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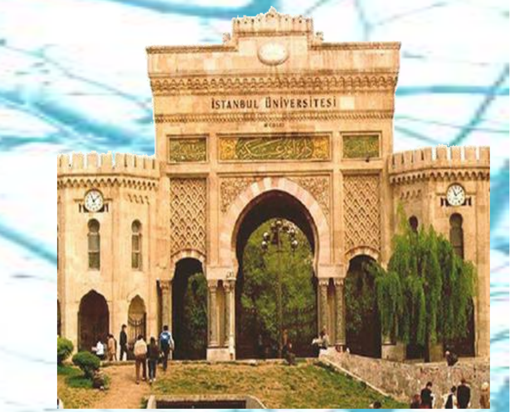

ISTANBUL, TURKEY

INVESTIGATION OF MEDIA EFFECTS ON REMOVAL OF HEAVY METALS IN BIORETENTION C

ABSTRACT

Heavy metals are the most toxic elements at high concentrations, although some of them such as Cu and Zn are essential to plants, humans, and animals within a limited value. It is very important to control and reduce heavy metal concentration in urban storm water runoff. There are several methods to remove the aforementioned toxic metals such as electrolyte extraction, chemical precipitation, ion-exchange, reverse osmosis, membrane filtration, adsorption, cementation, and electrochemical treatment technologies. However, these methods are highly expensive and hard to implement for treatment of big volumes of water such as storm water. For this purpose, Low Impact Development (LID) Best Management Practices (BMPs) have become popular to collect, infiltrate, and treat toxic metals in storm water runoff in recent years. Bioretention is an example of LID-BMP application of which usage has recently been started in storm water treatment. Researchers have been investigating the advantages of bioretention systems and this study contributes to these research efforts by seeking for the media effects of bioretention on heavy metal removal. For this purpose, batch sorption experiments were performed to determine the distribution coefficients and retardation factor of copper (Cu), lead (Pb), and zinc (Zn) for bioretention media such as mulch, turf, local or vegetative soil, sand and gravel. Furthermore, sorption reaction kinetics of Cu, Pb and Zn are tested in order to assess the sorption equilibrium time of these metals for 5 bioretention media.

BACKGROUND
Low Impact Development (LID) Best Management Practices (BMPs)

Low Impact Development (LID) Best Management Practices (BMPs) have become popular to collect, infiltrate, and treat toxic metals in storm water runoff in recent years. LID-BMP is a land planning method which is used to manage storm water runoff and improve water quality by reducing contaminant in storm water runoff. There are several LID type of storm water BMPs such as bioretention facilities, green roof, rain barrels, vegetative swales and permeable pavements.

(a) (b) (c) (d)

Figure 1. Types of LID in the literature (a) green roofs (TonyTheTiger, 2008), (b) vegatative swale (Pennsylvania Stormwater Best Management Practices Manual, 2006), (c) permeable pavement (JJ Harrison, 2011), (d) rain barrel (Abby Hall, U.S. EPA).

BACKGROUND
Bioretention

One of the most efficient and frequently used types of the LID-BMPs is bioretention. Bioretention is used to decrease the pollutant loading in surface and ground water through a variety of mechanisms including sorption, filtration, plant uptake, and microbial biodegradation.

Glass and Bissouma (2005) observed removal efficiencies of 81% for copper, 79% for zinc, 75% for lead in a parking lot bioretention cell over a 3-month period.

Six different filter media were tested and the total copper, lead, and zinc removals above 90% were observed for all soil mixtures by Hatt et al. (2007).

Figure 2. Bioretention pictures in the literature (Davis, 2001, 2003, 2009).

Aim of this study

- **To determine the heavy metal removal capacity of bioretention cells.**
- **To conduct batch sorption experiments**
- **To determine the type of isotherm**
- **To calculate distribution coefficients and retardation factor of selected heavy metals, i.e, Copper, Lead and Zinc, for 5 different bioretention media used in bioretention cells.**
- **To determine the sorption equilibrium time of Cu, Pb and Zn for each of bioretention media is assessed separately.**
- **To observe impacts of bioretention media on removal of toxic metal and effects of hydraulic conductivity are observed.**

MATERIALS AND METHODS

Batch Experiments

Solutions consist of 1 control solution (0 mg/L) and 5 solutions with concentrations of 0.01 mg/L, 0.1 mg/L, 1 mg/L, 10 mg/L and 100 mg/L .

In order to obtain more accurate results for turf and local soil, additional solutions with concentrations of 0.5 mg/L, 5 mg/L and 50 mg/L are prepared and tested.

The chemicals used in heavy metal solutions are Lead chloride ($PbCl_2$), Zinc chloride ($ZnCl_2$) and Copper chloride dehydrates ($CuCl_2x2H_2O$)

Figure 3. Photos of mulch, torf, local soil, sand and gravel (left to right) samples used in bioretention columns.

Solid waste and solution ratio is 1:5
(100 g of each dried sample and 500 mL of heavy metal solutions)

After 48 hours, 50 ml sample is taken from each bottle in order to measure Zn, Pb, and Cu adsorption

Figure 4. Photos of mulch, torf, local soil, sand and gravel with heavy metal solution.

Reaction Kinetics Test

- **Heavy metal solution with 1 mg/L concentrations of Cu, Pb and Zn is prepared**
- **5 polyethylene plastic bottles**
- **solid waste and solution ratio is 1:10**
- **to determine the equilibrium time, the residual metal concentrations are determined by taking 10 mL of samples after 0.5, 1.5, 3, 5, 7, 24, 48 and 72 hours from the beginning of the experiment from the bottles**
- **Atomic absorption spectrophotometer (Perkin Elmer AAnalyst 300 Spectrophotometer) is used to measure the amount of heavy metal remaining in the solution after sorption.**

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RESULTS AND DISCUSSION

Mechanical and Chemical Analyses of soil types used in bioretention columns

Particle size analyses of sand and local soil used inbioretention columns are conducted by using sieves and hydrometer.

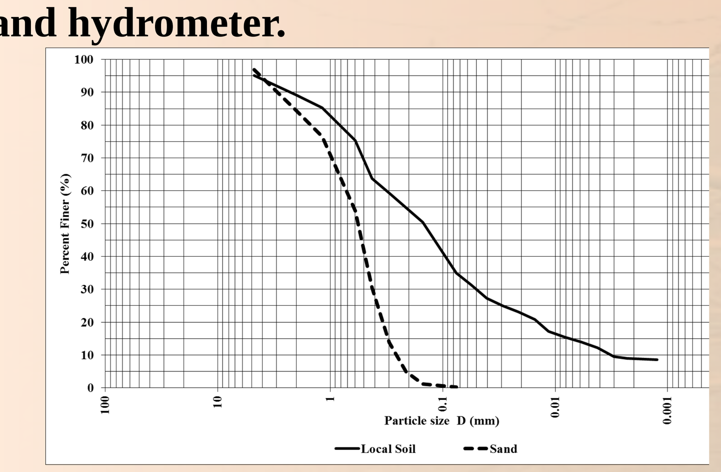

Figure 5. Particle size distribution curves for sand and local soil in Istanbul, Turkey.

Table 1. Results of mechanical (or physical) and chemical analyses.

Media	Organic content (%)	Zn (mg/L)	Cu (mg/L)	Pb (mg/L)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	d_{60}/d_{10}	Classification
Sand	0.86	$<4x10^{-4}$	$<4x10^{-4}$	$<4x10^{-4}$	3.04	96.79	0.17	0.00	2.67	sand
Local Soil	6.41	$<4x10^{-4}$	$<4x10^{-4}$	$<4x10^{-4}$	5.00	48.50	37.50	9.00	106.67	loamy sand
Gravel	0.19	$<4x10^{-4}$	$<4x10^{-4}$	$<4x10^{-4}$	100	0	0	0	NA	gravel
Turf	47.37	$<4x10^{-4}$	$<4x10^{-4}$	$<4x10^{-4}$	NA	NA	NA	NA	NA	NA
Mulch	67.23	$<4x10^{-4}$	$<4x10^{-4}$	$<4x10^{-4}$	NA	NA	NA	NA	NA	NA

NA= Not Applicable

- **Mechanical sieve and hydrometer analyses**
- **Organic contents of all media are determined by loss on ignition (550°C for 4 hours and reweighed)**
- **Moisture content is determined in the oven at 103 ^{0}C for 1 hour**
- **Specific gravity is measured for each sample by using Pico meter**

Table 2. Moisture content and unit weight of soil types.

Media	Natural unit weight (gr/cm^3)	Dry unit weight (gr/cm^3)	Moisture content (%)	Specific Gravity	Porosity (n)	Bulk density of the porous media (gr/cm^3)
Gravel	1.705	1.697	0.471	2.747	0.382	1.053
Sand	1.502	1.490	0.805	2.644	0.436	0.848
LocalSoil	1.191	1.057	12.68	2.332	0.547	0.540
Turf	0.636	0.499	27.45	0.982	0.492	0.323
Mulch	0.388	0.301	29.12	0.564	0.467	0.207

Batch Sorption Experiments

Linear isotherm is the best model which represents the adsorption of all heavy metals tested in this study (i.e. Cu, Zn and Pb) in all bioretention media.

Linear sorption Isotherm Equation is given as follows:

$$q_e = \frac{X}{M} = k_d C_e^n$$

Retardation Factor may be calculated for each bioretention media by the following equation:

$$R_f = 1 + \frac{\rho_b k_d}{n_p}$$

Table 3. Linear isotherm constants, correlation coefficients and retardation factors.

Heavy metal	Mulch			Turf			Local Soil			Sand			Gravel		
	K_d	R^2	R_f	K_d	R^2	R_f	K_d	R^2	R_f	K_d	R^2	R_f	K_d	R^2	R_f
Cu	0.347	0.995	1.154	3.500	0.996	3.297	0.759	0.972	1.749	0.011	0.977	1.022	0.004	0.938	1.011
Pb	1.511	0.997	1.670	26.85	0.997	18.63	5.279	0.876	6.211	0.029	0.984	1.057	0.050	0.989	1.138
Zn	0.141	0.998	1.063	0.899	0.949	1.591	0.077	0.801	1.076	0.006	0.970	1.011	0.001	0.748	1.053

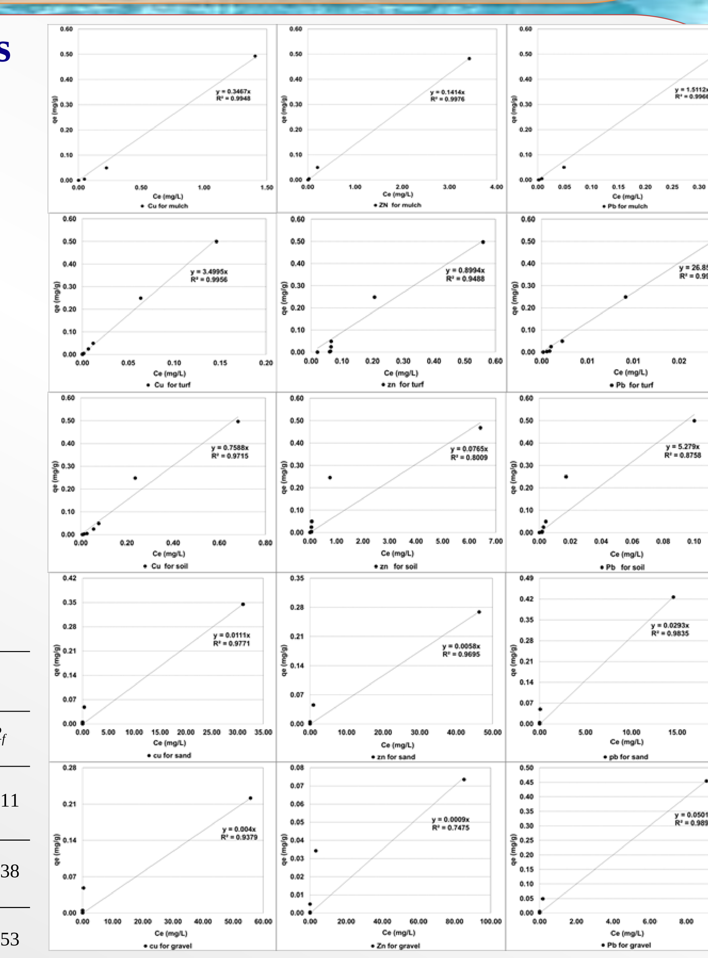

Figure 6. Adsorption of Cu, Zn and Pb in bioretention media.

Reaction Kinetics Experiments

Therefore, the equilibrium time concentrations of all metals for all media used in bioretention columns are measured in this part of the study. This result implies that sorption process is fast for all of the heavy metal ions (Cu, Pb and Zn) investigated in this study. The equilibrium time of bioretention column media range from 1 to 6 hours as seen in Figure 7. Therefore, it is found that bioretention column media has great capacity in treating contaminant in first flush runoff.

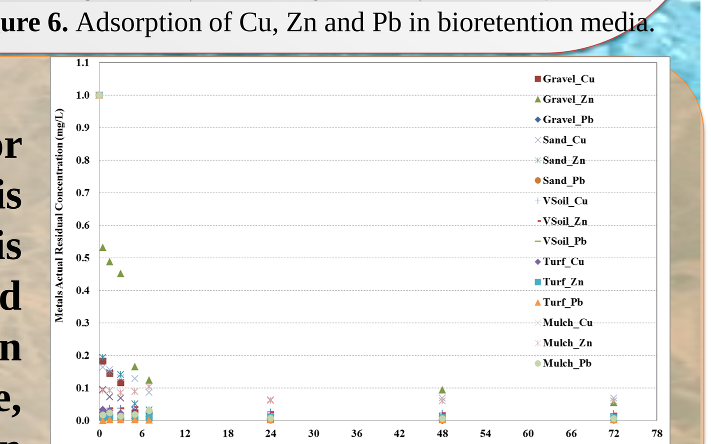

Figure 7. Change in actual residual metal concentrations.

CONCLUSIONS

The results of sorption test show that turf has higher sorption capacity than mulch and local soil for heavy metals used in the experiment. On the other hand, sand and gravel have relatively lower sorption capacities. Linear equilibrium isotherm represents sorption of these metals for all bioretention media. The highest sorption is observed for Pb followed by Cu and Zn for all bioretention media. The time required for reaching equilibrium conditions for bioretention column media is ranged from 1 to 6 hours for each metal investigated.