



# Soil amendments for heavy metals removal from stormwater runoff discharging to environmentally sensitive areas



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## SUMMARY

Concentrations of dissolved metals in stormwater runoff from urbanized watersheds are much higher than established guidelines for the protection of aquatic life. Five potential soil amendment materials derived from affordable, abundant sources have been tested as filter media using shaker tests and were found to remove dissolved metals in stormwater runoff. Blast furnace (BF) slag and basic oxygenated furnace (BOF) slag from a steel mill, a drinking water treatment residual (DWTR) from a surface water treatment plant, goethite-rich overburden (IRON) from a coal mine, and woodchips (WC) were tested. The IRON and BOF amendments were shown to remove 46–98% of dissolved metals (Cr, Co, Cu, Pb, Ni, Zn) in repacked soil columns. Freundlich adsorption isotherm constants for six metals across five materials were calculated. Breakthrough curves of dissolved metals and total metal accumulation within the filter media were measured in column tests using synthetic runoff. A reduction in system performance over time occurred due to progressive saturation of the treatment media. Despite this, the top 7 cm of each filter media removed up to 72% of the dissolved metals. A calibrated HYDRUS-1D model was used to simulate long-term metal accumulation in the filter media, and model results suggest that for these metals a BOF filter media thickness as low as 15 cm can be used to improve stormwater quality to meet standards for up to twenty years. The treatment media evaluated in this research can be used to improve urban stormwater runoff discharging to environmentally sensitive areas (ESAs).

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## 1. Introduction

The management and treatment of urban stormwater – both in terms of quantity and quality – is a widely recognized, vexing problem faced by stormwater authorities the world over (Clark and Pitt, 2012). Build out, paving activities and the installation of stormwater infrastructure reduce infiltration and promote rapid conveyance (Barbosa et al., 2012; Elliott and Trowsdale, 2007). Urban runoff quality is subject to deterioration as a result of physicochemical pollutant additions resulting from changes in catchment utilization. Pollutant constituents are myriad and include total suspended solids (TSS), heavy metals, hydrocarbons, nutrients and – in seasonally cold climates – chlorides from salt application (Perera et al., 2013; Winston et al., 2012; Fuerhacker et al., 2011; Kumpiene et al., 2008). There are many sources of pollutants, but highway runoff in particular has been recognized as

posing a substantial environmental risk to receiving environs due to the fact that it frequently contains all of the aforementioned pollutants in one complex cocktail (Baek et al., 2014; Kayhanian et al., 2012; Helmreich et al., 2010; Hallberg et al., 2007; Barrett et al., 1998; Amrhein et al., 1992; Pitt and McLean, 1986; Pitt and Bozeman, 1982). In some cases, runoff pollutant concentrations entering ground and surface waters can be orders of magnitude greater than what has been deemed safely permissible from either a consumptive or aquatic exposure standpoint (CCME, 1999, 2008; Amrhein et al., 1992). Fig. 1 summarizes the range of concentrations for Cu, Pb and Zn as reported in 12 different studies (Wang et al., 2013; Stagge et al., 2012b; MacKay et al., 2011; Davis and Birch, 2010; Finney et al., 2010; Gan et al., 2008; Li and Barrett, 2008; Flint and Davis, 2007; Hallberg et al., 2007; Barrett et al., 2006; Wu et al., 1998; Hoffman et al., 1985).

With the adoption of low impact development (LID), sustainable urban drainage systems (SUDS) and other distributed approaches to stormwater management, there is a growing recognition that simply matching pre- and post-development hydrograph peaks is insufficient; total volumes and quality characteristics also warrant consideration (Elliott and Trowsdale, 2007; Butler and Parkinson, 1997). Given the linearity of their design,

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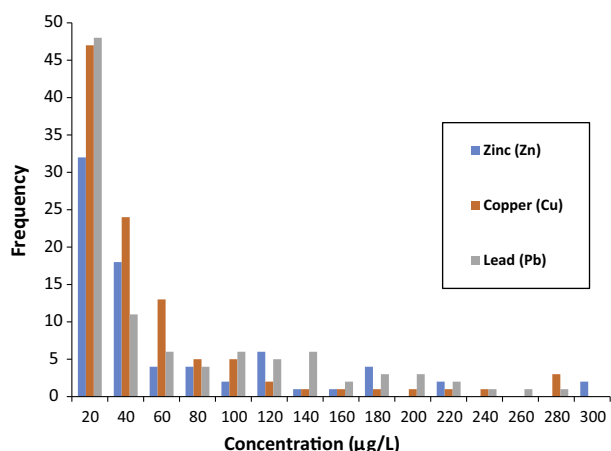


Fig. 1. Histogram of metal concentrations in stormwater runoff (µg/L); CCME guidelines for Cu, Pb, and Zn are 2, 2, and 30 µg/L, respectively.

highways are served primarily by ditches and swales, with a focus on conveyance (Stagge et al., 2012a, 2012b; Ingvertsen et al., 2012b; Zakaria et al., 2003). Roads are classified as linear nonpoint sources (NPS) of pollution, and the challenges of dealing with the diffuse characteristics of this feature type are well-documented (Yousef et al., 1987). In areas where drinking water and sensitive aquatic species are at risk due to the physicochemical burden associated with highway runoff, infiltration swales enhanced with pollutant-specific treatment media may be used, and work in this regard has progressed substantially (e.g. Guo, 2013; Davis et al., 2012a, 2012b; Ingvertsen et al., 2012a, 2012b; Stagge et al., 2012b; Clark and Pitt, 2011; Trowsdale and Simcock, 2011; Achleitner et al., 2007; Yousef et al., 1987).

As some of the stormwater flowing through a swale is infiltrated it comes in contact with the treatment media and some, most or all of the pollutants in the particulate-bound and dissolved phases are removed. Treatment media can include physical, chemical, or biological stock, or combinations thereof (Gotvajn and Zagorc-Končan, 2014; Winston et al., 2012; Kim et al., 2010; Blecken et al., 2009). Although the long-term hydraulic performance of such systems is well recognized, the water quality aspects of their performance remain rudimentary at best (Davis et al., 2012a; Ingvertsen et al., 2012b). At the level of the soil itself, work related to the incorporation of geotextiles, optimized particle size distributions (PSDs) and dual porosity approaches have also been investigated, with consideration given to the effects of pH, hydraulic loading, hydraulic retention time (HRT) and temperature, and these elements are reflected in design standards (Singh et al., 2013; Melbourne Water, 2005).

In Southern Ontario, Canada – home to 1/3 of the Country's population – concerns surrounding the dual issues of highway stormwater runoff and road salt management in environmentally sensitive areas (ESAs) are paramount (Trenouth et al., 2015; Perera et al., 2013). We define ESAs as any areas which have both a noted exceedance of stormwater pollutant concentrations above the CCME guidelines and where sensitive or at risk species are present. Pollutants washing off of roads have been noted to adversely impact threatened species in receiving streams, and the seasonal application of road salt has been identified as an agent of soil dispersion and subsequent pollutant mobilization (Baek et al., 2014; Norrström and Bergstedt, 2001; Hillel, 1998; Granato et al., 1995). Compounding this problem are findings suggesting that, for certain heavy metal species, the bulk of their annual wash off occurs during the winter months due to seasonally-intensive wear-ing of the road surface (Bäckstrom et al., 2003). In light of this,

there is a pressing need to identify, test and quantify the performance of novel, low-cost, locally available treatment media derived from waste materials for their ability to remove some of the most common highway stormwater pollutants, chiefly sediments and heavy metals. However, their performance under simultaneous exposure to high concentrations of chlorides (primarily from NaCl) is also of interest, as this is representative of anticipated field conditions in seasonally cold regions.

## 2. Background

Increasingly, credence is being given to the use of amendments used in conjunction with soil – either added as a blend within the soil matrix or layered at one or more depths within the soil profile (Lim et al., 2015; Ingvertsen et al., 2012a; Hsieh and Davis, 2005; Oste et al., 2002). Different soil amendments have demonstrated competence in various aspects of water quality improvement, but their performance while under simultaneous exposure to chlorides remains poorly characterized (e.g. Murakami et al., 2008; Dimitrova and Mehandgiev, 1998). Amendments have been studied in a variety of contexts including agricultural, industrial and urban settings.

Drinking water treatment residuals (DWTR's) amended into agricultural soils have been shown to immobilize nutrients like phosphorous ( $\text{PO}_4^{3-}$ ) (Agyin-Birikorang et al., 2006; Novak and Watts, 2005). However, related work has demonstrated that  $\text{PO}_4^{3-}$  adsorption to alum occurs across a wide range of pH conditions, and that  $\text{Cl}^-$  anions can also be adsorbed within the inner sphere in some instances (Yang et al., 2006). Work by Rahmani et al. (2010) suggests that nanostructure alumina is able to absorb Pb, Ni and Zn, but these findings are not easily extrapolated to filter alum. Although there are some concerns surrounding the heavy metal content of land-applied DWTRs, earlier work has shown that of three separate DWTRs tested, all had metal concentrations that are well below permissible limits, and that the metal species of greatest concern were not present in a bioavailable form (Elliott et al., 1990).

Zero-valent iron and goethite (a naturally occurring iron hydroxide species) have also been considered as materials which have the potential to remove heavy metals from stormwater and also capture and detain chloride ions via displacement reaction (Mariussen et al., 2015; Fronczyk et al., 2010). Research found that the aforementioned iron species have the ability to capture and detain approximately 140 mg of chloride  $\text{dm}^{-3}$ , and that other water quality benefits are also accrued by using this material. In particular, zero-valent iron has the ability to displace metal cations in solution, and it does so more effectively than activated carbon (Fronczyk et al., 2010). The use of goethite ( $\alpha\text{-FeOOH}$ ) as an agent to capture chlorides has been shown to have some efficacy (Rennert and Mansfeldt, 2002). However, despite these positive findings, it has also been shown that chlorides are loosely bound to goethite via a displacement reaction; in particular by displacing ferricyanide from goethite complexation surfaces. This has important implications with respect to ferricyanide-based anti-caking agents, as chloride ion substitution may result in their mobilization if they are present in salt spread mixtures (Rennert and Mansfeldt, 2002; Paschka et al., 1999). In light of previous findings, an iron-rich overburden from an Ontario coalmine was selected for use in this experiment.

Blast furnace slag has been shown to remove 99.9% of As(III) at initial concentrations of 1 mg/L, and up to 100% of influent bacteriophages under certain conditions (Park et al., 2014; Kanel et al., 2006). Agyei et al. (2002) achieved upward of 75%  $\text{PO}_4^{3-}$  removal from synthetic wastewater, and this was achievable regardless of the contact time between the material and the solution. These

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