Ability of Wood Fiber Materials to Attenuate Heavy Metals Associated with Highway Runoff

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16. Abstract

Wood chips were evaluated for their ability to attenuate heavy metals in roadway runoff. Column experiments with controlled synthetic runoff composition and flowrate were used to assess effects of flowrate (intercepted sheetflow from a 3-m wide roadway section), runoff salt concentration, wood exposure to alternating wetting and drying cycles, wood aging, competition among dissolved heavy metals, and removal of particle-associated heavy metals. Overall, wood chips damped the 'pulse' of copper in the synthetic runoff such that the effluent was characterized by lower concentrations (3 – 25% of input) over longer periods of time, but with little retention of the total copper mass. The most effective treatment was wood chips aged up to 9 months. Increased aging and chip water content reduced effluent concentrations, relative to no treatment. Flowrate had no effect on effluent concentrations. The presence of salt (> 2 mS/cm) or dissolved lead (500 µg/L) in the runoff caused greater effluent concentrations than the no treatment case. Removal of suspended particles (and associated contaminants) was greater than 85% with an estimated capacity of $0.16\ g/g_{wood}$. Field evaluation with concentrated flow to a gutter containing a wood chip treatment showed little effect on total or dissolved copper and zinc runoff concentrations and indicated that wood chips may be a source of contaminants in subsequent storm events. Applications of wood chips to treat roadway runoff would not provide a significant decrease in total maximum daily load (TMDL) contributions (*e.g.*, kg/d); however, there may be some scenarios for which wood chip treatments to decrease peak stormwater concentrations of dissolved heavy metals in sheetflow runoff is desirable.

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimetres	mm
ft	feet	0.305	metres	m
yd	yards	0.914	metres	m
mi	miles	1.61	kilometres	km
		AREA		
in^2	square inches	645.2	millimetres squared	mm^2
ft^2	square feet	0.093	metres squared	m^2
yd^2	square yards	0.836	metres squared	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	kilometres squared	km^2
		VOLUME		
fl oz	fluid ounces	29.57	mililitres	mL
gal	gallons	3.785	Litres	L
ft^3	cubic feet	0.028	metres cubed	m^3
yd^3	cubic yards	0.765	metres cubed	m^3

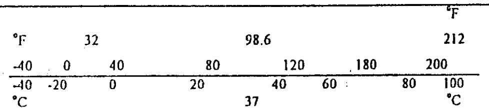
NOTE: Volumes greater than 1000 L shall be shown in m^3

Symbol	When You Know	Multiply By	To Find	Symbol
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5(F-32)/9	Celcius temperature	°C

* SI is the symbol for the International System of Measurement

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimetres	0.039	inches	in
m	metres	3.28	feet	ft
m	metres	1.09	yards	yd
km	kilometres	0.621	miles	mi
		AREA		
mm^2	millimetres squared	0.0016	square inches	in^2
m^2	metres squared	10.764	square feet	ft^2
ha	hectares	2.47	acres	ac
km^2	kilometres squared	0.386	square miles	mi^2
		VOLUME		
mL	millilitres	0.034	fluid ounces	fl oz
L	litres	0.264	gallons	gal
m^3	metres cubed	35.315	cubic feet	ft^3
m^3	metres cubed	1.308	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.102	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	Celcius temperature	1.8C+32	Fahrenheit temperature	°F



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List of Variables

C_0 (μg/L) initial dissolved metal concentration in batch sample

C_{in} (μg/L) inlet concentration of solute metal in column experiment

C_{out} (μg/L) effluent concentration of solute metal in column experiment

C_s (μg/kg) sorbed metal concentration

C_w (μg/L) dissolved metal concentration

K_d^{eff} (L/kg) effective sorption coefficient

M_0 (μg) initial mass of solute metal in batch sample, or delivered to column in synthetic runoff 'pulse'

M_s (kg) mass of solids

M_w (μg) mass of solute metal in aqueous phase, or eluted from column

Q (mL/min) volumetric flowrate

t (min) time

V_p (mL) column pore volume

V_w (L) volume of water in batch sample

Ability of Wood Fiber Materials to Attenuate Heavy Metals Associated with Highway Runoff

1. Introduction

1.1 Problem Statement

Roadway runoff constitutes an important non-point source of contaminants to surface waters in the US. Hoffman *et al.* 1985 estimated that 50% of polycyclic aromatic hydrocarbon (PAH) mass input to the Pawtuxed River, RI could be attributed to flushing of road surfaces within this urban watershed. In addition to toxic contaminants, such as PAHs and heavy metals, stormwater runoff from roads also contributes excess nutrients and suspended solids to streams and rivers. The extent to which roadway runoff impairs surface- and groundwater quality in other watersheds throughout New England and the US is little known. To protect future water quality as vehicle volumes continue to increase and as usage shifts from automobiles to trucks, there is an urgent need to assess feasible remediation techniques to attenuate the transfer of roadway-derived contaminants to surface- and groundwaters.

Stormwater management and treatment to attenuate roadway-derived contaminants is inherently challenging. Some of the engineering constraints include erratic contaminant deposition patterns on roadways, variable runoff flows, and pre-existing stormwater management approaches. The types of roadway-derived contaminants are diverse, including metals, organic compounds, ionic and nonionic species that may be dissolved in the stormwater or associated with particulate matter in the stormwater. Furthermore, it is preferable that an effective remedial approach for these diverse contaminant types be of low-cost.

1.2. Goals and Objectives

Woody materials constitute a cheap, abundant material with the potential to attenuate the diverse suite of contaminants associated with roadway runoff.

The goal of this research was to identify the key parameters that affect the efficacy of wood fibers for removing heavy metal and suspended solid contaminants from roadway runoff.

This goal was achieved by completing the following objectives:

1. Using laboratory column studies to assess the effects of the following variables on contaminant retention by wood fibers:
    a. runoff flow rate;
    b. runoff salt concentration;
    c. wood exposure to alternating wet-dry cycles;
    d. wood-aging effects, and
    e. competition among dissolved heavy metals.
2. Making field observations to validate laboratory outcomes.

1.3. Scope

The objective of this research was to identify the key parameters that affect the retention of roadway-derived dissolved and particle-associated heavy metals by woody materials. The scope of this work was limited to laboratory studies in which flows were carefully controlled so that contaminant mass balances could be completed, thus indicating mass percentages retained by the woody materials. The laboratory experimental design was implemented in a manner that enabled the retention effectiveness of various treatments to be assessed in parallel experiments with only one variable modified at a time. Multi-variable effects, such as all combinations of salt concentration and wood fiber aging time, were not assessed. Contaminant removals focused on copper, zinc, lead, nickel and cadmium, roadway-derived heavy metal elements of greatest concern because of the combined effects of high runoff concentrations and known aquatic toxicity.

Flow configurations in the experimental design achieved a balance between field representation and practical implementation. The laboratory experimental set-up was designed to simulate interception of sheetflow runoff by the woody materials. Other flow configurations would have required enormous quantities of water (~ 1000s L) for each experiment that could not easily be produced by a laboratory water purification system, or treated for waste disposal, if required. Since it was important to validate the outcomes of the laboratory assessment of wood fiber effectiveness for attenuating roadway contaminants, a limited number of field measurements were obtained. Field measurements were obtained from a configuration that consisted of intercepting guttered runoff with woody materials, and thus differed from the laboratory set-ups. A field trial of woody materials intercepting sheetflow would have required a trenching system that was precluded by the available budget on this project.

The significance of the research from this project is that the results may be used to:

- identify key design parameters for remedial structures incorporating woody materials to be used for stormwater management in future roadway projects, and
- enable the future evaluation of the contaminant-attenuation effectiveness of current stormwater flow management techniques that incorporate woody materials, such as mulches used in slope stabilization and berm construction.

1.4. Report Organization

This final report on NETC Project 03-1 is organized into five sections:

- **Section 2. State of Current Knowledge.** Typical characteristics of roadway-derived contaminants are reviewed including factors that contribute to the presence of contaminants on roadway surfaces and the mobilization during precipitation events. Prior studies demonstrating the effectiveness at wood materials for removing similar contaminants under other treatment scenarios (*e.g.* industrial wastewater treatment) are highlighted. Finally, the mechanisms by which roadway contaminants are anticipated to interact with wood materials are described to provide background to the experimental design approach of this study.
- **Section 3. Attenuation of Dissolved Heavy Metals by Wood Chips.** The methodology of the laboratory experiments is described in detail, including the theoretical basis for interpretation of the laboratory data. Discussion of the effects of runoff flowrate, salt content, wet-dry cycles, wood aging and contaminant competition are presented.
- **Section 4. Attenuation of Particle-Associated Heavy Metals by Wood Chips.** Evaluation of wood material effectiveness for removal of particle-associated heavy metals was separated from the evaluation of dissolved heavy metal removal because the mechanisms of interaction with wood fibers differs between these two “groups” of contaminants. Modifications of the

general laboratory experimental methodology (Section 3) are explained. Comparisons between particle-associated and dissolved heavy metal removals are discussed.

- **Section 5. Field Evaluation of Heavy Metal Removals by Wood Chips.** The experimental design of the field set-up to evaluate heavy metal removals by wood chips is described. Discussion of the effects of wood chip treatment on stormwater concentrations of dissolved and particle-associated heavy metals, and of suspended solids are presented.
- **Section 6. Conclusions and Recommendations.** General considerations for implementation of stormwater remedial measures using wood chips are presented with consideration for the regulatory framework and findings from Sections 2 – 5.

2. State of Current Knowledge

2.1. Characterization of Roadway-Derived Contaminants

Rain and snow melt water from roadways contains heavy metals, suspended solids, bacteria, organic compounds and nutrients (Barrett *et al.*, 1998; Drapper *et al.*, 2000). These runoff constituents originate from exhaust byproducts, tire and pavement wear, fluid leakage, wet and dry deposition and roadway maintenance activities. The relative contributions of different roadway-derived contaminants (*e.g.*, copper-to-nitrogen-to-suspended solids ratio) depend strongly upon land-use patterns surrounding the road (Choe *et al.*, 2002). Mobilization of these contaminants from the road surface and entrainment in stormwater runoff is influenced by the precipitation intensity of the storm event and by the antecedent dry event. Furthermore, the total contaminant load in stormwater varies throughout a runoff event. The so-called "first flush" volume, roughly 20% of the total runoff volume (Deletic, 1998), has contaminant concentrations that are at least an order of magnitude greater than the mean concentration of the event (Shinya *et al.*, 2000; Choe *et al.*, 2002). The extent to which first-flush concentrations exceed mean concentrations is influenced by the duration of the dry period preceding a particular runoff event (Sansalone and Buchberger, 1997a). Consequently, the contaminant input for a roadway runoff remedial measure is not well-known because concentrations and loads of roadway contaminants vary both spatially and temporally.

Despite the variable magnitude of contaminant loads in runoff events, the distribution of toxic contaminants among dissolved and particulate phases in the first flush appear to be consistent among studies. Copper, lead and zinc are particle-associated and exhibit a negative correlation with particle size (Colandini *et al*., 1995; Sansalone and Buchberger, 1997b). PAH compounds are present in both dissolved and particulate forms, although the most toxic compounds in this class are particle-associated (Shinya *et al.*, 2000). Cadmium and nickel are dissolved in runoff water, and also may be associated with fine particles that pass through the filters used to separate the particulate fraction (Sansalone and Buchberger, 1997b; Shinya *et al.*, 2000). Although these trends have been observed in multiple studies, it has not been possible to develop predictive correlations between dissolved or particle-associated contaminant concentrations and bulk water quality parameters (*e.g.*, total suspended solids) due to the variable nature of contaminant deposition patterns on roadways.

Roadway runoff characterization studies do give insight into treatment strategies that will be most effective for immobilizing contaminants. For example, to attenuate copper concentrations, the runoff remediation technique must remove very fine particles effectively.

The remediation strategy must be effective for immobilizing dissolved constitutents, if cadmium and soluble PAH concentrations are to be decreased also. Dissolved and fine-particle associated contaminants are not well-removed by present stormwater management practices such as ditches and detention basins, that employ gravitational settling. However, present stormwater management techniques could be improved by adding the capacity for fine particle filtration and dissolved contaminant sorption. Woody materials are readily-available and cheap materials that could be incorporated into storm water management practices to attenuate concentrations of roadway derived contaminants that are dissolved or associated with fine particulate matter.

2.2. Contaminant Uptake by Woody Materials

The uptake of dissolved organic compounds and metals by wood, and other fibrous plant materials, has been studied in controlled laboratory studies (Dao, 1991; Severtson and Banerjee, 1996; MacKay and Gschwend, 2000). Partitioning of organic compounds into wood is proportional to the lignin content of the wood tissue (Xing *et al.*, 1994; Severtson and Banerjee, 1996; MacKay and Gschwend, 2000). The uptake capacity of dissolved organic compounds by wood is expected to continue over long times in the field. Wood degradation processes preferentially deplete cellulosic components, leaving lignin structures to undergo very slow transformation (Higuchi, 1980). Additionally, colonization of wood surfaces by bacteria populations may facilitate the transformation of entrapped organic contaminants to less toxic compounds.

The mechanisms of dissolved metal uptake by wood tissues are less understood than for the case of organic sorption to wood (Han *et al.*, 1999). Contradictory results have been obtained in the case of metal sorption by lignin. Isolated lignins were found to have high metal binding capacities for copper, iron and aluminum (Nasr and MacDonald, 1978; Camire and Clydesdale, 1991); however, copper binding capacities were negatively correlated with lignin content in whole wood and plant tissues (Han *et al.*, 1999). This last observation may be consistent with the explanation that wood extractives are the most important component for complexing metals (Han *et al.*, 1999). Generally, the extractive fractions decrease as plants become more woody (Stamm, 1964). If metal binding sites are associated with the extractable components of wood, metal uptake may decline over time as stormwater flushes these components from the wood particles. Chemical modifications have been employed to increase the metal uptake capacity of lignin and cellulosic components of wood (see review by Han *et al.*, 1999); yet, consideration of wood pre-treatment costs may yield benefits for removal of dissolved metals from runoff, in comparison with the use of untreated wood particles.

Ultimately, the effectiveness of wood particles to take up dissolved contaminants from the aqueous phase depends on the relative rates of (1) stormwater flushing past wood particles and (2) contaminant diffusion to sorption sites inside the wood tissue. We characterized the uptake kinetics of organic compounds by wood particles in previous work (MacKay and Gschwend, 2000). The rate of contaminant removal from the aqueous phase was inversely related to the wood particle size and uptake rates were inversely proportional to compound solubilities (MacKay and Gschwend, 2000). Thus, poor uptake of large molecular weight compounds may be limited by slow diffusion rates, relative to stormwater flushing velocities through a wood treatment medium (Boving, 2002). Increased wood particle size is also expected to slow the uptake rate of dissolved metals into wood; however, no studies have yet proposed a mechanistic model that would enable prediction of metal diffusion rates in wood tissues.

The filter effectiveness of woody materials for removing particulate matter from water has not been addressed in previous studies. Wood particles have had limited application in air filtration where they have been shown to filter mold spore particles (Juneson *et al*., 2001; Martens *et al*., 2001). According to classical filtration theory, the filter efficiency increases when the filter media size is decreased or the media surface area is increased (Yao *et al.*, 1971). Thus, mechanical grinding of bark materials (*e.g.*, cedar mulch) will produce a more effective filter medium than wood chip waste.

Note that immobilization of roadway-derived particles in a wood filter does not ensure that contaminants are also immobilized. When particles are first flushed from the road surface, associated contaminants may not be at equilibrium with respect to distribution between the particle and aqueous phases (Sansalone and Buchberger, 1997b). As stormwater continues to flow past particles immobilized in the wood filter medium, heavy metals and organic compounds may desorb from the particles into the aqueous phase. Contaminants desorbed off particles can be taken up by wood fibers themselves. Important water quality parameters of roadway runoff that will affect the redistribution of contaminants between immobilized particles and flushing water include pH and salt concentration (Stumm and Morgan, 1996). Changes in runoff composition between storm events may also induce desorption of organic and metal contaminants that were previously taken up in the wood tissue.

2.3. Applications of Woody Materials in Stormwater Management

The USDA Forest Products Laboratory tested a fiber-based filter system to treat storm water at the outlet of a detention basin draining a parking lot (Han *et al.*, 1999). The outlet culvert was retrofitted with a box lined with eight individual packets of kenaf fibers. Kenaf fibers exhibited an uptake capacity of 8.5 mg of copper per gram of fiber, and were one of the highest capacity fibers tested (Han *et al.,* 1999). Copper concentrations of 2 – 3 μg/L were only decreased by 24 to 29% from the filter inlet to the filter outlet, despite an excess amount of sorption capacity contained within the 54 kg of fibers in the filter system. The poor field performance of kenaf fibers were not discussed in detail in the study report; however, possible explanations could be slow diffusion kinetics of copper from stormwater into fibers or the presence of particulate copper in stormwater vs. dissolved copper ions in lab tests. Other problems were reported with the filter configurations, including flow short-circuiting, filter clogging with trash and leaves, and wood warpage in the winter when the filters froze. These implementation problems may or may not have been the cause of the minimal nickel, chemical oxygen demand, phosphate and total suspended solids removals by the filters.

Boving has also proposed a point source treatment of water from stormwater detention ponds using wood (Boving, 2002). Laboratory studies were used to demonstrate the feasibility of removing dissolved PAHs from water with long (30 cm), thin (0.1 cm) shavings of aspen wood. Slow diffusion of these dissolved contaminants into the aspen particles over timescales greater than a week may limit field applications to detention systems with much greater retention times. It is proposed that 400 m^3 of aspen particles would be required to attenuate dissolved PAH concentrations from typical urban detention basin.

In addition to ‘end-of-the-pipe’ treatments of detention basin effluent, woody materials incorporated into erosion-control and other stormwater control structures may also attenuate contaminant concentrations in roadway runoff. Mulches and wood waste products are used for slope stabilization in roadway design. The purpose of these stormwater control structures is to promote infiltration of runoff while minimizing sediment erosion from road embankments. As stormwater percolates through these woody materials, dissolved metals and organic compounds may sorb to the mulch materials and particulate matter may be filtered out. Similarly, mulch berms used to slow stormwater runoff retain an unknown fraction of roadway contaminants dissolved or suspended in the rain or snow melt. Demars and Long have developed guidelines for use of woody materials for stormwater control, but did not investigate contaminant retention characteristics (Demars *et al.*, 2000). Better understanding of contaminant removal mechanisms by woody materials is necessary to evaluate the extent to which current wood fiber-based stormwater control measures attenuate roadway contamination runoff and to guide the future design of erosion control and berm structures to control flows *and* to attenuate contaminants in roadway runoff.

2.4. Runoff Factors Affecting Contaminant Retention by Woody Materials

Figure 1 shows a schematic representation of contaminant transport mechanisms in wood materials used in a stormwater control application. Dissolved contaminants may be transferred from the aqueous phase to the wood phase by chemical interactions (sorption) with components of the woody material (lignin, cellulose, extractives) (Fig. 1, [1]). Fine particles, and associated contaminants, suspended in the runoff may be removed from the stormwater by physical entrapment in small pore spaces between wood particles (Fig. 1, [2]). Retention of dissolved and particle-associated contaminants may be a reversible process, such that these contaminants could be re-mobilized into stormwater flowing through the wood-containing control device at a later time. Trapped particles carrying associated contaminants may be scoured from small pore spaces, for example with increased stormflow velocity (Fig. 1, [3]). Contaminants associated with trapped particles may be transferred from the particles to the aqueous phase without particle mobilization, contributing to the dissolved contaminant load in the stormwater (desorption, Fig. 1, [4]). Dissolved contaminant concentrations in the stormwater may also increase through the transfer of contaminants previously-sorbed to the wood phase (Fig. 1 [5]). Both of these desorption processes would occur in response to aqueous phase dissolved contaminant concentrations that were lower than the dissolved concentrations of the aqueous phase contacting the particles or woody materials at the time that contaminants became solid-associated.

Consideration of the contaminant transport mechanisms in wood materials and the characteristics of roadway runoff suggests several factors that are anticipated to affect contaminant retention by woody materials. First, contaminant retention by woody materials would be influenced by the flowrate of runoff through the woody materials. Increasing the stormwater flowrate would decrease the contact time between the aqueous and wood phases, possibly limiting sorptive transfer of dissolved contaminants to the woody materials. Increased flowrates could also increase turbulent fluid mixing in pore spaces between wood particles, thereby inhibiting particle entrapment in small pore spaces. Stormwater flowrates vary through the course of any storm event; however, flowrates would be lower generally for wood treatment applications that employ sheet flow (*e.g.*, slope erosion control, berm, Fig. 1 (a), (b)) than for applications with concentrated flow (*e.g.*, 'point source' treatment, Fig. 1 (c)).

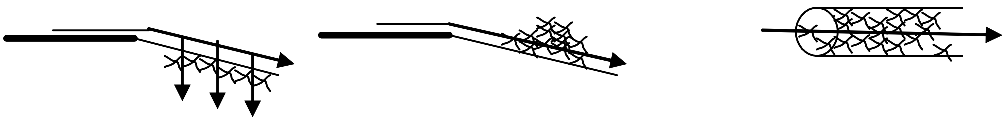
Second, salt concentrations in runoff would alter retention of dissolved ionic contaminants. Salt cations (sodium, calcium) may out-compete heavy metal cations for sorption sites on the surfaces of wood materials (Stumm and Morgan, 1996). Salt anions may form negatively-charged chloride complexes with heavy metal cations that would not interact with the wood surface (Morel and Hering, 1993). Salt concentrations in roadway runoff vary throughout the year in response to winter snow and ice maintenance activities.

Third, the episodic nature of precipitation events could alter the long-term retention of contaminants by woody materials. The flow configurations represented in Fig. 1 would result in intermittent periods of wetting and drying of the woody materials. Wetting (drying) of woody materials induces a slow swelling (shrinking) of the wood tissue (Stamm, 1964). At the beginning of a storm event, the initially-dry, shrunken wood materials may have few accessible sites for chemical interaction of dissolved contaminants. Dissolved contaminant access to sorption sites in the internal wood tissue would be exposed gradually by swelling during the storm event. In addition, the sharp increase in stormwater flow past the woody materials when a storm event commences may scour trapped particles (with associated contaminants) from a prior precipitation event, thereby mobilizing particle-associated contaminants.

Fourth, the changing properties of the wood material that occur during exposures to environmental conditions may influence contaminant retention. Sunlight, moisture content and temperature can promote chemical or microbial alterations of the wood tissue (Fiest and Hon, 1984). The ratio of wood components (lignin, cellulose, extractables) could change over time (Stamm, 1964), resulting in changes in the availability of sites to sorb dissolved contaminants. The development of small fissures in wood particles (Fiest and Hon, 1984) could increase accessibility of internal sorption sites for dissolved contaminants, or create more surface roughness to retain particles carried in stormwater. The growth of biofilms on the wood surface may provide additional sorption sites for dissolved contaminants (Martinez and Ferris, 2001).

Finally, the presence of multiple contaminants in stormwater runoff (*e.g.*, heavy metals) may result in competition between dissolved contaminants for sorption sites on wood materials (Stumm and Morgan, 1996). The importance of competition from other species for any one contaminant depends upon both the concentrations of the contaminants and the strength of the chemical interaction of the sorbed contaminants with the wood tissue (Stumm and Morgan, 1996).

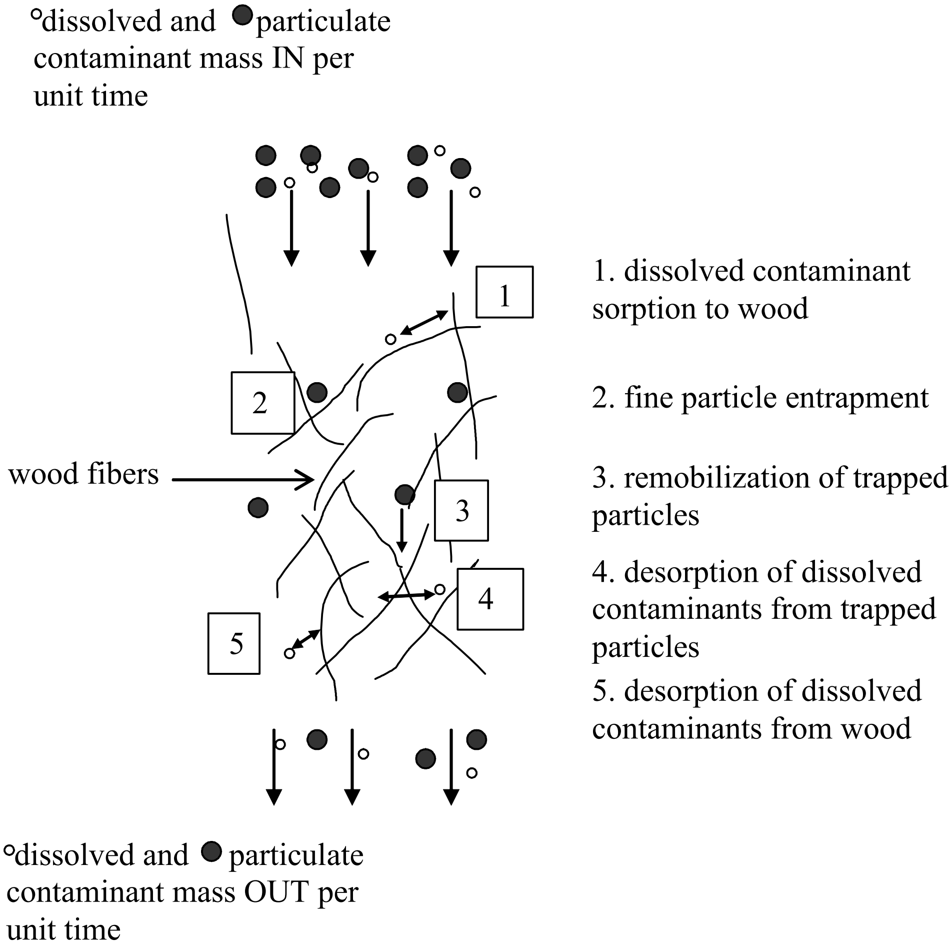
Figure 1. Interaction of stormwater with woody materials in stormwater control structures and processes affecting the retention of roadway-derived contaminants by woody materials.



(a) slope erosion control

(b) berm

(c) 'point source' culvert or detention basin outlet



3. Attenuation of Dissolved Heavy Metals by Wood Chips

Evaluations of heavy metal attenuation by wood chips were separated for dissolved and particle-associated contaminants because differing column construction schemes were required (see Section 3.1.3.1) and because differing runoff factors are anticipated to be important for these two types of contaminants.

3.1. Materials and Methods

3.1.1. Wood Chips

Wood chips were obtained from the Town of Vernon, CT, Parks and Recreation Department. The Vernon Parks and Recreation Department, like many Connecticut and New England municipalities, generates chips from wood collected during routine maintenance and pruning of vegetated areas. Typical tree species include oak and maple. Vernon chips were selected over wood chip samples from the Connecticut towns of Colchester, Avon and Mansfield after particle size distribution measurements showed Vernon chips to have a more uniform shape and a lower content of fines than the other chip samples. The uniform shape and size distribution of the Vernon chips would enable comparison among different samples. The small fines content of the Vernon chips would enable comparison between laboratory and field observations by reducing artifacts induced by wash-out of fines in a field setting.

All of the wood chips used for the experimental observations reported in this study were obtained a single sub-sample of the Town of Vernon wood chip stockpile. About 120 gal of wood chips were transported to the University of Connecticut. The wood chips were manually mixed on a large plastic sheet to homogenize the batch such that all aliquots used for experiments were assumed to have the same wood source composition and particle size distribution (Fig. 2). The wood chips were allowed to air dry for several days before being

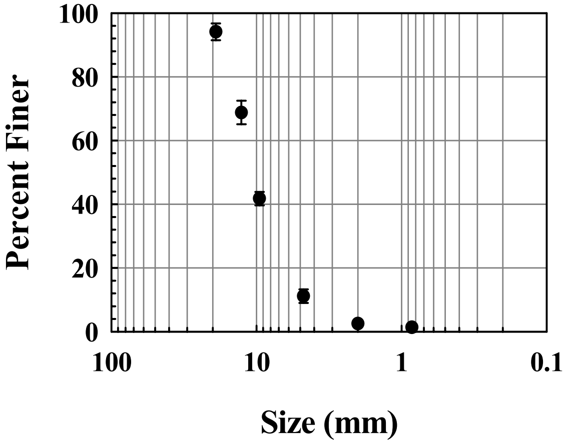


Figure 2. Particle size distribution of Vernon wood chips used for all experimental evaluations. Error bars show the range of particle sizes for three replicate measurements of particle size distribution obtained by dry sieving. Where not evident, error bars are smaller than the symbol size.

stored in 40 gal containers with loosely-closed lids. Unless specifically noted, stored, air-dried wood chips were used for all experiments.

Aliquots of wood chips were exposed to environmental conditions so that the effect of wood aging on heavy metal retention could be evaluated. The wood chips were contained within a wooden frame with three compartments and coarse mesh on the top and bottom. The frame was placed outside at the University of Connecticut Plant Science Research Facility in Mansfield, CT. The frame sat about 2.5 cm above the ground so that precipitation would flow through the wood chips and air could circulate below the bottom. Wood chips were added to a compartment in the structure periodically, such that separate aliquots were aged for 3 months (Dec. 2004 – Feb. 2005), 6 months (Sept. 2004 – Feb. 2005), and 9 months (Jun. 2004 – Feb. 2005).

3.1.2. Batch Sorption Measurements

The kinetics of water uptake and dissolved copper uptake by wood chips were examined in batch systems. Water content was determined by soaking a known mass of wood chips in high purity water. Periodically, the wood chips were weighed after draining the water from the chips and gently patting them with paper towel to remove residual water on the chip surfaces. The mass of water in the wood chips at each time point was calculated by difference between the wet mass of the wood chips and the initial dry mass. The fraction water saturation at each time point was determined by comparison with the mass of water in the wood chips after 480 hours (20 days) when the wet wood chips had reached constant mass.

Dissolved copper uptake by both dry and water-saturated wood chips was monitored as a function of time. Water-saturated wood chips were obtained by soaking dry wood chips in high purity water for 480 h until they had reached constant mass. Kinetic samples were obtained by adding 0.5 g of either initially dry-, or previously saturated wood chips to 250 mL of high purity water containing 300 μg/L of copper (added as copper sulfate, Fisher Scientific, Pittsburgh, PA). Wood chips were chosen to be of similar size for each sample bottle so that the rate of metal uptake would be similar across all bottles and all experiments. Duplicate samples were assembled for both dry and water-saturated wood chips and mixed end-over-end. Periodically, an aliquot of the solution phase was removed from each sample bottle to measure the copper concentration, as described in 3.1.4. Analytical. Sorbed copper concentrations in the wood chips were calculated by difference:

$$C_s = \frac{(C_0 - C_w)V_w}{M_s} \tag{1}$$

where C_s (μg/kg) is the sorbed concentration; C_0 (μg/L) is the initial aqueous phase concentration; C_w (μg/L) is the aqueous phase concentration at the time that the sample was obtained; V_w (L) is the volume of water, and M_s (kg) is the mass of solids.

Batch experiments were conducted to obtain effective sorption coefficients for heavy metals on wood chips. Independent measures of copper, lead, zinc, nickel and cadmium sorption were obtained so that they would not be confounded by competition among metals. Batch sorption samples were assembled in high density polypropylene bottles (250 mL, Nalgene, Rochester, NY). Metals were added to buffered high purity water as dilutions from a certified standard solution (1000 mg/L in 2% nitric acid, Fisher) to give 7 initial concentrations from 0 to 600 μg/L (8000 μg/L for copper). The aqueous phase was buffered using 10 mM MES (2-(Nmorpholino)ethanesulfonic acid), a buffer that does not form complexes with metals (Yu *et al.*, 1997). Solution pH was adjusted to 5 with addition of concentrated sodium hydroxide. Total solution volume was 240 mL. A pre-weighed mass of 0.5 g aged (9 months) wood chips was then added to each sample bottle. Wood chips were chosen to be of similar size for each sample bottle so that the rate of metal equilibration would be similar across all bottles and all experiments. The aqueous- and wood chip phases were allowed to mix end-over-end for 24 hours. Duplicate bottles were prepared for 3 of 7 concentration points. In addition, wood-free controls were included to account for metal losses to polypropylene bottles. Metal-free controls were assembled to account for metal contributions from the wood chips.

After the 24-hour contact time, aqueous and wood chip phases were separated for analysis. Aqueous metal concentrations were measured directly, as described in 3.1.4. Analytical. Solid phase concentrations (Cs, µg/kg) were calculated by difference:

$$C_s = \frac{M_0 - M_w}{M_s} \tag{2}$$

where M_0 (µg) is initial mass in the sample bottle contributed by the wood chip and the added metal stock; M_w (µg) is the mass of metal in the aqueous phase after 24 hours, and M_s (kg) is the added wood chip mass. Effective metal sorption coefficients, K_d^{eff} (L/kg), were obtained by linear regression of the sorbed concentration versus the aqueous concentration (C_w, µg/L) after 24 hours, such that:

$$K_d^{eff} = \frac{C_s}{C_w} \tag{3}$$

Mass balances on 25% of the tubes, including the metal-free wood control, were obtained using acid extraction. After separating the aqueous and wood chip phases, the wood chips were contacted with 30 mL of 5% nitric acid for 48 hours. The nitric acid extract was analyzed to quantify the metal concentrations.

3.1.3. Column Set-Up

Attenuation of dissolved heavy metals by wood chips was assessed using flow-through laboratory column experiments. The variables expected to affect dissolved heavy metal retention by wood chips were runoff flowrate, runoff salt content, wood chip wetting and drying cycles, wood chip aging and competition among dissolved heavy metals. These variables were evaluated using laboratory experiments so that they could be carefully controlled while applying synthetic runoff to wood chips with one-dimensional flow. Reproducible evaluations of these variables could not be obtained easily using field observations, as storm-to-storm heterogeneity in runoff flows and water quality parameters could mask specific variable effects.

A brief overview of the column experimental design is provided here (Fig. 3). A column that was packed with test media received flow in the downward vertical direction from a peristaltic pump. The pump was connected to by way of a three-way stopcock to two reservoirs – one containing synthetic runoff and the other containing high-purity water. Reservoir selection during the course of an experiment was made by manually switching the stopcock. At the start of the experiment, flow to the column was first directed from the high-purity water reservoir. This high purity water "pre-flush" (Fig. 3 (a)) was followed by flow from the synthetic runoff reservoir and finally, flow again from the high-purity reservoir. The resultant inlet concentration

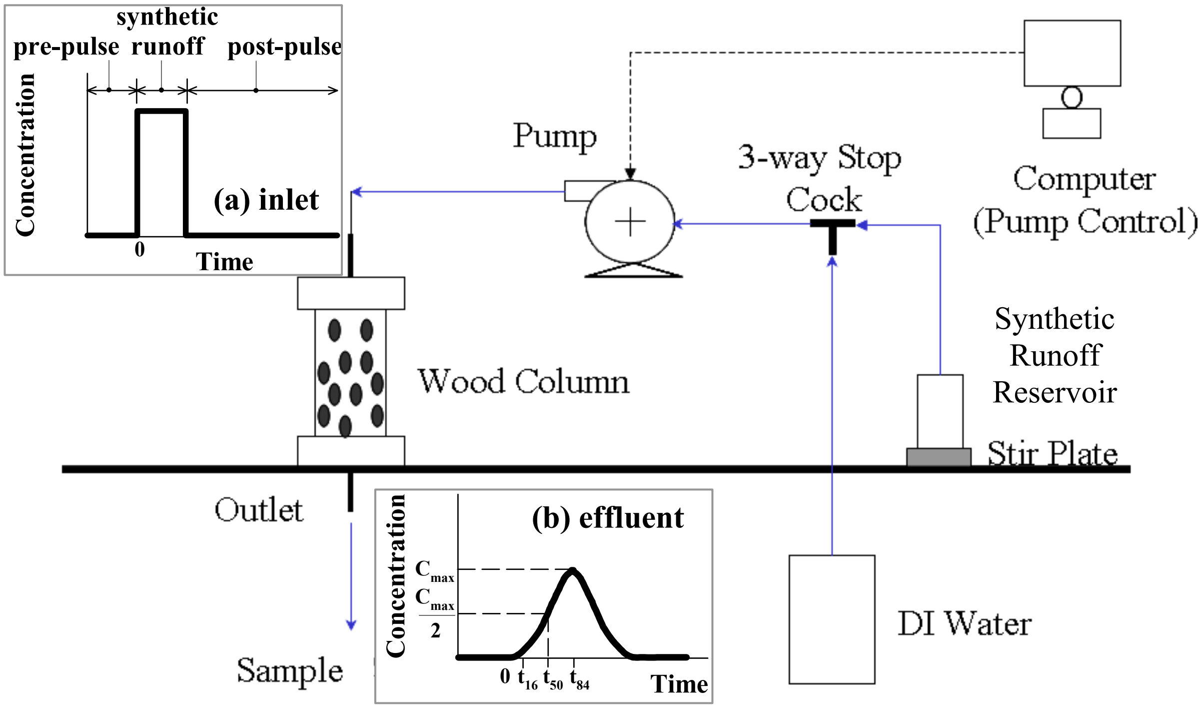


Figure 3. Schematic diagram of experimental column set-up. Inset figure 'a' shows the change in inlet water quality parameter concentration as a function of time. Inset figure 'b' shows a typical breakthrough curve of effluent water quality parameter concentration as a function of time.

of dissolved heavy metals for the column as a function of time (Fig. 3 (a)) mimics a typical "pulse" profile observed for runoff during a storm event (Sansalone and Buchberger, 1997a). Effluent samples were collected periodically at the outlet of the column to construct a breakthrough curve (Fig. 3 (b)) for assessing heavy metal attenuation by the column media.

3.1.3.1. Column Construction

Transparent schedule 40 polyvinylchloride (PVC) columns were used for all experiments (Fig. 4). The column dimensions were an internal diameter of 15.2 cm and a length of 30 cm. The top and bottom of the column were closed with solid plates attached by flange fittings glued to the outside of the column ends. The column end plates were sealed with Norprene gaskets and bolts. Flow was delivered to the top of the column and collected from the bottom of the column through 0.64 cm (0.25 in.) inner diameter tubing. The columns were packed with appropriate material. Then, the media was topped with 4 layers of mesh. The mesh sheets were layered in a "criss-cross" pattern to help distribute flow across the entire column diameter.

Figure 4. Experimental column set-up.

The column media used to assess dissolved heavy metal removal by wood chips was a mixture of wood chips and gravel. A preliminary experiment using a column packed entirely with wood chips showed that a non-sorbing salt tracer was transported through the column, but that dissolved copper was strongly sorbed with effluent concentrations that were below the limit of quantification (5 μg/L) during 8 hours of effluent sampling. Assessment of the effectiveness of wood chips for attenuating dissolved heavy metal concentrations required that detectable concentrations be obtained in the effluent. Consequently, columns were packed with a lesser quantity of wood chips, mixed with an inert solid (gravel) so that breakthrough curves with detectable concentrations would be obtained within a reasonable experiment duration and volume of runoff applied. The final column composition was 500 g wood chips mixed with 6400 g of gravel. A fresh column was packed for each variable evaluation. Thus, all breakthrough curves reported here were obtained from columns containing media that had not previously contacted synthetic runoff. The only exception was during the wet-dry cycle evaluation wherein the same column was subjected to repeated periods of drying followed by flushes with synthetic runoff. One column was packed with only gravel to verify that copper-gravel interactions were minimal. The gravel was chosen to have a similar particle size as the wood chips.

3.1.3.2. Synthetic Runoff

Dissolved heavy metals were delivered to the column in synthetic runoff prepared using high purity water. High purity water was obtained from a Diamond NanoPure (ThermoScientific, Barnstead, Waltham, MA) treatment system. Treatment consisted of reverse osmosis followed by polishing by ion exchange and activated carbon media. Produced water has a resistivity of greater than 18 MΩ·cm and an organic carbon content less than 5 μg/L. Metal concentrations were below the limit of quantification: 5 μg/L for copper, lead, cadmium and nickel; 10 μg/L for zinc. High purity water was air-equilibrated and had a pH of 5.5.

Copper was used as a representative dissolved metal for all experiments. Copper was chosen because it is a common contaminant in roadway runoff and it has a high toxicity to aquatic organisms. The nominal concentration of copper in synthetic runoff was 300 μg/L, a value chosen to be representative of field observations and to enable detection in effluent samples (Driscoll *et al.*, 1990; Sansalone and Buchberger, 1997b; Barrett *et al.*, 1998; Drapper *et al.*, 2000). Copper was added to high purity water as copper sulfate salt (Fisher). To minimize competition between copper and other metals typically present in roadway runoff, no other metals were present in synthetic runoff for experiments to evaluate method reproducibility, flowrate, wet-dry cycles and wood chip aging. General conclusions obtained for copper would also apply to other heavy metals of concern (lead, zinc, nickel, cadmium) because the aqueous chemistries of these elements are similar (Morel and Hering, 1993).

Effects of roadway runoff salt content on dissolved copper attenuation by wood chips were evaluated by adding sodium chloride to synthetic runoff. Three sodium chloride concentrations were tested: (1) 0.1 g/L (0.2 mS/cm), typical of summer conditions; (2) 1 g/L (2 mS/cm), the average salt content in runoff generated following winter deicing treatment, and (3) 10 g/L (20 mS/cm), a maximum winter value. Runoff salt concentrations were obtained from a detailed study of roadway runoff in Massachusetts (Granto and Smith, 1999) and were assumed to apply throughout New England.

Effects of competition among heavy metals on attenuation by wood chips were evaluated using synthetic runoff with copper, lead, zinc, nickel and cadmium. Nominal concentrations were added to be representative of those typically observed in roadway runoff (Driscoll *et al.*, 1990; Sansalone and Buchberger, 1997b; Barrett *et al.*, 1998; Drapper *et al.*, 2000): 300 μg/L copper, 500 μg/L zinc, 500 μg/L lead, 50 μg/L nickel and 50 μg/L cadmium. Metals were added by dilution from certified standards (1000 mg/L in 2% HNO_3, Fisher).

A summary of experimental conditions for all column experiments is provided in Table 1.

3.1.3.3. Flow Profile

A constant column flowrate of 74.2 mL/min was used for all experiments. This value was obtained by considering the amount of sheet flow intercepted by a treatment device during a typical rainfall event in Connecticut. The 2-year recurrence interval storm was characterized by a rainfall intensity of 0.16 mm/min and a 6-h duration (Ogden, 1998). Runoff was assumed to be generated from the crown of a two-lane road with paved shoulder. Flow interception by the treatment device was assumed to occur as sheetflow at the edge of the shoulder. Thus, the drained area was 3 m (12 ft) by 0.15 m (6 in. column diameter) and the resultant flowrate was 74.2 mL/min.

The effect of runoff flowrate on wood chip attenuation of copper was evaluated by conducting experiments at constant flowrates of 46.1 mL/min and 135 mL/min.

A "first-flush" (Sansalone and Buchberger, 1997a; Deletic, 1998) of contaminants was simulated in the column experiments by varying the inlet concentration of copper with time (Fig. 3(a)). Unlike a field setting in which the "first flush" derives from both changing contaminant concentrations and runoff flowrates, a constant flowrate was maintained through each experiment. First, the column was wetted with high purity water for 40 min (2900 mL flushing volume, equivalent to turning over the column pore space one time). Then the stopcock was switched to draw flow from the synthetic runoff reservoir containing the copper solution. Flow of synthetic runoff was maintained for 9.8 min (730 mL, equivalent to 0.25 pore volume turnovers) in copper-only experiments. (A synthetic runoff flow duration of 12.1 min was

Table 1. Summary of experimental conditions for all column experiments. Numbered entries (*i, ii, iii*) indicate parameter values varied in separate experiments.

Parameter	**Synthetic Runoff**	**Flowrate (mL/min)**	**Salt (mS/cm)**	**Wood Age**
Dissolved Heavy Metals				
Reproducibility	300 µg/L copper	74.2	0	0 mos
Flowrate	300 µg/L copper	*i.* 46.0 *ii.* 74.2 *iii.* 135.1	0	0 mos
Salt Concentration	300 µg/L copper	74.2	*i.* 0 *ii.* 2 *iii.* 20	0 mos
Wet-Dry Cycles	300 µg/L copper	74.2	0	0 mos
Wood Chip Aging	300 µg/L copper	74.2	0	*i.* 0 mos *ii.* 3 mos *iii.* 6 mos *iv.* 9 mos
Heavy Metal Competition	300 µg/L copper, 500 µg/L zinc, 500 µg/L lead, 50 µg/L nickel, and 50 µg/L cadmium	74.2	0	9 mos
Particle-Associated Heavy Metals				
Particle-Associated Heavy Metals	*i.* 200 mg/L SiO_2 *ii.* 2000 mg/L SiO_2	74.2	0	0 mos

maintained for the competition experiments.) Following synthetic runoff, flow was switched back to high purity water for at least 200 min (14.8 L, 5 pore volume flushes).

A conservative (non-sorbing) tracer was introduced to the column to characterize physical flowpaths in the column after the high purity water post-pulse flush was completed. The tracer solution of 5 g/L sodium chloride was introduced to the column at 74.2 mL/min for 9.8 min followed by high purity water flow for 40 min. The column tracer characterization followed the copper experiment so that the salt content of the tracer would not affect copper interactions with the wood chips.

Throughout the experiments, effluent samples (15 mL) were collected for analysis of water quality parameters. Samples obtained during the pre-pulse, synthetic runoff, and post-pulse intervals were acidified and analyzed for total copper (and lead, zinc, nickel, cadmium in competition experiments) (see Section 3.1.4). Samples obtained during the tracer characterization were analyzed for electrical conductivity as a surrogate measure for salt concentration.

3.1.4. Analytical Methods

Metal concentrations were quantified by graphite furnace atomic absorption spectrophotometry (GFAA, Perkin Elmer 5100 with palladium- and magnesium nitrate matrix modifier) or by inductively coupled plasma, optical emission spectrometry (ICP-OES, Perkin Elmer 3300XL with nitric acid digestion, EPA Method 200.7). All analyses were conducted at the University of Connecticut Center for Environmental Science and Engineering following accepted Quality Assurance/Quality Control standards. Instruments were calibrated with 5-point curves. Each set of 12 sample analyses contained a blank sample, a sample of known concentration (standard) and a sample with a known added mass of metal (standard addition).

Tracer concentrations were measured using an electrical conductivity probe (Orion 115Aplus).

3.1.5. Data Interpretation

Column effluent concentrations of heavy metals and of the tracer as a function of time were plotted as breakthrough curves (Fig. 3(b)). Effluent concentrations, C_{out}, were reported as reduced concentration by normalizing to the inlet synthetic runoff reservoir concentration, C_{in}:

$$\text{Reduced Concentration} = \frac{C_{out}}{C_{in}} \tag{4}$$

where dissolved metal concentrations were measured in units of μg/L and tracer concentrations were measured in units of mS/cm. Reduced concentrations were used in these plots to normalize for differences in inlet runoff reservoir concentrations: Solutes with identical transport through the column and identical wood interactions should have identical breakthrough curves when plotted as reduced concentration. Comparisons between breakthrough curve shapes among solutes can be used to infer differences in transport and/or wood interactions between solutes.

Tracer effluent breakthrough curves were used to obtain information about solute travel times through the column. Under ideal conditions of constant linear velocity for all flowpaths in the column, the effluent concentration of tracer should instantaneously rise to the runoff reservoir concentration (*i.e.*, reduced concentration = 1) at time equal to the travel time through the column (velocity/column length). Similarly, when flow is switched from the runoff reservoir to tracer-free high purity water at time ‘t’, the effluent concentration of tracer should decrease to zero at time equal to ‘t + travel time’. Thus, the ideal tracer breakthrough curve would have an identical shape to the inlet curve, Fig. 3(a), but shifted in time by an amount equal to the travel time through the column.

In a real column, tortuous flow paths around the wood chips give rise to a distribution of travel times through the column. This phenomena, called dispersion (Domenico and Schwartz, 1990), causes the actual tracer breakthrough curve to have a sigmoidal shape as it rises to a maximum reduced concentration and then decreases back to 0 (Fig. 3(b)). For tracer curves that reach a maximum reduced concentration of 1, as occurred in our experiments (*e.g.*, section 3.3), the average travel time through the column can be approximated by the time at which the reduced solute concentration of a non-sorbing tracer is 0.5 (t_{50}, Fig. 3(b)). A greater amount of dispersion in the column gives more spreading around t_{50}. Various approaches to compare dispersion among columns utilize the ratio, or difference, between the times at which the reduced concentration is equal to 0.16 (t_{16}, Fig. 3(b)) and 0.84 (t_{84}, Fig. 3(b)) of the maximum value (Domenico and Schwartz, 1990). The amount of dispersion determined from a non-sorbing tracer is assumed to be the same for solutes that interact with wood because all solutes follow the same tortuous flow paths through the column (Domenico and Schwartz, 1990).

Solute-wood interactions, such as by heavy metals, will cause differences in breakthrough curve shape compared to a non-sorbing tracer. First, the average travel time of a sorbing solute will be longer than for a non-sorbing solute because a portion of the solute mass in the column is non-mobile while interacting with the wood media. Second, the breakthrough curve shape of a sorbing solute can be more spread out than from dispersion alone if there are mass-transfer kinetics associated with the solute-wood interaction, such as diffusion into internal pore spaces (Brusseau *et al.*, 1991). Both the longer travel time and the increased spreading can lead to maximum reduced concentrations that are less than 1 for a pulse-shaped column input. Thus, the breakthrough curve of a sorbing solute is delayed in time and more “spread” out than that for a non-sorbing tracer in the same column.

Three metrics are used herein to make comparisons between breakthrough curves and to assess whether test variables had an effect upon copper transport through the column: (1) the maximum reduced concentration, (2) the degree of curve spreading, and (3) the mass of copper eluted at a time equal to 4 times the duration of the synthetic runoff pulse. Comparison of the mass of copper eluted from the column with the mass of copper known to be introduced to the column in the synthetic runoff indicates the degree of reversibility of the copper-wood interaction. Ideally, the mass of copper eluted from the column would be obtained by integrating the area under the breakthrough curve; however, integration of the low effluent concentrations sustained over long time periods during the post-pulse high purity water flush – the breakthrough curve “tail” – can introduce error into the mass calculations because effluent concentrations for the tail are at, or near, the analytical detection limit. Furthermore, an unknown amount of copper was leached from the wood chips themselves during each experiment. The mass of copper eluted from the columns was calculated at a time equivalent to 4 times the duration of the synthetic runoff pulse to minimize uncertainty from poor characterization of the breakthrough curve tail.

3.2. Copper Sorption to Wood Chips

Preliminary observations were made to assess the mass transfer kinetics associated with dissolved metal uptake by the wood chips. Wood chip deployments to attenuate heavy metals in the field were envisioned to be configurations in which roadway runoff would contact initially-dry wood chips. Under dry conditions, wood fibers shrink to have low internal porosity (Stamm, 1964). Thus, only sorption sites on the chip surface would be available for dissolved heavy metal uptake during early stages of a storm event, when contaminant solute concentrations in runoff may be greatest. Over increasing time of contact with water, wood chips would swell to have larger internal porosity and to become saturated with water. Saturated wood chips should have a greater sorption capacity for dissolved heavy metals because internal sites would be present in water-filled pores. The extent to which these internal sorption sites may be available

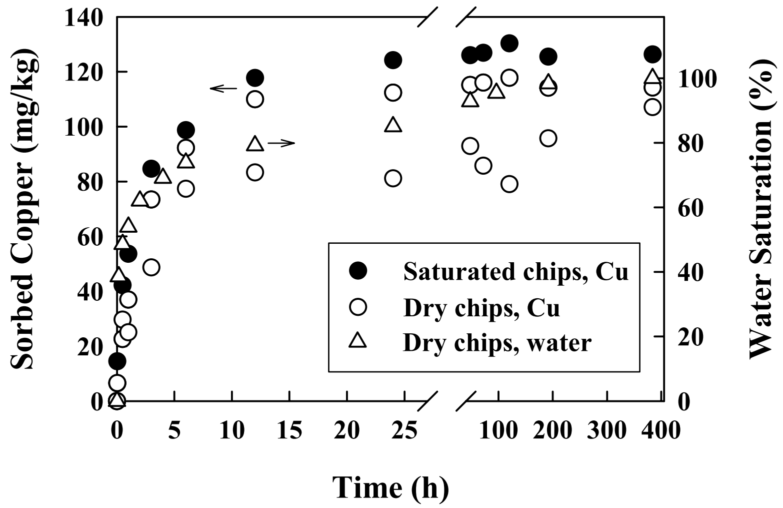


Figure 5. Uptake of copper and water by wood chips. Copper uptake in by saturated wood chips was obtained for wood chips that had soaked in water for 480 h prior to contact with a copper-containing solution.

for dissolved heavy metal uptake in a field configuration may be limited by the short contact times between runoff and wood chips (order minutes in our sheetflow column scenario), and by the long time scales to achieve chip saturation (order weeks for centimeter-sized chips (MacKay and Gschwend, 2000)).

Although weeks were required to fully saturate Vernon wood chips, saturation level had little effect on the kinetics of dissolved copper uptake over short timescales of contact (Fig. 5). Over the first hour of contact with a 300 μg/L copper solution, sorbed copper concentrations in initially dry wood chips (○, Fig. 5) were indistinguishable from those in wood chips that had been pre-saturated by soaking in water for 20 days (●, Fig. 5). Concurrently, during the first 30 min of solution contact, the dry wood chips would take up an amount of water equivalent to 50% of the saturated value. At contact times longer than 1 hour, sorbed copper concentrations in initially dry wood chips were lower than those for pre-saturated wood chips, indicating slower copper uptake kinetics for dry wood chips than for wet wood chips. The rate of water uptake by wood chips (▲, Fig. 5) also slowed after 1 hour, suggesting that the rate of copper sorption to initially dry wood chips was kinetically-limited by water uptake. Eventually, sorbed copper concentrations in initially dry wood chips at 380 hours did reach levels comparable to those in pre-saturated chips. The agreement in sorbed copper concentrations between initially dry- and pre-saturated wood chips after 380 h is consistent with the dry chips having attained the same level of saturation as the pre-saturated chips by this time. Overall, the results of this kinetic investigation indicate that heavy metal uptake by wood chips will occur over short time scales, whether or not wood chips are fully saturated with water.

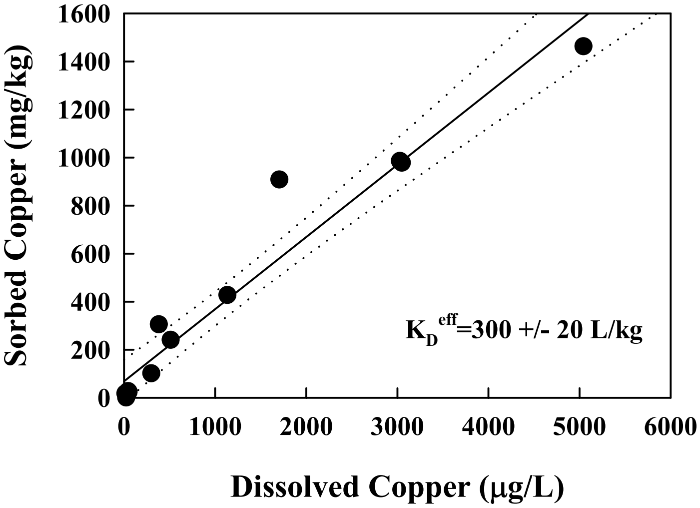


Figure 6. Copper sorption isotherm for initially dry wood chips. Dissolved copper concentrations were measured after 24 h of contact time between the wood chips and the copper solution.

An effective copper sorption coefficient of 300 (± 20) L/kg was measured for dry wood chips after a 24-h contact time (Fig. 6). A contact time of 24 h was chosen to minimize kinetic artifacts during sample tube assembly and manipulation. An effective sorption coefficient obtained for a contact time of several minutes would have been more representative of field conditions; however, sample handling would not be reproducible over that time scale because of the rapid change in water saturation and copper concentration over that time period (Fig. 5). With a 24-h contact time, the relationship between the sorbed and dissolved copper concentrations was linear, indicating that saturation of copper sorption sites was not observed with initial copper concentrations as high as 8000 µg/L that were about two orders of magnitude greater than typically observed in roadway runoff (Driscoll *et al.*, 1990; Sansalone and Buchberger, 1997b; Barrett *et al.*, 1998; Drapper *et al.*, 2000).

3.3. Reproducibility

Replicate tests of tracer and copper transport through the column were conducted to verify that our column assembly method was reproducible. Column assembly entailed packing media that was heterogeneous in both composition (wood/gravel mix) and particle size. Since a new column was packed for each variable evaluation (e.g. low-, intermediate-, high flowrate, etc.), copper transport through the column could be affected by both changes in the variable tested and by column-to-column differences in packed mixture composition and particle size distribution. Non-sorbing sodium chloride tracer transport through columns was used to assess similarities in physical flowpaths among columns. Copper transport through the columns was used to assess similarities in wood chip sorption interactions among columns.

Tracer breakthrough curves indicated that flowpaths among columns were similar (Fig. 7). For each of the breakthrough curves, the maximum tracer reduced concentrations were within 10% of each other. The shape of the breakthrough curve was reproducible from tracer test to tracer test with a sharp increase in the reduced concentration following the start of the

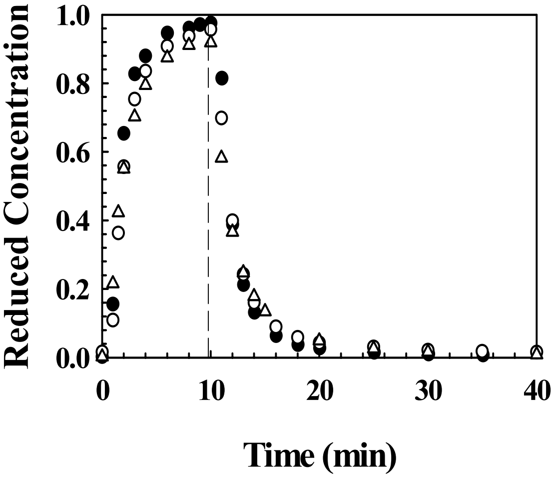


Figure 7. Triplicate tracer breakthrough curves from wood-gravel columns. The vertical dashed line indicates the time at which flow to the column was switched from the tracer-containing runoff reservoir to high-purity water.

tracer pulse, and a sharp decrease in tracer concentration at the end of the tracer pulse. Consequently, flowpaths for copper were assumed to be the same in all columns and any differences in copper breakthrough curves could be ascribed to differences in sorption.

Copper breakthrough curves indicated that wood chip interactions were similar among columns (Fig. 8). Three of four breakthrough curves were virtually identical (●,○,□, Fig.8), while the fourth (△) had a similar shape, but a lower maximum reduced concentration. The synthetic runoff inlet copper concentration could not explain differences among the four curves since the △ curve concentration (244 μg/L) was intermediate to the other three (225 – 295 μg/L). Inlet concentration could have an effect on breakthrough curve shape if a non-linear relationship between aqueous and sorbed copper concentration were suspected. Since the copper isotherms suggested a linear relationship (see Section 3.2), the breakthrough curves were taken to represent the range in transport variations of a sorbing tracer resulting from column packing.

Reduced concentrations observed at 8 min for the four breakthrough curves in Fig. 8 were used to calculate confidence intervals for subsequent copper transport tests. The average reduced copper concentration at 8 min was 0.23 with a population standard deviation of 0.05 units. Therefore, copper breakthrough curves were interpreted to differ from one another if their maximum reduced concentrations (6 min < t < 10 min) were separated by more than 0.1 units.

3.3.1. Copper Sorption to Wood

Several lines of evidence suggested that interaction between dissolved copper and wood occurred during column transport. The copper breakthrough curves from the wood-gravel columns had markedly different shapes than for tracer curves in the same column (Fig. 8). The maximum effluent concentration of copper from the experiment with C_0 = 225 μg/L

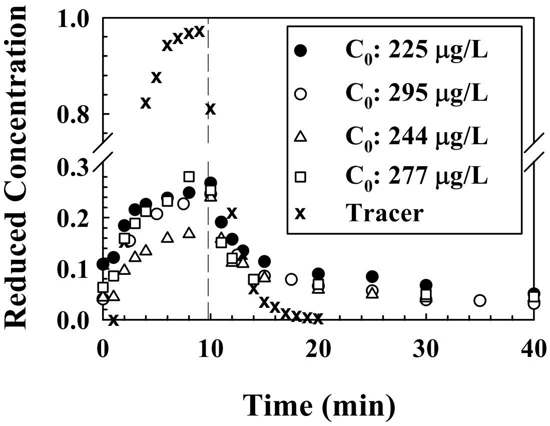


Figure 8. Replicate copper breakthrough curves from wood-gravel columns. The dashed vertical line indicates that time at which flow was switched from the synthetic runoff reservoir to the high purity water post-pulse flush.

(●) was only 0.25 times the inlet synthetic reservoir concentration, whereas the tracer reached a reduced concentration of almost 1 (Fig. 8). The change in breakthrough curve shape at times coincident with the beginning (t = 0 min) and ending (dashed line, t = 9.7 min) of the synthetic runoff pulse delivery to the column was much steeper for the tracer than for copper, with copper exhibiting long tailing beyond 40 min. Furthermore, the fraction of compound mass eluted occurred much later in time for copper than for the tracer. After 40 min (synthetic runoff pulse plus three equivalent volumes of high-purity water post-pulse), between 33 and 49 % of the copper mass had been eluted from the column (Tab. 2), compared to greater than 96% for the non-sorbing tracer. Similar observations could be made for the other copper breakthrough curves (○,□,△, Fig. 8); however, comparative tracer curves were not shown in Fig. 8 to reduce crowding. Together, these observations support the conclusion that copper transport through the column was influenced by a sorptive interaction with the wood chips.

Note that copper interactions with the gravel in these "mixed" wood-gravel columns could be excluded because the breakthrough curve for copper in an all-gravel column differed little from the tracer breakthrough curve in the same column (Fig. 9). As the tracer curve shape indicates dispersive effects from the distribution of tortuous flow paths within a column, a coincident copper breakthrough curve indicates that copper transport through the gravel column is influenced only by dispersion. Thus, no sorptive interactions would occur between copper and the gravel used in the "mixed" gravel/wood columns and any differences between tracer and copper breakthrough curves in the mixed columns must be attributed to copper interactions with wood particles.

The sorptive interaction between copper and the untreated wood chips was likely a reversible process. At the time that the experiments were truncated (180 – 200 min), between 60

Table 2. Summary of breakthrough curve characteristics for dissolved heavy metal column experiments.

Parameter	**Copper C/C_0 (Maximum) ($6\ \text{min} < t < 10\ \text{min}$)**	**Copper M_w/M_0 (%) ($t = 4 \times$ pulse length)**
Dissolved Heavy Metals		
Reproducibility	0.28	49
	0.25	39
	0.27	48
	0.24	33
	Average: 0.26 ± 0.02	Average: 42 ± 7
Flowrate – *i.* 46 mL/min	0.29	50
ii. 135 mL/min	0.3	50
Salt Concentration – *i.* 2 mS/cm	0.4	60
ii. 20 mS/cm	0.56	67
Wet-Dry Cycles – dry column	0.26	41
i. 2-d dry period	0.26	25
ii. 5-d dry period	0.24	30
iii. 15-d dry period	0.24	26
Wet-Dry Cycles – wet column	0.11	17
i. 2-d dry period	0.17	19
ii. 5-d dry period	0.19	22
iii. 15-d dry period	0.21	23
Wood Chip Aging – *i.* 3 mos	0.11	27
ii. 6 mos	0.05	10
iii. 9 mos	0.03	3
Heavy Metal Competition – Copper	0.2	46
	0.14	29
Zinc	0.13	37
	0.11	27
Lead	0.05	6
	0.02	2

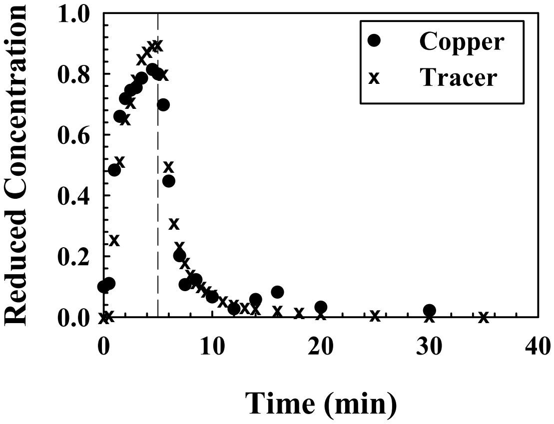


Figure 9. Tracer and copper breakthrough curves for an all-gravel column. The dashed vertical line indicates that time at which flow was switched from the synthetic runoff reservoir to the high purity water post-pulse flush.

and 90 % of the copper mass in the synthetic runoff pulse had been eluted from the column. It is likely that the low copper concentrations, close to the analytical detection limit, would have continued to be observed in the effluent if the high-purity water post-pulse flush had been maintained for a longer time. Thus, permanent retention of dissolved copper by the wood chips was not observed, rather wood chips served to attenuate the concentration of dissolved copper in time so that a longer sustained low-concentration of copper was released from the wood column compared to the short, high-concentration pulse input to the column.

3.4. Flow Rate

Flowrate had little effect on the attenuation of copper by wood chips. The comparison plots of flowrates that differed from a factor of 2 from the standard 74.2 mL/min are shown in Fig 10 with reduced time on the x-axis. Use of the variable reduced time normalizes for the difference in absolute time to deliver the same volume of synthetic runoff using different flowrates:

$$\text{Reduced Time} = \frac{t \times Q}{V_p} \tag{5}$$

where t (min) is time, Q (mL/min) is flowrate of experiment, and V_p (mL) is volume of empty pore space in column (2900 mL). Little difference in breakthrough curve shape was observed for the experiments. The maximum reduced concentrations for each case were within ± 0.05 and the curves showed similar extents of tailing. The copper mass eluted at 40 min was 50% for the 46 and 135 mL/min flowrates, within the range observed for the standard 74.2 mL/min (Tab.2). Greater than 80% of the copper mass was recovered by the termination of the experiment. Thus,

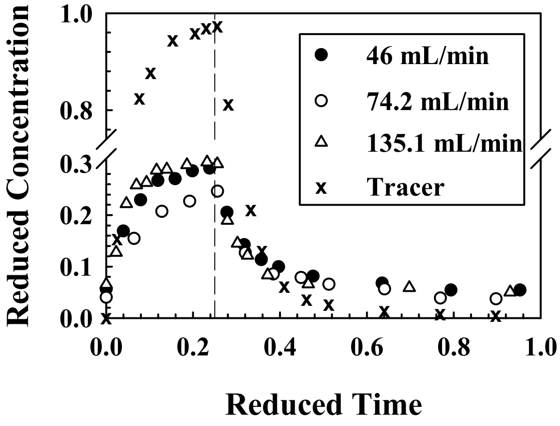


Figure 10. Effect of flowrate on dissolved copper breakthrough. The dashed vertical line indicates that time at which flow was switched from the synthetic runoff reservoir to the high purity water post-pulse flush. Time is plotted as reduced concentration to account for differences in travel times among the flowrates tested.

copper interaction with wood chips was not sensitive to column flowrate over a range corresponding to sheetflow runoff from a 12-h duration storm (46 mL/min) or a 2-h duration storm (135.1 mL/min) with a 2-year recurrence interval. (The flowrate of 135.1 mL/min also corresponds to a 5 to 50-year recurrence interval storm with a 3- to 10-hour duration.)

3.5. Synthetic Runoff Salt Content

The presence of salt in synthetic runoff suppressed the interaction of dissolved copper with the woodchips (Fig. 11). The maximum reduced copper concentration increased from 0.28 to 0.39 to 0.55 as the salt concentration was increased from summer (0 mS/cm, ○, Fig. 11), to average winter (2 mS/cm, ●, Fig. 11), to maximum winter (20 mS/cm, △, Fig. 11) conditions, respectively. The mass of copper also eluted earlier with increasing salt concentration. After 20 min (synthetic runoff pulse plus one equivalent volume of high-purity water post-pulse flush), the mass of copper eluted from the 0 mS/cm column was 22% (± 4%) of the mass input in the synthetic runoff pulse, whereas, 34% copper mass was recovered from the 2 mS/cm column and 50% from the 20 mS/cm column (Tab. 2). Ultimately, all of the copper mass was recovered from the latter two columns by the end of the post-pulse flush. Thus, the presence of salt in roadway runoff diminishes the attenuating effect of the wood chips on copper concentrations of the effluent, relative to the pulse input.

Two factors could contribute to decreased attenuation of copper by wood chips in runoff with high salt content. First, the much greater concentration of sodium ions (36 000 ×) could out-compete low levels of copper ions for cation exchange sites on wood surfaces despite overall

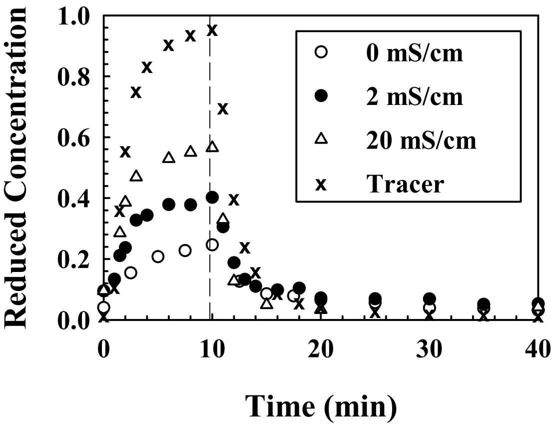


Figure 11. Effect of salt concentration on dissolved copper breakthrough. The dashed vertical line indicates that time at which flow was switched from the synthetic runoff reservoir to the high purity water post-pulse flush.

weaker strength of sodium complexes than copper complexes (Stumm and Morgan, 1996). Second, copper-chloride complexes in the aqueous phase may have less affinity for the wood surface because of lower net charge (neutral or anionic) than the cationic cupric ion (Morel and Hering, 1993). Together these factors would indicate that wood chips provide poor treatment for runoff generated in winter conditions when deicing salts are applied to roadways.

3.6. Wet-Dry Cycling

Dissolved copper transport through columns subject to alternating wet and dry conditions was investigated to represent field conditions. Wood chip deployments in the field were envisioned to occur as treatments that would receive intermittent flows. Dissolved heavy metal concentrations in stormwater runoff generated in a storm event would be attenuated by wood chips, after which the wood chips would experience a period of drying as rainfall events are typically separated. There was concern that metals retained by wood chips from one storm event could be mobilized by flow from a subsequent storm event such that the wood chips could serve as a source of dissolved metals in subsequent storms. Repeat runoff events were simulated with four alternating wetting and drying cycles on the same columns, one packed with initially-dry wood chips and the other with pre-saturated (480-h) wood chips. A synthetic runoff ‘event’ was simulated for each column and followed by a 2-d drying period. A second runoff ‘event’ was followed by a 5-d drying period. A third runoff ‘event’ was followed by a 15-d drying period and then the fourth ‘event’. Synthetic runoff ‘events’ are differentiated according to the duration of the antecedent drying period (0 d, 2 d, 5 d, 15 d).

Copper breakthrough curves for columns subjected to intermittent wetting and drying periods suggested that dissolved copper attenuation by wood chips was more effective for wet wood chips. Comparison was first made between the copper breakthrough curves obtained for

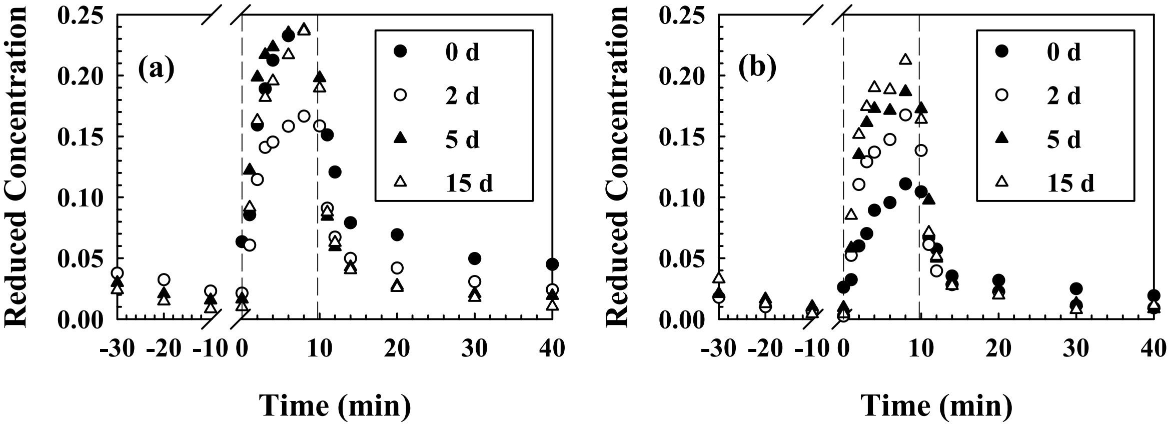


Figure 12. Effect of repeat wet-dry cycles on copper breakthrough. (a) Column containing air-dried wood chips at the time of the first synthetic runoff pulse. (b) Column containing water-saturated wood chips at the time of the first synthetic runoff pulse. The legend scale denotes the duration of the antecedent drying period before the synthetic runoff pulse was introduced. The dashed vertical line indicates that time at which flow was switched from the synthetic runoff reservoir to the high purity water post-pulse flush. Note the change in y-axis scale, relative to Fig. 7 – 11.

the first synthetic runoff pulses (0 d antecedent drying period) introduced to columns that contained initially dry wood chips (●, Fig. 12 (a)) and pre-saturated wood chips (●, Fig. 12 (b)). The maximum reduced copper concentration was decreased for the pre-saturated wood chip column (0.11) compared to the initially dry column (0.26) (Tab. 2). In addition, the mass of copper eluted from the pre-saturated wood chip column was lower than for the dry column (Tab. 2) both after 40 min of flushing (synthetic runoff pulse plus three equivalent times with high-purity water post-pulse flush) and at the conclusion of the post-pulse flush. These observations suggest that wetting of the wood chips increased the availability of copper interaction sites in the wood tissue, likely because of the concomitant swelling that would occur with saturation.

Little of the copper retained by the wood chips in either the initially-dry or pre-saturated column was released during subsequent "storm" events. Copper concentrations observed during the pre-flush (-30 to 0 min before the synthetic runoff pulse introduction) would be contributed by copper that originated from the wood chips because the column flushing solution during this period was copper-free high-purity water. Between -30 and 0 min, there was no significant difference (< 0.05) between the reduced copper concentrations preceding the second synthetic runoff pulse (2 d, ○) for the columns with the initially-dry (Fig. 12 (a)) and pre-saturated (Fig. 12 (b)) wood chips. The copper concentrations from the column with initially-dry wood chips (12 μg/L) were slightly higher than for the pre-saturated wood chip column (5 μg/L), despite greater fractional retention by this column of copper added during the first synthetic runoff pulse.

Greater mobilization (higher concentrations, more copper mass eluted) of copper might have been expected from the column with greater copper mass retained from the synthetic runoff pulse (*i.e.*, less copper mass eluted during the post-pulse flush); however, little change in copper reduced concentrations during the pre-pulse period (-30 to 0 min) was observed for either column (▲,△, Fig. 12 (a),(b)) confirming that copper was retained strongly by the wood chips.

The initial water level of the wood chips had little effect on copper attenuation after repeated cycles of wetting and drying periods. The maximum reduced concentrations for the third (5 d, ▲) and fourth (15 d, △) synthetic runoff pulses for both the initially-dry and pre-saturated wood chip columns were not significantly different from each other, or between the two columns (Fig. 12 (a),(b)). Similar trends were observed for the mass of copper eluted from the column. The column containing initially-dry wood chips exhibited a decrease in copper mass eluted, and the column containing pre-saturated wood chips exhibited an increase in copper mass eluted, but both columns reached similar levels of 23 to 26% at 40 min after three or four cycles (Tab. 2). It is likely that three or four cycles of wetting and drying periods caused the initially-dry and the pre-saturated wood chips to have similar, intermediate levels of water saturation. This intermediate water saturation level was sufficient to produce greater attenuation of copper (lower eluted concentrations, greater copper mass retention) than for the untreated wood chip case.

Results from this experiment examining effects of wood chip exposure to intermittent wetting and drying periods indicate that wood chips will provide more effective attenuation of dissolved copper in stormwater runoff during closely-spaced storms when wood chips are partially- or completely water-saturated. The overall effectiveness of partially saturated wood chips is unclear: Stormwater from closely spaced storm events may have lower concentrations of heavy metals that stormwater generated after a long antecedent dry period because the mass of contaminants deposited on the roadway surface could be lower between closely-spaced storms than for storm events separated by long periods of dry weather.

3.7. Wood Aging

Wood aging was the most effective treatment for attenuating dissolved copper. The maximum reduced concentration of copper decreased from 0.26 to 0.11 after aging wood chips outdoors for 3 months (○,●, Fig. 13). Additional decreases in the maximum reduced copper concentration were observed after 6 (△, Fig. 13) and 9 (▲, Fig. 13) months of aging; however, these differences were not significant within the reproducibility criteria of 0.05 units. In addition, the mass of copper eluted from the column during the post-pulse flush decreased with increasing extents of wood chip aging (Tab. 2). Wood chips that had been aged for 9 months retained greater than 97% of the dissolved copper introduced in the synthetic runoff pulse (Tab. 2).

The increased retention of copper mass among the aged wood chips suggested that the interaction between the copper and the wood chips may have changed to a more irreversible sorption mechanism. Certainly, the effective copper sorption coefficient for 9-month aged wood chips (790 ± 60, Tab. 3) was greater than for the untreated, 0-month aged wood chips. It is unknown what attributes of the wood chips may have changed during the aging process to increase the effectiveness of dissolved copper retention. Possible explanations could be the development of micro-fissures, allowing more access to internal wood tissue, or the formation of sorptive biofilms (Fiest and Hon, 1984). Wood chip saturation level could not explain the

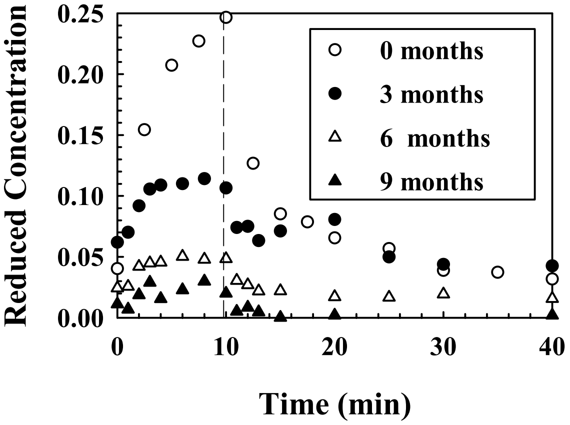


Figure 13. Effect of wood aging on copper breakthrough. The dashed vertical line indicates that time at which flow was switched from the synthetic runoff reservoir to the high purity water post-pulse flush. Note the change in y-axis scale, relative to Fig. 7 – 11.

differences in dissolved copper retention because all of the wood chips were retrieved on the same date so the last three months of environmental exposure was the same for all of the chips. Aging did result in noticeable coloration changes to the wood chips with increasingly darker coloration observed for chips that were aged 3, 6, and 9 months. Although the "0-month" wood chips were not collected freshly from a chipper and had spent an unknown period of time in a large outdoor storage pile, the blonde coloration of 0-month chips, similar to freshly-chipped wood, suggested that alterations of the wood were minimal during storage in the wood pile.

3.8. Competition Between Copper and Other Heavy Metals

Dissolved copper interactions with wood particles could be affected by competition for interaction sites from other dissolved heavy metals in stormwater since heavy metal cations have similar aqueous chemistries (Morel and Hering, 1993). Other heavy metals commonly present in stormwater include zinc, lead, nickel and cadmium. Along with copper, these elements constitute the heavy metals of greatest environmental concern when typical stormwater concentrations and toxicological impacts are considered.

3.8.1. Isotherms

Sorption isotherms were obtained for heavy metals commonly observed in roadway runoff to identify the relative strengths of interaction of these cations with wood particles. Independent systems containing only one heavy metal element were examined for copper, zinc, lead, nickel and cadmium using wood chips that had been aged for 9 months outdoors. The isotherms obtained for each of these elements were linear over the environmentally-relevant range of dissolved phase concentrations tested (0 – 600 μg/L). Effective metal sorption

Table. 3. Effective sorption coefficients for heavy metals sorbed to 9-month aged wood chips.

Metal	**Effective Sorption Coefficient, K_D^{eff} (L/kg)**
Copper	790 ± 60
Lead	2400 ± 140
Zinc	560 ± 60
Nickel	190 ± 50
Cadmium	470 ± 60

coefficients increased in the order: lead >> copper > zinc > cadmium > nickel (Tab. 3). The relative ranking of metal sorption coefficients suggested that, when present at similar concentrations, dissolved lead may provide the strongest competition for copper interaction sites. Ultimately, the net effect of competition between heavy metals for wood chip interaction sites depends upon both the strength of interaction (K_D) and the abundance (dissolved concentration) in the aqueous phase (*e.g.*, a high concentration of a weakly-sorbing heavy metal may out-compete a strongly-sorbing metal cation present at a very low concentration).

3.8.2. Column Studies

The presence of other heavy metals in synthetic runoff suppressed the interaction of copper with wood chips. The effects of competition on copper attenuation were investigated using wood chips that had been aged for 9 months because this wood chip treatment had yielded the greatest copper removal (▲, Fig. 13). In contrast, the copper breakthrough curve obtained using synthetic runoff containing 300 µg/L copper, 500 µg/L zinc, 500 µg/L lead, 50 µg/L nickel and 50 µg/L cadmium (○, Fig. 14) exhibited characteristics that were more similar to the case of untreated wood (*e.g.*, Fig. 8). The maximum reduced copper concentration increased from about 0.03 to about 0.15 and the copper mass eluted from the column increased from 3% to about 40% of the mass introduced. Thus, the presence of other dissolved heavy metals in stormwater reduces the effectiveness of dissolved copper attenuation by wood chips.

Examination of the breakthrough curves for the other heavy metals indicated that lead had the strongest interaction with the wood, as suggested by the isotherms (Tab. 3). The maximum reduced concentration for lead was between 0.02 and 0.03, and the lead mass eluted was 2 – 6 % of the mass introduced in the synthetic runoff pulses after 50 min (12-min pulse duration plus 3 equivalent durations of high-purity water post-pulse) (Tab. 2). The zinc (△, Fig. 14) breakthrough curves exhibited similar characteristics to copper (●, Fig. 14): Effluent concentrations were decreased relative to synthetic reservoir levels; however, all of the input zinc mass was eventually recovered.

Note that all nickel and cadmium concentrations were below the detection limits (5 µg/L). Concentrations were attenuated, relative to the influent synthetic runoff concentration (50 µg/L). No assessment of removals was possible; however, the lower K_D values of nickel and

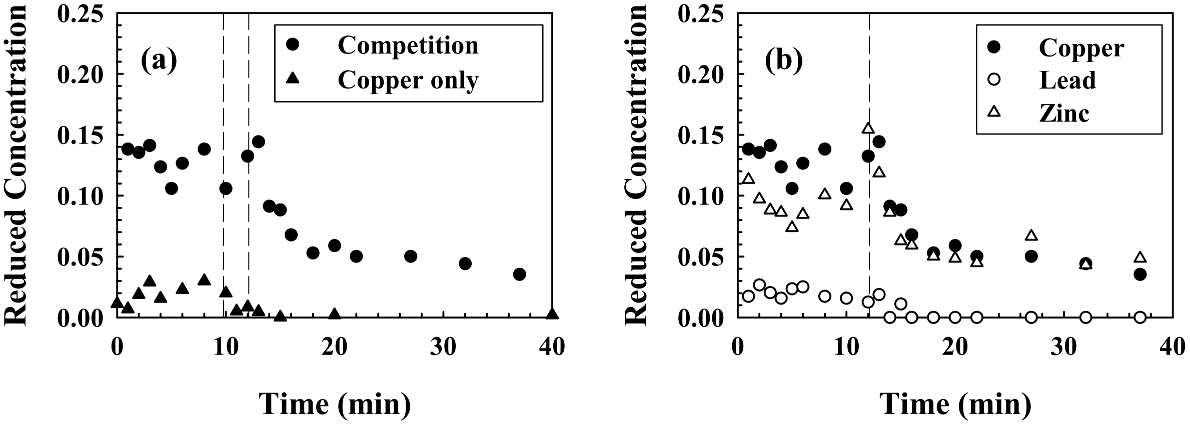


Figure 14. Effect of competition on copper breakthrough with 9-month aged wood chips. (a) Comparison between copper breakthrough curves obtained using synthetic runoff containing only copper with synthetic runoff containing copper, lead, zinc, nickel and cadmium. (b) Comparison between breakthrough curves for copper, lead and zinc obtained using synthetic runoff containing copper, lead, zinc, nickel and cadmium. The dashed vertical line indicates that time at which flow was switched from the synthetic runoff reservoir to the high purity water post-pulse flush (9.7 min for copper only; 12.1 min for competition). Note the change in y-axis scale, relative to Fig. 7-11.

cadmium, than for copper and zinc (Tab. 3), suggested that little irreversible removal likely occurred for these metals.

4. Particle-Associated Heavy Metals

The attenuation of particle-associated heavy metals by wood chips was examined independently of dissolved copper attenuation because different stormwater factors would affect the removal these two pools of contaminants. Particle-associated heavy metals were thought to be retained within the small pore spaces between wood particles (Fig. 1, [2]). Consequently, this process could only be examined using columns that were packed with wood chips, not a wood-gravel mix, as necessitated for dissolved copper (see Section 3.1.3.1.). Wood columns were used to assess particle retention by this media, and hence, by inference, the retention of contaminants associated with those particles.

4.1. Methods

The methodology to assess particle-associated heavy metal attenuation followed the same general protocol as that used for assessing dissolved copper attenuation (see Section 3.1.).

Aspects of the experimental protocol that differed for particle-associated heavy metal attenuation are described below.

4.1.1. Column Set-Up

Columns were packed entirely with wood chips to assess particle-associated heavy metals. It was anticipated that heavy metals associated with particles in roadway runoff would be attenuated by retention of the particles by wood chips. Such retention is primarily a physical process, *e.g.* trapping in dead-end pore spaces. Representative pore spaces and flow paths could only be achieved with a 100% wood column.

4.1.2. Matrix

Untreated wood, used as received, was employed as the sorbent phase for all of the experiments because an insufficient quantity of aged wood chips was available to complete all of the experiments. Each column was packed with 1700 g of wood chips. The resultant total pore space volume was 4100 mL.

4.1.3. Synthetic Runoff

Silica particles were used as a surrogate for particle-associated heavy metals. By inference, attenuation of silica particles by wood chips would indicate the attenuation of associated heavy metals.

Silica particles were chosen to have similar settling characteristics to particles sampled from roadway surfaces (Roger *et al.*, 1998; Andral *et al.*, 1999). Silica comprises a large component of particles mobilized in roadway runoff and thus the particle surface charge is likely also representative. Silica particles with a median size of 17 μm were obtained from U.S. Silica Co. This particle size represents a conservative (smallest particles) representation of rainfall-runoff particles observed during storm events in urban areas (Kim and Sansalone, 2008). The concentration of silica particles in the synthetic reservoir for each experiment was initially set to be 200 mg/L so that it was representative of typical field conditions. Analytical detection necessitated that replicate experiments also be conducted with a silica concentration of 1800 mg/L to confirm that particle removal was occurring. The synthetic runoff reservoir containing the silica particles was maintained with constant stirring by a Teflon-coated stir bar so that silica particles remained in suspension. The pump intake tubing was placed close to the bottom of the reservoir to ensure a constant inlet concentration of silica particles to the columns. Numerous sub-samples were obtained from this reservoir set-up prior to any experiments to verify that the column inlet concentration of silica particles was constant.

4.1.4. Analytical

Silica concentrations were quantified by a gravimetric technique. A sample aliquot of known volume (~ 15 mL) was filtered through a glass fiber filter (1.2 μm nominal pore size, Fisher) followed by sample holder rinsing with high-purity water. Prior to sample contact, the filter was pre-combusted at 550°C for 24 h, cooled in a dessicator for 2 h and weighed. After filtering a sample, the filter was combusted at 550°C for 24 h to remove wood particle fines. The combusted filter was cooled for 2 h in a dessicator and weighed. The silica mass was calculated as the difference between pre-filtration and post-filtration filter masses. Filter blanks were included in each batch of sample filters combusted. Blanks were obtained by the same procedure by filtering a 15-mL "sample" of high purity water. A total of 15 filter blanks were used to

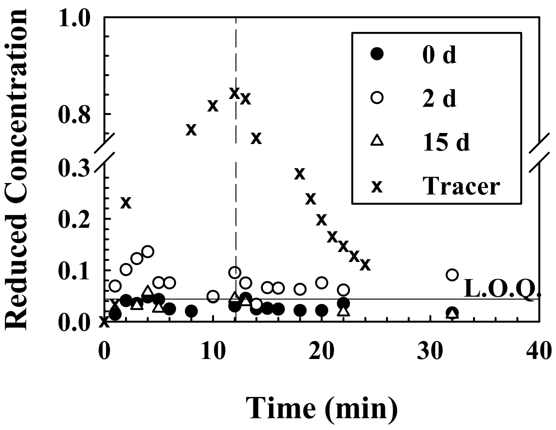


Figure 15. Silica particle breakthrough curves for initial synthetic runoff concentrations of 200 mg/L. The dashed vertical line indicates that time at which flow was switched from the synthetic runoff reservoir to the high purity water post-pulse flush. The solid horizontal line indicates the limit of quantification for silica particles.

compute a method detection limit of 8 mg/L silica, assuming 3 standard deviations around the mean mass loss of filter blanks.

4.2. Results

The experiments conducted with 200 mg/L silica particle concentration in the synthetic runoff yielded results that were inconclusive for assessing suspended solids removal by wood chips. The particle breakthrough curve differed from that for the non-interacting salt tracer (●,×, Fig. 15), indicating that some interaction between the suspended solids and the wood particles did occur. The full extent of the interaction is unclear because the effluent silica particle concentrations were less than the 8 mg/L limit of quantification throughout the experiment (●, Fig. 15). Consequently, the mass fraction of silica particles retained in the wood column could be from 0% (assuming effluent concentrations slightly lower than 8 mg/L) to 100% (assuming effluent concentrations close to 0 mg/L).

Repetition of column experiments using synthetic runoff concentration of 1800 mg/L silica particles indicated that wood chips were indeed effective for removing suspended solids from runoff. The maximum reduced suspended solids concentration was about 0.15 (Fig. 16). The fraction of suspended particle mass eluted from the columns was less than 15% of the suspended particle mass delivered to the column. Thus, wood chips are effective at retaining suspended solids (and associated contaminants).

Intermittent wetting and drying periods did not appear to induce release of particles retained during a prior "storm" event. The high particle mass retention for the columns with

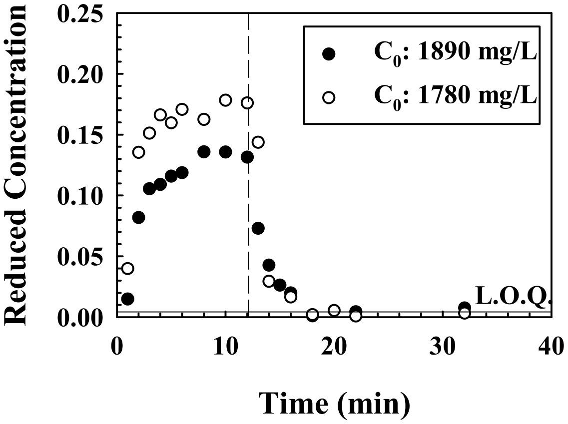


Figure 16. Silica particle breakthrough curves for initial synthetic runoff concentrations of 2000 mg/L. The dashed vertical line indicates that time at which flow was switched from the synthetic runoff reservoir to the high purity water post-pulse flush. The solid horizontal line indicates the limit of quantification for silica particles.

high suspended solids concentrations in the synthetic runoff (1800 mg/L) suggest that particle retention also occurred for the columns with runoff containing 200 mg/L suspended particles. Thus, silica particles from the first pulse (●, 0 d, Fig. 15) were likely present in the wood column at the start of the second runoff pulse (○, 2 d drying period, Fig. 15), and similarly between the second and third pulses (△, 15 d, Fig. 15). Effluent concentrations of particles in the subsequent pulses (○,△) were as high as 23 mg/L at some times, but there did not appear to be a concentrated release of particles upon resumption of flow after drying periods.

Observations from this experiment suggest wood chips are effective for removing suspended solids and hence, particle-associated heavy metals from roadway runoff.

5. Field Evaluation

Field evaluation of wood chips was undertaken to verify findings from the column experiments using actual roadway runoff. The primary difference between the laboratory and the field approaches was in the flow configuration. The flowrate, and hence column residence time, of the laboratory experiments was determined assuming sheet flow from the roadway surface (interception of flow from a 0.15 m inch length of road of 3 m width). Collection of runoff generated by sheet flow from the roadway surface could only be achieved with a constructed infiltration trench that was beyond the budgetary limitations of this project. As a result, the field configuration intercepted gutter flow, resulting in a volumetric runoff flowrate past the wood chips that was higher in the field than in the laboratory experiments. The contact time between the runoff and the wood chips was correspondingly shorter in the field than in the column setup.

5.1. Methodology

5.1.1. Sample Collection

The wood chip field evaluation was conducted in a small section of hot milled asphalt paved roadway. The site was located at the intersection of Rt. 195 and Rockridge Road, Mansfield, CT (41º 49' 56" N, 72º 18' 06"W). Rt. 195, the primary access route for the University of Connecticut, is a two-lane road with a paved shoulder. In the proximity of the study site, the shoulder was constructed with asphalt curbing. Periodic cuts in the curbing contain asphalt gutters (paved leakoffs) that direct stormwater flow from the roadway surface to forested land. The primary land use along Rt. 195 is light residential.

Untreated and wood chip-treated roadway runoff samples were collected from the same asphalt gutter to minimize source variations in runoff water quality parameters (Fig. 17). The drainage area was 97 m by 13 m (1290 m^2). Roadway runoff entering the gutter was directed through an H-flume to measure volumetric flow. An automated sampler collected untreated runoff as it exited the flume. Runoff then flowed through a 15-kilogram bag (0.9 m × 0.4 m × 0.4 m) of woodchips secured in a burlap bag. The burlap bag was staked to the asphalt gutter to maintain close contact between the wood chips and the surface of the gutter, thereby minimizing flow short-circuiting. Flow was not observed to overtop the wood chips. After contacting wood chips, runoff flowed through a second H-flume where a second automated sampler collected the wood chip-treated runoff. The average runoff flowrate was 730 mL/min.

Automated sampling was triggered by an ISCO 674 tipping-bucket rain gauge when rainfall intensity exceeded 1 mm/min. Volumetric flowrates of runoff in the two H-flumes were recorded every minute with ISCO 730 bubble flow meters. Runoff samples were collected every 15 min with an ISCO 6700 automated sampler. The sample carousel was equipped with 900 mL glass sample bottles. The glass sample bottles were soap-and-water washed, rinsed with high purity-water, acid-washed overnight with 10% nitric acid and rinsed repeatedly with high purity water.

5.1.2. Sample Analysis

Roadway runoff samples were returned to the lab for water quality parameter analyses. Runoff pH (accumet, Fisher) and electrical conductivity (Orion) were obtained by electrode emersion in the runoff. A 40-mL aliquot of runoff was removed from the top of each sample bottle with a plastic syringe. The aliquot was filtered (0.45 μm PTFE syringe filter, Fisherbrand, Fisher) and analyzed to determine dissolved metal concentrations. The sample was then agitated to suspend any particles that may have settled during sample transport. A second 40-mL aliquot of runoff was collected, acidified and analyzed for total metal concentrations.

A large (~800 mL) aliquot of each sample was used to quantify the suspended solids concentration. A known sample volume was filtered through a pre-tared glass fiber filter (1.2 μm nominal pore volume, Fisher). The filter was dried overnight in a 105°C oven and weigh ed. The suspended solids concentration was calculated by dividing the difference in filter mass by the volume of water filtered.

Metal concentrations were obtained by ICP-OES (see Section 3.1.4.).

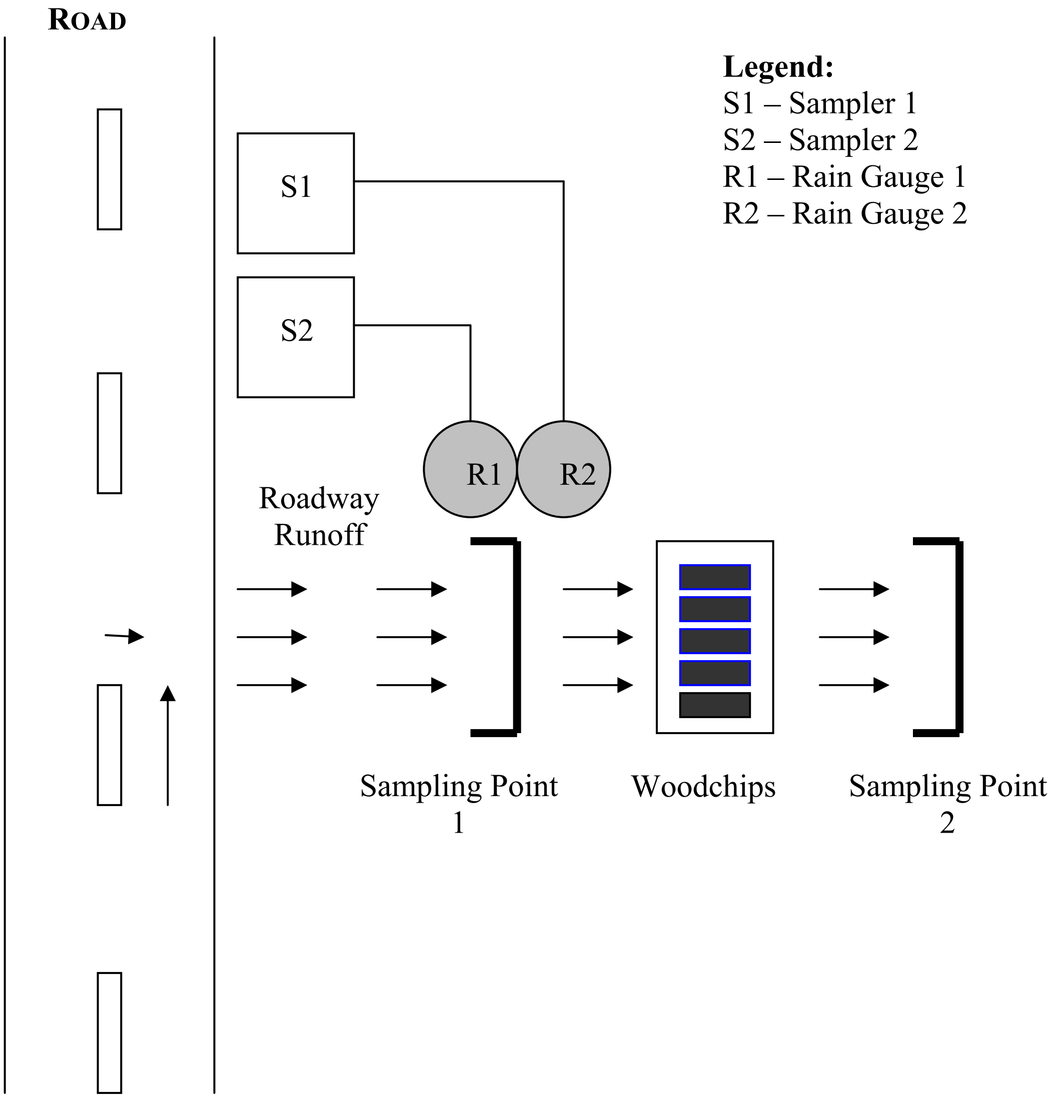


Figure 17. Schematic of field sample collection set-up.

5.2. Results

Attenuation of dissolved and particle-associated heavy metals by wood chips was less effective in the field treatment than in the laboratory evaluation. During the first storm event (Fig. 18), particle-associated copper and zinc and suspended solids were removed by the wood chips. (Runoff concentrations of lead, nickel and cadmium were at, or below, the limit of detection. Consequently, lead accounted for a negligible amount of competition with copper or zinc.) The untreated runoff flowing into the treatment device exhibited total copper concentrations (◆) that were greater than dissolved concentrations (■)(Fig. 18(a)). The difference between the total and the dissolved copper concentration at each time point is the corresponding particle-associated copper concentration in the water sample. The treated runoff leaving the wood chips had similar total (◇) and dissolved (□) copper concentrations over the course of the storm event (Fig. 18(a)), indicating that particle-associated copper was retained in the wood chips. Additional comparison showed little difference between the dissolved copper in the untreated (■) and the treated (□) runoff and hence, little removal of dissolved copper by the wood chips (Fig. 18(a)). A similar analysis for zinc (◆ *vs.* ■,◇ *vs.* □, ■ *vs* □, Fig. 18(b)) indicated that particle-associated zinc and a small amount of dissolved zinc were retained by the wood chips. The retention of particle-associated copper and zinc by wood chips was consistent with the decrease in suspended solids also observed (Fig. 18(d)). Note that there were no correlations between the particle-associated copper and zinc concentrations and the total suspended solids concentration, nor between the particle-associated copper and zinc removals (near constant throughout) and the total suspended solids removal (increasing through the storm event).

The wood chips were an apparent source of dissolved zinc and suspended solids to the treated runoff during the second storm event. Overall, the untreated roadway runoff had lower total concentrations of copper, zinc and suspended solids (◆, Fig. 19 (a),(b),(d)) in the second storm event than the first (compare to ◆, Fig. 18 (a),(b),(d)). Virtually all of the copper and zinc in the untreated roadway runoff was dissolved during the second storm event (◆ *vs.* ■, Fig. 19 (a),(b)). The treated runoff exiting the wood chips had total zinc concentrations (◇, Fig. 19 (b)) that were greater than for the untreated runoff (◆, Fig. 19 (b)) at the beginning of the storm event. Little particle-associated zinc was released (◇ ≈ □, Fig. 19 (b)) in the treated runoff, although particles were released from the wood chips during this time (total suspended solids ◇ > ◆, Fig. 19 (d)). Zinc released from the wood chips during the early times of the second storm may have desorbed into the stormwater from previously retained particles (Fig. 1, [4]). Release of previously retained copper from the wood chips during the second storm event was less evident than for zinc, with a small amount of dissolved copper retained removed from the untreated runoff (■ *vs.* □, Fig. 19 (a)).

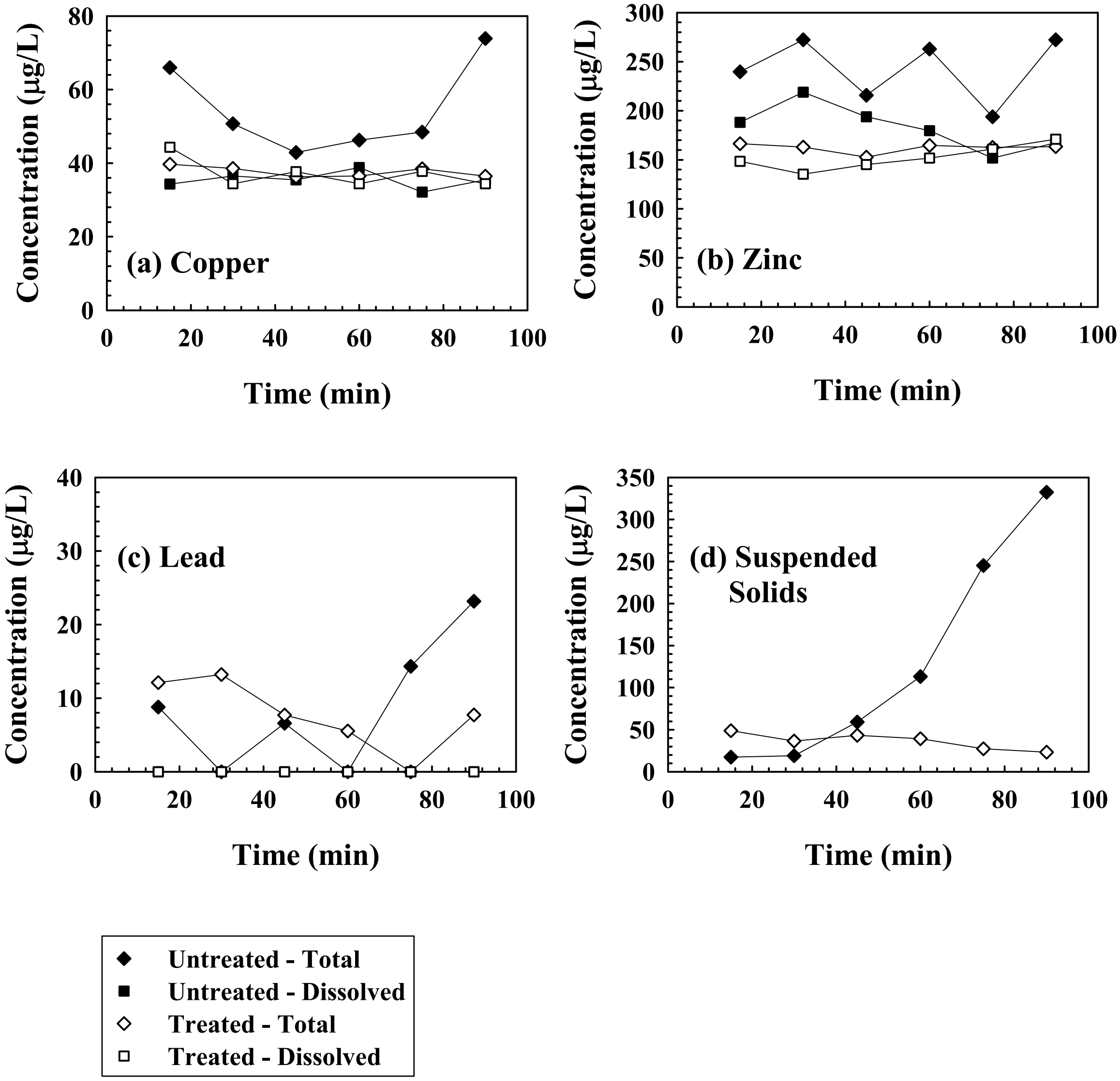


Figure 18. Heavy metals and total suspended solids in untreated- and wood chip-treated roadway runoff from the first storm event.

The most likely explanation for the decreased effectiveness of wood chips to attenuate dissolved or particle-associated heavy metal concentrations in the field evaluation was the difference in flow configurations between the field and laboratory. Sheet flow was simulated in the laboratory columns with a resultant volumetric flowrate of 74.2 mL/min. 'Contaminated' synthetic runoff was delivered to the columns (500 g wood chips) for durations of about 10 min. The concentrated runoff from the roadway section in the field evaluation resulted in a volumetric flowrate of 730 mL/min. Contaminant-containing stormwater runoff contacted the 15-kg mass

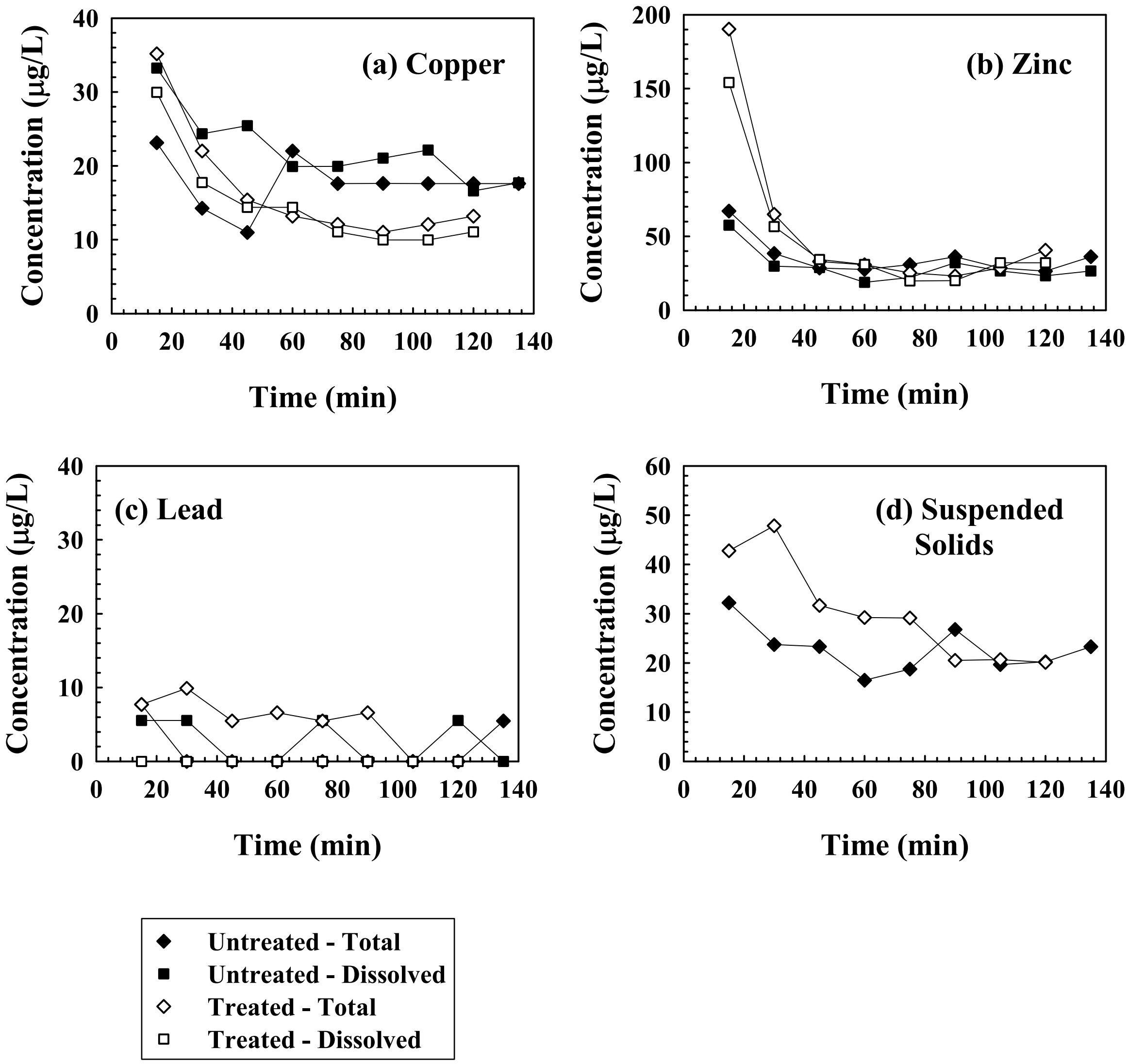


Figure 19. Heavy metals and total suspended solids in untreated- and wood chip-treated roadway runoff from the second storm event.

of wood chips in the field for 90 (storm 1) to 130 minutes (storm 2). Although the actual dissolved and total concentrations of copper and zinc in roadway runoff were lower than simulated in the column experiments, the sustained flow in the field evaluation resulted in 2 (copper) to 3 g (zinc) of total mass applied to the wood chips. The applied mass of copper and zinc in the field was about 6700 times that in the lab experiment and yet the wood chip treatment only contained an amount of wood chips that was 30 times greater than in the laboratory.

6. Conclusions and Recommendations

Evaluation of wood chips for attenuating heavy metal contaminants in roadway runoff must be undertaken within the context of the anticipated regulatory frameworks for stormwater management. Treatment of stormwater from roadway surfaces may be mandated in some locations, as stipulated by Stormwater Phase II Final Rule, Small MS4 Stormwater Program (USEPA, 2000). Alternatively, regulation of roadway runoff may occur in some locations where, for example, direct discharge of stormwater to impaired waterways must be controlled to achieve environmental restoration goals. In either case, the guiding framework for establishing stormwater contaminant treatment objectives is the watershed Total Maximum Daily Load (TMDL) (Section 303(d), Clean Water Act, 1992 Amendments, US Code). TMDLs are calculated by accounting for the mass of contaminant contributed per unit time from all of the sources within the watershed. Typically, calculations are undertaken on a 'per day' timescale basis. Hence, stormwater remediation measures, such as the use of wood chips to attenuate heavy metals in roadway runoff, must demonstrate effective decreases in stormwater contaminant masses for timescales of a day, or greater.

Removal of dissolved heavy metals from roadway runoff using treatment with wood chips likely would have little impact upon TMDL calculations. Evaluation of the dissolved copper breakthrough curves obtained from the mixed wood-gravel columns showed suppressed peak effluent concentrations, relative to the synthetic runoff concentrations. Although lower effluent than influent concentrations were observed over a longer time than the synthetic runoff pulse duration, the total mass of copper collected in the effluent was ultimately the same as the mass of copper introduced to the column. Thus, although the wood chips did not achieve irreversible removal of copper mass, a necessary condition for reducing stormwater contaminant mass-per-day loadings for TMDL goals, the wood chips did serve to "damp" the pulse of dissolved copper in the synthetic runoff, relative to no treatment.

There may be some scenarios for which wood chip treatments to decrease peak stormwater concentrations of dissolved heavy metals may be desirable. Contaminant concentrations in the aqueous phase, as opposed to total mass, are correlated to organism toxic responses. A decrease in stormwater dissolved heavy metal concentrations by wood chips could yield a lowered toxic response. The greatest decrease in dissolved metal concentrations in roadway runoff would occur with the use of aged wood chips that have been partially wet to expand the wood tissue. Further reductions would be achieved by increasing the mass fraction of wood in the treatment device, *e.g.*, all wood treatment. Overall, the concentration reductions that would be achieved are on the scale of one order of magnitude for wood chip treatments that are implemented in a sheetflow configuration.

Wood chips were demonstrated to reduce the mass of total suspended solids in synthetic roadway runoff; however, the suspended solids capacity of the wood chips may limit treatment applications for removing particle-associated heavy metal contaminants. The maximum suspended solids capacity of the wood chips was estimated assuming that all the pore spaces between the wood chips were filled with suspended solids. The travel time of the non-sorbing salt tracer through the column (t_{50} = 1.5 min) corresponded to a water-filled pore space of about 110 mL for a 1770-g wood chip column. For suspended solids with a density of 2.65 g/mL, the retention capacity of the wood chips was estimated to be 0.16 g suspended solids per g wood.

Results of this research are translatable to other transportation districts in the U.S. A primary difference between New England and other regions of the country is rainfall pH, being less acidic in other regions. Higher pH runoff will enhance dissolved heavy metal interactions with wood chips somewhat as wood sorption sites are increased (Morel and Hering, 1993), but will have little effect upon particle retention by wood chips (Yao *et al.*, 1971).

Note that field applications of wood chips to attenuate heavy metal contaminants in stormwater must also consider disposal of the contaminated wood chips and leaching of organic matter from the wood chips, issues not addressed in this study.

7. References

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