



Research article

Removal of metals from mine drainage waters by in situ mineral sorbent-based pilot filter systems

Heini Postila^{a,*}, Elisangela Heiderscheidt^a, Tiina Leiviskä^b^a Water, Energy and Environmental Engineering, P.O. Box 4300, FIN-90014, University of Oulu, Oulu, Finland^b Chemical Process Engineering, P.O. Box 4300, FIN-90014, University of Oulu, Oulu, Finland

ARTICLE INFO

Keywords:

Purification efficiency
Mining waters
Slag
Recycled mineral
Sorption

ABSTRACT

Discharge of metal-containing wastewater streams into the environment is an environmental concern because these pollutants do not degrade and tend to bioaccumulate. A number of laboratory-based investigations on the effectiveness of a wide range of filter materials for metal removal from diluted wastewater streams have been reported. However, only a few pilot or full-scale investigations have been conducted. Therefore, this study investigated the metal retention capabilities of mineral-based filter materials (commercially available mineral product (5–15 mm), recycled mineral material (2–4 mm) and slag by-product (2–4 and 4–16 mm)) when used in pilot-scale filter systems under continuous operation in a closed mining area in North Ostrobothnia, Finland, between June and October 2017. The influence of material particle size on system function and on metal retention efficiency was also evaluated. The results revealed that system performance was dependent on material composition and particle size (smaller particle size being more effective). The highest metal removal efficiencies (Zn, Ni, Cd, Cu and Pb) and largest amount of water treated (per volume of material applied) were achieved by an aluminium oxide-based recycled mineral material (2–4 mm). While smaller-grained materials performed better in terms of removal efficiency, the removal rates achieved by coarser-grained, commercially available mineral product (5–15 mm) were comparable to those achieved by small-grained slag (2–4 mm). Full-scale systems using the recycled mineral product (2–4 mm) would have an approximately two-fold longer material replacement time than systems using the slag (2–4 mm). Replacement time for the larger-grained materials tested could not be determined, due to problems with freezing. Overall, the recycled mineral material tested can be recommended for full-scale tests, especially when high zinc removal rates are required.

1. Introduction

Release of metals contained in e.g. mining-influenced waters (The Coal Authority, 2014), urban runoff (Valtanan et al., 2014; Westerlund et al., 2003) etc. can impair surface water quality and the general health of the receiving aquatic ecosystem, as these pollutants do not degrade and tend to bioaccumulate in the environment (Simate and Ndlovu, 2014). As regards mining-influenced waters, concentrations of metals can vary depending on the type of mine and on where the water originates from inside the mine site (drainage, process etc.) (Akcil and Koldas, 2006; Palmer et al., 2015). Any water treatment system aimed at reducing metal load into the environment must therefore cope with water quality variations. At operational mining sites with highly polluted waters (e.g. mining process waters), active purification methods for metal removal, such as chemical precipitation, distillation, evaporation, electrolysis and activated carbon, are employed (Fu and

Wang, 2011; The Coal Authority, 2014). Passive methods such as wetlands, filters and bio-filters can be applied for removal of metals from diluted streams such as mining area drainage water and for pollution control at closed mining sites (Clar et al., 2004; Fu and Wang, 2011). The suitability of passive methods depend on different factors such as location, available space, and amount and quality of water to be treated. For example, if available space is the limiting factor and water amount is not too large (drainage area maximum 0.8–4 ha; Clar et al., 2004), a filter-type system can be a feasible alternative. When planning a filter-type system, important factors to be taken into consideration are the quality of the inflow water, and the particle size and composition of the filter material. The effectivity of different materials depend on the type and concentration of metals contained in the water (Clark et al., 2005) as ions compete for sorption sites. The pH of the water affects the surface charge of materials and the speciation of metals, thus affecting sorption efficiency. Particle size influences bulk porosity and the risk of

* Corresponding author. Water, Energy and Environmental Engineering, P.O. Box 4300, University of Oulu, FIN-90014 Oulu, Finland.

E-mail addresses: heini.postila@oulu.fi (H. Postila), elisangela.heiderscheidt@oulu.fi (E. Heiderscheidt), tiina.leiviska@oulu.fi (T. Leiviskä).

clogging, with finer-grained materials being more susceptible to clogging than coarser-grained materials (Vohla et al., 2011). On the other hand, finer-grained materials provide a larger surface area (higher number of sorption sites), which increases the capability of the filter medium to retain metal ions (Chuah et al., 2005). Moreover, high metal content in the material can cause leaching (Lim et al., 2015) and increased concentrations in outflow water.

A number of laboratory-based investigations into the effectiveness of a wide range of filter materials for metal removal from wastewater streams have been reported (e.g. Genç-Fuhrman et al., 2007; Gogoi et al., 2018; Hatt et al., 2008; Lim et al., 2015; Reddy et al., 2014). However, reports on pilot-scale or full-scale tests are scarce (Assmuth, 2017; Clark et al., 2005). While laboratory-scale experiments are important and provide the opportunity to investigate processes and mechanisms in more detail, pilot- and full-scale tests are needed to fully assess the suitability of materials and systems (Hatt et al., 2008). Such tests should submit materials and systems to the challenges faced in real-life applications, such as variations in water quality, temperature and/or volume.

Based on the identified need for pilot- or full-scale experiments, the aim of this study was to assess the metal retention capabilities of different mineral-based filter materials (commercially available mineral product, recycled mineral material and slag by-product) when used in filter-type pilot-scale systems. Tests were carried out in a closed mine site (Northern Finland) and real mine area drainage water was used. The influence of filter material type and particle size on the system's function and metal retention efficiency were evaluated.

2. Material and methods

2.1. Pilot design and operation

Filter pilot systems were tested in a closed mining area in North Ostrobothnia, Finland, from mid-June to late October 2017. Inflow water for the systems was pumped from a ditch carrying leachate from an old mine tailing area. The study was conducted as part of the HuJa (ERDF) project. "Enhancing the treatment of metal-containing stormwaters and wastewaters using natural materials". Material selection was based on preliminary laboratory-based studies (Gogoi et al., 2018 and unpublished data) and suggestions from project collaborators. Important factors taken into consideration were metal retention capacity (especially for Zn), high hydraulic conductivity and material grain size. Selected materials were: recycled mineral product ALOXrc (2–4 mm; referred to as Mineral R) and commercial available mineral sorbent product PalPower M10 (5–15 mm; referred to as Mineral P) from Aquaminerals Finland Oy, OKTO JT-sand (2–4 mm) and OKTO chippings (4–16 mm) by-product slags from ferrochrome production by Outokumpu Chrome Oy (referred to as Slag).

The pilot systems consisted of plastic boxes (about 55 cm × 35 cm × 30 cm), where compartments were created (inlet, filter media and outlet) using perforated plastic walls (holes 5 mm, located 2.5–3 cm apart) and 1 mm plastic netting. The adsorbent materials were placed in

the compartments in a layer measuring around 35 cm × 35 cm × 15 cm (Fig. 1). Slots for inlet pipe (inner diameter 4 mm) connection were installed at three different depths (−1, −5.5 and −10 cm from the top). This was done to overcome any variation in pressure head during the tests, so that flow velocity could be kept as stable as possible. The outlet pipe (inner diameter 6–8 mm) was placed at 12 cm from the bottom of the unit and was fitted with a 1 mm plastic net at the entrance to prevent blocking of the pipe with leaves and other materials transported with the water. The pilot systems (boxes) were covered to prevent the entry of foreign material.

Pilot operations started in mid-June 2017 with two filter boxes filled with the finer-grained (2–4 mm) Slag and Mineral R materials (Table 1). In August, clogging of the system using the Slag material was observed, so the material in the box was changed to a larger-grained Slag material (4–16 mm) and a third filter box was established and filled with larger-grained Mineral P material (5–15 mm). The desired water residence time in the systems was about 30 min, which would be a suitable scaling up parameter for filters to be constructed in the existing ditches. Volumetric inflow rate to each pilot was set as accurately as possible based on the three inlet depths (−1, −5.5 and −10 cm from the top of box) to meet the desired residence time.

During the tests, water was pumped from the ditch to a 90-L container by one (operation with two pilot filter units) or two (operation with three pilot units) pumps (Biltema: model 25–2751; Fig. 2). The water storage container was filled by intermittent activation of the pumps, controlled by ON/OFF timers. The storage tank was filled every 90 min during operation with one pump and every 45 min during operation with two pumps. From the 90-L water container, the water travelled by gravity via the inlet pipe to the filter pilot inlet compartment. Gravity was also the driving force behind the flow of water through the filter material (around 0.5–1.5% longitudinal slope) to the outlet area and from there to the outlet pipe. The outlet pipe discharged to a small container, where electric conductivity (EC) and pH were measured. From the small container, the water discharged to the same ditch downstream of the pump extraction point (see Fig. 2).

2.2. Monitoring

The EC measurements were carried out continuously (frequency 15 min) by HOBO-loggers installed at the water storage tank and at the outflow of the pilot systems to monitor changes in the ionic strength of the water. In addition, manual pH and EC measurements (WTW Multi 350i-meter) were made and water samples were taken at the same points during field visits, which were made every day or every second day at the start of the test and every 2 weeks for the rest of the operating period. Inflow and outflow samples were taken from the 90-L water container and outlet pipe, respectively. Monitoring of water flow conditions and maintenance work such as unblocking and cleaning pipes etc. were carried out during site visits.

Due to the intermittent pumping, the water level inside the water storage container varied, which caused flow velocity variations in the pilot systems. For that reason, inflow rate was determined on a few

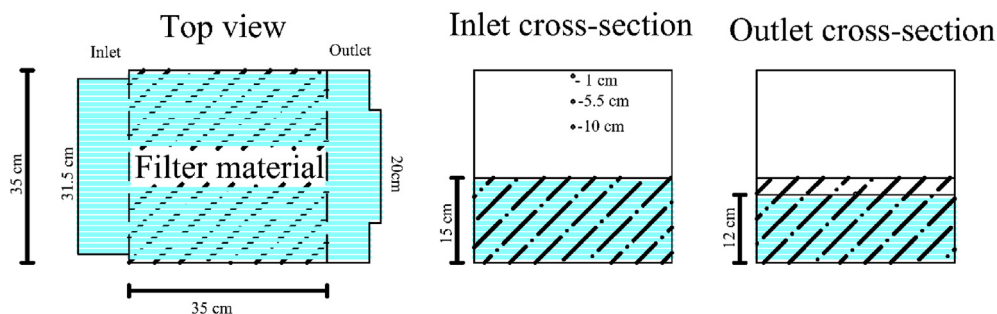


Fig. 1. Top view of the pilot-scale filter system and cross-section of the inlet and outlet.

Table 1

Information on operation of the different filter units, amounts of material tested, test period and reason for test interruption.

Material	Amount of material		Test period ^a	Test time (d)	Reason for ending the test
	(kg)	(m ³)			
Mineral R (2–4 mm)	18.60	0.018	13.6–11.10.17	120	Clogging
Slag (2–4 mm)	29.74	0.019	13.6–16.8.17	64	Clogging
Mineral P (5–15 mm)	20.79	0.018	16.8–11.10.17	49	Freezing 23.10.17
Slag (4–16 mm)	31.27	0.019	16.8–11.10.17	49	Freezing 23.10.17

^a The coarser material units operated until 23.10.17 (61 days), but the water amount and water quality data were only recorded until 11.10.2017. Therefore, only collected data was used in calculation of treated water volume.

occasions by collecting the water discharging from inlet pipes. Water was collected at different times, i.e. different water pressure levels inside the same pumping cycle, into a volumetric container for a specific amount of time (e.g. 3 min). The average inflow rate was determined from the measured values, taking into consideration how water level varied in the storage tank due to pumping regime. Outside those occasions, if disturbed flow conditions were noted in a specific pilot, e.g. due to clogging problems in pipes, inflow rates were estimated based on the water level in the 90-L water container relative to the pumping cycle (e.g. how much water was in the container just before each new pumping cycle).

2.3. Analytical and other determination methods

During the test period, inflow water samples were collected on 13 different occasions and on five of these occasions, a portion of the water collected was filtered (glass fibre (GF) 0.45 µm syringe filter). From the outflow of units containing Mineral R (2–4 mm), Slag (2–4 mm), Mineral P (5–15 mm) and Slag (4–16 mm), the number of samples (unfiltered/filtered) taken was 13/5, 8/2, 6/3 and 6/3, respectively. Filtered and unfiltered samples (acidified as pre-treatment) were sent for elemental analysis to an accredited laboratory. Elements analysed (SFS-EN ISO 11885:2009) using ICP-OES method were Ca, K, Mg, Na and Si. Elements analysed (SFS-EN ISO 17294-2:2016) using ICP-MS method were Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, U, V and Zn. When total concentrations (unfiltered samples) were analysed (SFS-EN ISO 17294-2:2016), the ICP-MS method was used for Cd, Ni, Cu, Cr, Zn, As and Pb. Note that, the total concentrations were determined significantly more often than the dissolved concentrations of different metals. Thus, it was not possible to establish a direct correlation between the average dissolved and total concentrations determined.

On two occasions, inflow samples were also analysed for: total nitrogen (Tot.N, SFS-EN ISO 11905-1), sum of nitrate and nitrite nitrogen (NO₂₊₃-N, SFS-EN ISO 13395), ammonia nitrogen (NH₄-N, Sis. A56

Skalar analytical method no.158.), dissolved organic carbon (DOC, Sartorius Minisart® 0.45 µm membrane filter, SFS-EN 1484), total phosphorus (Tot.P, SFS-EN ISO 15681-2, CFA-technics), phosphate phosphorus (PO₄-P, SFS-EN ISO 15681-2, CFA-technics) and chloride (Cl, SFS-EN ISO 10304-1), and, on one occasion, sulphate (SO₄, SFS-EN ISO 10304-1). The determination accuracy and detection limit of the methods used are presented in Table S1 (Supplementary material). In the calculations performed, values under the detection limit were assumed to be 80% of the limit. Variation in inflow water (elements or compounds) concentrations was presented as standard deviation (*s_d*) if *n* > 2.

Average inflow rate and inflow and outflow concentrations for two consecutive field visits were used as the inflow or outflow value of that period. Outflow rates were assumed to be equal to inflow rates, due to the small size of the system, and thus no significant effect of e.g. evaporation should have occurred. Inflow and outflow pollutant load was calculated based on average discharge rates and the average inflow and outflow concentrations between two consecutive sampling times. Load was calculated as the sum of average inflow rates and concentrations between two consecutive sampling times and load removal as the difference between the sum of inflow and outflow load. Removal efficiency, RE (%), was calculated based on the difference between load entering the system (*L_{in}*, mg) and load leaving the system (*L_{out}*, mg) in the whole test period:

$$RE = \frac{L_{in} - L_{out}}{L_{in}} * 100\% \quad (1)$$

The minimum and maximum values and standard deviation (if *n* > 2) for removal efficiencies calculated for each sampling period are presented. The non-parametric Kruskal-Wallis test was used to evaluate if the difference in removal efficiency values distribution obtained from pilot systems using different filter media was statistically significant (*p* < 0.05). The test was performed using SPSS statistical software.

Water residence time was determined at the start and end of pilot system operation. At the start of the tests, the residence time (*t_r*, min)

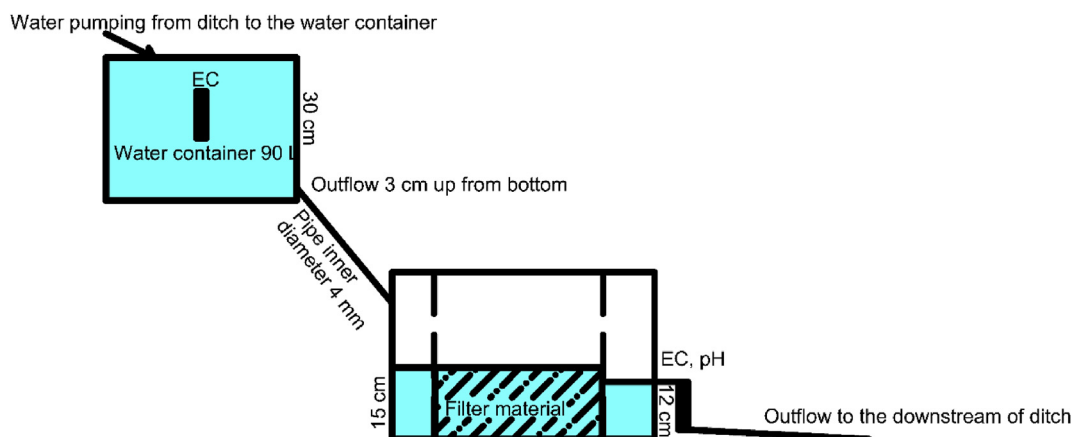


Fig. 2. The pilot filter system and water flow routes.

Table 2

Information on operation of the different filter units, porosity, residence time, discharge rate and treated water volume.

Material	Test duration (d)	Porosity	Residence time		Discharge av. (L/d)	Treated volume (m ³)	Treated volume/material volume (m ³ /m ³)	Treated volume/mass of material (m ³ /t)
			start (min)	after (min)				
Mineral R (2–4 mm)	120	0.81	31	83 ^b	425	51	2785	2743
Slag (2–4 mm)	64	0.49	19	51 ^b	406	26	1403	874
Mineral P (5–15 mm)	49 ^a	0.45	20	46 ^c	469	23	1304	1106
Slag (4–16 mm)	49 ^a	0.78	26	74 ^c	592	29	1518	927

^a The coarser material units operated until 23.10.17 (61 days), but the water amount and water quality data were only recorded until 11.10.2017 (49 days).^b The tracer test was interrupted before the electric conductivity values returned to the levels observed at the beginning of the test. Therefore, the determined residence times cannot be considered accurate, but they can give good estimation/indication of real values.^c Last water sample taken on 11.10.2017. Tracer tests were conducted in laboratory after thawing of the pilot on 1.11.2017.

and porosity of filter media (Φ) was determined based on equations (2) and (3).

$$t_r = \frac{V_s * \Phi}{Q_{in}} \quad (2)$$

$$\Phi = \frac{((t_{in} - t_{out}) * Q_{in}) - V_w}{V_s} \quad (3)$$

where:

V_s = volume of filter media (ml) at 12 cm height (outflow point)

Q_{in} = inflow (ml/min)

t_{in} = time (min) when water started flowing into filter system

t_{out} = time (min) when water started to discharge from filter system

V_w = volume of water (ml) in the inlet and outlet compartments (water filled) of filter systems at 12 cm height (outflow point).

At the end of the tests, the system residence time was determined by a conservative tracer experiment in which sodium chloride (NaCl; 3.5 g in 0.5 L; feed in 1–2 min pulse) was used as tracer and changes in the electric conductivity of outflowing water were monitored. A detailed description of determination of mean residence time using the conservative tracer method can be found in Postila et al. (2015). The residence time in the filter compartment was calculated by subtracting the water residence time in the inflow and outflow compartments from the system's residence time determined. Due to low temperatures, some of the water inside filters containing the coarser-grained materials was found to be frozen on the last site visit. The pilot systems were then transported to university laboratory facilities and tracer experiments were conducted after complete thawing was observed. A water sample for that tracer experiment was collected from the feeding ditch. Before tracer experiments were carried out, a small sample of the filter materials was removed for characterisation analysis.

Elemental composition of fresh material and spent material (collected after pilot experiments, before tracer tests) was analysed (one fresh and one spent material sample per product taken close to inlet area of pilots). Materials were first crushed to about 2 mm grain size ($> 80\% < 2\text{ mm}$ and $< 20\% > 2\text{ mm}$) with a Rocklabs Boyd Crusher and then crushed samples (containing both fractions) were pulverised to $< 75\mu\text{m}$ size ($> 95\%$) with an Essa LM2 mill. The pulverised samples (containing both fractions) were then mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace (1050 °C, ~3 min). The molten melt was immediately poured into a solution of 5% nitric acid containing an internal standard, and mixed continuously until completely dissolved (~30 min). The samples were analysed for major oxides and trace elements by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian Vista 735 ICP) and inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer Sciex ELAN 9000). For major oxides, determination accuracy is within 5% above 100x detection limit, while for minor and trace elements it is within 10% above 100x detection limit. X-ray diffraction

analysis of fresh and crushed materials was performed using a Panalytical X'Pert Pro diffractometer equipped with a Cu X-ray source and an X'Celerator detector. The XRD patterns were recorded in the 2 θ range of 5–70° with a step size of 0.017°. The amount of metals retained (m_{ret} , mg) in the filter media material was calculated based on equation (4) (based in one sample of fresh and spent material of each sorbent):

$$m_{ret} = c_{out} * m - c_{in} * m \quad (4)$$

where:

c_{out} = metal concentration (ppm) in spent material. If value under detection limit, it was assumed to be 80% of the limit.

c_{in} = metal concentration (ppm) in fresh material. If value under detection limit, it was assumed to be 80% of the limit.

m = mass of material in pilot (kg)

3. Results

3.1. Treated water amount, residence time and field measurements (pH, EC)

Interruption of tests due to clogging of the system occurred only for the materials with small particle size (Table 1). The amount of water treated by the Mineral R material was significantly larger than that treated by the Slag (smaller particle size) product (Table 2). Measured water residence time was lowest in the Slag (2–4 mm) and Mineral P (5–15 mm) pilots and highest in the Mineral R (2–4 mm) pilot at the start and end of the test period. Measured water residence times were more than two-fold longer at the end of the tests than at the start in all filter systems.

The pH of the water discharging from all filter systems increased relative to inflow pH (7.5). Outflow water pH peaked inside the first hour of operation for all materials and the maximum pH value observed for Mineral R (2–4 mm), Slag (2–4 mm), Mineral P (5–15 mm) and Slag (4–16 mm) products was 9.9, 12.1, 8.6 and 9.4, respectively. The increase in pH was due to dissolution of alkaline compounds from the filter materials. After the initial increase, outflow water pH decreased and values between 7 and 8 were recorded after few days of operation in all units except that with the Slag (2–4 mm) material, in which pH was over 8 for nearly the whole test. The EC values measured in outflow waters was very similar to those observed in the inflow water for all filter materials tested (Tables S2–S6, Supplementary material).

3.2. Inflow and outflow water quality

Concentrations of water quality parameters analysed in inflow and outflow samples collected from the filters are presented in Tables S2–S6, respectively (Supplementary material). For reference, average concentration of Tot.Zn, Tot.Ni and Tot.Fe in inflow samples was 542, 8.2 and 270 $\mu\text{g/L}$, respectively, while the concentration of Tot.N was 1.1 mg/L and that of DOC was 3.7 mg/L. The average outflow

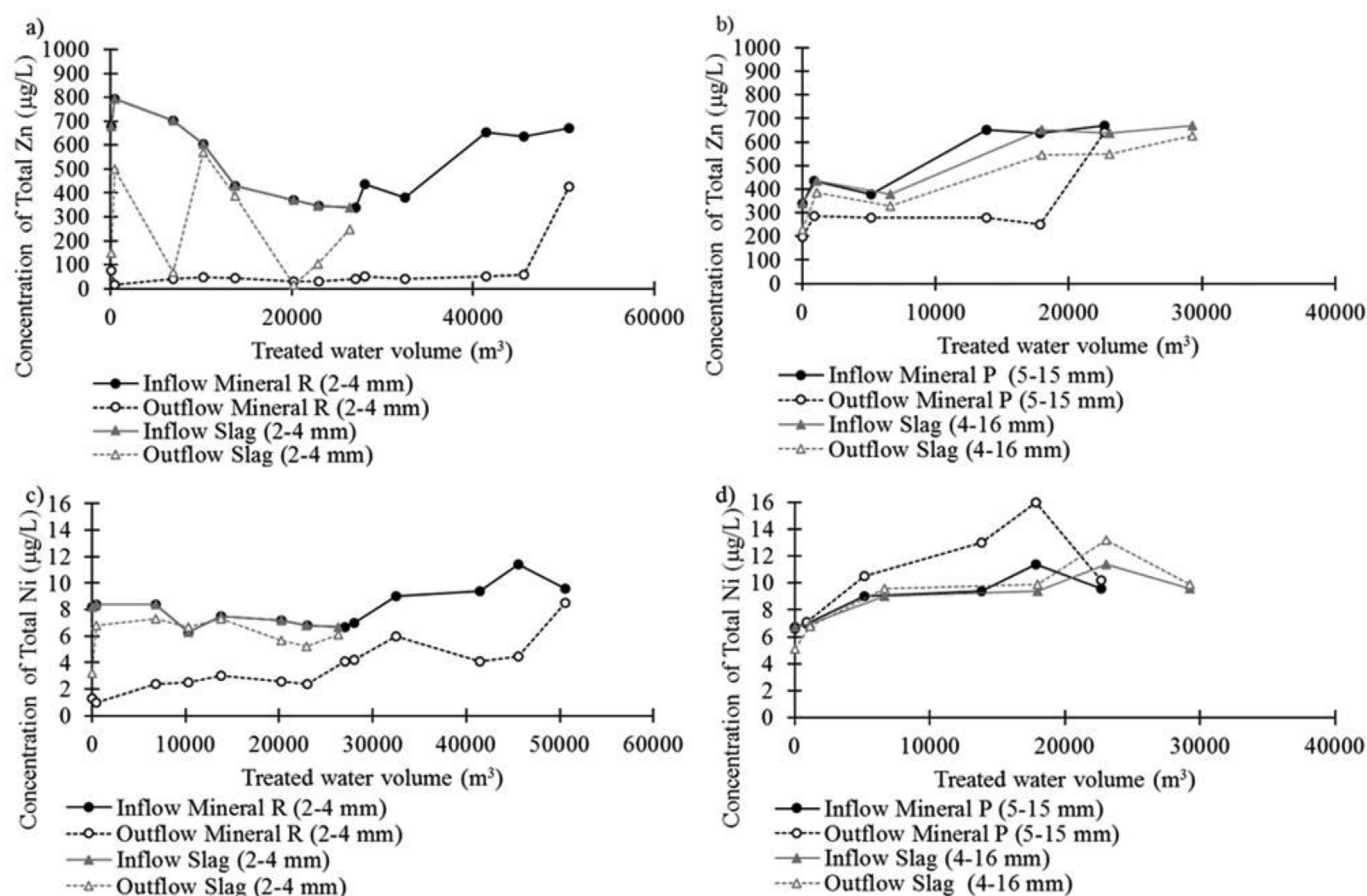


Fig. 3. Inflow and outflow concentrations ($\mu\text{g/L}$) of (a, b) total zinc from fine-grained and coarse-grained filter material, respectively, and (c, d) total nickel from fine-grained and coarse-grained filter material, respectively.

concentration of Tot.Zn, Tot.Ni and Tot.Fe found in samples collected in the pilots containing Mineral R (2–4 mm), Slag (2–4 mm), Mineral P (5–15 mm) and Slag (4–16 mm) was (respectively): 74, 255, 322 and 444 $\mu\text{g Tot.Zn/L}$, 3.6, 6.0, 10.6 and 9.1 $\mu\text{g Tot.Ni/L}$ and 129, 244, 218 and 316 $\mu\text{g Tot.Fe/L}$. Outflow Tot.N was at the same level as in inflow water. Variations in Tot.Zn and Tot.Ni concentration in inflow and outflow water samples with increasing treated water volume are presented (Fig. 3). Due to the fact that Zn and Ni were present mainly in dissolved form in the inflow water and because total concentrations were analysed more often, only total concentrations are reported (Fig. 3). Moreover, focus is placed on the concentrations of Zn and Ni in outflow samples, because they were present in higher concentrations in the inflow water than e.g., other heavy metals such as Cd, Cu and Pb (Table S2, Supplementary material). Total and dissolved concentrations of all parameters analysed in inflow and outflow samples are shown in Tables S2–S6 (Supplementary material).

3.3. Removal efficiency

Best removal of Zn and Ni was accomplished by the smaller-grained samples of the materials tested, especially by the Mineral R product

(Fig. 3; Tables 3 and 4 and S8 and S9, Supplementary material). Based on Kruskal-Wallis test, there were statistically significant differences in the removal efficiencies of Zn and Ni between the pilots. In pairwise comparison, it was possible to identify that Ni removal efficiencies achieved by Mineral R were statistically significant different from those achieved by the coarser-grained materials, while the removal of Zn achieved by Mineral R was statistically significant different from that in all other materials tested. Leaching of Ni occurred from the units with Mineral P material (Fig. 3). Variations in Ni concentration observed in inflow and outflow samples from the systems filled with Slag material (4–16 mm) were mainly within the determination accuracy ($\pm 10\%$) of the method used.

Other elements analysed (Cd, Cr, Cu and Pb) were found in very low concentrations in the inflow water, with Cr concentrations being mainly under the detection limit ($0.2 \mu\text{g/L}$) of the method used (Table S2). Although very low concentrations were present in the water, satisfactory removal of Cd, Cu and Pb was observed, especially by the Slag and Mineral R materials with smaller particle size (Tables 5–7 and Tables S10–S12, Supplementary material). Some retention of Fe was achieved in all pilot systems except that with Slag (4–16 mm), where Tot.Fe leached (although, based on analysis method determination accuracy,

Table 3

Inflow concentration of total zinc (Zn, $\mu\text{g/L}$), load (mg), removed load (mg), load-based removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. $\pm$ sd (min-max) ($\mu\text{g/L}$)	Load (mg)	Removed load (mg)	RE $\pm$ sd (min-max) (%)	n
Mineral R (2–4 mm)	542 $\pm$ 160 (339–794)	26869	23742	88 $\pm$ 8 (63–96)	13
Slag (2–4 mm)	533 $\pm$ 182 (339–794)	13883	7101	51 $\pm$ 23 (8–84)	8
Mineral P (5–15 mm)	519 $\pm$ 151 (339–671)	12300	5249	43 $\pm$ 11 (31–59)	6
Slag (4–16 mm)	519 $\pm$ 151 (339–671)	15849	2171	14 $\pm$ 8 (10–32)	6

Table 4

Inflow concentration of total nickel (Ni, µg/L), load (mg), removed load (mg), load-based removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. ± sd (min-max) (µg/L)	Load (mg)	Removed load (mg)	RE ± sd (min-max) (%)	n
Mineral R (2–4 mm)	8.1 ± 1.4 (6.3–11.4)	421	231	55 ± 17 (36–86)	13
Slag (2–4 mm)	7.4 ± 0.8 (6.3–8.4)	196	24	12 ± 20 (-1–61)	8
Mineral P (5–15 mm)	8.9 ± 1.8 (6.7–11.4)	212	–54	–26 ± 16 (-39–1)	6
Slag (4–16 mm)	8.9 ± 1.8 (6.7–11.4)	274	–19	–7 ± 14 (-11–24)	6

values were similar for two-thirds of the measurements) (Table S13, Supplementary material). Clear leaching of Cr was observed from all filter media tested apart from Mineral R. Leaching of As was observed from the Mineral P filter system (Table S14, Supplementary material) while Al leaching occurred from the Mineral R (2–4 mm) material and leaching of dissolved Al also from the Slag (4–16 mm) material (Table S15, Supplementary material). Overall, leaching decreased with increasing treated water volume. Based on Kruskal-Wallis test, there were statistically significant differences between the removal of Al, As, Cd, Cu, Fe and Pb achieved in the filter boxes. In pairwise comparison, it was identified that statistically significant differences in Al removal occurred mainly between Mineral R and Mineral P materials, while for As removal statistically significant differences were mainly between Mineral R and Slag (2–4 mm) and between Mineral R and Mineral P materials. Differences in Cd and Cu removal were identified between Mineral R and the coarser-grained materials, while differences in Fe and Pb removal occurred between Mineral R and Slag (4–16 mm) materials.

3.4. Material characterisation

X-ray diffraction (XRD) analysis (Fig. S1) showed that Mineral R is an amorphous material containing aluminium oxide and that Mineral P mainly contains magnesite and quartz, but also some other phases (biotite, chlorite, talc, calcite, periclase and portlandite). Calcium was the main element in the slag materials and XRD showed that many phases were present (akermanite-gehlenite, larnite, bredigite, merwinite, monticellite, cuspidine, magnesiochromite and periclase). All spent filter materials (collected after the pilot tests) showed higher Zn content (Table 8) than fresh samples. In particular, Zn concentrations were higher in the recovered Mineral R product (~800 ppm) than in fresh samples, which was a result of excellent retention of Zn by Mineral R during the pilot tests. Higher Ni concentrations were observed in all spent filter media samples than in fresh samples except for Mineral R. High concentrations of Cr were found in all filter materials (used and fresh) except in the Mineral R product. Full elemental composition can be found in Table S7 (Supplementary material).

4. Discussion

4.1. Removal efficiency

As expected, metal removal was higher in filter systems containing materials with smaller particle size, although in the case of Pb, Mineral P (5–15 mm, consisting mainly of magnesite and quartz) achieved slightly higher removal than the Slag material (2–4 mm, calcium as main element). Because of the larger surface area of smaller particles, and therefore the higher availability of sorption sites, it was expected

that smaller-grained materials would be more effective in retaining metals (Chuah et al., 2005). Therefore, pilot operations were started with filter units filled with materials of smaller particle size. Among the small-grained materials tested, Mineral R (aluminium oxide as main component) achieved the best removal rates for the majority of the metals analysed (Zn, Ni, Cd, Cu, Pb). Overall, the removal efficiencies achieved in this study were slightly lower than those reported by Assmuth (2017) for sand and sand-biochar filter media tested for storm water treatment (e.g. 97–99% Zn removal from inflow containing 10–560 µg Zn/L; mostly over 90% Ni removal from inflow containing a mean of ≤5 µg Ni/L). In a previous study, Mineral P was tested in columns for urban runoff and the following removal rates were obtained: Zn 48% (inflow 210 µg/L), Ni 13% (inflow 39 µg/L), Cd 20% (inflow 0.056 µg/L), Cu 40% (inflow 69 µg/L) and Pb 67% (inflow 0.48 µg/L) (Gogoi et al., 2018). These removal rates are similar to, or on occasion better than, those reported here.

The amount of metals retained in the filter media was calculated based on the elemental composition of fresh and spent material (only rough estimation since only one sample/per material was collected). Increased Zn concentrations in spent materials account for 60, 15, 28 and 37% of removed Zn by Mineral R, Slag (2–4 mm), Mineral P and Slag 4–16 mm material, respectively. The increased concentration of Ni and Cu in spent materials of some of the sorbents accounted for hundreds of times the load of Ni and Cu removed from inflow water (Tables 4 and 6). It is important to note that, only one sample of fresh and spent materials were sent for characterisation analysis and that sampling of spent material was conducted near the inlet area of pilots. As concentration of metals in the water decrease with residence time in the system, it is safe to assume that, larger portion of metals are retained in the inlet area of the filters. Therefore, extrapolating metal concentration values found in the spent material sample collected at the inlet to the whole filter media can result in substantial overestimation of metals retained in the system. By dividing the metal load removed during the whole test period by the mass of sorbent in the system; it is possible to conduct a more viable comparison among metal retention capacity of the tested materials. The amount of Ni, Zn and Cu removed by Mineral R were 12.4, 1276 and 3.2 µg/g of sorbent respectively while 0.8, 239 and 0.2 µg of Ni, Zn and Cu were respectively retained per g the Slag (2–4 mm) material.

Leaching of As, Ni, Al and Cr was observed from different materials during this study. Leaching of As occurred from the Mineral P filter, but As concentrations in outflow (average 1.5 µg/L, maximum 5.9 µg/L) were under the Finnish drinking water quality limit (10 µg/L; D 1352/2015). The Ni concentrations found in outflow samples of systems using materials with larger particle size (maximum concentration 16 µg/L) were also under the Finnish drinking water quality limit (20 µg/L). Leaching of Al from the Mineral R filter resulted in outflow

Table 5

Inflow concentration of total cadmium (Cd, µg/L), load (mg), removed load (mg), load-based removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. ± sd (min-max) (µg/L)	Load (mg)	Removed load (mg)	RE ± sd (min-max) (%)	n
Mineral R (2–4 mm)	0.44 ± 0.11 (0.30–0.64)	22.5	13.1	58 ± 17 (27–83)	13
Slag (2–4 mm)	0.38 ± 0.05 (0.3–0.44)	9.9	2.4	24 ± 29 (-13–78)	8
Mineral P (5–15 mm)	0.50 ± 0.12 (0.35–0.64)	11.9	2.7	22 ± 9 (6–29)	6
Slag (4–16 mm)	0.50 ± 0.12 (0.35–0.64)	15.4	0.2	1 ± 8 (-6–14)	6

Table 6

Inflow concentration of total copper (Cu, µg/L), load (mg), removed load (mg), load-based removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. ± sd (min-max) (µg/L)	Load (mg)	Removed load (mg)	RE ± sd (min-max) (%)	n
Mineral R (2–4 mm)	1.8 ± 0.8 (1.1–3.8)	97	60	62 ± 10 (49–82)	13
Slag (2–4 mm)	1.4 ± 0.2 (1.1–1.6)	36	6	16 ± 9 (4–32)	8
Mineral P (5–15 mm)	2.4 ± 1.0 (1.1–3.8)	58	3	5 ± 13 (-27–8)	6
Slag (4–16 mm)	2.4 ± 1.0 (1.1–3.8)	74	–3	–4 ± 6 (-12–4)	6

concentrations below the drinking water limit (recommendation < 200 µg/L) except in the first sample collected (261 µg/L). Similarly, leaching of Cr from the Slag and Mineral P materials did not result in outflow concentration values above the Finnish drinking water quality limit (50 µg/L) apart from the first sample collected from the Slag filter system. Comparison to Finnish drinking water legislation was conducted to highlight the low concentrations of metals leaching from the materials however, it is important to note that leaching results in extra load to the environment and should be taken under considerations during material selection phase.

The type of filter pilot system tested here can potentially be used for metal removal from other loading sources such as urban storm water, the polishing phase of treatment for wastewater flows from active mine sites etc. In Finland, general metal concentration limits are not set for water discharge from closed mine sites and there are no regulatory limits on metal concentrations in storm water (Inha et al., 2013).

4.2. Metal removal mechanism

Possible mechanisms for metal removal were mainly sorption on the surface of the sorbents or, in case of Zn, precipitation as hydroxides due to dissolution of hydroxide from the materials. The characterisation results confirmed that Zn content was higher in the spent materials (especially Mineral R), but the exact mechanism was not revealed. As Zn concentration in the runoff water was significantly higher than that of other metals and the pH of outflow water increased above levels where Zn starts to precipitate (as zinc hydroxide, Zn(OH)₂), precipitation cannot be excluded. On the other hand, the Zn concentration in the outflow water was lower than that required for minimum solubility of zinc hydroxide (Reichle et al., 1975).

Slag with smaller particle size (2–4 mm) produced fine precipitate, which was collected for analysis. It contained mostly calcium carbonate (CaCO₃) and some magnesium hydroxide (according to XRD), but also a high content of Zn (870 ppm, according to elemental composition). This fine precipitate might have been one reason for the clogging observed with the filter system with 2–4 mm Slag material. With Mineral R material, fine precipitate was not observed, thus clogging must have originated from different mechanisms, which were not revealed in this study. Different ions may attach via different mechanisms (adsorption, precipitation) on calcium carbonate (Sturchio et al., 1997; García-Sánchez and Álvarez-Ayuso, 2002). Zinc might have co-precipitated on the CaCO₃ precipitate formed. García-Sánchez and Álvarez-Ayuso (2002) suggest that Zn retention on CaCO₃ occurs by precipitation as hydrozincite (Zn₅(OH)₆(CO₃)₂) on the surface, a suggestion generally supported by X-ray photoelectron spectroscopy data.

4.3. Functioning of the filter systems

An important parameter in filter-type water treatment systems is the material replacement time, as material replacement inevitably becomes necessary due to decreasing removal efficiency or clogging. The useful working time for different filter systems and filter materials varies between 5 and 10 years (Wendling et al., 2017) or between 1.5 and 9 years (Monrabal-Martinez et al., 2017). However, these values are based on the sorption capacity of materials tested under laboratory or pilot test conditions (possible clogging of real or full-scale systems is not taken into consideration). From the results obtained in the present study, it was not possible to evaluate accurately the material replacement time of full-scale systems. However, it was possible to make rough estimates for the small-grained materials, which reached the clogging stage during the experiment. In the example of a filter system within a ditch network treating 10 m³ of inflow water (of similar quality to the inflow water used in this study) per day, the system would require the following dimensions: 6 m × 1.5 m × 0.8 m (length × width × height). The filter material replacement time would be 5.5 years for Mineral R (2–4 mm), while it would be 2.8 years for the Slag (2–4 mm) product. The material replacement times were estimated based on the relationship between treated water volume and the material volume identified during the pilot tests (Table 2). Another important factor to be considered on up-scaling the filter systems is the decrease in hydraulic capacity over time (Hatt et al., 2008) and, at high latitudes, clogging of the filter due to freezing.

5. Conclusions

Continuous in situ pilot-scale tests of filter systems were conducted in the field, where varying inflow water quality and temperature offered more realistic conditions for evaluating the suitability of filter materials than column or batch experiments in the laboratory. Filter performance was dependent on material composition and particle size (smaller particle size being more effective). The highest metal removal efficiencies and largest amount of water treated (per volume of material applied) were achieved by aluminium oxide-based recycled mineral material (2–4 mm). In general, while smaller-grained materials performed better in terms of removal efficiency, the removal rates achieved by coarser-grained commercially available mineral material (5–15 mm) were comparable to those achieved by slag material with small particle size (2–4 mm).

Due to the diluted nature of the water treated and the composition of the materials tested, leaching of some metals occurred. For example, Al concentrations were higher in outflow than inflow for units filled with recycled mineral material. Similarly, As was leached from commercial mineral product and higher Cr concentrations were found in the

Table 7

Inflow concentration of total lead (Pb, µg/L), load (mg), removed load (mg), load-based removal efficiency (RE, %) and number of samples (n).

Material	Inflow av. ± sd (min-max) (µg/L)	Load (mg)	Removed load (mg)	RE ± sd (min-max) (%)	n
Mineral R (2–4 mm)	0.29 ± 0.55 (< 0.05–2.1)	7.3	4.0	54 ± 41 (-53–72)	13
Slag (2–4 mm)	0.38 ± 0.70 (< 0.05–2.1)	3.9	0.7	18 ± 12 (7–37)	8
Mineral P (5–15 mm)	0.14 ± 0.08 (0.06–0.28)	3.3	1.2	36 ± 62 (-113–52)	6
Slag (4–16 mm)	0.14 ± 0.08 (0.06–0.28)	4.3	0.7	17 ± 59 (-130–23)	6

Table 8

Elemental composition of fresh and spent materials for selected contaminants.

Analyte	Mineral R 2–4 mm	Mineral R 2–4 mm used	Slag 2–4 mm	Slag 2–4 mm used	Mineral P 5–15 mm	Mineral P 5–15 mm used	Slag 4–16 mm	Slag 4–16 mm used
FUSION ICP-OES								
SiO ₂ , %	0.27	1.56	26.94	24.75	27.77	26.32	30.1	26.56
Al ₂ O ₃ , %	87.2	83.92	4.46	4.38	3.5	2.65	4.06	4.59
Fe ₂ O ₃ , %	0.34	0.2	6.64	10.43	7.02	7.57	2.48	3.48
MnO, %	0.003	0.016	1.144	1.213	0.102	0.112	1.007	1.074
MgO, %	0.04	0.29	9.57	10.93	27.54	32.46	11.13	9.21
CaO, %	0.05	0.95	47.68	40.04	11.57	7.28	47.38	46.41
Na ₂ O, %	1.12	0.25	0.06	0.06	0.16	0.08	0.06	0.04
K ₂ O, %	0.01	0.04	0.02	0.02	0.57	0.34	0.01	0.01
TiO ₂ , %	0.006	0.005	1.038	0.954	0.136	0.103	1.03	0.904
FUSION ICP-MS								
Cr, ppm	< 20	60	> 10000	> 10000	1440	1660	> 10000	> 10000
Ni, ppm	20	20	3880	6390	800	1320	1740	1920
Cu, ppm	< 10	< 10	210	310	40	30	60	130
Zn, ppm	< 30	800	< 30	60	100	170	< 30	50
As, ppm	< 5	< 5	< 5	7	53	77	< 5	< 5
Pb, ppm	< 5	< 5	< 5	< 5	6	< 5	< 5	< 5

outflow of all filter systems except those with recycled mineral material. Leaching can also be expected from full-scale systems if the materials are used for treatment of similarly dilute streams to that tested in this study.

Based on the results obtained, full-scale systems using the recycled mineral product (2–4 mm) would have an approximately two-fold longer material replacement time (effective working time; treated water vol/vol of material ≈ 2800) than systems using the slag (2–4 mm) product (treated water vol/vol of material ≈ 1400). Material replacement time could not be estimated for the coarser-grained materials due to test interruption (freezing). Therefore, clogging because of precipitate accumulation or armouring was not reached. Overall, the recycled mineral material tested can be recommended for full-scale tests, especially for applications where high Zn removal is required.

Acknowledgements

This work was funded by the European Regional Development Fund/Centre for Economic Development, Transport and the Environment for North Ostrobothnia as part of the HuJa project, “Enhancing the treatment of metal containing storm waters and wastewaters by using natural materials”. The other funding bodies and partners in project were Outokumpu Chrome Oy, Oulun Jätehuolto Oy, Pudasjärven vesiosuuskunta, Taivalkosken vesihuolto, Oulun Vesi, Pölkky Oy, Kuusamon energia- ja vesiosuuskunta, Naturpolis Oy, City of Kuusamo, Finnish Water Utilities Association, Maa- ja vesiteknikan tukiry., Ranuan Vesihuolto Oy, Napapiirin Energia ja Vesi Oy, Vesikolmio Oy, Aquaminerals Finland Oy and University of Oulu. We would like to acknowledge Veikko Pekkala and Tuomo Pitkänen for their help in practical issues related to the field tests. We also want to thank the Aquaminerals Finland Oy and Outokumpu Chrome Oy for donating the test materials.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2019.01.115>.

References

- Akcil, A., Koldas, S., 2006. Acid mine drainage (AMD): causes, treatment and case studies. *J. Clean. Prod.* 14, 1139–1145.
- Assmuth, E., 2017. Performance of Roadside Filtration Systems in the Treatment of Stormwater (Master's thesis). Aalto University.
- Chuah, T.G., Jumasiah, A., Axni, I., Katayon, S., Thomas Choong, S.Y., 2005. Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview.

- Desalination 175, 305–316.
- Clar, M.L., Barfield, B.J., O'Connor, T.P., 2004. Stormwater Best Management Practice Design Guide. National Risk Management Research Laboratory, Office of research and Development, U.S. Environmental Protection Agency, Cincinnati, OH.
- Clark, S.E., Johnson, P., Pitt, R., Gill, S., Pratap, M., 2005. Filtration for metals removal from stormwater. In: 10th International Conference on Urban Drainage, Copenhagen/Denmark, pp. 21–26 August 2005.
- D 1352/2015, 2015. Sosiaali- ja terveystieteiden ministeriön asetus talousveden laatuvaatimuksista ja valvontatutkimuksista. In: In Unofficial English Translation: the Ministry of Social Affairs and Health Decree of Drinking Water Quality Standards and Monitoring Studies.
- Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manag.* 92, 408–418.
- García-Sánchez, A., Álvarez-Ayuso, E., 2002. Sorption of Zn, Cd and Cr on calcite. Application to purification of industrial wastewaters. *Miner. Eng.* 15, 539–547.
- Genç-Fuhrman, H., Mikkelsen, P.S., Ledin, A., 2007. Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from storm water: experimental comparison of 11 different sorbents. *Water Res.* 41, 591–602.
- Gogoi, H., Leiviskä, T., Heiderscheidt, E., Postila, H., Tanskanen, J., 2018. Removal of metals from industrial wastewater and urban runoff by mineral and bio-based sorbents. *J. Environ. Manag.* 209, 316–327.
- Hatt, B.E., Fletcher, T.D., Deletic, A., 2008. Hydraulic and pollutant removal performance of fine media stormwater filtration systems. *Environ. Sci. Technol.* 42, 2535–2541.
- Inha, L., Kettunen, R., Hell, K., 2013. Quality of the Runoff Water from Roads. Finnish Transport Agency, Infrastructure technology. Helsinki 2013. Research reports of the Finnish Transport Agency 12/2013. (In Finnish, abstract in English).
- Lim, H.S., Lim, W., Hu, J.Y., Ziegler, A., Ong, S.L., 2015. Comparison of filter media materials for heavy metal removal from urban stormwater runoff using biofiltration systems. *J. Environ. Manag.* 147, 24–33.
- Monrabal-Martinez, C., Ilyas, A., Muthanna, T.M., 2017. Pilot scale testing of adsorbent amended filters under high hydraulic loads for highway runoff in cold climates. *Water* 9.
- Palmer, K., Ronkanen, A.-K., Kløve, B., 2015. Efficient removal of arsenic, antimony and nickel from mine wastewaters in Northern treatment peatlands and potential risks in their long-term use. *Ecol. Eng.* 75, 350–364.
- Postila, H., Ronkanen, A.-K., Marttila, H., Kløve, B., 2015. Hydrology and hydraulics of treatment wetlands constructed on drained peatlands. *Ecol. Eng.* 75, 232–241.
- Reddy, K.R., Xie, T., Dastgheibi, S., 2014. Removal of heavy metals from urban stormwater runoff using different filter materials. *J. Environ. Chem. Eng.* 2, 282–292.
- Reichle, R.A., McCurdy, K.G., Hepler, L.G., 1975. Zinc hydroxide: solubility product and hydroxy-complex stability constants from 12.5–75 °C. *Can. J. Chem.* 53, 3841–3845.
- Simate, G., Ndlovu, S., 2014. Acid mine drainage: challenges and opportunities. *J. Environ. Chem. Eng.* 2, 1785–1803.
- Sturchio, N.C., Chiarello, R.P., Cheng, L., Lyman, P.F., Bedzyk, M.J., Qian, Y., You, H., Yee, D., Geissbuhler, P., Sorensen, L.B., Liang, Y., Baer, D.R., 1997. Lead adsorption at the calcite-water interface: synchrotron X-ray standing wave and X-ray reflectivity studies. *Geochem. Cosmochim. Acta* 61, 251–266.
- The Coal Authority, 2014. Metal Mine Water Treatment Review. URS Infrastructure & Environment UK Ltd 47068625/MARP001rev4.
- Valtanen, M., Sillanpää, N., Setälä, H., 2014. The effects of urbanization on runoff pollutant concentrations, loadings and their seasonal patterns under cold climate. *Water Air Soil Pollut.* 225, 1977.
- Vohla, C., Köiv, M., Bavor, H.J., Chazarenc, F., Mander, Ü., 2011. Filter materials for phosphorus removal from wastewater in treatment wetlands—a review. *Ecol. Eng.* 37, 70–89.
- Wendling, L., Koimula, K., Kuosa, H., Korkealaakso, J., Iiti, H., Holt, E., 2017. Storm-filter material testing summary report. In: Performance of Stormwater Filtration Systems, VTT Research Report VTT-R-05545-17.
- Westerlund, C., Viklander, M., Bäckström, M., 2003. Seasonal variations in road runoff quality in Luleå, Sweden. *Water Sci. Technol.* 48, 93–101.