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Metal removal by bed filter materials used in domestic wastewater treatment

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ABSTRACT

Bed filters using reactive materials are an emerging technology for on-site wastewater treatment. Used materials, which are enriched with phosphorus, can be used as a fertiliser or soil amendment. However the materials can also be enriched with metals from the wastewater. Six materials (opoka, sand, Polonite[®], limestone, two types of blast furnace slag) exposed to long-term wastewater loading in columns and in a compact filter well filled with Polonite were investigated for metal removal and accumulation. Wastewater applied to the columns had low heavy metal concentrations in the order Zn > Cu > Mn > Ni > Cr. All columns were able to remove 53%–83% of Zn except those filled with sand. Polonite demonstrated a high removal capacity of Mn (>98%), while only the slag materials were able to remove Ni. All materials showed increased Cu, Cr(III), Mn, Pb and Zn content after filtration. Speciation calculations showed that high concentrations of dissolved organic matter might have prevented efficient metal removal, particularly in the case of Cu. The low content of toxic heavy metals in the studied filter materials studied would probably not restrict their use as a fertiliser or soil amendment.

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1. Introduction

On-site disposal systems are considered a legitimate form of wastewater treatment in rural areas and in such cases a septic tank system combined with an unsaturated soil adsorption bed is the most common design. However, other treatment systems have been developed during recent decades, with constructed wetlands being the most widely applied [1]. A new alternative on-site system that provides treatment prior to disposal into soil or a receiving water body consists of a self-contained flow-through unit with an incorporated reactive mixture, also known as substrate, medium, material or sorbent [2]. This system has the advantage of being very efficient in the removal of phosphorus (P) [3–5]. However, a problem with the use of these materials is that they also may adsorb heavy metals from wastewater. This poses a risk of soil contamination when the spent materials are used in agriculture as a fertiliser or soil amendment [6,7].

Blast furnace slag, an industrial by-product, has been suggested as a suitable substrate for removing metal from wastewater [8]. Slag and similar materials produced from the steel-manufacturing industry have also demonstrated potential as P-sorbing agents in wastewater treatment [5]. In addition, their alkaline character renders them suitable as agricultural liming materials [9,10].

Bed filters using reactive materials may provide an effective, low cost and low maintenance approach for on-site wastewater treatment. Application of this technology can limit the amount of P entering surface water systems and groundwater from wastewater effluents, and may provide significant environmental benefits in rural areas with no sewage systems. Reactive materials can be classified into two distinct groups. One type promotes chemical reactions that destroy the contaminant or transform it to a more benign species (e.g. reductive dehalogenation, denitrification, biodegradation). The second attempts to transfer the contaminant mass from the aqueous phase to the solid phase (e.g. adsorption, ion exchange or precipitation). The latter provides environmental benefits by concentrating the contaminant mass in a finite and known volume of material, which then allows for easier collection and future disposal, or possibly even acceptable rates of release [2].

The possibility of recycling the spent reactive materials or sorbents to agriculture as a fertiliser and soil conditioner has been investigated in some studies [7,11,12]. Their P content might be low compared with industrial fertilisers but their alkaline properties have positive effects on acid soils [7,13]. However the benefits of using these materials in agriculture can be outweighed by their content of heavy metals, which can be transferred from soil to crops by plant uptake and become hazardous for man and the environment. Domestic wastewater contains different amounts of metals depending on its source [14]. These metals can accumulate in the filter material during filtration of the wastewater and add to any indigenous content that might be present [15]. Investigations

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carried out on treatment of landfill leachate and urban stormwater clearly show the ability of reactive materials to remove metals from the liquid to the solid phase, but also leaching from the filter matrix [16,17].

Several mechanisms, such as sorption, complexation and precipitation, can control metal concentrations in effluent from bed filters employed for wastewater treatment. Divalent metal cations tend to favour sorption on colloidal particles with negatively charged sites, calcite, clay minerals, organics and oxides of Fe, Mn, Al and Si [18]. Complexation is the combination of metal ions with non-metallic ligands by covalent bonds. The humic-like substances formed from wastewater decomposition can serve as ligands for metal complexes [19]. Precipitation occurs when a metal species falls out of solution as a solid. Sulphides and carbonates are capable of forming precipitates with Cd, Ni, Zn, Cu and Pb [20,21].

A large-scale dynamic column experiment was conducted over a long time period to assess the removal of metals from water by different reactive materials subjected to domestic wastewater loading. Additionally, an analysis was made of the indigenous heavy metal concentrations in the filter material Polonite, which is used in full-scale, on-site wastewater treatment. The long-term experiment simultaneously investigated P and N removal, the results of which are presented elsewhere [11,22].

The aim of the present paper was to (i) study and compare the capacity of six filter materials for metal uptake or release under conditions of intermittent wastewater loading; to (ii) investigate whether equilibrium with solid phases might have controlled metal solubility in the materials; and to (iii) quantify the content of metals in the filter materials, in particular the Polonite used in small-scale wastewater treatment, and to relate that content to statutory limits on metal content in sludge for use in agriculture. In addition, the removal mechanisms were examined with particular reference to the possibilities of preventing metal contamination of the reactive materials.

2. Materials and methods

2.1. Column experiment and characterization of materials

Six filter materials were used for the column experiment, which was performed indoors (20 °C) at the Loudden wastewater treatment plant, Stockholm. The design of the research set-up and the physical parameters of the wastewater treatment materials are described in detail elsewhere [11]. The materials, their particle size and total weight in columns were: amorphous blast furnace slag 0.25-4 mm, 46.9 kg (ASC); crystalline blast furnace slag 0.25-4 mm, 44.8 kg (CSC) and 2-7 mm, 38.9 kg (CSVC); limestone from Ignaberga in southern Sweden, 1-2 mm, 45.9 kg; opoka, a bedrock from Poland, rich in CaCO₃ and SiO₂ and formed from marine sediments [23], 2-5.6 mm, 36.4 kg; a calcinated opoka with the brand name Polonite, 2-5.6 mm, 27.2 kg; and washed quartz sand, 0.2–2 mm, 54.1 kg, used as a model for the sand commonly used in infiltration beds in Sweden. For additional characterization, see Table 1. Two materials were tested in duplicate columns (CSC, Polonite). The nine 30 cm wide columns were filled to a height of 50 cm.

On average, $0.5 L h^{-1}$ of wastewater was filtrated through each column intermittently every second hour for 67 weeks. Before being applied to the columns, the wastewater was pretreated in a two-chamber septic tank so that coarse, suspended material and organic particles precipitated out. Before treatment in columns, the wastewater had the following characteristics (mg L⁻¹): SS 130 ± 11 , BOD₇ 85 ± 15 , TOC 70.7 ± 9.5 . Equal subsamples of pre-treated wastewater were distributed from a distribution tank to all columns. The columns, tanks and tubing were made from polyvinyl chloride (PVC). At the top of each column, a 2.5 cm thick layer of

mineral wool was placed as an additional barrier to prevent any larger remaining organic particles in the wastewater from entering the filter materials. The mineral wool also had the function of distributing the wastewater equally over the filter surfaceand was changed in all columns three times during the experiment period to avoid clogging and preferential flow tendencies.

2.2. Full-scale treatment system experiment

A reactive bed filter system for a one-family house, situated 20 km NE of Uppsala city in Sweden, was used for studies of treatment efficiency. The reactive material used was Polonite mixed with 8% peat (w/w), which emerged as the most promising filter among materials tested in previous research [12,24,25]. The system consists of a pre-treatment step with septic tank and biofilter followed by a filter well filled with Polonite (volume 800 L, dry weight 560 kg), receiving wastewater intermittently in relation to its production in the household. After 2 years and 3 months of operation, the filter material was removed and exchanged with a new Polonite filter. The total phosphate (PO₄-P) removal was 90% for that period.

2.3. Analyses and calculations

Column influent and effluent samples were collected in 100 mL acid-washed plastic vessels at least fortnightly. The pH was determined and the samples then filtered through a $0.45 \,\mu$ m micropore filter (Sartorius). Biochemical oxygen demand (BOD₇) was determined after 45, 50 and 58 weeks of the column system operation according to Swedish Standards (SS 028143-2 mod. and SS-EN 25814-1).

Samples taken from the influent and each column during periods of approximately every 6 weeks were mixed to one representative sample for analyses of elements. In total, 11 samples were obtained from influent and column effluents, covering the whole experimental period. The filter materials were excavated with a plastic spoon in downward direction of the columns, in the 0–5, 5–10, 10–20, 20–30, 30–40, and 40–50 cm layers and dried at room temperature. The Polonite material from the filter well was similarly sampled and, in addition, three samples were taken randomly from the whole filter mass after mixing (in total 14 samples). Metal concentrations in the virgin materials, in the liquids and in the solids from the column and full-scale experiment were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

The removal capacity of the filter materials (R_m , %), i.e. the retention or leaching of dissolved elements during the infiltration of wastewater, was calculated according to the equation:

$$R_{\rm m} = \left(1 - \frac{C_{\rm e}}{C_{\rm i}}\right) 100\tag{1}$$

where C_e is the effluent concentration and C_i is the influent concentration.

The total metal content $(mg kg^{-1})$ of filter materials in the columns was calculated as the average of the content in each layer. Analyses were performed in duplicate for the 0–5 cm layers.

To investigate whether equilibrium with solid phases might have controlled metal solubility in the materials, Visual MINTEQ ver. 2.53 [24] was applied for speciation of the column effluents. Reactions for aqueous complexes and solid phases, including equilibrium constants for these, were taken from the Visual MINTEQ standard thermodynamic database [24]. In these calculations, complexation with dissolved organic matter (DOM) in the effluents was estimated using the Stockholm Humic Model [25] assuming that 70% of the DOM consisted of fulvic acid [24]. Because measurements of alkalinity and dissolved organic carbon (DOC) were made only for a few samplings, the results should be considered approximate.

Table 1

Filter materials used, their origin, pH and chemical composition at start of the experiment.

Filter material	Origin	рН	Main chemical composition
Blast furnace slag; (a) crystalline (b) amorphous	Industrial, by-product	9.6 9.9	SiO ₂ (36%), CaO (35%), MgO (13%), Al ₂ O ₃ (10%)
Opoka	Natural, crushed bedrock	8.3	SiO ₂ (45%), CaO (40%), Al ₂ O ₃ (4%), Fe ₂ O ₃ (2%), K ₂ O (1%)
Polonite®	Man-made from opoka	12.5	SiO ₂ (45%), CaO (45%), Al ₂ O ₃ (4%), Fe ₂ O ₃ (2%), K ₂ O (1%)
Limestone	Natural, crushed bedrock	8.9	SiO ₂ (8%), CaO (49%)
Sand	Natural, sieved fraction	6.5	SiO ₂ (69%), Al ₂ O ₃ (13%), K ₂ O (3%), Fe ₂ O ₃ (3%)

3. Results and discussion

3.1. Characteristics of wastewater

The pH and BOD₇ values for the wastewater used in the experiment and the changes after filtration through the filter materials are presented in Table 2. Wastewater pH was unusually high, sometimes approaching values of 9.3, most likely due to loadings other than from domestic sources, e.g. industrial effluent, storm water and effluent from the adjacent harbour. Organic compounds measured as BOD indicated normal concentrations for this type of mixed wastewater.

The screening with ICP-AES encompassed a total number of 25 elements in the influent and effluent of the columns. Dissolved concentrations of As, Cd, Co, Mo, Pb, Ti, V and Y in influent wastewater were very low, below the detection limit of the ICP instrument. Other elements in the wastewater applied to the columns showed low concentrations and followed the order Ba > Zn > Cu > Mn > Mg > Ni > Cr. The influent concentrations and the concentrations found in effluent from each of the column materials are shown in Table 4. It is obvious from this data that wide variations occurred in metal concentrations, most likely caused by the above-mentioned sources of pollution (cf. [14]). In fact, metal concentrations in influent were lower than typical effluent discharge limits with the exception of Cu [19]. Thus, the wastewater used in the column experiment had very low dissolved metal concentrations. The treatment preceding the filtration through the column materials most likely removed the majority of metal species. These

Table 2

Characteristics of column influent and effluent samples of wastewater.

Filter material ^a	Influent		Effluent	
The material	рН	BOD ^b	рН	BOD ^b
_	8.18-9.28	87 ± 13	-	_
Sand			6.05-9.27	1.3 ± 0.6
Opoka			8.29-9.95	3 ± 0.6
Polonite			8.23-12.84	2 ± 0.9
CSC			8.09-9.88	1.7 ± 0.5
ASC			8.93-9.73	2 ± 0.4
CSVC			8.49-9.75	2 ± 1
Limestone			7.63-9.81	2.7 ± 0.6

^a ASC = amorphous slag, coarse; CSC = crystalline slag, coarse; CSVC = crystalline slag, very coarse.

^b mg L⁻¹, n = 3.

Table 3

Percentage removal of dissolved metals by the filter materials.

Filter material	Removal (%)							
	Ba	Cu	Cr(III)	Mg	Mn	Ni	Zn	
Sand	0	0	0	0	00	0	0	
Opoka	36.2	0	11.6	0	61.7	0	68.6	
Polonite [*]	0	15.9	0	98.6	98.7	0	62.2	
CSC [*]	44.3	12.9	0.38	0	0	29.6	82.5	
ASC	27.1	27.9	9	0	83.8	32.9	80.1	
CSVC	47.6	2.8	0	0	0	24.9	74.6	
Limestone	13.6	7.2	0	0	44.9	0	53.7	

Average for duplicate materials.

can be trapped by gravity settling of suspended solids in a primary clarifier, e.g. septic tank [26,27].

3.2. Removal and release of dissolved metals in columns

Differing removal rates of dissolved metals were observed for the filter materials (Table 3). The apparent tendency for removing metals among the materials studied here followed the order Polonite > ASC > opoka > CSC > limestone > CSVC > sand. Zinc was removed by all materials, except the sand, in the range of 53%–83%. Only the three blast furnace slags (ASC, CSC, CSVC) were able to remove Ni. Polonite removed over 98% of dissolved Mg and Mn in the wastewater, while reasonably efficient removal of Cu was demonstrated by the ASC.

Analyses of metal concentrations in the leachate (effluent) from columns (data not shown) showed significant (p < 0.05) release, i.e. an increase in concentration, of some elements from sand, CSC, ASC and CSVC. Sand released Cu and Zn, while CSC and ASC showed increased concentrations of Mg. The very coarse crystalline slag (CSVC) exhibited a large loss of Mn, though only in the beginning of the experiment.

3.3. Speciation modelling

According to speciation calculations with Visual MINTEQ, a very large fraction of dissolved copper in the column leachates were bound to the DOM (the median value was 99.99%). The corresponding figures for Cr(III) (assuming that all dissolved Cr existed as trivalent chromium), Zn and Ni were 93%, 59% and 24%, respectively. Other ions such as Mn, Ca and Ba were less strongly bound to the DOM.

The wastewater that trickles through the filter matrix and colloidal matter can attach to the surface of each mineral particle [28]. Bacteria create a biofilm where microbial adsorption of heavy metals can occur [29] and where adsorption and precipitation processes can also retain the metals. The increased concentrations of dissolved metals in the effluent may therefore be the result of leaching from the materials. The blast furnace slag, from which Mg and Mn were obviously released, demonstrates this, as did the results of a previous study [16].

Calcite is a principal component of opoka and limestone. The differences between these materials in terms of metal sorption capacities may be due to their affinity to the surface of calcite [30]. It has been claimed that the mechanisms involved in metal retention by blast furnace slag are ion exchange on particle surfaces and/or precipitation on Al(OH)₃ and SiO₂ [31]. Sorption/precipitation to sulphidic compounds in blast furnace slag may also be important. However, sulphur was leached to a large extent from blast furnace slag columns in the beginning of the present experiment (data not shown), as was previously observed in a column experiment with landfill leachate [16]. In the case of limestone and opoka, chemisorption of metal ions to their rough calcite surfaces can be one mechanism for removal [32,33]. Moreover the dissolution of alkaline minerals, particularly in the case of Polonite, can increase the pH of the percolating wastewater above solubility point, which causes metals to precipitate, most likely as metal oxides and metal carbonates [34].

Element	Influent	Column effluent	Column effluent							
		Sand	Opoka	Polonite**	CSC**	ASC	CSVC	Limestone		
Ba	62.2 ± 21.3	68.4 ± 12.6	39.7 ± 12.3	90.4 ± 24.7	34.7 ± 8.9	45.3 ± 9.9	32.6 ± 7.6	53.7 ± 26.9		
Cr	1.71 ± 0.52	2.71 ± 3.52	1.51 ± 0.34	26.8 ± 32.6	1.68 ± 0.53	1.55 ± 0.5	1.75 ± 0.52	1.72 ± 0.59		
Cu	16.2 ± 10.8	26.4 ± 9.6	18.1 ± 6.4	13.6 ± 7.4	15.01 ± 14.1	11.6 ± 4.8	15.7 ± 5.5	15.0 ± 8.6		
Mg [*]	6.26 ± 0.66	6.88 ± 1.86	7.68 ± 1.25	0.09 ± 0.06	32.1 ± 5.99	28.4 ± 10.3	7.26 ± 0.86	26.3 ± 7.03		
Mn	10.9 ± 3.1	31.2 ± 32.2	4.21 ± 4.0	0.24 ± 0.19	29.3 ± 65.3	1.77 ± 2.15	82.6 ± 203.1	6.04 ± 6.7		
Ni	4.64 ± 1.6	10.1 ± 5.7	5.52 ± 1.58	6.37 ± 4.15	3.26 ± 0.77	3.11 ± 0.49	3.48 ± 1.34	5.79 ± 5.01		
Zn	37.5 ± 11.8	221.3 ± 164.5	11.8 ± 5.5	14.2 ± 10.2	6.57 ± 1.96	7.47 ± 1.63	9.54 ± 2.86	17.36 ± 23.5		

Influent and column effluent concentrations of elements. The unit is $\mu g L^{-1}$, unless otherwise stated (average, SD).

 * mg L⁻¹.

Table 4

* Average and SD for duplicate materials.

The organic ligands present in wastewater can bring about enhanced, suppressed or unaffected adsorption of metal ions on clay minerals [35]. An enhanced effect is often seen at low pH, whereas at neutral to high pH (as in the present investigation) the DOM is likely to suppress metal sorption, especially for Cu. Predicted purification efficiencies calculated from adsorption isotherms are therefore never reached [36].

3.4. Metal content in the filter materials

All filter materials used in the columns generally showed enhanced concentrations of the heavy metals Cu, Cr(III), Mn, Pb and Zn after wastewater filtration (Table 5). The clearest increase in content for all materials was found for Cu. In the sand, all metals were found in increased concentrations. A small release of Cr(III) was apparent from opoka, Polonite and CSVC.

Chemical analyses of filter layers showed that Zn had a clear distribution pattern in all materials, with its highest concentrations in the surface layer and lowest in the bottom layer of the columns. This was also true for Cu in columns filled with the fine-grained materials ASC, CSC and limestone.

In Table 6, the concentrations of heavy metals in the experimental material Polonite are compared against the permissible limits of metal content in sludge for use in agriculture. The field data included from a domestic filter well differed from the data obtained from the column in that much higher Cr(III), Cu and Mn contents were found in the Polonite used for treating the wastewater from one household than the two columns fed with municipal wastewater. However the systems were operated quite differently. The loading to the columns was 1.5 times higher, where unsaturated conditions existed, whereas the filter well used an intermittent cyclic process with complete saturation of the material.

It is interesting to compare the results on removal of dissolved metals from wastewater (R_m , Table 3) with those from analyses of metal concentrations in the materials (Table 5). The sorption of Cu was clear in all materials regardless of pH conditions and particle size distributions. However, a rather moderate removal was found for the materials with ASC, the highest values recorded being about 28%. Sand did not show any apparent removal of dissolved Cu, but analysis of material from the column showed presence of the metal. All columns removed BOD efficiently, which indicates that organic matter was retained and partly decomposed.

With regard to the mechanisms for metal sorption/dissolution, speciation modelling with Visual MINTEQ suggests that Ba was close to equilibrium with barite (BaSO₄) in all column leachates (Fig. 1), as the calculated ion activity products were close to the solubility constant of this mineral phase. This may explain why Ba was removed in the CSC and CSVC columns, since these columns generate an increase in dissolved SO_4^{2-} , which would cause barite precipitation. Additionally, the Ni appears to be solubility-controlled by nickel hydroxide, Ni(OH)₂, in all column leachates except the opoka column. Dissolved chromium was in most cases

slightly lower than predicted by equilibrium with Cr(III) hydroxide. For copper, the results suggest that CuO or a similar phase in the Polonite columns (but not in the other columns) might have controlled the dissolved Cu. Dissolved zinc was very much undersaturated with respect to any zinc mineral phase, suggesting that the processes controlling zinc are likely to involve adsorption/desorption and weathering processes. In addition, lead was found to be far from equilibrium with any mineral phase. Magnesium was close to equilibrium with brucite in the Polonite columns early in the sampling period, suggesting that magnesium removal by Polonite involved the precipitation of this mineral. However in the latter part of the experiment there was also undersaturation in the Polonite leachates despite a continued high Mg removal in these columns (>95% throughout the experiment). A possible explanation to this phenomenon is that the pH remained high for a longer time in small pores of the material, permitting brucite precipitation, despite the observed undersaturation in the bulk leachate. This suggests that for successful chemical transport modelling, different flow domains need to be considered (for example using the dual-porosity approach) as recently found for waste materials [37].

The mechanisms for determining metal sorption or desorption therefore appear to be different for different metals. For Cu and Cr the binding to organic ligands in the dissolved phase is likely to suppress efficient precipitation of these ions in the materials. Barium and nickel are solubility-controlled, with little influence of organic complexation. Zinc is neither solubility-controlled nor strongly affected by organic ligands, and so this metal may be controlled by adsorption to inorganic components in the materials.

3.5. Metal flow in wastewater and consequences for filter material recycling

The origin of metals in domestic wastewater is complex, as indicated even by the limited results presented here (Table 6). The reason for elevated concentrations of Cr(III) and Mn in Polonite used in the treatment system for the private house can be related to the specific water supply (drilled well) and tubings. The filter well where Polonite is used is made of stainless steel, which may be a source of additional contamination. The high levels of Mg in influent wastewater may originate from a number of sources, e.g. hard drinking water and seawater intrusion to the sewage system.

Polonite is one of the most promising materials for P removal and subsequent recycling as a soil conditioner [11,13], but the ability to accumulate metals is a disadvantage for this material. However, it must be stressed that one of the metals (Mg) investigated here are considered non-hazardous in the environment and that only Polonite among the materials studied removed Mg from the wastewater.

A further disadvantage is the leaching of dissolved heavy metals from the materials and the indigenous content. However, if the effluent concentrations do not exceed the permissible limits for discharge to receiving water bodies, this should not be a problem. The

Table 5

Concentration of heavy metals in the filter columns (mg kg $^{-1}$). Average values \pm SD for the six layers investigated of each material. Values for virgin materials are shown in brackets.

Element (mg kg ⁻¹)	Filter material								
	Sand	Opoka	Polonite	CSC	ASC	CSVC	Limestone		
Cu	$11.8 \pm 2.7^{*}$	9.5 ± 1.5 (2.02)	6.9 ± 1.3 (1.2)	$3.6 \pm 1.7^{*}$	$3.6 \pm 1.3^{*}$	$3.6\pm0.8^{*}$	$4.3\pm2.9^{*}$		
Cr(III)	$3.4\pm0.8^{*}$	5.7 ± 1.1 (8.8)	$13.9\pm 3.8(22.5)$	$9.8 \pm 1.7 (9.5)$	15.8 ± 3.3 (17.9)	$6.2 \pm 1.1 (9.5)$	$0.5\pm0.1^{*}$		
Mn	$22.9\pm3^{*}$	$108 \pm 12.9 (51.8)$	76.8 ± 13.1 (57.7)	$3689 \pm 279 (3647)$	$3268 \pm 513 (3355)$	$2312\pm 357(3648)$	$505.9 \pm 122.5(296)$		
Pb	$8.6\pm4.5^{*}$	$14.1\pm4.3(13.5)$	$8.6 \pm 4.9(10.1)$	$4.5 \pm 3.1 (0.5)$	$5.3 \pm 3.3^{**}$	$5.7 \pm 3.1 (0.5)$	$10.1 \pm 6.7 (5.1)$		
Zn	$17.5 \pm 14^{*}$	$50.1\pm15.8(32.6)$	$57.9\pm30.7(30.8)$	$32.3\pm37.5(14.6)$	$31.2\pm29.6(18.3)$	$23 \pm 11.8 (14.6)$	$33.4\pm24.9(14.5)$		

* Below detection limit.

** Not analysed.

Table 6

European Union and Swedish statutory limits for sludge disposal on arable land compared with the content of heavy metals in the reactive material Polonite exposed to wastewater filtration in long-term column¹ and field-scale experiments² (mg kg⁻¹).

	Pb	Cd	Cr (III)	Cu	Ni	Hg	Zn	Mn
EU directive 86/278/EEC	750-1200	20-40	1000-1500	1000-1750	300-400	16-2.5	2500-4000	n.d.
Sweden	100	2	100	600	50	2.5	800	n.d.
Polonite ^{1***}	8.6 ± 4.9	*	13.9 ± 3.8	6.9 ± 1.3	*	*	57.9 ± 30.7	$\textbf{76.8} \pm \textbf{13.1}$
Polonite ²	n.d.	*	61 ± 9.7	13.1 ± 5.3	21.7 ± 3.1	*	32.0 ± 21.6	$200{\pm}~63.1$

n.d. no data, * not analysed, ** below detection limit, *** average for two columns.



Fig. 1. The logarithm of the ion activity products for BaSO₄(s) (barite), Ni(OH)₂(s), Cr(OH)₃(s), Zn(OH)₂(s) and Mg(OH)₂(s) (brucite) during the experiment. The black vertical lines correspond to the solubility products of these mineral phases at 20 °C according to Visual MINTEQ calculations (Gustafsson, 2007).

blast furnace slags used in this study had low concentrations of toxic metals compared with other types of slag [38], and the effluent metal concentrations measured were low to intermediate according to Swedish guideline values for natural concentrations of metals in surface water [39].

As can be seen in Table 6, the concentrations of selected heavy metals in the Polonite were far below the European limits for sludge disposal and also much below the stricter Swedish limits. On the basis of the results from the present study it is recommended that for on-site wastewater treatment using reactive filter materials, the preceding treatment steps must be efficient at organic matter removal. This can be achieved by large septic tanks and/or prefiltration prior to treatment in the reactive filter. In this way metal contamination of the filter material can be avoided and thus there is no risk associated with disposal of the material in agriculture. However, sludge from the septic tank must then be monitored if intended for use as a soil amendment on arable land.

4. Conclusions

This long-term column experiment showed that dissolved metals in wastewater were removed in various amounts by the studied filter materials. The fine-grained, amorphous blast furnace slag showed sorption capacity for all the metals investigated except Mg, which was only removed by the Polonite[®]. According to speciation calculations with Visual MINTEQ, a large fraction of dissolved Cu and Cr(III) in the column leachates were bound to the DOM.

Leaching from the materials can contribute to the metal flow, increasing the concentration in the effluent. However the observed metal concentrations in this study were low compared with the Swedish guideline values for natural surface water.

The Polonite material used in both on-site wastewater treatment and the column experiment showed heavy metal concentrations that are much lower than the European limits for sludge disposal. Hence the low content of heavy metals in the filter materials will not interfere with their use as a fertiliser or soil amendment. However for confirmation of the results obtained in this study, more used filter materials from different treatment plants should be collected and analysed.

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