reservoirs is the least problematic and most promising method discussed in this paper. HOS systems have already been successfully installed and are a
A proven method located in four lakes in the Guadalupe River watershed, San Jose, California (McCord et al. 2016). These lakes are contaminated from mercury tailings and mining activities from New Almaden Quicksilver mine.

Using an HOS system presents to control the release of mercury into ambient waters presents a large number of benefits. The most important benefit is that abiotic conditions prevents mercury bioaccumulation in fish and other aquatic biota, by preventing the methylation and subsequent release of mercury into the food web. Furthermore, an oxygenated hypolimnion prevents sulfate and iron reducing bacteria from methylating mercury.

Equally advantageous is the fact that HOS causes no ecological harm to the body of water being treated. In fact, HOS systems increase dissolved oxygen levels and decrease ambient water temperatures, which fish and aquatic plants need to survive. This improves overall abiotic conditions, keeps lakes oxygenated, while still maintaining cool temperatures that stratification sportfish species and consumable fish species need to survive even in summer months. Also, increased DO levels and cool temperatures benefit downstream habitats and improve drinking water quality if reservoirs are using this as potable.

The benefits to both in-lake and downstream water quality make HOS the ideal choice for environmental managers when compared to other remediation techniques. HOS does not cause remobilization of mercury like capping or dredging. It is a much less invasive technique and does not damage benthic systems like capping does. It does not subject to the surrounding ecosystem to an aggressive invasive plant species like the phytoremediation method.

In terms of cost, installing an HOS system is not the cheapest method, nor is it the most expensive. Expenses relating to this method include the purchase of machinery, installation cost, energy requirements and purchase of liquid or gaseous oxygen, which costs about $100/ton (Moore et al. 2016). While the initial equipment costs of HOS are high, it should be viewed as an investment for the community that uses the lake for recreation and for improvement of aquatic environments. HOS has the added bonus of limited energy requirements. The system only needs to be run 6-8 months out of the year. Lakes and SRB’s in the benthic sediments are not as biologically active during the winter months and do not produce as much methylmercury. Lakes and reservoirs during the winter also have a more even distribution due to mixing. Mixing results in homogenized lake layers, increased levels of DO and lower temperatures, preventing anoxic conditions in the benthic layer.
Unlike dredging or phytoremediation, an HOS system does not remove mercury from an already contaminated lake or reservoir. However, it does prevent it from being methylated by controlling abiotic conditions within an aquatic system. In order for this remediation method to be most effective, it should be implemented before the spring turnover and lake stratification occurs. This will help prevent hypoxic conditions in the hypolimnion and deliver an adequate concentration of oxygen. However, these systems should not be viewed as a way to turn a hypoxic lake into an oxic lake. HOS systems are designed to deliver a set concentration of DO. If anoxic conditions are extreme, there just is just not enough oxygen being delivered to overcome this deficit. These systems need to be implemented proactively, and not retroactively in late winter or early spring.

Another benefit of the HOS method is that the system is completely adaptable to both small and large bodies of water, depending on the selection of the delivery device. Not all devices are appropriate for all aquatic systems. For relatively shallow lakes and reservoirs (≤ 10 m) speece cones should be installed in the hypolimnion (Moore et al. 2016). Speece cones deliver high concentrations of oxygen rich waters over a smaller area of sediments. Also, they are more cost effective compared to implementing them over a large area. Deeper lakes and reservoirs (≥14m) should have line diffusers installed. Line diffusers can cover and oxygenate a much larger area than speece cones can and are economically feasible for this purpose (Moore et al. 2016).

Implementing line diffusers can also create weak circulation within the hypolimnion, without destratifying layers of a lake. This can prevent methylmercury in the water column from being brought to the surface where it then becomes bioavailable to phytoplankton. The velocity of outflow and bubble size can be adjusted to suit a variety of water quality needs. So much so that the released plume from the device rises to the top of the hypolimnion, spreads out horizontally, and then becomes negatively buoyant and will sink down to the benthic layer of the lake, oxygenating the bottom. The variety, flexibility, and control over these devices makes it an ideal choice when attempting to control the release of mercury into aquatic systems.

Over time, scientists and engineers have developed a variety of methods to control the release of mercury and minimize risks of exposure in both wildlife and humans. Each method addressed in this paper is effective, in that it either removes mercury from a system, or prevents the process of methylation. However, there is no one infallible remediation method applicable to
all freshwater systems in the State of California. To choose the most appropriate method, or combination of methods, environmental managers will have to prioritize their own criteria to determine the most appropriate method for their site.
Recommendations

Implement Hypolimnetic Oxygenation for Effective Mercury Control

A comprehensive approach is necessary to achieve effective remediation control of methylmercury contamination within lakes and reservoirs. There are three general options to address mercury remediation: control the process of methylation of mercury found in aquatic systems, prevent the introduction of mercury into the environment in the first place; and minimize exposure risk to humans by preventing consumption of mercury contaminated fish. The recommendations suggested here will attempt to provide a variety of options for environmental managers, policy makers and the general public.

The most efficient way to prevent methylation of mercury in an aquatic system is to implement hypolimnetic oxygenation. HOS is the least problematic remediation choice when choosing a method to control the release of mercury into aquatic systems compared to the other four methods I analyzed. HOS controls the release of mercury, and prevents its’ methylation and bioavailability. The increase of dissolved oxygen prevents hypoxic conditions, therefore inhibiting the growth of sulfate reducing bacteria. This then prevents the methylation and release of methylmercury into the food web.

The in situ aqueous capping method physically isolates it from ambient water, yet still allows for the production of methylmercury underneath the cap. There is a risk of puncturing the cap and subsequent mercury release into ambient waters. However, capping can still be a viable method to control mercury if the cap is made of proper material and thick enough to prevent puncture. In order to be extremely effective, continuous monitoring is necessary to determine if the mercury is contained in the aqueous cap.

HOS will not cause eutrophication and does not pollute drinking water like the nitrate additions method. The use of nitrate as a remediation method to control the release of mercury into the environment is not recommended in California. Excess nitrate in aquatic systems in California can cause eutrophication and fish kills, thereby decreasing the oxygen levels in a lake and creating conditions for sulfate reducing bacteria to flourish and methylate mercury. Successful pilot studies have been conducted east of the Mississippi River where phosphorous is the limiting nutrient, however, studies of this kind have been conducted on the West Coast where nitrogen is the limiting nutrient. Further small-scale studies need to be conducted to determine
additional mechanisms of mercury control and why nitrate additions are a viable option based on geographic region without creating eutrophication.

Dredging is a viable method for cleaning up point source pollution or sites with a high risk of direct mercury exposure to the public. However, the majority of lakes in the State of California do not fall into this category. Further, the hydraulic and mechanical removal of sediment comes at a high risk of remobilizing sediment contaminated with mercury. This risk of mercury remobilization and the high cost of dredging make other remediation methods advisable.

Phytoremediation can be used to remove mercury from a contaminated system over time. However, this method risks the introduction of invasive plant species into endemic California ecosystems. HOS implementation does not increase this risk. Plant species that accumulate mercury, like the water hyacinth and sea rush, can be invasive and problematic if not controlled properly. Although HOS does not remove mercury from a system like phytoremediation does. If implemented proactively, can prevent mercury from entering the food web by arresting the production of methylmercury. Installing and operating an HOS system is much more expensive than phytoremediation due to the purchase of an HOS device, its installation and cost of energy use. While costs for phytoremediation only include the cost of propagating the plants and their transport. Installation of plants can be conducted by trained volunteers, with minimal cost. For these reasons, hypolimnetic oxygenation is the ideal remediation method to control mercury release into freshwater aquatic systems.

**Statewide Ranking of Contaminated Lakes**

Realistically, there is not enough State funding for every mercury-contaminated lake to be completely remediated. I recommend that each lake or reservoir should be ranked and prioritized for remediation action. Ranking criteria should be weighted and based on the following: volume of each lake, the level of mercury contamination (high, medium, low), presence of sport or consumable fish and their population size, proximity to vulnerable communities that rely on subsistence fishing, and high hydrodynamic flows (risk of mercury transport). Site assessments should then be conducted and a statewide report would be compiled, ranking each lake or reservoir from highest remediation action, to the lowest. Using these criteria, an additional geospatial analysis should be conducted to identify lakes with high priority for remediation, and
their proximity to vulnerable communities that depend on subsistence fishing. These analyses and site visits could help environmental managers to target remediation actions and identify communities most at risk for mercury exposure and mitigate these risks.

*Monitor Mercury Concentrations at Lower Trophic Levels*

Traditionally, mercury concentrations are analyzed from fish species relatively high on the food chain or taken from sediment cores. Mercury concentrations found within fish tissues give a relatively accurate proxy of how much methylmercury is in biota in an aquatic system (McCord et al. 2016). However, monitoring methylmercury concentrations at lower trophic levels would give more accurate concentrations within biota in a lake. Monitoring and analyzing mercury concentrations of species lower on the food chain will quickly tell environmental managers if their remediation methods are effective (McCord et al. 2016). If there is little to no mercury uptake in these species, that is an indicator that the remediation methods are working and mercury is not becoming bioavailable or accumulating (McCord et al. 2016). By monitoring methylmercury concentrations within various organisms, like benthic invertebrates, or even phytoplankton, researchers can quickly identify whether or not methylmercury is bioavailable. Using fish tissue as a way to identify methylmercury concentrations is a delayed monitoring method. It takes months to years for methylmercury to bioaccumulate up the food chain and fish to be large enough to obtain appropriate tissue samples (Gochfeld 2003). Further research is necessary to improve methodology to accurately for accurately assessing methylmercury concentrations in an aquatic system. In addition to this, the mechanisms and reasons for methylmercury uptake by phytoplankton is still unknown. These processes need to be elucidated first, before methods can be improved. In the interim, monitoring methylmercury concentrations in benthic invertebrate species might be a viable substitute.

*Reduce Atmospheric Mercury Emissions*

Globally, the majority of mercury that is released into the environment comes from atmospheric emissions. By decreasing atmospheric mercury emissions, the amount of mercury that is deposited into watersheds decreases. Curbing global mercury emissions will prevent mercury from entering watersheds and bioaccumulating in aquatic organisms. Reducing atmospheric
emissions will therefore reduce the amount of methylmercury that is bioaccumulated in aquatic organisms. The majority of mercury atmospheric emissions that are deposited onto the State of California come from eastern Asia (Steding and Flegal 2002). Reducing these emissions will reduce the amount of mercury that is deposited in the State of California.

Mercury emissions can be controlled or decreased in several ways. Switching to a more environmentally friendly energy source would also lower atmospheric emissions of mercury both locally and globally. Emerging energy markets of hydropower, solar, nuclear, and wind energy are increasing in popularity. Currently, China has the largest atmospheric mercury emissions by country per capita (Hu and Cheng 2016). This phenomenon will eventually decrease the dependence on coal-combustion for energy and displace coal-fired energy, decrease mercury emissions, while still supporting a country’s energy growth needs. Decreasing emissions in both developing and developed countries will collectively decrease mercury emissions, mercury transport and deposition. In China, coal fired power generation is projected to decrease from 54% to 35% by 2030 due to the switch to alternative energy (Hu and Cheng 2016). This phenomenon will eventually decrease the dependence on coal-combustion for energy and displace coal-fired energy, decrease mercury emissions, while still supporting a country’s energy growth and needs. California estimates that 29 percent of its electricity sales in 2016 were met by renewable energy from wind, solar, geothermal, biomass and hydroelectric (CEC 2017). And by 2030, 50% of its retail sales will come from renewable energy (CEC 2017). This demonstrates a significant shift away from fossil fuel dependence. Decreasing fossil fuel use will decrease atmospheric mercury deposition. Atmospheric mercury can stay suspended for six months to two years before being deposited to the earth (Steding and Flegal 2002). This long residence time allows for wind transport and deposition of mercury far away from the point source. Much of California’s atmospheric mercury that is deposited here comes from eastern Asia, specifically China. Controlling the release of mercury, by switching to alternative energies and decreasing dependence on fossil fuels in China will decrease the amount of mercury deposited in California.

Until alternative energies are the primary source of power, it is necessary to implement legislation to control mercury emissions from stationary coal burning power plants. About 9.9 percent of all energy consumed in the U.S. in 2015 came from renewable sources and in 2012 the U.S. was the world’s largest consumer of renewable energy (IER 2017). However, a significant increase in consumption and production of renewable energy is necessary to combat fossil fuel
dependence. The Environmental Protection Agency (EPA) in December of 2011 enacted a rule that would decrease emissions of mercury and other hazardous air pollutants from both existing and new coal and oil based power plants with an energy capacity greater than 25 megawatts (EPA 2017). The Mercury and Air Toxics Standards (MATS) was the first national standard to reduce mercury and other toxic air pollutants since the 1990 Clean Air Act (EPA, 2017). Approximately 1400 coal and oil fired power plants in the U.S. are active, a majority of which do not control their emissions of toxic pollutants (EPA 2017). Currently 50% of mercury emissions from the U.S. come from power plants and more stringent mercury control is necessary. This stringent ruling will help prevent 90% of mercury from stationary coal burning power plants from being emitted, reduce 88% of acid gas emissions and reduce sulfur dioxide emissions by 41% (EPA 2017). This single regulatory action is a strong example of stricter emission controls and prevention of mercury releases into the environment. Ideally this ruling could be used as an example for other countries who need to adopt stricter laws concerning mercury emissions, like Brazil, China and India.

Advanced pollution control equipment should be installed and implemented to control mercury releases in coal-based power plants. An estimated 44% of all coal fired power plants lack advanced pollution control equipment (EPA 2017). Installing advanced control methods would decrease emissions of harmful air pollutants, mercury included. Air pollution control devices like fabric filters, electrostatic precipitators and activated carbon injection, can all capture a variety of different mercury species from coal fired power plant emissions (Table 4). These advanced control devices also have the added benefit of removing other hazardous air pollutants, like NOx, SOx, and particulate matter (Hu and Cheng 2016). Combined actions of legislation and advanced pollution control devices would have a positive impact on human health and the environment.
Table 4. Summary Table of Advanced Air Pollution Control Devices (Hu and Cheng 2016)

<table>
<thead>
<tr>
<th>Control measure/device</th>
<th>Intended air pollutant control</th>
<th>Impact on mercury removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion controls</td>
<td>$NO_x$, dioxins, and furans</td>
<td>Mercury can be controlled as a co-benefit</td>
</tr>
<tr>
<td>Coal washing</td>
<td>Particulate matter and $SO_2$</td>
<td>Significant fractions of mercury are also removed from the coal</td>
</tr>
<tr>
<td>Electrostatic precipitator</td>
<td>Particulate matter</td>
<td>Mercury (primarily particulate mercury) can be removed as a co-benefit</td>
</tr>
<tr>
<td>Fabric filter</td>
<td>Particulate matter</td>
<td>Mercury (primarily particulate mercury) can be removed as a co-benefit</td>
</tr>
<tr>
<td>Cyclone</td>
<td>Particulate matter</td>
<td>Mercury (primarily particulate mercury) can be removed as a co-benefit</td>
</tr>
<tr>
<td>Dry scrubber</td>
<td>Acidic gases ($SO_2$ and $HCl$), and some particulate matter (when combined with downstream particulate matter control devices)</td>
<td>Can remove some mercury as a co-benefit</td>
</tr>
<tr>
<td>Wet scrubber</td>
<td>Acidic gases ($SO_2$ and $HCl$), and some particulate matter</td>
<td>Can remove some mercury as a co-benefit</td>
</tr>
<tr>
<td>Wet flue gas desulfurization</td>
<td>$SO_2$</td>
<td>Mercury (primarily oxidized mercury) can be removed as a co-benefit</td>
</tr>
<tr>
<td>Selective catalytic reduction</td>
<td>$NO_x$</td>
<td>Mercury can be removed (primarily through causing mercury oxidation) as a co-benefit</td>
</tr>
<tr>
<td>Selective non-catalytic reduction</td>
<td>$NO_x$</td>
<td>Has little or no effect on mercury emission reduction</td>
</tr>
<tr>
<td>Activated carbon injection</td>
<td>Mercury, dioxins, and furans</td>
<td>Mercury can be effectively removed (primarily through adsorption) as a co-benefit or as the target pollutant</td>
</tr>
</tbody>
</table>

Consumption of Fish Species Lower on the Food Chain

Consuming fish as a low fat, high protein animal meat has dietary benefits, including but not limited to intake of omega 3 fatty acids that help cell development in the body and are essential for brain development in young children (Wenstrom 2014). However, due to the increase of mercury contamination in freshwater systems and bioaccumulation, there is the risk of exposure to mercury in humans when eating fish. Eating fish or shellfish that is found lower on the food chain will reduce mercury intake. The people who subsist on freshwater fish often are subsistence anglers, immigrant communities, or in low socioeconomic groups. They depend on easily accessible freshwater fish to feed themselves or their families. Fish found in freshwater systems are an easy and inexpensive animal protein.

Although all fish found in mercury-contaminated lakes and reservoirs are exposed to mercury, the tertiary species accumulate the highest levels of mercury in their tissues. Therefore, eating smaller fish lower in the food chain will minimize the intake and exposure to mercury, reducing the risk of adverse health effects. Generally speaking, older, larger fish have lived longer and have accumulated higher concentrations of mercury in their tissues. Consequently, eating smaller sized fish can reduce a person’s mercury intake.

The California Office of Environmental Health Hazard Assessment (OEHHA) has published a number of online documents and interactive tools that can aid the general public about identifying species of fish that are suitable to eat and how often these species can be consumed with a minimal risk of mercury exposure. The Fish Consumption Advisories and Safe
Eating Guidelines tool can be found at: https://oehha.ca.gov/fish/advisories. People who consume fish can navigate to this tool online and look up their location by county, waterbodies found in California, and fish species (Figure 9). After typing these data into the tool, the tool shows a tabular breakdown of the fish species by location that are safe to consume, as well as any subsequent fish consumption advisories or warnings. The fish consumption advisories and Safe Eating navigation tool can also be accessed via a mobile device with access to the internet. This tool is incredibly powerful, allowing the general public to become educated and make smarter dietary choices, thereby reducing their overall exposure to mercury.

Figure 11. Fish consumption advisories and Safe Eating navigation tool (CalEPA 2016)

In order to reduce this risk, the public should be educated to eat fish low on the food chain, or to cut out fish consumption entirely for a vegetarian or vegan diet, if economically feasible. Both the U.S. Food and Drug Administration and the Environmental Protection Agency published nation-wide advisory as of 2004 (FDA 2017). This education program is still relevant today. These consumption advisories have been, and will continue to reduce the risk of exposure to mercury in humans and sensitive groups.

The advisory recommends that children, young women, or women that may become pregnant, avoid fish that contain high levels of mercury. The three-main recommendations that stem from this advisory are the following:

1. Do not eat shark, swordfish, king mackerel or tilefish. They have high levels of methylmercury
2. On average eat two means a week consisting of a variety of fish and shellfish that have low methylmercury concentrations
3. Adhere to local fish consumption advisories before consuming fish in local lakes, rivers and coastal areas
a. If no advice is available, on average, eat one meal per week of fish that is caught in local waters, and do not consume any other fish during that week

   i. One serving of fish is considered approximately the width and thickness of the palm of a hand. Therefore, an adult serving of fish should be larger and thicker than a serving for a child (Figure 11).

   ![Serving Size of Fish for Children and Adults](image)

   Figure 12. Approximate serving size of fish for children and adults (CalEPA 2017)

In addition to adhering to the FDA and EPA fish consumption advisories, it is also recommended to increase signage, warning the public about the dangers of mercury consumption in contaminated fish. In addition to this, the number of languages found on each sign should be increased. Many subsistence anglers either do not speak English, or English is not their first language. Overcoming this language barrier will make fish consumption advisories more accessible to the public. Increasing the number of languages and number of signs will educate the public and reduce the risk of exposure due to consumption of contaminated fish in freshwater systems.
Literature Cited


