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Thomas B. Boving

Joshua Klement

Bethany Thienel

Beverly J. Johnson

Bates College, bjohnso3@bates.edu

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Runoff Treatment with Aspen Wood

Thomas B. Boving¹, Joshua Klement¹, Bethany Thienel², Beverly Johnson²

¹University of Rhode Island, Dept. Geosciences, Kingston, RI 02881
²Bates College, Lewiston, Maine 04240

Abstract. Runoff from roadways and urban areas is often contaminated with heavy metals such as zinc and copper. The use of aspen wood (Populus tremula) was investigated as a potential sorbent for these metal contaminated runoff waters. The objective was to design an alternative runoff treatment technology based on a renewable resource, i.e. wood. Laboratory isotherms and column experiments were conducted in order to investigate the sorption and desorption of dissolved copper and zinc to and from aspen wood fibers. Sorption of Cu(II) and Zn(II) followed non-linear Freundlich isotherms. The aspen wood-water partition coefficient values revealed that Cu(II) had a greater tendency to sorb to the aspen wood than Zn(II). The column experiments indicated that, at least initially, both metals were being rapidly sorbed. During later stages of the sorption experiments, slower, but steady transport of the metal ions into the wood fibers appeared to be the dominating removal mechanism. Desorption of copper with E-pure water was faster than zinc, but the total amount of metal mass released from the wood was small in both cases, i.e., only 2% to 4% of the amount sorbed. Although initial dissolved metal removal data from an ongoing field test is inconclusive, it was shown that a proto-type wood filter and a viable runoff treatment technology can be build around wood-based filter materials.

Keywords. Metal contaminants, remediation, runoff treatment, wood filter

Introduction

Stormwater runoff pollution is a problem in urban and suburban areas and along roadways. Associated pollutants, such as heavy metals and petroleum hydrocarbons, are quite difficult and expensive to remediate once discharged to surface and ground water resources. While conventional best management practices (BMP), such as detention ponds, are effective in removing contaminants sorbed to suspended solids, they typically do not address the dissolved contaminants (Boving and Neary, 2006). To close this gap, multi-stage BMPs have been implemented that rely on “created wetlands” or artificial filtration materials to attenuate dissolved contaminants. A major shortcoming of created wetlands is that their treatment effectiveness is very seasonable, i.e. the gross contaminant removal is greatly reduced when the vegetation dies off during the cold season. (Neary, 2004). Artificial filter materials, such as activated carbon, are expensive. Wood filters on the other hand work on the same principle as wetlands, i.e. sorption of the contaminants to organic matter and, to some extent, co-sedimentation with suspended particulates (Boving and Zhang, 2004), but maintain their filtration capacity year-round. Also, wood is inexpensive relative to other filter materials, which ensures that these filters are economically. This study was designed to substantiate these claims under field conditions and explore the fate of the loaded wood filters.

Organic and inorganic pollutants originate from various sources, including automotive and industrial emissions as well as domestic use of a great variety of chemicals. For instance, metal concentrations in urban stormwater runoff were found to range between 5.3 and 35 µg/L for total Cu(II) and between 39 and 210 µg/L total Zn(II) (Pitt et al., 2004). The major concern with respect to Cu and Zn is ecotoxicity (Kjolholt, 2001). For instance, the Danish regulations for discharge of stormwater to surface water bodies have limit values of 12 and 110 µg/L for Cu and Zn, respectively (DEPA, 2007). Higher concentrations are tolerated in drinking water regulated by the United States Environmental Protection Agency (EPA), i.e. up to 1.3 mg/L Cu(II) (USEPA, 2002). Currently, there is no EPA drinking water limit established for Zn(II), although 5 mg/L is often considered a threshold concentration for this compound.

Plant materials, such as cornhusks, peat, and hazelnut shells, have been studied as low-cost remediation for wastewater, especially in the cleanup of heavy metals (Brown et al., 2000; Ciminio et al., 2000; Ricordel et al., 2001) or organic compounds (MacKay and Gschwend, 2000; Boving and Zhang, 2004). For example, Annadurai et al. (2003) found that banana peels removed up to 7.97 mg Pb(II) per gram peel. The exact
processes of metal-solid interactions remain uncertain (Ong and Swanson, 1966; Deczky et al., 1978; Bloom and McBride, 1979, Brown et al., 2000).

Even less is known about wood-metal interaction processes and the possible application of wood for remediation of metal contaminated water. Wood is a heterogeneous material composed of three major components: cellulose, hemicellulose, and lignin. Cellulose makes up 40-45% of the dry weight of wood (Siau, 1983). Cellulose is a collection of linear polysaccharides of 2,000-26,500 molecules (Higuschi, 1997). Layers of the cellulosic polymers are stacked by van der Waals’ forces to form a strong crystalline structure (Stamm, 1964). Water commonly enters the crystalline structure of cellulose and binds to the abundant hydroxyl groups by hydrogen bonding (Stamm, 1964, Siau, 1983). Hemicellulose makes up the wood matrix. It is formed by five- and six- carbon ring sugars, and has a lower molecular weight than cellulose (Siau, 1983). Lignin is a hydrophobic polymer and responsible for preventing decay of the wood and increasing the strength of the plant tissue. Lignin comprises approximately 20% of aspen wood (Fengel and Wegner, 1989). It consists of complex three-dimensional building blocks involving six-carbon rings and functional groups such as methoxyls, phenolic hydroxyls, phenolic ethers, aliphatic hydroxyls, and carbonyls (Siau, 1983).

Han (1999) used lignocellulosic materials (including aspen wood chips) for attenuating metals (Ni, Cu, Zn) in stormwater runoff. It was found that the potential of lignocellulosic fibers to act as filters for metals is directly related to their extractives content and surface area, and inversely related to their lignin and cellulose content. Similar results were reported by Lee and Rossell (2004). Said et al. (1993) proposed that once a hydrated-metal complex is adsorbed to cellulose through hydrolysis, a positively charged metal ion interacts with the cellulose’s hydroxyl groups. Other potential sorption sites on the cellulose surfaces may include carboxyl and carbonyl groups. Crist et al. (2002) investigated the sorption of Pb(II), Zn(II) and Cu(II) onto kraft lignin, a waste product from paper production. Their data indicates that the metal-wood partition coefficient, K, depends on pH. Crist et al. (2002) also suggest that metal sorption onto lignin is in direct relation to the aqueous metal concentration and the solid surface of the lignin. Srivastava et al. (1994) found that increasing the temperature increased the sorption of Pb(II) and Zn(II) onto black liquor, another product of the paper industry. They applied Gibb’s free energy equation to their data to calculate the spontaneity of the sorption of these metals onto the adsorbent. Data from this study also correlates well with the Freundlich and Langmuir isotherm models. Srivastava et al. (1994) noticed immediate sorption of the metals onto lignin, followed by slow diffusion of the metals onto lignin.

The focus of this study was on aspen wood and its interaction with dissolved zinc (Zn(II)) and copper (Cu(II)) and the performance of a wood-based filter under field conditions. The major objective was to design an alternative runoff treatment technology based on a renewable resource, i.e. wood. Based on preliminary results (Thienel, 2004) and previous studies of the effectiveness of aspen wood fibers for PAH adsorption (Boving and Zhang, 2003), it was hypothesized that aspen wood effectively removes dissolved pollutants typically present in runoff. A series of batch and column experiments were conducted to determine qualitative and quantitative descriptors for the wood-contaminant interaction. These experiments were followed by a field study (still ongoing at the time this manuscript was presented). The results of our experiments are summarized in the following and discussed in the context of possible application of wood filters for remediating contaminated runoff.

Materials and Methods

The contaminant treatment effectiveness of aspen wood (Populus tremula) was demonstrated in isotherm and column experiments. Aspen wood fibers are commercially available from American Excelsior, Inc., Arlington TX, and consisted of strands about 2-20 cm in length, with a diameter of approximately 1 mm. Before use, the wood was washed with deionized water to remove dust and other impurities. The water content of the aspen wood was determined by saturating wood fibers with deionized water for four weeks. Wood saturation was achieved when the water content of wood samples remained constant over three successive measurements. After saturation, the wood was oven-dried (24 hr at 105°C) and weighed. The mass difference between saturated and dry wood translated into an average water saturation of 58%. Trace metal grade, concentrated HNO₃, Zn(II) (as zinc sulfate, ZnSO₄ x 7 H₂O), and Cu(II) (as copper sulfate, CuSO₄ x 5 H₂O), were obtained from Aldrich Inc. (A.C.S. purity grade) and used as received. All solutions were prepared using E-pure water free of detectable traces of the target metals. Only pre-cleaned containers were used for sample storage and handling.

Adsorption Isotherm Experiments: In preparation of the sorption isotherm experiments, the aspen wood fibers were soaked in deionized water for two days. Then, 200 mL of a copper sulfate or zinc sulfate solution ranging from 0 mg/L to 5 mg/L (as Me(II) concentrations) were added to 1.445 g (dry weight) aspen wood. The concentrations used in these experiments were about two orders of magnitude higher than those found in
typical freeway runoff (Pitt, 2004). No significant sorption differences between wet and dry aspen wood were found during preliminary experiments. Samples of 2 ml to 5 mL of each batch were collected over a period of one week to 12 days. It was assumed that the incremental removal of liquid from the test vessel did not affect the isotherm results. Each sample was acidified with 20 µL concentrated HNO₃ using an autopipette with a high-density plastic tip. The metal concentration of each sample was analyzed on an Optima 300 XL ICP-OES in the Geology Department at Bates College. The mass of metal in solution for a given sample was subtracted from the mass in the starting solution to obtain the metal mass sorbed per gram of wood wool. The Freundlich isotherm was used to model the metal sorption onto the wood:

\[ C^* = K C^j \]  

Eqn. 1

where \( C^* \) is the mass of solute sorbed per dry mass of the solid absorbent (mg/g), \( C \) is the concentration of the solute in equilibrium with the solid absorbent (mg/L), \( K \) is the partition coefficient and \( j \) is the Freundlich exponent (Fetter, 1993). To calculate \( K \) values, equilibrium solute concentrations were plotted against the mass of metal sorbed per gram of wood and a best-fit curve was determined. The equilibrium value \( K \) was obtained once sorptive uptake of a compound to aspen wood stabilized, i.e., no more changes in the aqueous metal concentration were measurable over three consecutive measurements. Any background metal concentrations in the wood were determined by microwave digestions followed by ICP analysis. All samples had background concentrations less than the copper and zinc detection limits (0.1 ± 0.01 mg/g).

**Column Experiments:** The purpose of the column experiments was to investigate the sorption and desorption of Cu(II) and Zn(II) to and from aspen wood fibers. Conservative tracer tests (sodium chloride) were conducted prior to flushing with metal solution to estimate the potential for hydraulic shortcutting due to preferential flow. Tests results (not shown) showed that preferential flow was not occurring. A 5% nitric acid-washed Kontes brand Glass Chromatography column (5 cm long and 2.5 cm I.D.) was packed with 1.445 g (dry weight) aspen wood. Prior to experimentation, a Fisher Variable Flow Peristaltic Pump (Pump II Model 3385) was used to flush E-pure water (pH 6.4 and electrical conductivity of <5 µS/cm at 22°C) through the packed column until all trapped air was removed. During the sorption experiment, the column was flushed with a metal solution at average flow rates that ranged from 0.5 mL/min to 0.7 mL/min. Periodic column effluent samples were collected in 15 mL polypropylene conical test tubes and acidified with 20 µL concentrated HNO₃. The sorption experiment concluded when the relative concentration (\( C/C_0 \), the ratio of effluent to influent concentration) reached a value close to 1 (influent concentration = effluent concentration). For the desorption experiments, the column was then flushed with E-pure water (pH = 5.6) in an attempt to flush out sorbed metals. Again, periodic samples were collected and acidified as described above. All samples were analyzed for metal concentration using an ICP-OES (see Table 1). The column experiments lasted for 3-10 days each.

![Figure 1](image1.png)

Figure 1. A pre-cast concrete structure was constructed for the wood filter field experiment in Providence, Rhode Island. The filter’s inside dimensions were 1.4*1.2*3.3 m (H*W*L) - equivalent to about 5 m³ volume. The filter was outfitted with 27 wood filter modules containing about 115 kg of (dry) shredded aspen wood.

**Field Testing:** Tests are being conducted on a pre-cast concrete filter (Figure 1). The filter’s inside dimensions are 1.4*1.2*3.3 m (H*W*L) - equivalent to about 5 m³ volume. The filter was outfitted with 27
wood filter modules, each containing about 4.25 kg of (dry) shredded aspen wood, 115 kg in total. Runoff from surrounding urban and highway areas in Providence, Rhode Island, was discharged to a detention pond on the test site. From the detention pond, runoff was pumped into the initially empty wood filter using a gasoline-powered, cast-aluminum pump (Honda) connected to 10 cm (i.d.) PVC pipe. All other parts of the filter system were non-metallic. The average flow rate was 0.187 m$^3$/min and the theoretical filter residence time was 26 minutes. Water samples were taken from designated influent and effluent samples ports. No significant changes in pH or dissolved oxygen (DO) were observed. The principal test parameters were dissolved copper (Cu(II)), and zinc (Zn(II)). Samples were also collected for polycyclic aromatic hydrocarbons (PAH), nutrients (nitrate and phosphate) and bacteria (E.coli), but for space limitations these results are not discussed herein. Whatman 0.45 micron cellulose nitrate filters were used to filter the metal samples. Metal samples were filtered immediately after returning from the field, preserved with analytical grade nitric acid (Aldrich), and analyzed by a Thermo X-Series II Quadrupole ICP-MS at the University of Rhode Island. Total dissolved solids (TSS) were measured in filter influent and effluent. Two conservative tracer tests (NaCl) were performed on the wood filter system with the goal to determine runoff residence times in the filter system and the filter’s porosity.

Results and Discussion

Both laboratory and field experiments were carried out to study the interaction of aspen wood with heavy metal contaminants typically present in runoff. The following section provides a discussion of the observed results.

*Adsorption Isotherm Experiments:* Isotherm experiments provide insight into the sorptive uptake of the metal contaminants to the wood sorbent. Figure 2 shows the results of the Zn(II) and Cu(II) adsorption isotherm experiments. In both cases, sorption equilibrium was reached within 168 hours (Figure 3). The sorptive metal uptake was nonlinear over the range of concentrations analyzed (0 mg/L to 5 mg/L; initial concentration). Applying the Freundlich isotherm, an equilibrium $K$ value of 0.51 l g$^{-1}$ and 0.77 l g$^{-1}$ was calculated for Zn(II) and Cu(II), respectively. The Freundlich exponents, $n$, for both metals were similar, i.e., 0.29 for Zn(II) and 0.31 for Cu(II). The higher $K$ value for Cu(II) indicates that Cu(II) tends to sorb more effectively to aspen wood relative to Zn(II).

![Equilibrium solute data for Cu(II) and Zn(II) plotted alongside best-fit Freundlich isotherms. A $K$ value of 0.77 l g$^{-1}$ and 0.51 l g$^{-1}$ was calculated for Cu(II) and Zn(II), respectively. The Freundlich exponents for Cu(II) and Zn(II) were similar (0.31 and 0.29, respectively). The equilibration time was 168 hours.](image-url)
Column Experiments: Figure 4 summarizes the results of a column experiment using a 10 mg/L Cu(II) solution flushed through 1.445 g (dry) aspen wood fibers. After 30 hours of flushing with Cu(II) solution, the sorption experiment was followed by flushing the wood with deionized water to investigate Cu(II) desorption. Over the first hour of the sorption experiment, the relative Cu(II) effluent concentration increased sharply, i.e., from zero to approximately 0.3 C/Co. Afterwards, the effluent concentration continued increasing, but at a much slower rate. The effluent concentration approached the influent concentration (C/C0=1.0) after about 30 hours of flushing. At this time, 974 ml of Cu(II) solution, containing 9.74 mg Cu(II), had been flushed through the column. It is to note that the apparent equilibrium was reached about 120 hours faster when compared to the isotherm experiments (Figures 2 and 3). However, during the column experiments the wood came in contact with two to five times more concentrated copper solution (10 mg/L Cu(II)) than during the isotherm studies. For this reason, an earlier decline in filter efficiency during the column flushing was not unexpected.

During the following desorption experiment, the Cu(II) concentration dropped below 0.2 mg/L within 6 hours (87 ml total flushing volume). Over the course of the sorption experiment, 2.3 mg Cu(II) per gram of aspen wood were removed from solution. Compared to the Cu(II) mass input, this is equivalent to a removal efficiency of about 34%. During the desorption experiment, only 0.1 mg Cu(II) was released back into the flushing solution (deionized water) over a 6 hour period (4% of amount sorbed). Similar results were obtained for zinc (results not shown).
The column experiment indicates that the removal of dissolved Cu(II) by aspen wood was most effective during the first 12 hours of the experiment, when the rate of Cu(II) uptake was the greatest. The high degree of initial removal effectiveness can be explained by rapid surface complexation of the metal ion onto the wood surface. Once the easily accessible surface complexation sites were filled up, further metal uptake was slow, but steady. This observation can be explained by diffusive transport of metal ions into the wood matrix.

![Mass balance for the copper (a) and zinc (b) sorption and desorption experiment using 10 mg/L Cu(II) solution. Input (diamonds) is the cumulative mass of dissolved metal entering the column. Triangles are the mass of metal sorbed and desorbed per gram of dry wood.](image)

Figure 5a shows the changing removal effectiveness in terms of metal Cu(II) mass entering and leaving the column. The difference between input and output was equal to the amount of Cu(II) sorbed to the wood (per gram). From Figures 5 it is evident that the metal removal effectiveness decreased with time. For example, after about 25 hours of flushing, the mass of sorbed Cu(II) remained essentially constant (2.3 mg Cu(II) per gram of aspen wood). This implies that around this time the wood filter had reached its maximum removal effectiveness. The desorptive release appeared to be steady and linear. Extrapolating the linear part of the desorption curve, it would take (theoretically) about 470 hours (ca. 19.6 days) to remove all the sorbed Cu(II). Thus, the desorptive release of Cu(II) is much slower compared to the sorptive uptake.

Compared to the Cu(II) experiments, the experiments conducted with Zn(II) solution exhibited similar results (Figure 5b). The main differences were that (i) the effluent Zn(II) concentration reached C/Co=1 sooner and (ii) the desorptive release of the Zn(II) from the wood was lower. The total measurable amount of Zn(II) desorbed accounted for about 2% to 7% of the mass sorbed to the wood.
Field experiment: Although still ongoing at the time this manuscript was written, first results indicate that the wood filter is working as designed. Figure 6 shows the results of a conservative tracer test with sodium chloride that was undertaken to test the runoff residence time in the filter. The travel time of runoff in the filter was 26 min, which agreed well with the theoretical travel time calculated from the average flow rate. This period of time is, as shown by the column experiments, sufficiently long to attenuate dissolved metal contaminants. Further, because there was limited early breakthrough, the flow through the filter was not significantly influenced by preferential flow conditions. Based on the tracer test, the filter’s porosity was determined to be about 94%. The density of wood packed inside the filter was 21.9 kg/m$^3$. Both, packing density and porosity were comparable to those used in the column experiments.

Preliminary dissolved zinc and copper data indicate that there is no removal taking place. Possible reasons for this unexpected result may have to do with sampling and analytical uncertainties and, probably more important, erosion of metal contaminated particulate matter from the concrete structure itself. For instance, the analysis of concrete samples broken off the filter and then analyzed with a wave-length dispersive X-ray fluorescence spectrometer (Bruker S4 Pioneer) showed that, on weight basis, the concrete contained 16.8±0.3 mg/kg and 119.8±0.1 mg/kg copper and zinc, respectively. Leaching studies are needed to further quantify the mobility of these concrete impurities. Nitric acid aided digestion of fresh aspen wood filter samples and testing the pumping equipment influent and effluent excluded either as the source of the metals.
Further, we are currently investigating if keeping the wood filter consistently submerged under water – as simulated during the laboratory experiments - will improve the filter performance. This is likely because submerged wood swells which may activate sorption sites and, at least under field conditions, permits reactive biofilm growth.

**Conclusion**

The results presented herein demonstrate that under laboratory conditions aspen wood is a promising filter media for dissolved metal contaminants typically present in roadway runoff. The measured $K$ values from adsorption isotherms suggest that Cu(II) has a greater tendency to sorb onto the aspen wood than Zn(II). The non-linearity of the adsorption isotherms indicated that sorptive uptake was more effective at lower metal concentrations. The results from the column experiments support this finding. This means that under field conditions, where typical dissolved metal concentrations are much lower than tested herein, wood filters should last sufficiently long, i.e. several months, to make them an attractive filter medium. Further experiments, however, are needed to determine the filter’s maximum live time. The column experiments also indicate that sorption of Cu(II) to aspen wood was effective for a longer period of time compared to Zn(II). At least initially, both metals were being rapidly removed from solution, most likely being sorbed to easily accessible sites on the surface of the wood fibers. During later stages of the sorption experiments, slower, but steady diffusive transport of the metal ions into the wood fibers appeared to be the dominating metal removal mechanism. Desorption of Cu(II) was faster than Zn(II), but the total amount of mass released from the wood was small in both cases, i.e., only 2% to 4% of the amount sorbed. Although the sorption capacity of aspen wood for Cu(II) and Zn(II) appears limited, their slow desorption results in almost permanent removal of those metals.

Field test data show that a wood filter can be built around the findings of the laboratory experiments. The tested filter does not hinder the flow-through of the runoff and provides ample residence time to permit attenuation of the dissolved metal load. However, preliminary zinc and copper data showed that the filter is not removing those metals from the runoff. It appears that, next to analytical and sampling uncertainties, leaching of those metals from the concrete may interfere with the experiment. If the concrete is confirmed as the source of excess metals, additional experiments need to be carried out by placing the wood inside fiberglass containers.

Besides being a natural and renewable resource, aspen wood is inexpensive and wood filters are easy to manufacture. Also, once the wood’s sorption capacity is reached, these filters can be economically disposed of, for example, by incineration in a waste treatment plant. For these reasons, aspen wood filters may therefore be attractive for use in metal clean-up.

The experiments described herein did not further explore the mechanism (-s) responsible – including the possible impact of biofilm growth on the wood - for removing metal ions from aqueous solutions. In an effort to increase the efficiency of wood filters, more research is therefore needed to distinguish the wood component (-s) and mechanism (-s) responsible for the metal uptake. Investigation of other types of woods and other contaminant classes are also necessary to further explore the feasibility and possible application of wood filters.

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**References**


Han, J. S., 1999: Stormwater filtration of toxic heavy metal ions using lignocellulosic materials selection process, fiberization, chemical modification, and mat formation. In: 2nd Inter-Regional Conference on Environment-Water 99: September 01-04, 1999; Lausanne, Switzerland. S.l., 11 pgs.