



Peat filter performance under changing environmental conditions

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ABSTRACT

Peat is a candidate filter material for in situ treatment of urban runoff, contaminated groundwater and landfill leachates. Until now research has focused on peat sorption in batch experiments and there is a lack of knowledge on peat performance in filter beds. In this project column tests were carried out to evaluate the capacity of peat to remove As, Cd, Cu, Cr, Ni, Pb and Zn in multi-metal solution under a range of environmental conditions that may be encountered in real-life applications (draining, water stagnation, freezing, change in pH and metal concentrations, input of NaCl and elevated DOC). The removal capacity was 91–98% for Cd, Cu, Zn, Ni and Pb and the efficiency was unaffected by the changes of physical factors, but temporarily inhibited for solutions containing NaCl. Leaching of DOC from peat was detected in the initial samples and temporarily decreased metal removal. The peat filters showed high removal rates for Cd, Cu, Zn, Ni and Pb under all experimental conditions and are recommended for treatment of waters containing these elements. In contrast, peat was not found to be efficient for treatment of As and Cr in the multi-metal contaminated water at the pH range (6.7–8.0) studied.

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1. Introduction

The European Union Water Framework Directive [1] commits member states to good chemical and biological status for all water bodies (surface, estuarine and groundwater) by 2015. This implies the treatment of contaminated water before release into receiving waters. However, several types of contaminated waters including urban runoff and leachates from landfills and contaminated sites are not connected to the wastewater treatment system and are often not treated. Permeable reactive barriers (PRB) and bed filters are effective options for treatment of contaminated waters [2,3]. Several materials have been tested for use in PRB and bed filters, including activated carbon, iron oxides and natural materials [3]. *Sphagnum* peat moss has been found to efficiently remove heavy metals, oil, detergents, dyes, pesticides and nutrients from contaminated waters [4–6], and several examples of peat use in filter beds for contaminated waters have been reported in the literature [7–11]. Peat moss is a promising material for use in filters because of its availability, low price and its high sorption capacity relative to commercial sorbents [4,12,13].

Previous research on peat as a filter material focused on mechanisms of sorption and sorption capacity of the peat [14–18].

However, the influence of the actual running and maintenance conditions for peat filters is rarely addressed. A peat filter may be subject to changing environmental conditions, including temperature, redox potential, water load and water quality. Operating periods may be interrupted and filters left dry, stagnated in water or frozen. One of the objectives of this study was to investigate peat filter performance under realistic conditions. Another issue is the durability of the peat. Peat is an organic material that decomposes with time and decomposition may affect the filter performance. Peat in its natural state is one of the most slowly decomposing organic materials as it is usually formed in environments poor in nutrients and under the water table in anoxic conditions. Such conditions inhibit the microbial activity responsible for decomposition. Moreover, the *Sphagnum* plants in particular contain compounds which are resistant to or inhibit decay [19]. It is however possible that the decomposition rate of peat might accelerate when it is used in a filter. First of all, the redox conditions could be changed and more air could become available for microbial decomposition. Fluctuations of redox conditions seem to accelerate peat deterioration [20]. In addition, increase in pH has been shown to stimulate microbial growth in peat [21].

In this project a study on the influence of actual running and maintenance conditions on metal sorption by peat filter has been conducted. The influence of the following parameters was investigated in column experiments: time, draining, freezing, stagnation in water, input of NaCl, rise in pH or metal concentration. The findings have important implications for the use of organic-based filter materials.

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2. Materials and methods

Metal sorption to *Sphagnum* peat moss was studied in columns for a period of 6 weeks. Detailed physico-chemical characterization of the peat material has been provided elsewhere [17]. Seven identical peat columns, 60 mm × 300 mm, were packed with 60 g (DW) peat, with organic content of 94% (DW), water content of 85% and packing density of 0.08 g cm⁻³. Columns were eluted at 1 mL min⁻¹ with upward flow at a constant temperature of 24 °C. During the first 3 weeks (period I) multi-metal solution was passed through the columns, the total volume being 26 L. During the following 3 weeks, columns were exposed to drainage (open column with no water flow), water stagnation or freezing, and thereafter followed by a 3-week period (II) of elution with the same solution. The metal solution contained 100 µg L⁻¹ of the metals As, Cd, Cu, Cr, Ni, Pb and Zn prepared from analytical grade metal nitrates (Sharlau, extra pure) and buffered at pH 6.7 with 0.02 M sodium phosphate (Sharlau, extra pure).

The remaining columns were run directly for another 3 weeks, but input metal solutions were modified as follows: metal concentrations increased to 1 mg L⁻¹, pH increased to 8.0, and 6 g L⁻¹ NaCl was added. Two reference columns were run continuously, one with a constant metal solution and another with the buffer solution without metals.

An aliquot was collected from each column leachate every 48 h and filtered through a 0.45 µm cellulose-acetate filter. Dissolved metal concentrations were determined by inductive coupled plasma mass spectrometer (ICP-MS) with a 10 µg L⁻¹ Rh internal

standard and using multi-element standard solutions (Merck XI CertiPUR) for calibration. Samples were preserved by addition of 1% suprapure HNO₃ (Sharlau) and kept at 4 °C.

3. Results and discussion

3.1. Assessment of peat filter for Cd, Cu, Ni, Pb and Zn sorption

All peat columns were found to efficiently remove metals during the 6-week experimental period with adsorption rates of 91–98%, except for the first sample (3 L) for which metal removal was lower (65–95%); see Fig. 1. The corresponding DOC level in the effluent suggests that the initially lower removal is due to a DOC flush that causes formation of dissolved metal–organic complexes instead of binding to the peat surface.

The retention of the metals was not significantly affected by freezing, rise in pH or higher metal concentration. A statistically insignificant decrease in Zn, Ni and Cu sorption was observed in the first samples after freezing and change in pH. This effect was similar to the raised metal concentration in the very first sample (Fig. 1, eluted volume 3 L) and may be attributed to the leaching of DOC. In the case of freezing, DOC accumulated in the column during the melting period was leached. Increase in pH of the solution caused an initial DOC flush due to increasing solubility of organic material with pH. This first flush effect was statistically significant directly after draining or stagnation of the column (Fig. 1, eluted volume 30 L) for Cu, Ni and Zn, but was not observed for Cd and Pb.

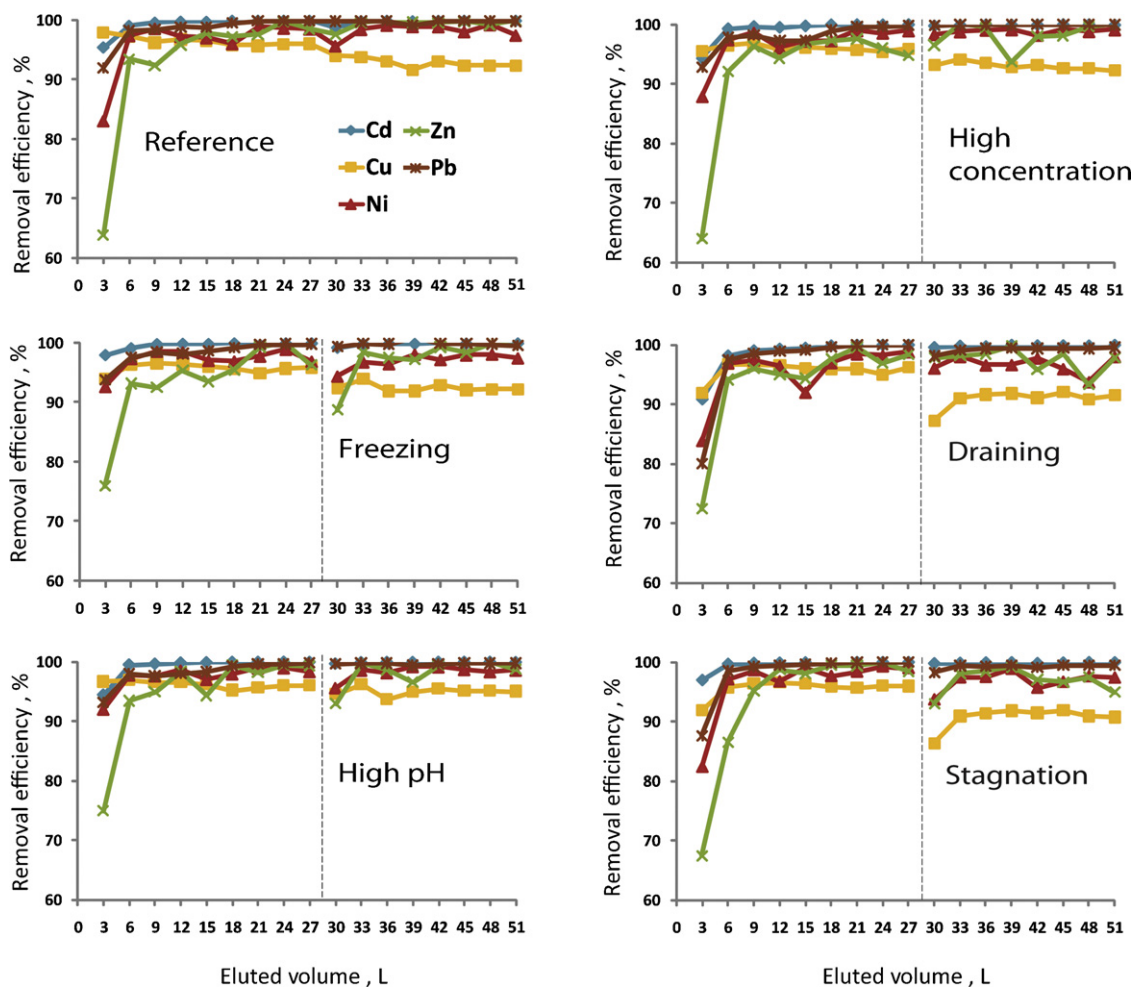


Fig. 1. Sorption of metals by peat columns under different environmental conditions; dashed line indicates change in conditions.

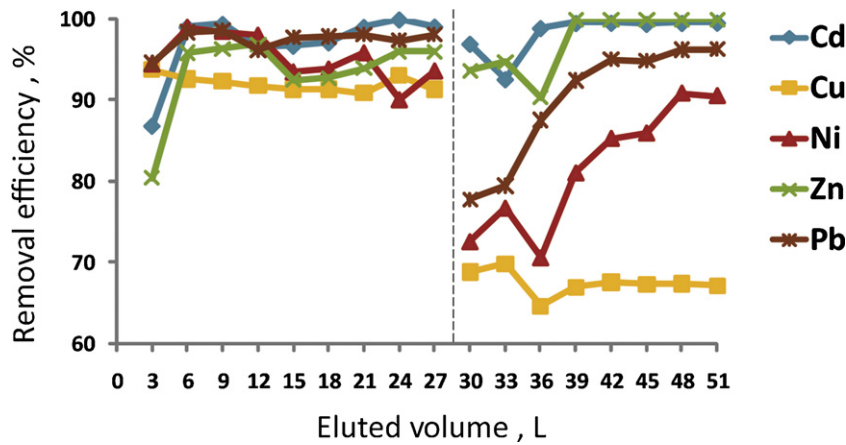


Fig. 2. Sorption of metals by peat from solution containing NaCl; dashed line indicates change in conditions.

It should be noted that Cu sorption decreased gradually with time in contrast to other metals. Copper is believed to be sorbed more specifically and is generally fixed by chelation with exchange of two neighboring carboxylate oxygens [22,23]. As the number of such sites is limited and decreasing with time, sorption conditions for Cu become less favorable. Because of its specific binding Cu is even less affected by the “first flush” effect.

3.2. Sorption from solutions with NaCl addition

Salt (NaCl) is widely used as a de-icing agent and may be found in high concentrations in urban runoff during cold seasons. The influence of NaCl on trace metal sorption to peat has, therefore, important implications for stormwater treatment by peat or other types of organic filters. The presence of NaCl in the input solu-

tion decreased sorption of all the metals for a short period (Fig. 2, eluted volume 30–39 L). Sorption was restored quickly for Zn and Cd and more gradually for Pb and Ni. Sorption of Cu was however reduced by 30%. Sodium has a lower affinity to the peat surface than studied metals owing to its lower charge and relatively larger ionic radii, and thus forms weak complexes with organic materials. Because Na concentration was one order of magnitude higher than that of the other metals, Na could have saturated carboxylate sites [24]. In addition, sorption of Na decreases the negative charge of the peat matrix and the attraction of metal ions to peat surface. The inhibition of metal sorption was temporary, as the number of the sites available for Na sorption gradually decreased and Na may also be exchanged by other metals with a stronger affinity for the peat surface. The effect on Cu sorption was permanent as Cu was reported to occupy carboxylate sites [22,23]. A decrease

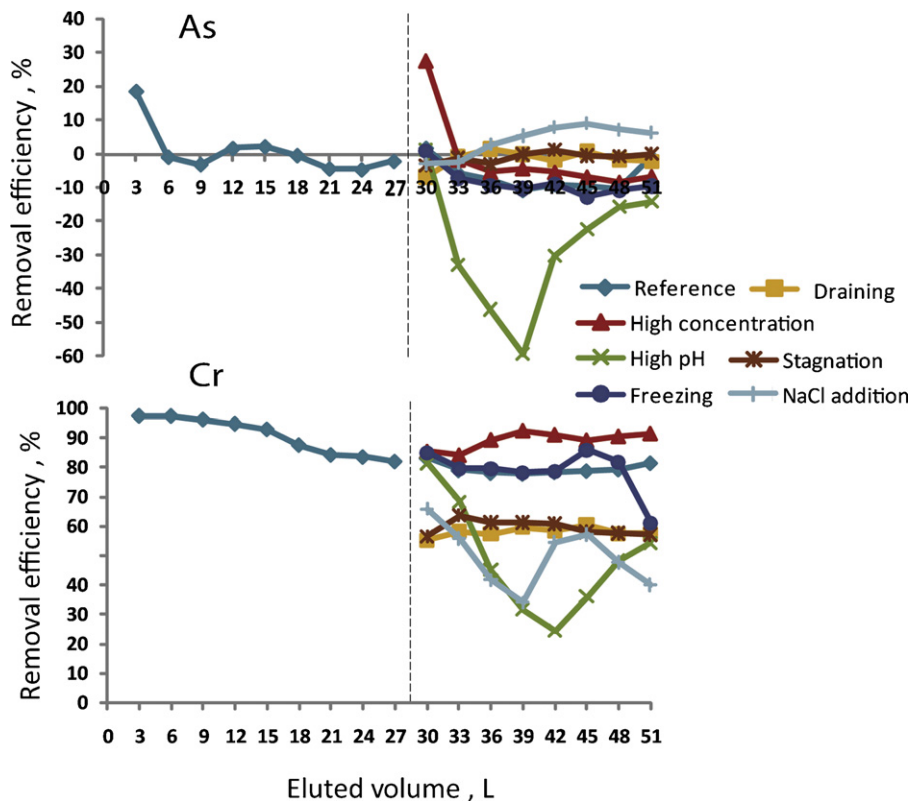


Fig. 3. As and Cr removal by peat under different environmental conditions; dashed line indicates change in conditions.

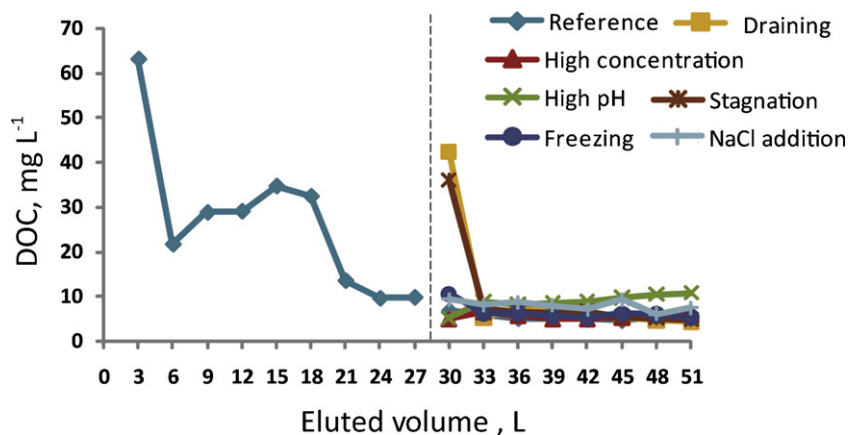


Fig. 4. Concentrations of DOC in peat columns effluent; dashed line indicates change in conditions.

of Cu sorption in the presence of Na was also shown elsewhere [25].

3.3. Assessment of peat filter for As and Cr sorption

The peat columns were not found to remove As, regardless of the applied environmental condition; see Fig. 3. This poor removal is attributed to the occurrence of arsenate/As(V) as negatively charged ions, i.e. H_2AsO_4^- or HAsO_4^{2-} in oxidizing conditions, or arsenite/As(III) as arsenous acid H_3AsO_3^0 in reducing environment, at the pH used in solutions (i.e. 6.7 and 8.0). Arsenic was only retained during a short initial period, when the natural pH of peat around 4 caused the pH of the solution to decrease. This may be explained by the higher adsorption affinity to iron hydroxides (occurring in peat) of As(V) at lower pH values; as pH increases, the sorption is weaker and, depending on hydroxides, surfaces change to negatively charged (Sracek et al., 2004). Changes in redox conditions, from highly oxidized in the solution to reducing in the peat column, could also affect As sorption by reductive dissolution of Fe hydroxides enhancing release of adsorbed As (Sracek et al., 2004). The removal of As sharply decreased as soon as the pH in the column was buffered by the higher pH of the solution (Fig. 3, eluted volume 6 L). The same initial sorption peak was also observed when the solution with high As concentration was introduced, but not for the other solutions. A leaching of previously sorbed As was observed for the solution when pH was increased to 8, enhancing leach of As(V) from hydr/oxides' surfaces (Fig. 3, eluted volume 30–51 L).

Chromium was removed effectively during the initial period, but thereafter the removal decreased from 97 to about 80%; see Fig. 3. The chromium removal was also affected by the changes in environmental conditions. Increasing pH to 8 resulted in 30% lower Cr sorption, due to the formation of soluble chromate CrO_4^{2-} . Addition of NaCl resulted in 30% and draining and stagnation in 20% lower Cr sorption, respectively. Chromium is believed to be removed through precipitation as a result of the changes in redox conditions from highly oxidized in the solution to reducing in the peat column, where Cr(VI) in the forms HCrO_4^- and CrO_4^{2-} is reduced to Cr(III) that precipitates as $\text{Cr}(\text{OH})_3$ at the actual pH of 6.7. Results for Cr and As suggest that peat should not be used for treatment of waters contaminated with these elements at neutral to basic pH.

3.4. Dissolution of DOC from peat

Peat moss has a high content of humic and fulvic acids which have considerable solubility in water and may be leached from the

peat matrix. The release of DOC from peat was determined to be in two stages: a first flush during which large quantities of DOC are released (Fig. 4, 3 L eluted volume) and a lower, more constant DOC release during the rest of the experiment. During the first stage, washout of the residual DOC contained in the peat pore-water occurs, while in the second stage newly produced DOC is probably leached as a result of the progressive degradation of the peat surface.

Leaching of organic material from peat could probably increase through peat decay when complex organic compounds are broken down into simpler compounds [26]. Peat in general is the most slowly decomposed organic material, but decomposition may be accelerated by factors promoting bacterial growth, e.g. oxidation, higher temperature or neutral to basic pH [21]. Oxidizing conditions, obtained by draining the column for 3 weeks, caused a DOC flush that quickly declined (Fig. 4, eluted volume 30 L). The cumulative DOC leached from this column by the end of the experiment was equal to that from the other columns, which suggests that no excessive DOC was produced but just accumulated. This was also confirmed by the equal DOC flush after stagnation of one of the columns in water for 3 weeks (Fig. 4). No other conditions, including freezing, elevated pH, metal concentration or NaCl addition, had any statistically significant influence on the DOC leached.

DOC leaching from peat soils with various organic content has been investigated [27]. The DOC leaching from peat in this study is consistent with leaching from organic-poor or azide-treated soil, where microbiological activity was eliminated. The organic-rich soils were characterized by DOC production and leaching, increasing with time. These findings suggest that metals present in the input solution suppress microbiological activity and thus peat decomposition. This hypothesis is also confirmed by development of an obvious algae growth in the column eluted with the buffer solution without addition of metals, in contrast to the rest of the columns.

As trace metals have high affinity for organic material, a DOC-facilitated transport of metals through peat filters may occur. A significant correlation ($R^2 > 0.8$, $P = 0.5$) between DOC and Cd, Ni, Pb and Zn concentrations was found in the column effluent, suggesting that these metals are transported as organic complexes. However, transport of metals with DOC was considerable only during the first two days of the experiment, when DOC leaching was the highest (Fig. 4, 3 L eluted volume). Thereafter, concentrations of DOC and metals were very low. In order to avoid initial transport of metals with DOC in a peat filter, washing of peat before use is recommended to remove residual and easily soluble organic material.

4. Conclusions

Peat columns removed Cd, Cu, Ni, Pb and Zn by 91–98% from artificial multi-metal solutions. The retention of metals was not affected by freezing, rise in pH and higher metal concentration. Draining and stagnation caused a marginal temporal decrease in Cu, Ni and Zn sorption. The presence of NaCl in the input solution decreased sorption of all the metals for a short period, except for Cu for which sorption decreased by 30%, possibly due to differences in sorption mechanisms compared to other metals. Peat columns removed almost no As, and had a lower efficiency for Cr, possibly due to the occurrence of these elements as negative ions at the pH range studied. Peat columns are not recommended for As and Cr sorption at neutral to basic pH.

The amount of DOC leached from the peat columns is significant ($40\text{--}70\text{ mg L}^{-1}$) only during a short conditioning of a new column or after a long period of stagnation or draining. During these periods higher metal concentrations are also found in the effluent. This problem may be easily overcome by washing of the new peat filter before use to remove excess of the easily leached organics and by re-circulating the initially eluted solution. The DOC leaching after the conditioning period is constant and low around 3 mg L^{-1} , and metal transport with the peat DOC in a filter is negligible.

Peat filters are recommended for treatment of water contaminated with Cd, Cu, Ni, Pb and Zn and can also be successfully used for stormwater treatment.

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