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Heavy metal removal mechanisms of sorptive filter materials for road runoff treatment and remobilization under de-icing salt applications

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ABSTRACT

The objective of this research study was to elucidate the removal and remobilization behaviors of five heavy metals (i.e., Cd, Cu, Ni, Pb, and Zn) that had been fixed onto sorptive filter materials used in decentralized stormwater treatment systems receiving traffic area runoff. Six filter materials (i.e., granular activated carbon, a mixture of granular activated alumina and porous concrete, granular activated lignite, half-burnt dolomite, and two granular ferric hydroxides) were evaluated in column experiments. First, a simultaneous preloading with the heavy metals was performed for each filter material. Subsequently, the remobilization effect was tested by three de-icing salt experiments in duplicate using pure NaCl, a mixture of NaCl and $CaCl_2$, and a mixture of NaCl and $MgCl_2$. Three layers of each column were separated to specify the attenuation of heavy metals as a function of depth. Cu and Pb were retained best by most of the selected filter materials, and Cu was often released the least of all metals by the three de-icing salts. The mixture of NaCl and $CaCl_2$ resulted in a stronger effect upon remobilization than the other two de-icing salts. For the material with the highest retention, the effect of the preloading level upon remobilization was measured. The removal mechanisms of all filter materials were determined by advanced laboratory methods. For example, the different intrusions of heavy metals into the particles were determined. Findings of this study can result in improved filter materials used in decentralized stormwater treatment systems.

1. Introduction

Parameters commonly monitored in runoff from traffic areas include solids, organic substances, heavy metals, and compounds of de-icing salts (Folkeson et al., 2009). Heavy metals such as Cd, Cu, Ni, Pb, and Zn are often measured because of their environmental relevance and can occur in notable runoff concentrations (Huber et al., 2016c). Chloride is also determined in high runoff concentrations from traffic areas with winter services because NaCl, $CaCl_2$, and $MgCl_2$ are widely used as de-icing salts (Bauske and Goetz, 1993; Nelson et al., 2009).

In recent years, dozens of manufactured decentralized stormwater treatment systems have been developed to treat traffic area runoff prior to discharge into surface water or local groundwater (Dierkes et al., 2015). To retain dissolved and particulate substances, commonly a mechanical step (e.g., sedimentation or filtration) followed by a subsequent treatment step with a filter material is necessary (Hilliges et al., 2013). The term “filter material” was deliberately chosen because it is commonly used by manufacturers and operators, although the removal mechanisms of filter materials consist not just of filtration (e.g., after precipitation), but also of sorption or ion exchange. These decentralized treatment systems for traffic area runoff can be approved for use after passing several tests (e.g., remobilization of Cu and Zn by NaCl; DIBt, 2015). However, no standardized testing method is provided among these approval processes to determine the impact of all relevant de-icing salts upon the remobilization of heavy metals that were previously retained by filter materials. Consequently, there is currently no manufactured decentralized treatment system for road runoff available in Germany with proven filter stability against NaCl, $CaCl_2$, and $MgCl_2$, although Cl^- and the corresponding cations can have an effect upon retained heavy metals. For example, during applications of NaCl in road maintenance, increases in Cd, Cu, Ni, and Zn

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concentrations were detected in the effluent of a constructed wetland (Tromp et al., 2012). Thereby, the Cu effluent concentrations were higher than the maximum influent concentration and the system itself became a source of contamination during the cold season. Hence, the consideration of heavy metal releases triggered by de-icing salts is relevant for systems treating traffic area runoff in moderate and cold climates.

A few studies have examined the remobilization behavior of heavy metals bound to roadside soils (e.g., Amrhein et al., 1992; Bauske and Goetz, 1993; Bäckström et al., 2004). Nelson et al. (2009) tested two soils for the effects of NaCl and $MgCl_2$ on heavy metal mobility (Cd, Cu, and Pb). Both soils exhibited different behaviors for each de-icing salt and heavy metal, in particular for Cu. The use of NaCl resulted in the largest remobilization of Cu and Pb. $MgCl_2$ released higher levels of Cd for both soils. Huber et al. (2014) published results concerning the remobilization of Cu and Zn by NaCl and $CaCl_2$ for two soils and five filter materials used for stormwater treatment. In some cases, both heavy metals were released and in other cases, only Zn showed higher mobility. These effects depended upon the material and the de-icing salt, e.g., some heavy metals were not released with NaCl alone but by a mixture of NaCl and $CaCl_2$. In addition, the pH of the effluent was often reduced by the use of de-icing salts in this study. However, neither of these studies experimented with all of the relevant five heavy metals and three de-icing salts. Thus, the focus of further research should be on the identification of the impact of relevant de-icing salts upon previously retained metals. Moreover, as more and more manufactured decentralized treatment systems are used, commercially supplied filter materials must be tested as these materials are much higher loaded than roadside soils because of their high ratio of drainage area to filter material surface area (Huber et al., 2014).

The objectives of this study were to elucidate the removal and remobilization behaviors of five heavy metals under the application of three de-icing salts using lab-scale column experiments. In addition, the removal mechanisms were specified for all six commercially supplied filter materials, and the influence of two preloading levels upon the remobilization was determined for the material with the highest removal capacity.

2. Material and methods

2.1. Filter materials and chemicals

The following filter materials were used in this study: granular activated carbon (GAC, Donau Carbon GmbH, Germany), a mixture (called alumina) of granular activated alumina (55%; Albemarle Corporation, USA) and porous concrete (45%; Xella Deutschland GmbH, Germany), granular activated lignite (lignite, Rheinbraun Brennstoff GmbH, Germany), half-burnt dolomite (dolomite, Rheinkalk Akdolit GmbH & Co. KG, Germany), and two granular ferric hydroxides with different calcium contents (FerroSorp, HeGo Biotec GmbH, Germany; GFH, Wasserchemie GmbH & Co. KG, Germany). Prior to conducting any experiments, lignite and dolomite were sieved to the size fraction of the other materials (0.5–2.0 mm) to minimize the influence of different size fractions of each filter material upon the heavy metal retention (Smith, 1998). Subsequently, all materials were dried at 105 ± 2 °C to achieve a constant weight, and finally stored in desiccators without additional treatment until use. The chemical and physical characteristics of all blank materials are presented in Tables 1 and 2.

The heavy metal salts used were $CdSO_4 \cdot {}^{8}/_{3}H_2O$ (AppliChem GmbH, Germany), $Cu(NO_3)_2 \cdot 3H_2O$ (AppliChem GmbH, Germany), $Ni(NO_3)_2 \cdot 6H_2O$ (Merck KGaA, Germany), $Pb(NO_3)_2$ (AppliChem GmbH, Germany), and $Zn(NO_3)_2 \cdot 6H_2O$ (AppliChem GmbH, Germany). Adjustments of pH values and preservation of all liquid samples were performed with nitric acid 65% p.a. (Merck KGaA, Germany). As de-icing salts, NaCl (AppliChem GmbH, Germany), dried, powdered $CaCl_2$ (AppliChem GmbH, Germany), and $MgCl_2 \cdot 6H_2O$ (AppliChem GmbH, Germany) were used.

2.2. Experimental setup

The experimental apparatus was constructed of glass and all pipes were made of polyvinyl chloride. The glass column had an inner diameter of 2.0 cm and a length of 40 cm, providing a filter material bed height of 14.4 cm. Thus, the ratio of the inner diameter to the largest particle was at least 10:1 to obtain appropriate lab-scale design parameters (Fanfan et al., 2005). A glass screen was placed at the bottom of the column to support the filter materials. The influent was directed through the glass columns in up-flow mode (from bottom to top) at ambient temperature (21 ± 2 °C). All sorbent samples were weighed using an analytical balance (MC1 Research RC 210D, Sartorius AG, Germany) with an accuracy of ±0.1 mg.

For heavy metal removal, lab-scale column experiments were conducted with influent concentrations of 0.625 mg/L (Cd), 2.5 mg/L (Cu, Ni, and Pb), and 5.0 mg/L (Zn). These concentrations are higher than most values measured in runoff from traffic areas (to shorten the duration of the experiments), and the different values were chosen to simulate realistic proportions (Huber et al., 2016c). The initial pH was 4.9 ± 0.3 to obtain dissolved metals. Deionized water (electrical conductivity <1 μS/cm) was used for influent preparation and no buffer was used to simulate a worst-case scenario for the determination of dissolved heavy metal removal (e.g., to avoid oversaturated conditions) (Huber et al., 2016a). The flow rate was adjusted to about 6.5 mL/min by a peristaltic pump (ECOLINE VC-MS/CA8-6, Ismatec SA, Switzerland). Thereby, the empty bed contact time was maintained at about 7 min. The experiments were performed in eight columns per material from Monday to Friday. During weekends, the filter materials were kept saturated without flow (representing dry-weather periods). The preloading part was terminated when the breakthrough of Zn was at least 50% in the effluent. This removal efficiency corresponds to the elimination criteria often requested by international regulations for stormwater treatment systems (Huber et al., 2016b). Consequently, a breakthrough of 50% correlates with the end of the service life (i.e., the maximum preloading of a real filter). In addition, one shorter preloading run was performed with the filter material that had the highest removal capacity to test the effects of different preloading levels on remobilization. At the end of the preloading, each column was flushed with deionized water for 60 min to remove the dissolved heavy metals, which were not fixed onto the filter material. The flushing process was controlled by measuring the heavy metal concentrations in effluent samples for all tests. Thus, the effluent concentrations measured in the subsequent de-icing salt experiments were only related to remobilization and no remobilization occurred during the previous deionized water flushes.

Six of the eight columns containing filter materials with preloaded heavy metals were used for the de-icing salt experiments. Two columns were operated with pure NaCl solution (10 g/L), two with a mixture of NaCl (10 g/L) and $CaCl_2$ (2.5 g/L), and two with a mixture of NaCl (10 g/L) and $MgCl_2$ hexahydrate (2.5 g/L). All de-icing salt concentrations were taken from the literature (Huber et al., 2015) and the experiments simulated a typical runoff event (6.0 L/(s·ha), which corresponds to 2.2 mm/h, for 200 min). The ratio of the filter surface area to the drainage area of the decentralized treatment system that was selected for the de-icing salt tests was 1:1820. Therefore, the corresponding flow rate was