The Midwest Hazardous Substance Research Center

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Constructed Wetlands for Metals Removal

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Summary of the Problem

Water draining from mines or mining waste frequently contains metals with potential negative human and environmental impact. Similarly, many industries discharge wastewaters with moderate levels of metals. Treating such water to remove metals is expensive using current technologies, and in cases of abandoned mines or tailings piles, may simply be impractical due to the remote nature and vast scale of these problems. A low-cost, minimal maintenance treatment option is needed.

Constructed wetlands for the treatment of acid mine drainage (AMD) were discovered after researchers noted that such toxic mine drainage was cleaner after passing through natural bogs or other wetlands. Constructing a wetland at the mine exit to treat the metal-laden seepage has become a popular but unpredictable treatment technology. Additionally, many mines leach water which is highly acidic. However, most industrial wastewater and water from lead mines, such as the mines in Missouri's three mining districts, is neutral or slightly alkaline. In the case of lead mines, the water is often saturated for lead and zinc. Lead has many effects on human organs, and of particular concern are the negative effects of lead on developing brains.

Researchers at the University of Missouri-Rolla are conducting studies on the fundamental mechanisms by which metals are removed in such constructed wetlands. Such understanding should help to explain:

- why some wetlands have failed,
- whether the removed metals are stable, and
- how to optimally design these treatment wetlands.

Beyond understanding removal mechanisms, the research also is attempting to determine long term fates for the metals in the wetlands in response to disturbance, changing conditions or abandonment.

Introduction

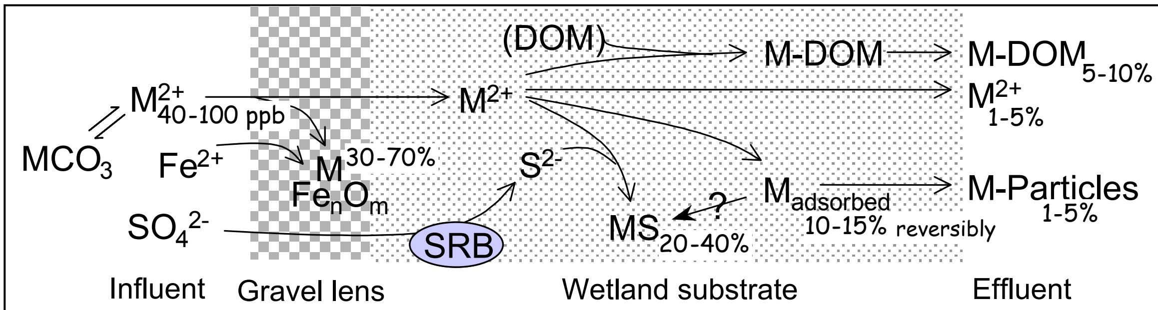
When successful, constructed wetlands result in a reduction in metals and toxicity at low cost. This project is focused on the use of such inexpensive constructed wetlands for the remediation of lead mine drainage. Lead mines are prevalent in Missouri, which produces roughly 90% of the lead mined in the U.S.; Missouri's most widespread major pollutant is lead from mining activities, with associated Superfund sites amounting to whole counties. Lead mine drainage is unlike acid mine drainage (AMD) because lead and zinc are found together in limestone formations, resulting in slightly alkaline (typically pH 8 vs. pH less than 5 for AMD) mine water. Given the difference in pH and that constructed wetlands for AMD sometimes fail, treatment of lead mine drainage by constructed wetlands was far from a sure success. Under laboratory conditions, this project has shown that wetlands successfully and reliably remove a large fraction of the lead, zinc, and sulfate in lead mine drainage, and has focused beyond efficacy on the removal mechanisms, bioavailability, and effects of disturbance.

The overall research effort began in 1997 with some funding from the Doe Run Company. In the lab, the constructed wetlands treating a synthetic lead mine drainage remove 60-70% of the zinc and 90-95% of the lead in the mine water, and have done so for six years. The toxicity of the resulting water, as measured using the EPA whole effluent toxicity method with *Ceriodaphnia dubia*, was less than the toxicity of uncontaminated water from a spring in the Mark Twain National Forest. Thus, constructed wetlands are quite effective for treating lead mine drainage.

In addition to simple efficacy, a concern is the long term fate of the metals in the wetlands; the wetland might become a source of metals rather than a sink, depending on how the metal is removed. An analogy might be found in the use of MTBE in gasoline – it was originally added to replace lead and make gasoline burn cleaner, but now MTBE is a significant groundwater pollutant due to gasoline spills and the low biodegradability of MTBE. To determine the likelihood that the metals, concentrated from the water into the wetland, might somehow be released, the research has examined the chemistry of the metals removal.

Removal Mechanisms

Much of the lab-scale work in the first year of this project funded by the EPA focused on removal mechanisms and is summarized in the figure below.



Wetland removal mechanisms for divalent metals Pb and Zn. Values are measured % distribution of Pb.

The mine water is generally saturated or supersaturated with lead at the observed carbonate concentrations, so some deposition of $PbCO_3$ is observed prior to entry into the wetlands. A similar issue of aqueous geochemistry is the formation of iron oxyhydroxides; within the influent oxic zone of the wetlands found in the gravel lens, iron oxides form and adsorb significant amounts of lead and zinc. The gravel lens is used to evenly distribute water flow into the sediment that is the main body of the wetland. Once the water passes into this organic material, adsorption and sulfide precipitation become dominant in the removal of the metals. The adsorption capacity of the organics is very high, and some of this adsorption occurs on dissolved organic matter (DOM). The wetland effluent generally has 10-20 ppb lead and 100-140 ppb zinc (reduced from 40-100 ppb lead and 170-300 ppb zinc in the influent), but 50-80% of the metals in solution are actually associated with the DOM. Thus, metal remains in solution but adsorbed. Such adsorbed material may be protected from removal as metal sulfides. This research is the first to definitively show the formation of metal sulfides in treatment wetlands. Precipitation as such metal sulfides is not as great as anticipated based on aqueous geochemical models and earlier speculations; the rate of sulfide precipitation in the wetlands is apparently significantly lower than the rate of adsorption. Some of the adsorbed metals are irreversibly removed; we now speculate that the metals slowly are converted to sulfides. The implication of this chemistry is that the metals are moderately stable as removed. So long as the gravel remains aerobic and the sediment remains anaerobic, very little metal could be released from the wetlands short of a major industrial acid spill at a treatment wetland.

With the metals chemistry and removal understood, two potential issues are currently being examined. One is the failure mode of the wetland – when they stop working, why do they stop working? For horizontal-flow wetlands at high flow rates, such failure is simply hydraulic. The adsorption kinetics in the wetlands are fast enough that the incoming water will have metals removed if it flows through unsaturated substrate for a few minutes, but at a high flow rate (in excess of 1.8 L/m^3/min), the water just runs over the surface rather than through the substrate. Vertical flow wetlands were constructed to operate the wetlands at higher loading These wetlands were run at a hydraulic retention times of approximately 5 min, corresponding to a surface loading rate of 17 L/m^2/min and volumetric loading rates of 100 L/m^3/min. Two vertical wetlands were constructed, one with a upflow pattern and the other using downflow. When challenged with this very high loading rate, zinc breakthrough was observed to propagate through the columns. Therefore, as expected, the failure mode at low HRT is breakthrough due to adsorptive kinetics. However, the vertical-flow wetlands used for these experiments were not mature – the Eh values were low and little sulfate reduction was observed. Therefore, when the wetlands are more mature (towards the end of this second year of research), experiments will be repeated to determine the extent to which sulfide precipitation increases removal.

Bioavailability

The second issue we are now focusing on is bioavailability, which appears to be modest. The two methods used here for examining bioavailability are to perform extractive assays and to measure metals in plant and insect tissues. The extractive assays on lab-scale wetlands have shown that the metals that might be considered bioavailable are in a range from 10% to roughly half of the lead in the wetland substrate and perhaps 1% of the zinc. As discussed above, the lead appears to adsorb reversibly and then slowly change to an irreversibly bound phase. The zinc, on the other hand, is preferentially in the phase co-precipitated with iron oxyhydroxides; if this phase is considered bioavailable, an issue of some debate, then roughly 70% of the removed zinc is potentially bioavailable. Confirmation of these results at field scale has just begun; samples from natural wetlands receiving lead mine drainage and lead tailings leachate and samples from constructed wetlands treating metals-containing wastewaters (from a landfill and a metals processing facility) are being obtained and similarly assayed.

Direct measurement of metals in plant and insect tissues from the lab-scale wetlands have shown no significant lead or zinc concentrations, based on somewhat limited observations to date. Three plant species that are dominant in local wetland environments, cattails (*Typha latifolia*), bulrush (*Scirpus validus*) and duck potato (S*aggitarria latifolia*), were planted in lab-scale wetlands. Cattails and bulrush had been planted in our original lab-scale wetlands, with no uptake apparent in these plants when assayed by total digestion.

Long-Term Fate

The final objective of the project is related to operational disturbances. In essence the question being asked is what happens when the mining operation shuts down, the wetlands dry up, or someone drives their ATV through the wetland? A wetland operating for 5 years that has been thoroughly sampled will be mixed by hand to simulate a substantial physical disturbance such as a vehicle running through the wetland. The effect on effluent metals concentrations will be determined. Thereafter the same wetland will be allowed to stagnate and air dry, followed by flushing with distilled water to determine the affect of aerobic conditions on metals release and to determine changes in metals chemistry as the sediment goes aerobic. This experiment will have great meaning with regards to the theory that the sulfides sequestered in the wetlands have potential to be re-released.

Impact

As a result of this project, The Doe Run Company, the leading producer of lead in the U.S., has proposed a constructed wetland for a facility near Buick, Missouri. The wetland will treat their effluent to reduce toxicity, and was designed based on publications from this project.

For more information:

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