KTH Land and Water Resources Engineering

PILOT TRIALS WITH COLUMNS FILLED WITH REACTIVE MATERIALS FOR STORMWATER TREATMENT

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JOANNA KOCYBA

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Master of Science Thesis

CONTENT

Preface

This Master's thesis was carried out as part of the Environmental Engineering and Sustainable Infrastructure program at the Department of Land and Water Resources Engineering, Royal Institute of Technology, Stockholm.

I graduated from the Interdisciplinary Department of Environmental Protection at Warsaw Agricultural University. I completed the research concerning Geographical Information System applied to the analysis of surface water resources, which was an experimental part of my Master degree. I decided to write this thesis in Stockholm, to develop my knowledge in the field of sustainable wastewater treatment systems.

This research was a part of the project performed for Stockholm Water Company (Stockholm Vatten AB) in the cooperation with the Swedish Road Administration (Vägverket). I would like to thank the Swedish Road Administration for the organisation and installation of the pilot plant. Stockholm Water Company I appreciate the technical support and laboratory analysis. Especially, I would like to thank Åsa Snith for the support, empathy and patience.

I want to thank my supervisor, Gunno Renman Associate Professor of Water Resources Engineering and Sustainable Management for his valuable advice, discussions and support during my work.

I also appreciate the great help of Magnus Hallberg in the installations of the pilot plant, and would like to thank him for introducing me to the specific subject of stormwater treatment technologies.

I also know that it would not be possible to complete my studies in Sweden if my beloved family and friends would not support me. Thank you Babciu Joanna and Konrad. I appreciate also all joyful as well as sorrowful moments, when my fantastic friends accompanied me. Thanks to all of you.

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Joanna Kocyba

Abstract

In this study, the investigations of different filter substrates that could be used for stormwater treatment with special regard to the uptake of heavy metals have been carried out. Selections of different filter materials were examined. Particularly, two organic materials: granulated activated carbon (GAC), pine bark and mineral materials: zeolite (clinoptilolite), Polonite® were used. The pilot trials with columns were installed within existing stormwater treatment system at Lilla Essingen Island in Stockholm. The influent used for distribution into the columns was previously treated in the sedimentation pond and mechanical filter. Selection of substrates was used with the aim of indicating the material that achieved the best sorption and hydraulic performance. The experiments were conducted in un-saturated and saturated hydraulic conditions. Field measurements comprised of such daily-monitored parameters as pH, electric conductivity and turbidity. Laboratory analyses encompassed ten elements: aluminium (Al), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn). In general, all examined materials achieved satisfactory results in the removal of manganese, iron, aluminium and zinc, which was related with mechanical filtration and removal of suspension containing complexes of Fe, Mn, Zn and Al. Overall, the metals uptake was found to be dependent on the concentrations in the influent. In the column experiments, the clinoptilolite material and the finer GAC 830W were found to be the most efficient in metals' sorption from aqueous solution. However, the highest efficiency in terms of hydraulic performance achieved cleaned and sieved Polonite® material.

Keywords: Heavy metals; reactive bed filter; removal efficiency; GAC, pine bark, Polonite®; zeolite

1. Introduction

Runoff from urban catchment areas, especially from roads, parking lots and build up areas, is highly polluted by such constituents as heavy metals (Cd, Cr, Mn, Co, Ni, Cu, Zn, V, Pb, etc.), organic chemicals (such as polyaromatic hydrocarbons, polychlorinated biphenyls, chlorinated methanes and phenols), organic compounds (such as oil, grease, hydrocarbons and alkyllead compounds) (Hares and Ward, 1999). The contamination originates mainly from the air deposition, traffic; brake linings, tires, asphalt, gasoline and oil and also from building materials like roof and fronts (Cu and Zn) and different galvanized materials (Zn) e.g. crash, safety barriers (Sörme and Lagerkvist, 2002).

Due to such anthropogenic pollutions that are discharged with urban runoff directly to the environment it is important to study and apply sustainable, environmentally friendly and economically efficient treatment facilities. Sedimentation ponds and constructed filters are the examples of such techniques. Detention ponds used for temporary storage to reduce or eliminate flow peaks are also designed to entrap sediments, decayed plant and animal debris in runoff water. The contamination is removed mainly by sedimentation process, since vast amount of pollutants are attached to solid particles. Also heavy metals can be eliminated from storm water through the scavenging by particulate or colloidal forms of complexes (Taillefert and Gaillard, 2001). Courser particles can be therefore removed in the process of sedimentation, however fine fraction along with dissolved pollutants can not be discharged to the natural recipient. For the purpose of pollution control, different treatment systems are of great interest (Aldheimer and Bennerstedt, 2003). Recently the reactive bed filter technology has been applied in stormwater treatment (Renman co). Its application however requires previous investigations of filter materials, its sorption capacity, and also filter dimension and operation aspects.

Some previous field study showed high efficiency of heavy metals removal for the same mineral and organic substrates that are investigated in this thesis project. These materials were natural and burned opoka (calcium silicate sedimentary rock), zeolite (clinoptilolite) and pine bark. All of the tested materials after polluted rainwater treatment showed high metal reduction level. The average removal for e.g. Cu was around 80% and for Zn between 63 – 79% depending on the variant of tested substrate (Färm, 2003).

The aim of this research project was to study filter materials for reduction of mainly heavy metals with special attention to the dissolved matter. In this case study a pilot scale trial was constructed within existing system in order to examine different types of filter media

(mineral and organic) in the polishing step of the storm water treatment plant. The treatment plant is located at the island Lilla Essingen in the City of Stockholm and captures polluted rainwater from parts of the traffic route Essingeleden (traffic load 120,000 vehicles/day), some local roads, parking lots and roof water from built-up area (Figure 1).
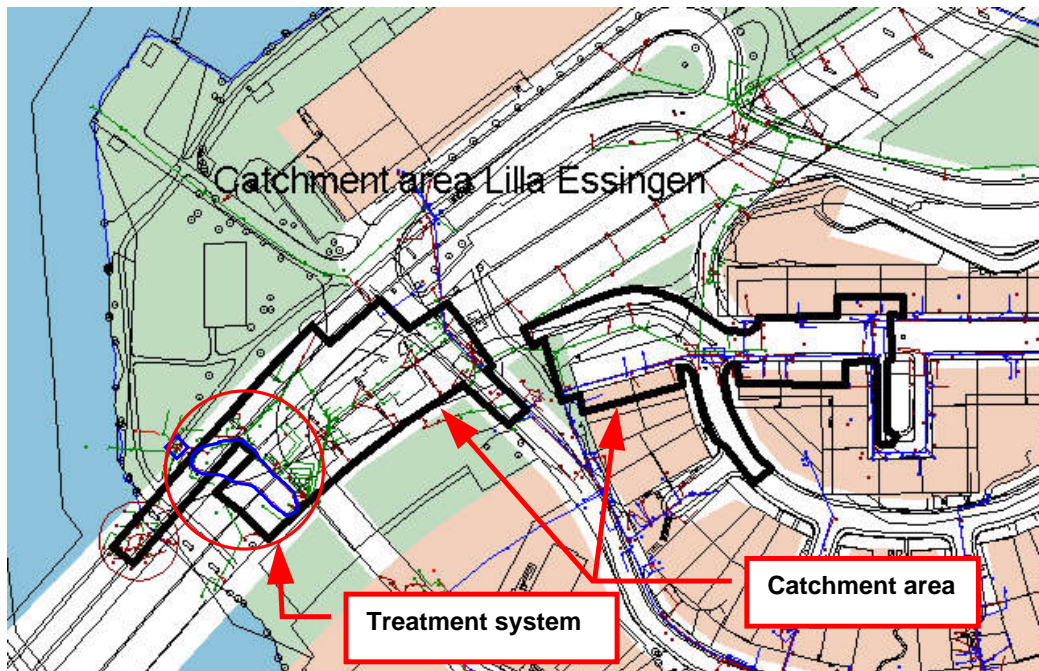
Figure 1. Topographic map (scale 1:2 000) over stormwater treatment system and its catchment area (black bold edge) (Stockholm Vatten AB)

The storm water is collected by the storm sever system from where it flows to the treatment plant by gravity. Sedimentation of coarse particles takes place in the detention pond, where water is directed from to the constructed filter system. It consists of mechanical and reactive pre-fabricated filters mounted in the manhole made from concrete. The system aims to remove particles, and immobilize metals and nutrients by sorption process.

The reactive filter manhole in the treatment plant (Figure 2) was used for the installation of the pilot scale experiment. A couple of filter materials were selected and tested in the same conditions with the aim of studying its hydraulic and adsorptive abilities along with effectiveness in the particular environment.
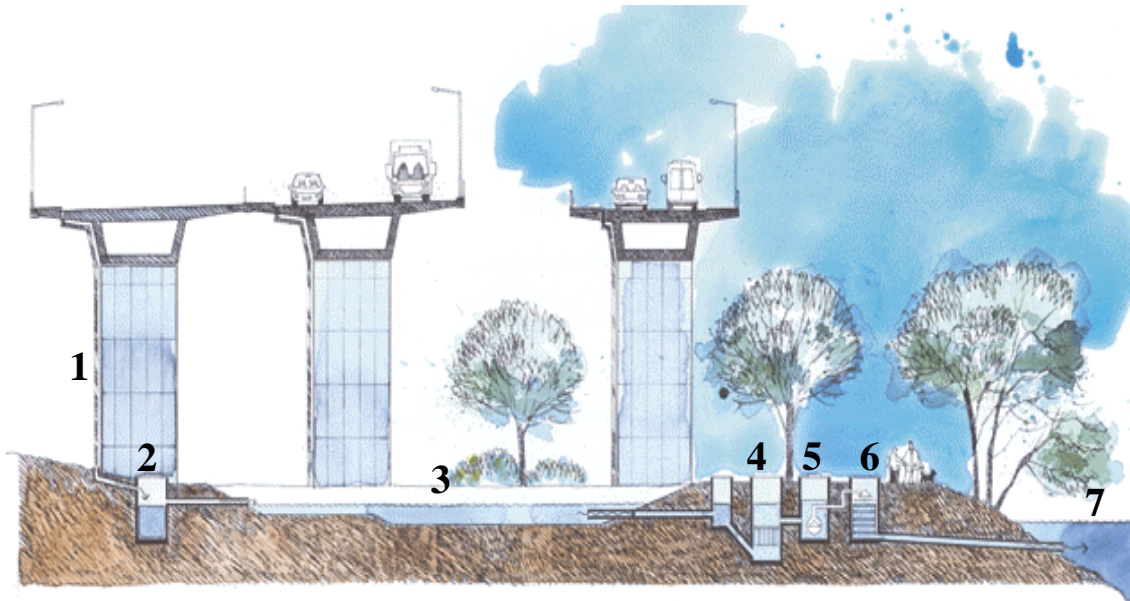
Figure 2. Schematic cross-section of stormwater treatment system at Lilla Essingen (1 – stormwater gutter, 2 – inlet-well, 3 – sedimentation pond, 4 – mechanical PIAB filter, 5 – pump station, 6 – reactive filter, 7 – recipient Lake Mälaren) (Stockholm Vatten AB)

Evaluation criteria were based on treated water quality analysis and compared to the polluted storm water. Used indicators were such as turbidity, conductivity, pH, temperature, TOC, DOC, TOT-N, TOT-P and concentration of following heavy metals (total): aluminium (Al), cadmium (Cd), chromium (Cr), cooper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), vanadium (V), and zinc (Zn). Assessment of the operation ought to check the effectiveness of pollutants removal by the filters. Still it should indicate the most suitable substrate for water pollution control within this particular catchment area. Nevertheless it should also give general guidelines that can be applied for the other comparable case studies.

2. Materials and methods

2.1. Filter materials

A selection of organic (granulated activated carbon, pine bark) and mineral (Zeolite, Polonite$^®$) filter media were studied in this field trial. Experiment was divided in two parts, within which selection of investigated materials differed. First field trial was carried out under hydraulic load of approximately 2.5 m/h under un-saturated conditions. The investigated variation in sorption capacities of the used materials comprised GAC (granulated activated carbon), Polonite$^®$ (sieved and un-sieved), zeolite (clinoptilolite) and pine bark. The second field trail was run with ca 1m/h under un-saturated and thereafter saturated conditions. It examined two types of GAC (finer and courser), zeolite and Polonite$^®$ (sieved). Thus the selection of tested media will be presented with regards to this division.

2.1.1. First field trial materials

NORIT GAC 830W

One of the organic materials that were examined was granulated activated carbon. It was chosen as a reference regarding to its known high adsorptive ability. The aim was to estimate differences in adsorptive and clogging properties of other used mineral media. This material is suitable in a wide range of applications such as purification of potable water and industrial process liquids. It is used for removal of e.g. natural organics, colour bodies, pesticides, detergents, chlorinated solvents and compounds causing taste and odour problems. The particular NORIT GAC 830W is produced by steam activation of coal (NORIT technical bulletin).

Table 1. Specification of NORIT GAC 830W (NORIT technical bulletin)

Components	
Particle size	0.60 – 2.36 mm
Total surface area	1150 m^2/g
Apparent density	485 kg/m^3
Effective size	0.9 mm
pH	Alkaline

Zeolite - Clinoptilolite

Zeolites are a group of complex hydrated alumino- silicate minerals with open frameworks. The tree dimensional structure of zeolite possesses large channels containing negatively charged sites resulting from Al^{3+} replacement of Si^{4+} in the tetrahedra. Sodium, calcium potasium and other positively charged exchangeable ions occupy the channels within the structure, and can be replaced with heavy metals (Bailey *et al.,* 1999). Zeolites are therefore characterised by their high cation exchange capacity due to its structure and large surface area. The zeolite used in this experiment was clinoptilolite that mainly contains silicate oxide (SiO_2) and aluminium oxide (Al_2O_3). It is often applied as a sorbent in pollution control and recovery of heavy metals. Chemical composition of this substrate is presented in Table 2 and the characteristic of physical properties can be found in Table 3.

Table 2. Chemical composition of clinoptilolite (Filipsson and Ekengren, 1998)

Element	Percentage content
SiO_2	71.48
Al_2O_3	10.81
Fe_2O_3	0.89
Na_2O	0.6
K_2O	4.08
MgO	1.01
CaO	2.45
TiO_2	0.15
Other constituents	3.08

Table 3. Physical properties of clinoptilolite (Filipsson and Ekengren, 1998)

Components	
Particle size	1 – 2 mm
Particles density	2.2 – 2.3 kg/l
Active surface area	200 – 500 m^2/g
pH	Alkaline
Adsorption capacity	1.2 – 0.2 cm^3/g
Ion exchange capacity	1.2 – 1.3 meq/g

Polonite®

This material is manufactured from the bedrock of Opoka. Opoka is the Polish term for silica-calcite sedimentary rock. Preparation of this material includes heating up the bedrock to 900 $^{\circ}$C and thereafter separation into suitable fractions for filtration processes. During the process of heating calcium carbonates decompose to oxides. Main components of Polonite® are SiO_2, CaO, Fe_2O_3 and Al_2O_3 (Brogowski and Renman, 2004). Polonite® was elaborated at the Royal Institute of Technology in Stockholm (KTH) in the cooperation with Warsaw Agricultural University in Poland (SGGW). It showed high removal efficiency of phosphorus and metals (Kietlińska and Renman, 2004; Färm, 2001). Also hydraulic properties of Polonite® were investigated in previous studies that revealed strong efficiency dependence on flow conditions, contact time of influent with filter bed (Meyer, 2004). This material was previously applied in the storm water treatment system at Lilla Essingen as a reactive filter after sedimentation process. Quantitative analysis of this material showed following chemical composition displayed in Table 4.

Table 4. Chemical composition of Polonite® (Brogowski and Renman, 2004)

Element	Percentage content
SiO_2	60.1
Al_2O_3	5.32
CaO	25.4
Fe_2O_3	2.7
K_2O	1.06
MgO	0.77
MnO	0.02
Na_2O	0.15
TiO_2	0.34
P_2O_5	0.11
Other constituents	4.03

Table 5. Physical properties of Polonite® (Brogowski and Renman, 2004)

Components	
Particle size	2 – 5.6 mm
Particles density	700-980 kg/m^3
Specific surface area	0.7 m^2/g
pH	12.6
Adsorption capacity	1.2 – 0.2 cm^3/g

Pine bark

The second organic substrate that was tested for pollution control of storm water was pine bark. It is commonly used as an adsorbent for cleaning of oil-polluted waters. This material is of interest due to its availability in large quantities as a low-cost sorbent, being a residual product from local cellulose and paper industries. As a natural material it can be composted or burnt after using it as a filter. However, metal contamination needs to be considered in relation to how the compost or ash will be used after treatment.

2.1.2. Second field trial materials

The second field trial was divided in two parts, which were carried out in un-saturated and saturated conditions respectively. In both parts of the experiment, the following filter media were used: Polonite®, zeolite (clinoptilolite), finer granulated activated carbon NORIT GAC 830W, and courser granulated activated carbon NORIT PK 3-5. The same selection of substrates in both of the conditions was examined with the hydraulic load of approximately 1 m/h.

NORIT PK 3-5

NORIT PK 3-5 is a granular activated carbon material, which can be used in a large range of water applications including potable water and process water treatment. This material is produced by steam activation of coal similarly as previously described activated carbon; however, this material comprises of courser grain size and thus can be also examined due to its hydraulic properties. It was chosen also in order to obtain a comparative scale for assessment of the efficiency with other used courser materials such as Polonite®.

Table 6. Specification of GAC NORIT PK 3-5 (NORIT technical bulletin)

Components	
Particle size	2.8 – 5.0 mm
Total surface area	875 m^2/g
Apparent density	260 kg/m^3
Effective size	3.0 mm
pH	alkaline

NORIT GAC 830W

The same finer granulated activated carbon was investigated as in the previous filed trial and used as a reference regarding to its already mentioned high adsorptive ability. Thus, the differences in adsorptive and clogging properties of other used media can be compared. However, it was significant also to make another study of this material with lower surface load and in different infiltration conditions. The detailed information concerning this material can be found in chapter 2.1.1.

Zeolite, Polonite[®]

Zeolite and Polonite[®] were chosen again for tests (for detailed information on its chemical composition and physical properties see sub-chapter 2.1.1.). However, operation conditions were set differently. Also the way that materials were prepared before installation was changed. The corresponding description on material preparation can be found in separated chapter 2.2.

2.2. Material preparation

2.2.1. First field trial preparation

The treatment of materials selection consisted of finer activated carbon GAC 830W and pine bark cleaning. The GAC preparation was carried out by flushing the material set up in a PVC tube with fresh tap water. Floating fine particles were removed with water in the process of decantation. In this case pore volume was measured by a direct method. The method consists in the estimation of the water volume, which was used for total saturation of the medium (up to material's head in the column). The pore volume was approximated to 42 % of the total material volume.

Pine bark had been cleaned also to remove dust and in order to increase its compaction abilities. This material was placed on sieve of 0.5 - mm pore size and washed with clean tap water.

No preparation was done for the mineral substrates. Un-sieved and sieved Polonite® and also zeolite were settled as rough material directly in the column without sieving and cleaning. The aim was to detect and retain similar filtration factors that could cause a failure of materials previously used in the Lilla Essingen stormwater treatment system. However, the tests required also further cleaning of un-sieved Polonite® and zeolite. Thus the portions of each material were placed on 0.5 - mm sieve and flushed with fresh tap water for the removal of fine fractions. Approximately 21 dm^3 of clean water was used to remove fine fraction from 4.75 dm^3 of the material volume.

2.2.2. Second field trial preparation

Before placing the materials in tubes they were washed with clean tap water using a standard 1 - mm sieve in order to remove very fine fraction and improve hydraulic conductivity. For further preparation, the pore volume was measured by different techniques. Thus, the pore volume of each used material was calculated as a difference in weight of hydraulically saturated substrate sample and dried one (assuming water density as 1 g/cm^3). For this purpose a glass flask of 200 ml volume was used to take samples of every substrate. Weighted material saturated with tap water, was dried at 105 ^{o} C. The same procedure was repeated using the material volume of 100 ml to diminish the risk of measurement error. Table 7 shows measured values for pore volume of each tested material. Much higher values were achieved for dried materials than for saturated with fresh water, which indicates material's ability to absorb water.

Table 7. Measured pore volume of filter materials (n.d. - no data)

Medium	Fraction [mm]	Pore volume of dried material [%]	Pore volume of saturated material [%]
Polonite®	2.0 – 5.6	61	34.5
NORIT GAC 830W	0.6 – 2.36	60	42
NORIT PK3-5	2.8 – 5.0	74	n.d.
Zeolite	1 –2	51	n.d.

2.3. Set-up and operation of filter columns

Transparent PVC tubes with internal diameter of 106 mm were used. Transparency of the columns facilitated the observation of hydraulic efficiency of water filtration through the material. Each column was 900 mm high and filled up to 500 mm with one of selected filter substrates. Thus, the volume of each material was equal to 4.41 dm^3. Stormwater was continuously pumped through the pipe system that was equally distributing the inflow into every column. As already mentioned, the experiment was divided in two parts. First field trial was carried out with the hydraulic load of approximately 2.5 m/h under un-saturated conditions and the second with approximately 1 m/h of hydraulic load under un-saturated and saturated conditions. The columns were mounted abreast in the manhole that is fated for a full-scale reactive filter installation within the already described rainwater treatment plant (Figure 3).

Figure 3. Column set-up in reactive filter manhole

2.3.1. First field trial

The columns were set up abreast and connected with a pipe system that evenly supplied stormwater into each tested filter bed (Figure 4). Every column was continuously operated with a downward flow at the measured hydraulic load approximately 2.5 – 3.0 m/h. The load was controlled by a pump regulator and by placing gaskets (flow control discs with the gap of a proper size) inside rubber hoses at the inflow to the tubes. The hydraulic load was

constantly controlled and recorded along with every measurement and sampling. This was done manually by measuring a precise time needed to fill a 500-ml cylinder with stormwater incoming to the column. Measurements were performed for each column. The column set-up was operated only in un-saturated conditions. For such conditions, the layer of a mineral fibre was additionally placed on the top of every material. The idea of using it was to disperse the influent equally onto the whole surface of a filter column. Consequently, the total volume of a filter could be in constant contact with the fluid. The mineral fibre was supposed to absorb the fluid and prevent the stream formation through a filter pillar.

Columns used in this experiment had also been equipped with a layer of a dense sintered porous plastic media (PIAB filter). The layer was placed on the bottom of tubes in order to prevent the fine fraction of material from escaping to the outlet.

Initially, granulated activated carbon, un-sieved and sieved Polonite[®] as well as zeolite were installed separately in each tube. The GAC material was operated with the measured hydraulic load of 3.1 m/h. Zeolite and both forms of Polonite[®] were directly placed in the column without sieving and cleaning. All filters were operated simultaneously. Measured hydraulic load amounted to 3.0 m/h for zeolite column. Both columns filled with Polonite[®] were run with the load at approximately 3.1 m/h.
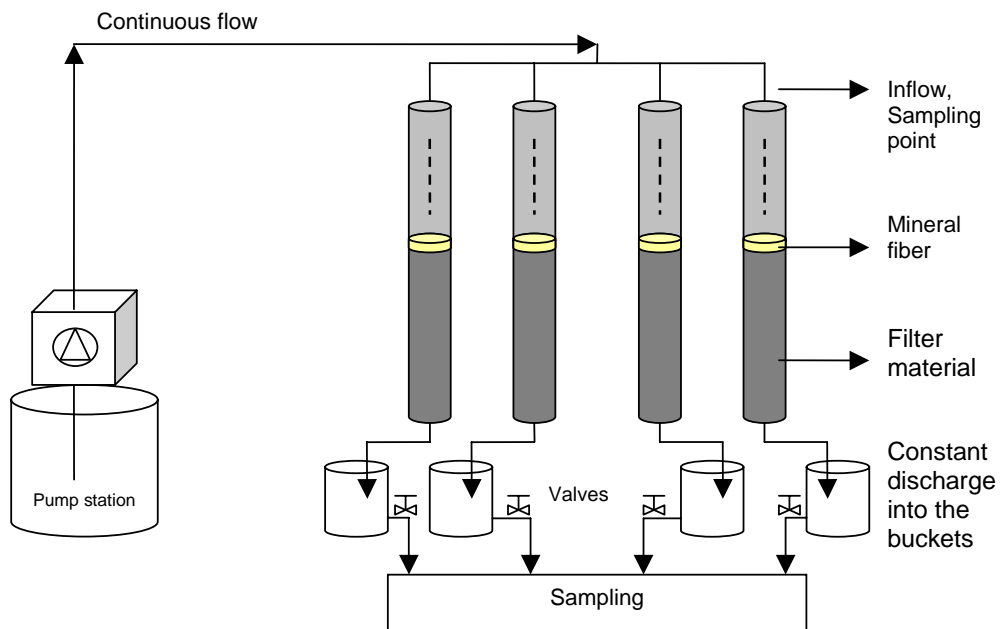
Figure 4. Column set-up, field trial – down-flow in un-saturated conditions

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Further on the columns after Polonite® and zeolite were also used to test blank trials. The tubes without filter substrates were investigated to estimate the filtration ability of the synthetic layer and the mineral fibre. Thus one of the columns was cleaned and equipped only with a new PIAB layer and operated without any filter material to verify when and if it clogs. The reinstalled column functioned with the hydraulic load of approximately 3.0 m/h. Samples of the effluent were taken for the field measurements and laboratory analysis. For the same purpose another column was used to run a blank trial with added mineral fibre and PIAB to compare how the mineral wool affects the filtration process and whether it discharges any pollutants. This was checked to monitor fibre's ability to change concentrations of monitored pollutants in the effluent from tested filters.

2.3.2. Second field trial

The second field study was divided in two parts with similar material selection. However, different saturation conditions were set. Thus, the performance of the filters was studied under un-saturated and thereafter saturated conditions with the same hydraulic load of approximately 1 m/h. Columns for the second trial were set up in the reactive filter manhole as in the previous study for un-saturated conditions (Figure 4). For saturated conditions the filters were additionally equipped as described in chapter 2.3.2.2. (Figure 5). The PIAB filter was also substituted by a mesh of 1.5 mm size of openings. The mesh was placed at the bottom of the columns to retain the filter material and to reduce the hydraulic resistance that was observed by using the PIAB filter.

2.3.2.1. Un-saturated conditions

Columns filled with four variations of medium: zeolite, Polonite®, NORIT GAC 830W, and GAC NORIT PK3-5 were operated with the downward flow at the hydraulic load ranging from 1 to 1.7 m/h. The load was also constantly measured by using a 500 - ml cylinder. Precise time needed to fill 100 ml of the influent was recorded and recalculated into the hydraulic load for the specific column dimension. Also a mineral fibre was placed on the top of each material pillar to spread the fluid.

2.3.2.2. Saturated conditions

The set-up of columns was similar to the former procedure. In order to generate a constant hydraulic saturation of the filter bed, a plastic hose was led from the discharge tap at the bottom of the tube to the level of 600 mm of the absolute column height (Figure 5). This technique stabilised the water level over the head of the filter bed. Additionally, three taps were installed by each column on different heights (level 1 – 120 mm, level 2 – 320 mm and level 3 – 470 mm) for sampling procedure (turbidity measurement). This enabled to monitor the treatment process on representative levels of the material pillar and to observe the clogging phenomenon.
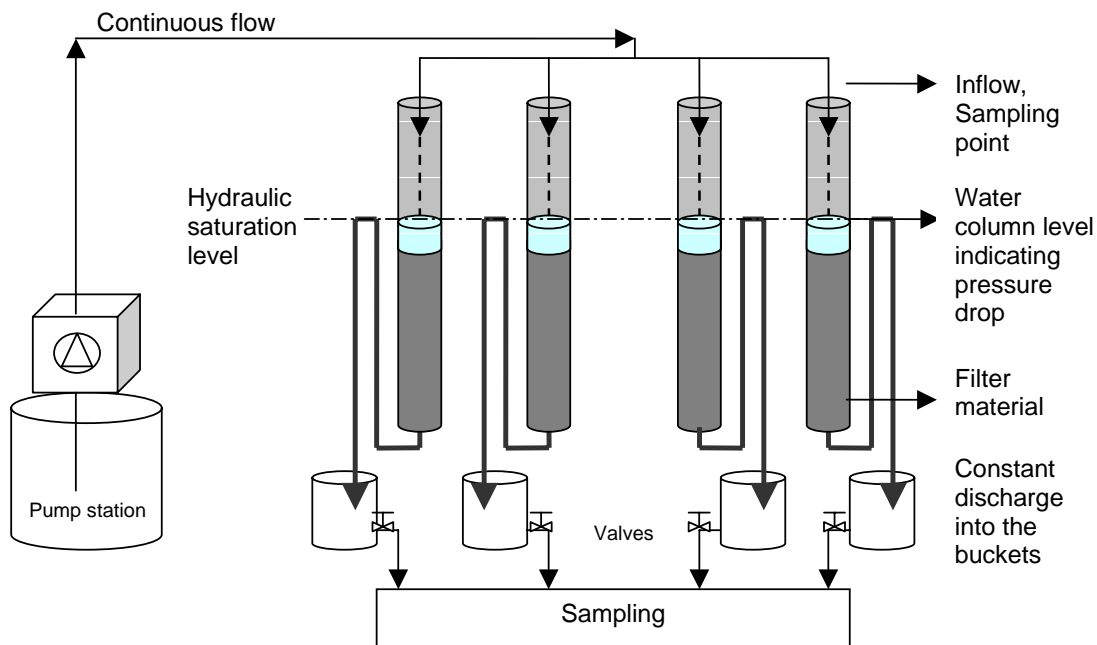

Figure 5. Column set-up, field trial – down-flow in saturated conditions

2.4. Field measurement

2.4.1. Turbidity

Samples for this measurement were taken from a plastic hose for the influent and from outlet containers connected with each column. Also, in the case of the experimental run in saturated conditions, the sampling was performed from every tap on three representative levels of the filter pillar, as described in chapter 2.3. Water from the sedimentation pond was also sampled daily for clarity control. Turbidity of the effluent was measured directly after sampling using a portable instrument 2100P Turbiditymeter, HACH Company. The average volume of light scattering over a defined angular range was determined. Results indicating a suspension value were displayed in NTU (Nephelometric Turbidity Units). This measurement was conducted approximately every 12 hours at the beginning of each experiment period, and afterwards once a day.

2.4.2. Electrical conductivity

A field conductivity instrument (FE 287 Portable Conductivity Meter, EDT Instruments Company) was used. Measurements were taken approximately every 12 hours at the beginning of each experiment period, and afterward once a day. This parameter was determined for the influent and each column effluent. Additionally, purity of water from the sedimentation pond was controlled daily. Since conductivity is only a quantitative measurement that corresponds to all ionic content and cannot distinguish particular conductive materials, some of the water samples were filtrated through 0.45 - µm filter in a laboratory before metal analysis. Conductivity was measured in mS/m units with accuracy of +/- 0.3% of a reading (not including cell errors) and automatic temperature compensation. Periodically the apparatus was calibrated and checked for distortions in a laboratory using control solutions of a standardised conductivity value 14.7 mS/m, 72 mS/m and 1290 mS/m.

2.4.3. pH and temperature

Standard measurement device (*sension™1* Portable pH/mV/Temperature Meter**,** HACH Company) was used for recording of this parameter. Measurement procedure was performed daily for the influent and each column effluent as well as for water from the sedimentation pond. Routine measurements included also periodical calibration of the instrument (using buffer solutions of pH values 4, 7, and 8) in order to decrease risk of distortions and raise the level of correctness. The water was sampled in glass vessels and the temperature parameter was measured simultaneously in °C by the pH meter. The instrument used requires the temperature readout to compensate for temperature - dependent pH readings (Instruction Manual).

2.4.4. Precipitation

Precipitation data was acquired from the Fredhäll and Eugenia rain gauge, which automatically records the level of rainfall in appropriate time intervals. Thus, it constantly monitors every rain event and measures the precipitation level in mm. An automatic sampling device for water samples permits remote-controlled and event-controlled collection of water samples. Twenty-four water samples can be collected and assigned to events such as time, tide, current or turbidity. From remote-collected and transmitted rain data hydrographs were created separately for each field trial.

2.4.5. Flow measurement

Flow of the influent water to the filter column was carried out manually by using a 'clock and bucket' method. The precise time was measured, during which 500 ml (during the first trial) and 100 ml (second trial) cylinder was filled with storm water incoming to the column through an inlet hose. This parameter was constantly controlled and recorded along with every measurement and sampling. The flow measurement was carried out separately for each of the columns.

2.4.6. Head loss

This parameter was monitored along with other measurements. Using a calibrated ruler placed by the site of each transparent tube, the level of water in a filter column was observed and recorded manually. The height of the water level noted in mm was measured from the bottom of the tube. However, the actual water column height was calculated later on by taking in to account the thickness of the bottom synthetic layers placed in columns.

2.5. Water analysis

2.5.1. Sampling

Samples were collected from the inlet pipe, outlet buckets (Figure 4 and 5) and also occasionally from the sedimentation pond (mainly after higher rain events). Stormwater was stored in plastic containers at the volume of 500 ml for each sampling point. Some of the samples were kept at a low temperature of 4 °C in a cooling room at a laboratory or 10 °C in the manhole for up to three days. No special conservation procedure, like stabilization by adding of acid, was done before a delivery to the laboratory. For the laboratory analyses every 250 ml was distributed for heavy metals (Cd, Cu, Zn, Cr, Ni, Pb, Fe, Mn, Al and V) analysis and the remaining 250 ml of water for other parameters (TOT-N, TOT-P, DOC, and TOC). The sampling was carried out daily. The detailed frequency of field measurements and sampling procedures is included in Appendix 1; tables 1.1, 1.2 and 1.3.

The removal efficiency of elements by each medium was calculated based on the differences between concentrations in the influent and effluent samples. Total mass (in mg/kg material) of each constituent entering and leaving the columns was estimated from the level of daily concentrations and the measured amount of treated stormwater.

2.5.2. Analytical methods

Heavy metals

A method used for the determination of heavy metals was an inductively coupled plasma mass spectrometry (ICP-MS). The chemical analysis was performed at a laboratory using Elan DRC-e ICP-MS analytical instrument (PerkinElmer Company). Before samples were introduced into the instrument, an addition of nitric acid (ρ (HNO_3) = 1.4 g/ml) was done and the pH was decreased to the value of 2 in laboratory conditions. Some of the samples were also filtered through a filter of the nominal pore size 0.45 µm and treated with nitric acid in order to determine the colloidal and dissolved part of metals present in the solution.

Uncertainty values of the described method differ depending on the level of metal concentration in an analysed solution, and thus the statistical accuracy of measurements increases along with higher levels of concentration. Table 8 shows uncertainty values in percentage rate for each analysed metal.

Table 8. Uncertainty rate for each analysed metal (Stockholm Vatten)

Heavy metal	Level of concentration (µg/l)	Uncertainty (%)
Al	2 - 200	36 - 13
Pb	0.1 - 50	36 - 13
Fe	2 - 200	34 - 15
Cd	0.01 - 5	39 - 18
Cu	0.1 - 50	31 - 17
Cr	0.1 - 50	32 - 16
Mn	1 - 200	17 - 13
Ni	0.1 - 50	35 - 17
V	0.1 - 50	27 - 16
Zn	2 - 200	23

Total organic carbon (TOC)

An analytical instrument used for the determination of total organic carbon (TOC) was Multi N/C 3000 (Analytic Jena AG). The method applied was SS-EN 1484-1. The measurement was carried out by a direct method that requires an initial addition of acid into the sample. This caused the liberation of total inorganic carbon (TIC) in the form of carbon dioxide. Thereafter, organic carbon that was left in the solution is released by combustion and the

carbon dioxide product was measured by the infrared spectrometry. Samples were stored in plastic containers in a refrigerator at the temperature of 4 °C. The samples of stormwater were biologically inactive and therefore no special preservation was necessary.

Dissolved Organic Carbon (DOC)

The method and the device used for the determination of dissolved organic carbon (DOC) is as previously described for the TOC laboratory analysis. However, before the analysis the samples were filtrated through a filter of nominal pore size 0.45 μm to remove the suspended total organic carbon.

Total Nitrogen

Total nitrogen concentration was measured by the use of the Multi N/C 3000 device (Analytic Jena AG). The method of nitrogen determination was EN 122 61, which is the oxidation of the sample containing nitrogen by catalytic combustion in an oxygen atmosphere at > 700°C, to nitrogen oxides. Some of the samples could not be analysed immediately and therefore were stored at 10 °C up to 3 days without stabilisation by acid. However, the procedure was acclaimed as sufficient on account of rainwater's low biological activeness.

Total Phosphorus

The laboratory determination of phosphorus was performed by the use of UV – 1601 SHIMADZU laboratory instrument. Method: SS 02 81 07-2 was applied, which is an ammonium molybdate spectrometric method. Samples delivered to the laboratory were collected in glass bottles washed with acid because of the low concentration of nitrogen in stormwater.

3. Results and discussions

3.1. First field trial

The first column experiment brought an immediate knowledge concerning mostly hydraulic properties of the materials. All the substrates showed a tendency of rapid clogging if installed as a raw material without any preparations. E.g. zeolite, since it was placed directly in column without sieving and cleaning, and contained a wide range of grains – from courser to very fine. Hence, this broad range on grain size caused a very fast occurrence o the hydraulic clogging phenomena (Figure 6).

Figure 6. Clogging visible as the effect of outwashing and sedimentation of zeolite very fine particles in the column

Under the surface load of 2.7 m/h, the zeolite material clogged after approximately 20 min. The reason was that the fine particles of the material were flushed down to the bottom zone of the substrate column and filled tightly the void structure. Figure 6 shows fine granules that were firstly lifted by water column and thereafter settled on the top of the material head. Zeolite was therefore detached from the tube and cleaned with fresh water stream using a mesh of the opening size equal to 0.5 mm, as described in chapter 2.2. The zeolite was tested again in the conditions as previously. However, despite the cleaning procedure the material was clogged again after about one hour. Also, the flow velocity through the bottom synthetic

layer (PIAB) from zeolite column was checked directly after the material removal. For that purpose the empty column with only the PIAB layer was filled with tap water roughly up to 0.5 m of the column height and the discharge flow was measured. This was done to check whether the filter material or the PIAB caused clogging. The measurement of flow through the PIAB layer showed the values of 6.2 m/h and 15 m/h before and after cleaning, respectively. It clearly indicated that the clogging phenomenon was caused by high content of the fine fraction of the used material (the hydraulic conductivity was worsened). Figure 7 (left side) shows the PIAB layer after the operation of the column and cleaning it with tap water. One can see that this synthetic layer to some extent had been blocked in. However, the colour of filling particles indicated that it originated from the medium fine fraction rather than from the water suspension.
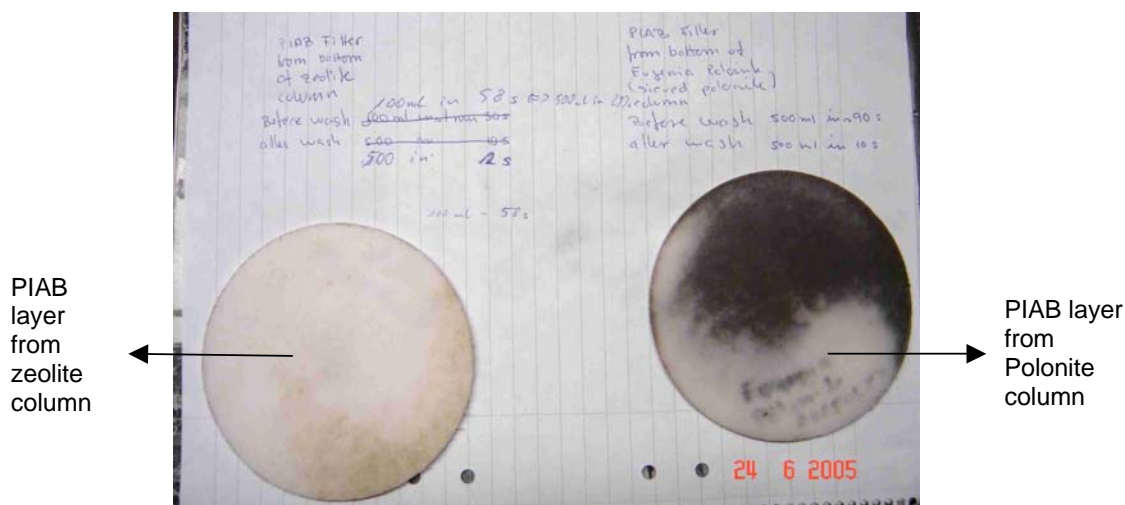

PIAB layer from zeolite column

PIAB layer from Polonite column

Figure 7. Cleaned PIAB layers from the bottom of zeolite and Polonite (un-sieved) column

For Polonite$^{®}$ (not sieved), with broad range of grains' size (from 5 mm to a few µm), a similar procedure was applied. The Polonite$^{®}$ column was operated at the hydraulic load of approximately 3.1 m/h. Clogging was observed also shortly after commencement of the operation, approximately after 30 min. Therefore, this column was removed but no reinstallation was carried out. Analysis of the bottom PIAB layer explicitly revealed blockage caused by fine particles originated from the un-sieved Polonite$^{®}$ (Figure 7). The flow measurement was performed by filling the emptied column, with the remaining PIAB layer, with tap water up to 0.5 m of the column height. The flow through the PIAB layer was 1.9 m/h and after its cleaning with fresh water and reinstallation in the column the flow amounted

to 18 m/h. Those large differences in the flow demonstrated that the fine fraction of the substrate as well as the small size of PIAB pores deteriorated the hydraulic conductivity.

The second form of Polonite® (sieved) was installed in the column without cleaning. The hydraulic load was calculated to be 3.1 m/h. The water column level was below the material's head shortly after installation and start-up of the pump. However, after approximately 15 hours of the constant flow the water column was stabilized at the level of 0.12 - 0.14 m above the material's head. This column was operated for approximately 22 hours. However, this medium was also clogged, and therefore was removed without reinstallation.
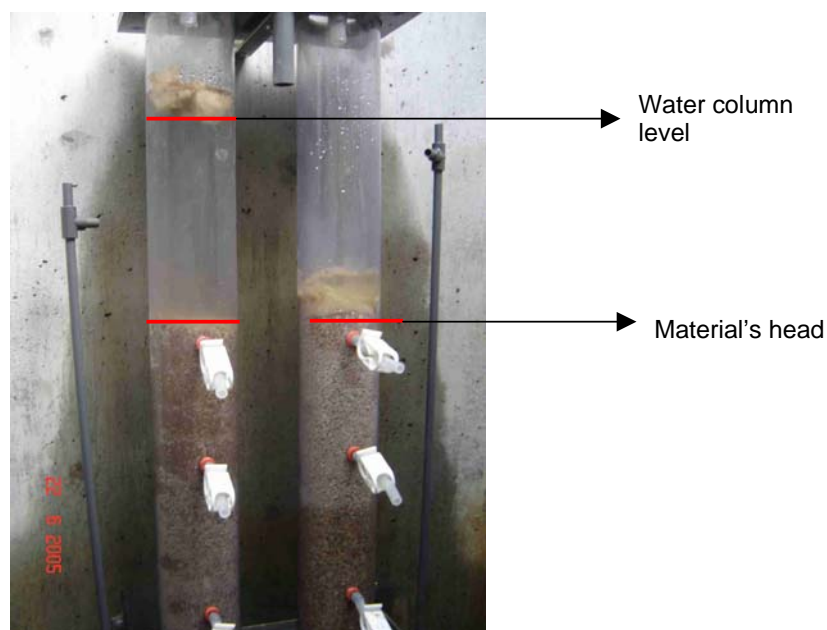
Figure 8. Not sieved and sieved Polonite® (from the left) – commencement of operation

Pine bark along with the activated carbon filling was tested as one of the organic materials. It was used to fill the column cleaned after the Polonite® study. The registered filtration velocity at the start up stage was around 3.0 m/h and remained roughly constant during the whole operation phase. The water column level stabilized at the height of 0.19 m above the material's head. The column with this medium was operated for 28 hours without clogging, though after next 23 hours an overflow was also recorded. It was possibly caused by higher concentration of suspended solids in the influent due to the rain event.

The blank trial showed also that PIAB layers and mineral fibres acted as filtration features. The blank columns were operated at the hydraulic load of approximately 3.0 m/h.

The blockage and overflow was observed only in the column containing PIAB layer and mineral fibre.

3.1.1. Field measurements

Field measurements during the first period of the conducted experiment provided useful information on hydraulic and filtration properties. The turbidity study of the sieved Polonite® material showed at the first period that very fine particles were settling in the bottom part of the column. The effect of flushing down by water stream caused the material's hydraulic resistivity. For instance the turbidity value of a sample from the lowest column zone came to 61 NTU. After around 7 hours of the operation it increased to 84 NTU. To compare, at the same measurement the turbidity of effluent was equal to 8.9 NTU. In case of the bark filling at the highest column level the turbidity value amounted to 6.72 NTU and at the lowest column level to 4.28 NTU after 51 hours of operation. This indicates that a material containing a very broad range in the granule size have a tendency to aggravate its hydraulic conductivity. Very fine grains of filter material are flushed downward the column and thus cause clogging of the filter bed.

The GAC material was operated under the hydraulic load accounted for 2.8 – 3.2 m/h. The water column level ranged constantly from about 0.115 m to 0.195 m above the material head but rather remained in this extent with a couple of cases when decreased entirely (<0.5m of total column height). No clogging phenomenon was observed during approximately 68 hours, after which an overflow appeared probably as the effect of increased suspended solids concentration in influent due to the occurrence of intensive rain event. As it was noted, the GAC material considerably adsorbed the suspended solids, i.e. the highest measured turbidity value in the influent (17.8 NTU) was reduced by the 150 % (to the value of 7.15 NTU), whereas the lowest registered value of 8.28 NTU was decreased by GAC to 3.91 NTU. In case of Polonite® these values differed insignificantly. It is important to emphasize that filter materials' function is to reduce dissolved and colloidal matter content, not to act as a physical filter for particles since the idea is to use the filter after a sedimentation process. However, some researches reveal that some of the heavy metals in stormwater at high pH predominate as particulate-bound fraction (Shinya et al., 2000, Pettersson, 1999, Sansalone, 1999). Therefore, physical filtering properties of filter's filling materials are also of interest.

3.1.2. Laboratory analysis results

The laboratory analyses of trace elements brought some preliminary results on materials' adsorptive abilities. The highest reduction was calculated for the GAC with an exception in the case of zinc and manganese. Those metals were much better reduced by Polonite®. Average rates of metals' reduction expressed in percentage are displayed in Table 9 for comparison. The average was calculated only for the period that the compared filters were tested simultaneously (2005-06-23). In the majority of the cases the reduction rate for the GAC material ranges from 70% (71% for total cadmium and 70% for total lead) to around 30% (33% for total manganese and 25% for vanadium) and for the other metals mean value equals 50 - 60%.

Concerning the sieved Polonite®, the average reduction was recorded for total zinc (Polonite® - 65%, to weigh against GAC - 55%) and manganese (Polonite® - 76%, GAC - 33%). Significant concentrations of chromium and vanadium appeared to be higher in the effluent, which indicates the release of these substances from the Polonite® material. The Cr and V concentration values in the effluent exceeded fourfold and 8-fold the values in the inflow, respectively. This phenomenon of metal release is the effect of Cr and V chemical content in the natural bedrock that is used to produce Polonite® (also observed by Kietlińska and Renman, 2005).

Pine bark reduction rates range from around 20% for Cu to around 42, 48 and the highest 64% for Pb, Fe and Al, respectively. No reduction for bark is noted of such heavy metals as Cd, Cr and Mn. However, higher concentrations of nearly whole heavy metals (except Al) were registered in the effluent samples taken after approximately 25 hours of the bark column operation.

Table 9. Comparison of reduction rates based on influent and effluent values (average value calculated for the period 2005-06-23 –2005-06-24)

Heavy metal symbol	GAC W830, reduction (%)	POLONITE (Sieved), reduction (%)	Bark, reduction (%)
Cd	71	71	0 and release
Cu	51	31	20 - release
Zn	55	65	27- release
Cr	58	release	0 - release
Ni	20-0	37	25-100 release
Pb	70	50	42- release
Fe	54	57	48- release
Mn	33	76	0- release
Al	66	45	64
V	25	release	20 and release

Blank trials provided some information mainly about the mineral fibre, which affected the filtration process. The analysis of metal concentrations revealed a decrease of iron (mean 45%), manganese (mean 40%) and zinc (mean 30%) in outflow water. However, the concentration of aluminium in the effluent from blank column with mineral fibre was lifted by ca 40% at the beginning of operation. Thereafter at the end the concentration was declined considerably by 64% against influent concentration. For other analyzed metals no reduction was observed. Such results might indicate initial release of aluminium compounds from the used mineral fibre. Regarding decreased concentration of iron, manganese and zinc one can conclude that the placement of this material could have considerable influence on monitored metals' concentration in effluents from tested media. Nonetheless, all presented results are burdened with the significant error value. The reason is that the initial concentrations were close to the level of detection limits, which could possibly affect the results of laboratory analysis. For this reason, the uncertainty rates amounts to above 30% (Table 8 in chapter 2.5.2.).

3.2. Second field trial

3.2.1. Un-saturated conditions

The successive experiment was performed with the following four types of materials: GAC W830, GAC PK3-5, Polonite®, zeolite. All of those filters were operated in un-saturated conditions during the period of four weeks. The filtration velocity was lowered to the values from 1.1 to 1.8 m/h. The desired stable hydraulic load of 1m/h was not possible to achieve due to technical problems. Since the hydraulic load was computed using manually measured flow rates into the columns, possible error should be also considered. The different flow rates through 0.106 m (internal diameter) columns correspond to the load of 1l/h = 0.11m/h.

During this experiment no clogging phenomenon was observed, which has been perceived as the result of sieving and washing away fine fraction of each material before the installation (see chapter 2.2.). It is important to emphasize that this procedure enabled to achieve hydraulic conductivity with special regard to the mineral materials that explicitly depicted a tendency for blockage during the first field experiment. The second factor, which apparently enhanced the hydraulic conductivity, was the larger openings of the mesh placed in the bottom of each column. During the test with the GAC column the permeability decreased step by step starting from the 25th hour of the experiment. The GAC column clogged completely after ca 5 days. This was the effect of suspended solids deposit on the mineral fibre that caused hydraulic resistivity of the top layer. The layer of mineral wool was changed into the new one and the water column level dropped entirely below the material head. The procedure was replicated for zeolite. However, the first overflow in the column appeared after about 50 hours. No clogging was observed for other materials.

3.2.1.1. Field measurement (turbidity, electrical conductivity, and pH)

During the whole experiment each material captured suspension and reduced its concentration. However, during the first period of this field trial the suspension in storm water (inflow) was low, and did not exceed the turbidity value of 4 NTU. According to the Swedish Environmental Protection Agency (SEPA) quality criteria of monitored values can be classify as a significant extent of turbidity (Table 10a, 10b). However, according to the Stockholm Vatten sources, 3.5 NTU is the mean value of clarity monitoring of Lake Mälaren waters.

Table 10a. Surface water quality criteria of water transparency (Swedish Environmental Protection Agency)

Class	Extent of Turbidity	FNU (=NTU)
1	None or insignificant	< 0.5
2	Slight	0.5-1
3	Moderate	1-2.5
4	Significant	2.5-7
5	Very large	< 7

Table 10b. Average values of turbidity in the effluents from the materials' columns, un-saturated conditions (n = 33) and saturated conditions (n = 27)

Average turbidity value [NTU]	Influent	Clinoptilolite	Polonite®	GAC 830W	GAC PK3-5
Un-saturated conditions	4.92	1.83	2.78	1.36	2.34
Saturated conditions	3.93	1.92	2.54	1.5	2.32

Relatively low influent turbidity values at the initial trial period were caused by a pre-treatment unit (sedimentation pond) during longer time without storm event. The highest process efficiency was calculated for finer activated carbon (GAC 830W) that decreased turbidity to a value oscillating at 1 - 2 NTU. Very similar results were observed for zeolite. Values 2 - 3 NTU reached the effluent from the Polonite® and courser GAC columns, thus, reduction rates remained rather low (Figure 9). Nevertheless, the reduction rates rose significantly after rain appearance (2005-07-16). Despite lifted concentration of suspended solids in the incoming water, turbidity values in effluents from filters remained low. The results of turbidity measurements showed again the highest efficiency in case of finer GAC filling and clinoptilolite filtration. The highest noted turbidity values of the influent of around 16.5 - 17 NTU were reduced to the value of 2.0 - 2.6 NTU by GAC and to the value of 3.0 - 3.6 NTU by zeolite (Figure 9). Such results for finer GAC and clinoptilolite were achieved due to the smaller void size. The finer grains enable the material to retain also smaller particles of the suspension, and therefore decrease its total quantity. The highest concentrations were recorded for Polonite® effluent (8.0 - 8.5 NTU), even though reduction reached ca 50%. Better results showed courser GAC, reducing amount of suspension to effluent values of 5.8 - 6.1 NTU.
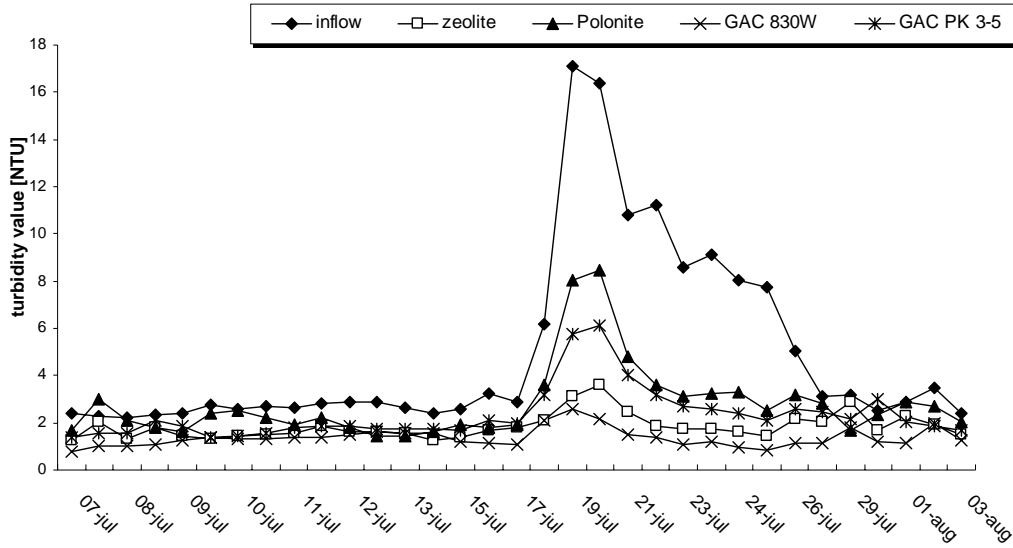
Figure 9. Turbidity reduction of all tested material under downward flow un-saturated conditions, period 2005-07-07/08-03

The conductivity field measurement of influent was decreasing constantly until the first rain event (2005-07-16). Afterwards, this parameter rapidly increased indicating lifted concentrations of the dissolved matter in the stormwater discharge. Exceptionally high values were recorded for Polonite® at the initial phase of the experiment (114 – 118.5 mS/m). Possibly calcium oxide (25% of the material content in dry mass) was washed out by filtrate. Also, elevated pH values were initially recorded in the effluent from the Polonite® column. It was equal to 11.4 after ca 8 hours from the operation start-up and dropped to 7.9 at the end of the test period (after 33 days).
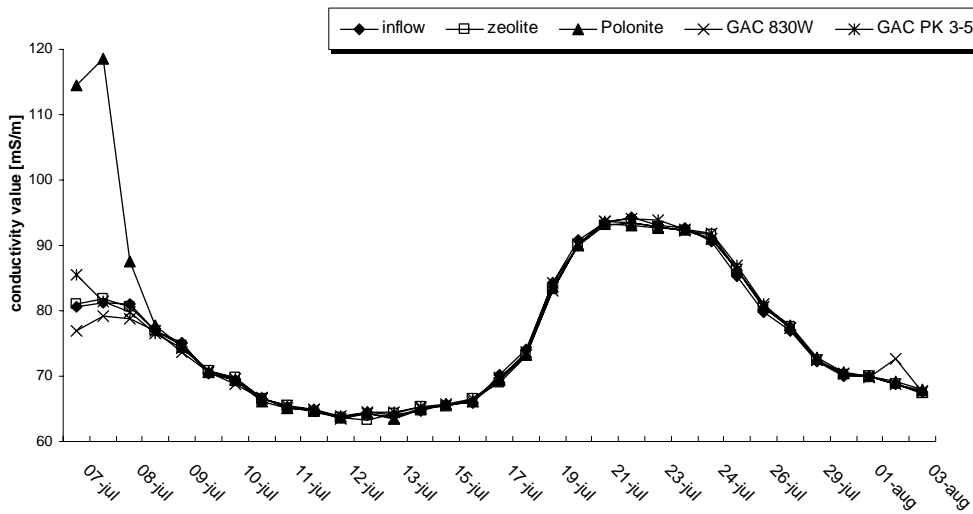

Figure 10. Conductivity values during the period of second field trial (2005-07-07/08-03), un-saturated conditions

30

For other materials, effluent conductivity values did not vitally diverge from the influent value. Thus, a general tendency was the initial slow decline of conductivity from around 80 (first sampling) to 64 mS/m, and afterwards the increase of up to 94 mS/m. This rapid increase was caused by a discharge of dissolved compounds in the run-off water from the catchment after the first rain event (Figure 10). Along with stormwater accumulation in the pond due to the constant rainfall, higher conductivity value remained stable for 4 days. Afterwards the concentration of ionised chemicals dropped within next 6 days to the value of 70.4 mS/m despite still maintaining atmospheric precipitation. Unchanged values of influent and effluents during the whole period of the experiment can indicate that the materials did not remove contaminants in the dissolved form. This could be achieved by such processes as adsorption of ions onto substrate surface, or chemical precipitation. However, no changes in conductivity in the case of all tested materials can be interpreted as the results of no occurrence of ions removal by adsorption. Instead mechanical removal of pollutant with the suspension is the process of heavy metals' uptake to take into account.
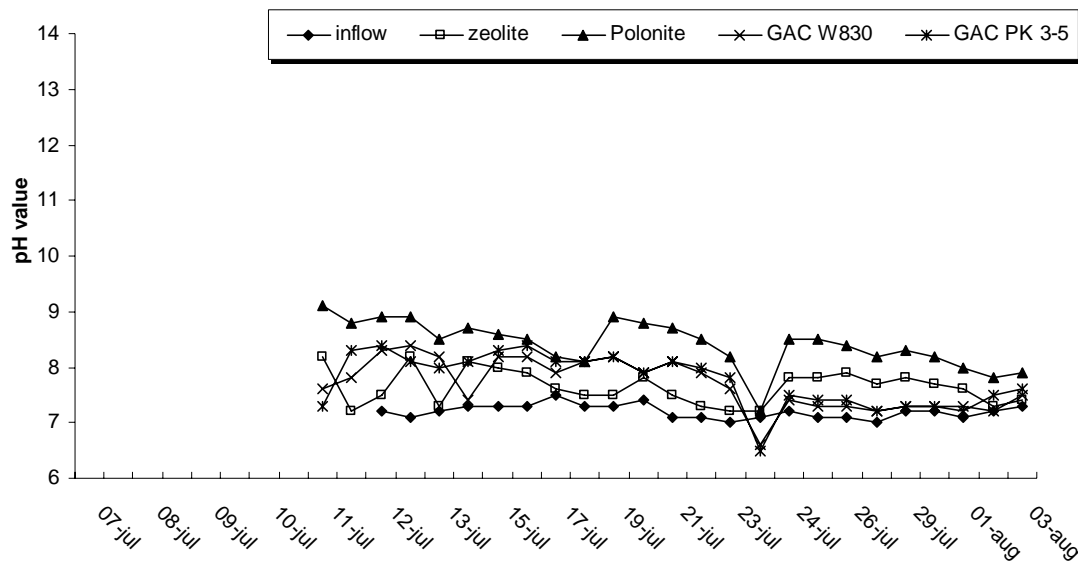
Figure 11. Variations in pH values in filters' effluent and influent (2005-07-07/08-03), un-saturated conditions

No significant variation in the inflow pH value was also observed and it ranged from value of 7.0 to 7.5. However, as already mentioned, the pH values of the Polonite® effluent showed a decreasing tendency and during the all experiment maintained on the level of approximately 8 - 9. Effluents from both types of activated carbon also showed alkaline pH

value of ca 8 at the initial part of the experiment and constantly decreased to the value of 7.3. The pH value of clinoptilolite effluent in the initial trial phase was slightly elevated. However, it did not vary considerably from the values of inflow. Figure 11 shows only data recorded from the second week of the experiment due to the lack of measuring instrument. However, it was assumed that the changes in pH values at the initial field trial was similar to those registered during the experiment performed in saturated conditions. This is discussed in the following chapter 3.2.2.

3.2.1.2. Laboratory analysis results

Laboratory analyses encompassed in total ten elements. Influent concentrations showed very low concentrations of cadmium (Cd; <0.01 – 0.03 µg/l) close to the instrument detection limits. Also low concentrations of lead (Pb; 0.8 – 5 µg/l), chromium (Cr; 0.8 – 3 µg/l) and nickel (Ni; 1 – 9 µg/l) were analysed. Therefore, one can assume that competitive role of those metals was rather less in the adsorption process. The reduction efficiency of those metals was consequently very low (see enclosed Table 12 below). The results of other screened metals showed large differences in their removal by all tested substrates, which was mainly depended on the concentrations of incoming water. The removal efficiency differed also for each filter material, still it remains rather low for all media comparing to the other reviewed studies (Kietlińska and Renman, 2004; Färm, 2001; Ouki and Kavannagh, 1996).

All examined filter substrates achieved good results for reduction of such metal as iron, manganese, aluminium, and zinc (total amount without partitioning into the colloidal and particulate fraction). Those metals appeared in analysed storm water at the highest concentrations during the whole period of sampling. Still, the highest removal efficiency was observed for activated carbon with smaller grain size (GAC 830W) and clinoptilolite. Removal of Zn, Mn, Al and Fe by those materials rose drastically with increasing concentrations of influent. This can be observed especially based on data obtained after storm event that appeared on July 16th (Figure 12, 13, and 14). In other words, effluent concentrations upheld at the same lowered level or were diminished even more despite elevated concentrations of influent.

Table 12. Values in percentage of removal efficiencies by four selected filter media (negative values indicate release of a particular metal); n=20, SD = standard deviation

Element	ZEOLITE		POLONITE		GAC 830W		GAC PK 3-5	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Mn	80.4	11.7	52.8	26.3	83.7	12.2	68.8	13.3
Al	48.3	30.2	5.0	37.5	47.9	24.0	16.9	39.0
Fe	39.8	17.6	20.7	26.2	46.7	17.5	33.8	12.9
Zn	35.7	9.2	26.6	18.4	49.0	13.1	33.8	30.8
Pb	20.8	22.8	10.9	20.7	31.0	28.1	14.2	19.2
Cu	12.1	35.5	6.2	58.1	51.1	24.9	25.1	70.1
Cr	11.2	46.5	-246.6	132.2	27.2	58.3	21.4	48.7
V	4.2	42.7	-108.3	137.0	16.8	34.7	9.6	61.5
Ni	3.6	55.0	11.4	43.7	-49.4	96.7	10.9	76.2
Cd	-3.0	97.0	10.6	52.3	40.9	27.1	11.4	55.0

Polonite[®] removal rate of Fe, Mn and Zn remained rather unchanged, and did not depend on variations in influent concentrations. Metals' uptake by Polonite[®] fluctuated in time. Polonite[®] revealed the highest removal efficiency for manganese, with the maximum rate equal to 85 % while the minimum only 31% based on whole data obtained from everyday effluent concentration measurement. In the case of zinc the removal efficiency was in the range of 17% - 50% and in case of iron 13.6% - 48.6%. For such metals as nickel, lead, cadmium, aluminium and copper Polonite[®] performed poorly. However, it is important to mention that high removal efficiency of e.g. nickel (50 - 77 %) and copper (up to 60 - 70%) was reached whenever the influent concentrations increased. Table 13 shows removal efficiencies for the selection of elements that were reduced weakly by Polonite[®], and the values of initial concentrations that influenced effectiveness of removal using this material.

Table 13. Removal efficiency variations of metal uptake by Polonite[®] dependent on initial concentrations

Analysed element	Median low influent concentration [µg/l]	Removal efficiency [%]	Elevated influent concentration [µg/l]	Removal efficiency
Al	40 – 50	0 or insignificant	300 – 450	79
V	3 – 5	Overshoot	10 – 13	40 – 60
Cu	10 – 15	< 25	22 – 42	68 – 74
Ni	1 – 3	0	6 – 9	50 – 77
Pb	1 – 3	0	> 3	30 – 60
Cd	0.01	0	0.02 – 0.03	33 – 50

Low removal efficiency of Polonite® in this study can indicate dependence on level of contamination in water introduced into the column, since the effect of initial concentration on metals removal is of great importance. The effect of initial concentration was reported in several studies (Athanasiadis and Helmreich, 2005; Petrus and Warchoł, 2005; Inglezakis and Grigoropoulou, 2004; Ouki and Kavannagh, 1996). Additionally, such infinitesimal uptake can be explained by a short contact time of influent with medium as the probable effect of hydraulic overload (high filtration velocity) established in this experiment. Still, in actual column operation, any volume element of the solution is in contact with a given layer of the bed for only a limited period of time, usually insufficient for attaining of equilibrium. Thus, the failure of attaining local equilibrium results in lower uptake of cations from the incoming solution (Helfferich, 1995). Precipitation of metals' hydroxide is the suggested removal mechanism for Polonite®, forming insoluble precipitates in bed filter at alkaline conditions (Kietlińska and Renman, 2004), thus also decrease of pH could slow this process or cause the release of already precipitated compounds. For example an overshoot in the uptake of iron, manganese, and zinc was observed simultaneously after approximately 73 hours of the continuous flow. It is visible as a peak in Figures 12, 13, and 14 showing Polonite® column performance. One possible assumption could be that the analysed sample was randomly contaminated. However, the release of particles, which attracted metal compounds and were rinsed out by water stream inside the column bed can be also taken into account. This explanation is probable since this experiment was conducted in unsaturated conditions, thus formation of water streams inside the bed (channelling) seems to be relevant. The change in the pH value inside the column could play an important role as well in the process of elution of already precipitated metals from the fixed bed. The alkalinity of Polonite® effluent was decreasing constantly from the pH value of approximately 12 to the value of 9. It was observed in parallel with the overshoot of metals.
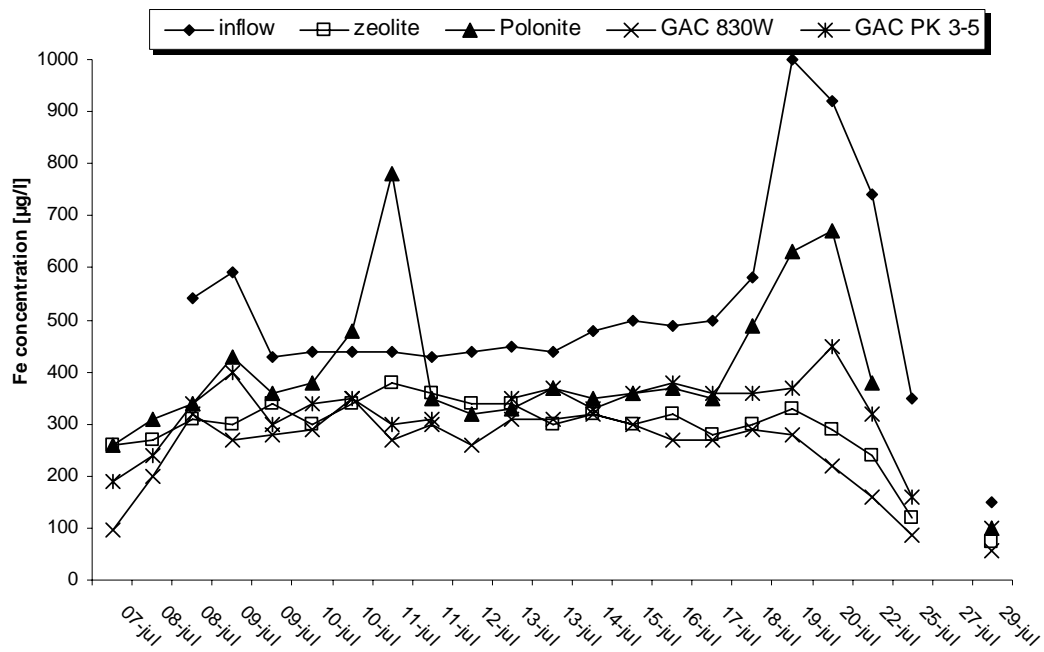
Figure 12. Total Fe concentration values in influent and effluent from filters selection, un-saturated conditions
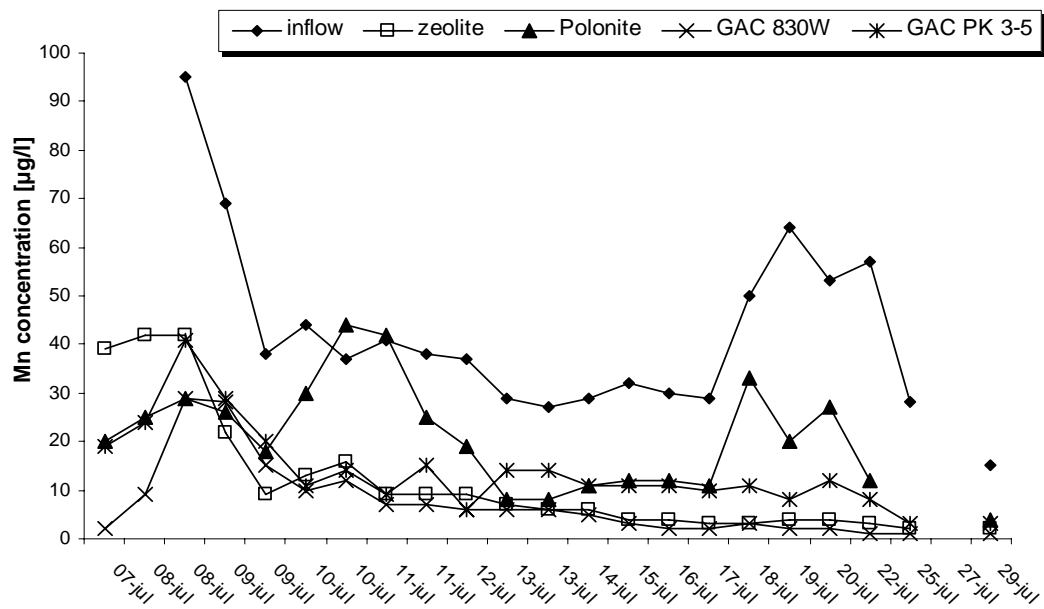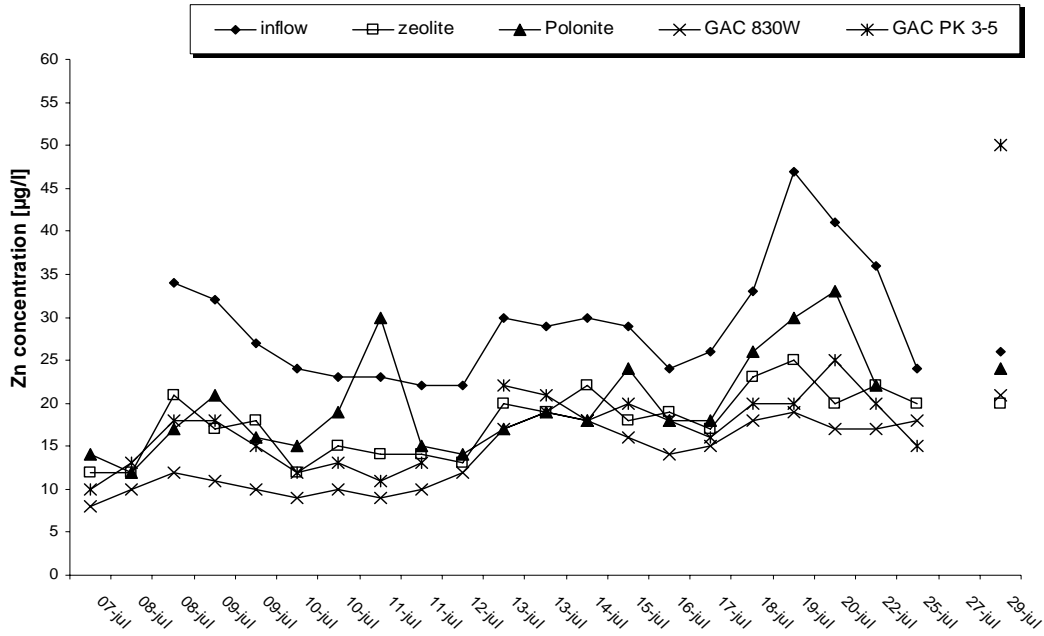

Figure 13. Total Mn concentration values in influent and effluent from filters selection, un-saturated conditions

35

Figure 14. Total Zn concentration values in influent and effluent from filters selection, un-saturated conditions

Metal uptake by the zeolite substrate was also found to be affected by such factors as initial concentration of pollutants, residence time (hydraulic load) and particulate matter in the influent. In this study the zeolite (clinoptilolite) material column performance showed better results comparing to the Polonite®, but slightly poorer than the finer GAC medium (see Table 12). For instance, manganese was removed on average 80.4 %, while finer GAC achieved 83.7 %. Iron, zinc and aluminium were similarly removed by zeolite and activated carbon. Lead, copper and chromium uptake by zeolite was, however, much lower, while nickel, cadmium and vanadium average removals were very poor and equalled only 3 – 4 %. From all daily monitored concentrations recalculated into the percentage of reduction, the manganese removal efficiency was in the range of 55 - 94.7% and iron of 13 - 68 %. Moreover, zinc maximum removal efficiency reached 51% and minimum 16% (Table 14). However, the increase of Mn, Fe, Al and Zn removal by clinoptilolite was correlated with the increase of suspended solids in the incoming water and its higher removal, which exemplifies Figure 15. This possibly indicates that the most effectively reduced by this material were metals bound to the particulate matter through the mechanical filtration. The effect of high filtration velocity and thus low contact time disabled to achieve an equilibrium of the ion exchange process (metal ions' uptake by clinoptilolite). Consequently, it resulted in lower removal rates when less amount of suspension was captured by this material
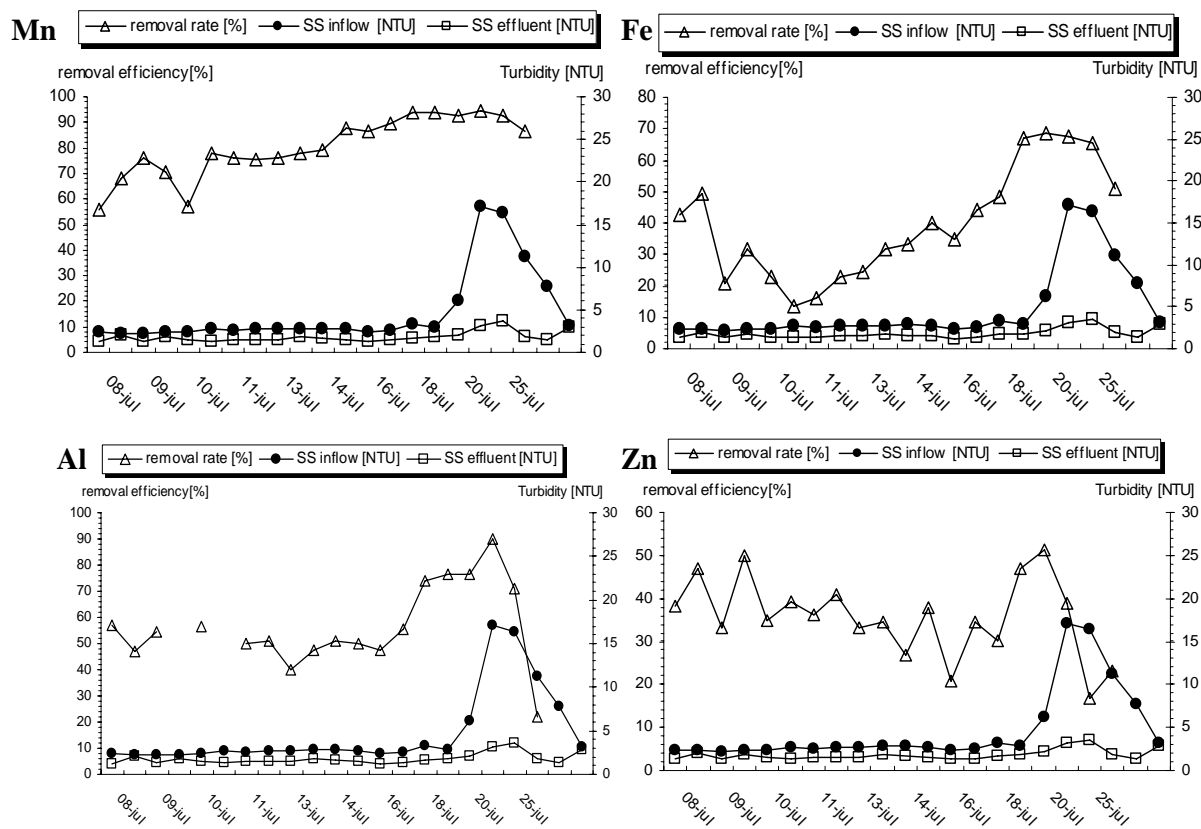
Figure 15. Increasing uptake of Mn, Fe, Al, and Zn by clinoptilolite at higher reduction of suspended solids, un-saturated conditions (Al – values of removal efficiency -9 and -43.5 were excluded from the chart)

For such metals as nickel, lead, cadmium, aluminium and copper the clinoptilolite substrate showed also better results at higher initial concentrations (Ni: maximum 77%, Pb: maximum 66%, Cd: maximum 66%) (see Figure 16). Nonetheless, the zeolite column performed with very broad range in removal rates during the whole time of columns' operation. At very low initial concentrations no removal was recorded. Thus, as in the case of the Polonite® experiments, also the removal efficiency in the zeolite column increased with initial higher concentrations of metals. Those good results achieved at higher pre-concentrations of the metals are not correlated with the level of suspension removal. It can be also connected with the content of Al and Si oxides in zeolitic chemical composition. This provides zeolites with negative framework favourable to ion-exchange capability for the metal cations. The negative charge in natural clinoptilolite is balanced by cations, most frequently sodium, potassium, calcium and magnesium, which can be exchanged with other cations present in storm water such as heavy metals. Thus, some part of the dissolved fraction in the influent could be possibly adsorbed by this medium.
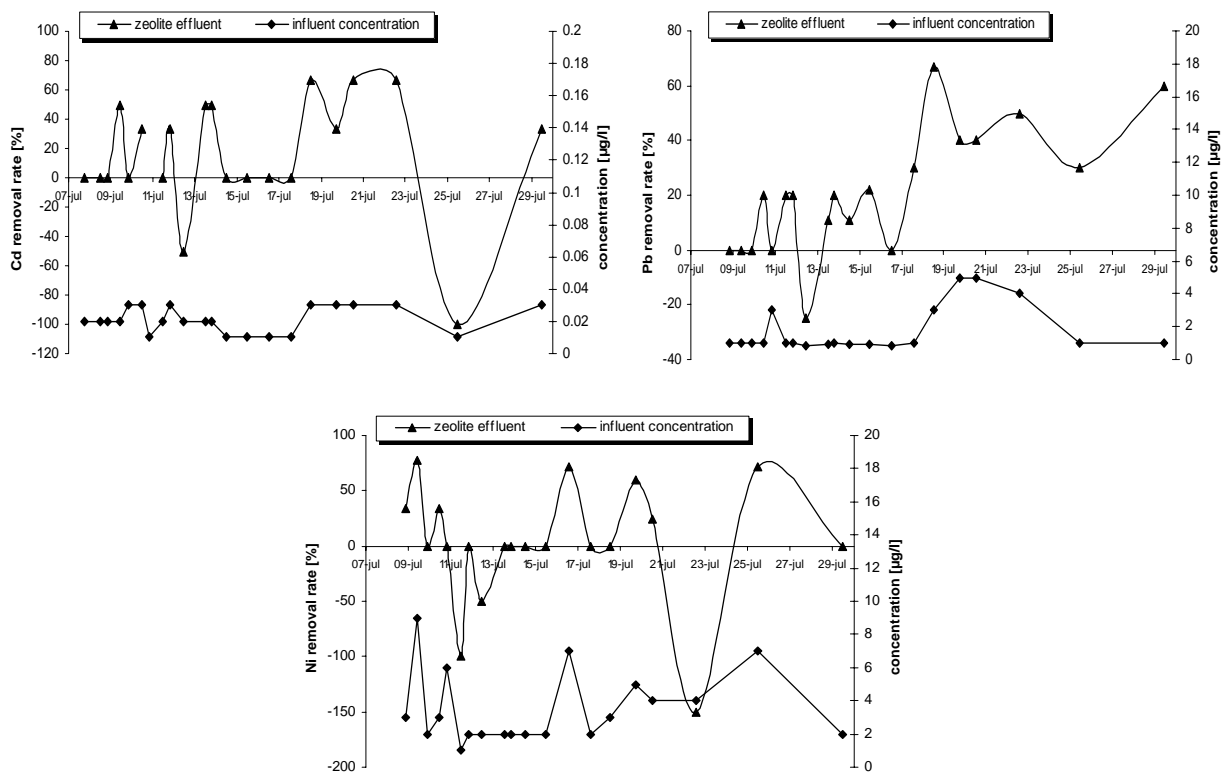
Figure 16. The fluctuations in Cd, Pb and Ni uptake by zeolite and dependence on initial concentrations

Table 14. Maximum and minimum metal removal efficiencies by zeolite.

Element	ZEOLITE	
	Maximum [%]	**Minimum [%]**
Mn	94.7	55
Al.	90	22
Fe	68	13
Zn	51	16
Pb	66	0
Cu	71	0
Cr	73	0
V	70	0
Ni	77	0
Cd	66	0

The selectivity series also characterises clinoptilolite and can be the result of various factors, which influence ion-exchange behaviour in zeolites. One factor is the framework structure of the zeolite itself. The dimensions of the channel formed by the tetrahedral units, which make up the zeolite must be large enough to allow passage of a hydrated metal ion (Ouki and Kavannagh, 1996). In this study, the clinoptilolite substrate also showed removal efficiency order (selectivity series). However, this was connected with the values of metal concentration in the influent. Ouki and Kavannagh (1996) also examined the effect of initial

concentration on metal removal by clinoptilolite for solutions ranged from 1ppm to 30 ppm. They reported that an optimum removal was achieved at an initial concentration of 10 ppm. In this trial, the metal concentrations did not exceed the value of 1 ppm (mg/l). One can conclude that low influent concentration, even at peak times, had a big impact on the occurrence of low reduction rates.

Some of analysed metals were also released in different amounts by tested materials. This was observed mainly for such elements as aluminium, chromium and vanadium, whose elevated concentration has been registered in the effluent from the Polonite® column. In the case of aluminium, percolating through filter bed, stormwater initially washed out some of its amount (Figure 17), after approximately 25 hours of operation the concentration in the effluent stabilised on the level of influent concentration. Kietlińska and Renman (2004) showed also leachate of Al, Cr, and V from Polonite® as the effect of natural content of those elements in the bedrock that is used to produce Polonite®.

Figure 17. Total Al concentration values in influent and effluent from filter selection, un-saturated conditions

Tests on Polonite® in those trials also revealed the same phenomenon of chromium and vanadium release. Higher amount of those metals was released at the initial phase of the column operation than in the case of aluminium. During the rest of the trial period Cr and V concentrations in the effluent were also slightly elevated (Figure 18, 19). The calculations of the total load of metals into the columns and the total reduction showed apparent release of Cr at the value of 4.03 mg/kg material and V for the release amounted to 6.71 mg/kg material (see Table 15).

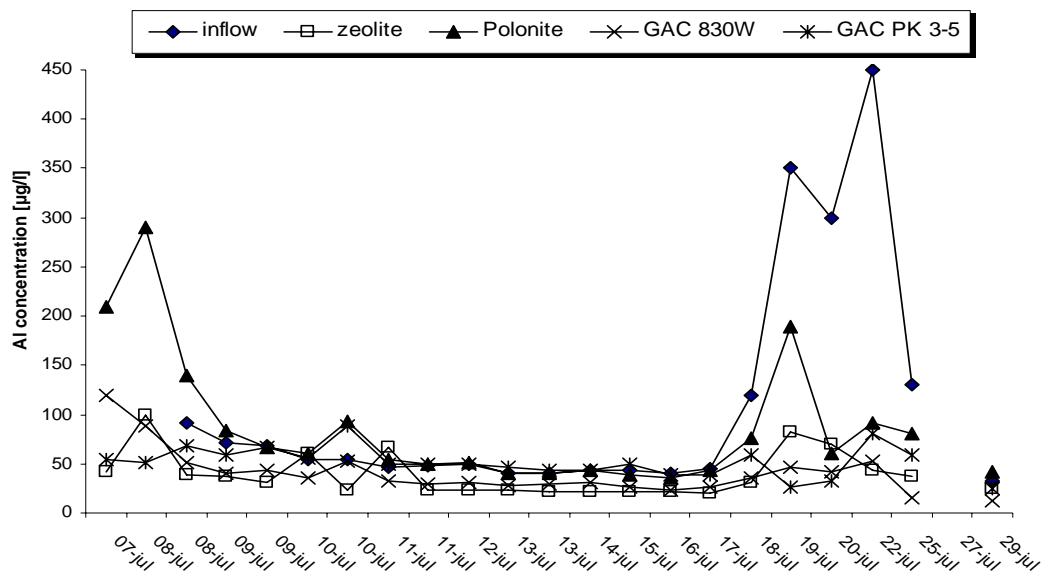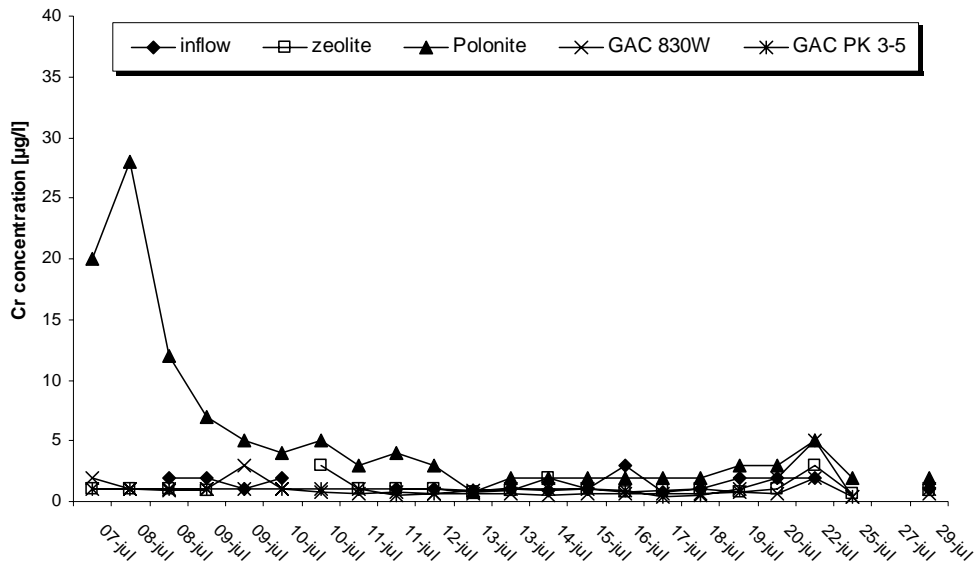*Figure 18. Total Cr concentration values in influent and effluent from filter selection, un-saturated conditions*
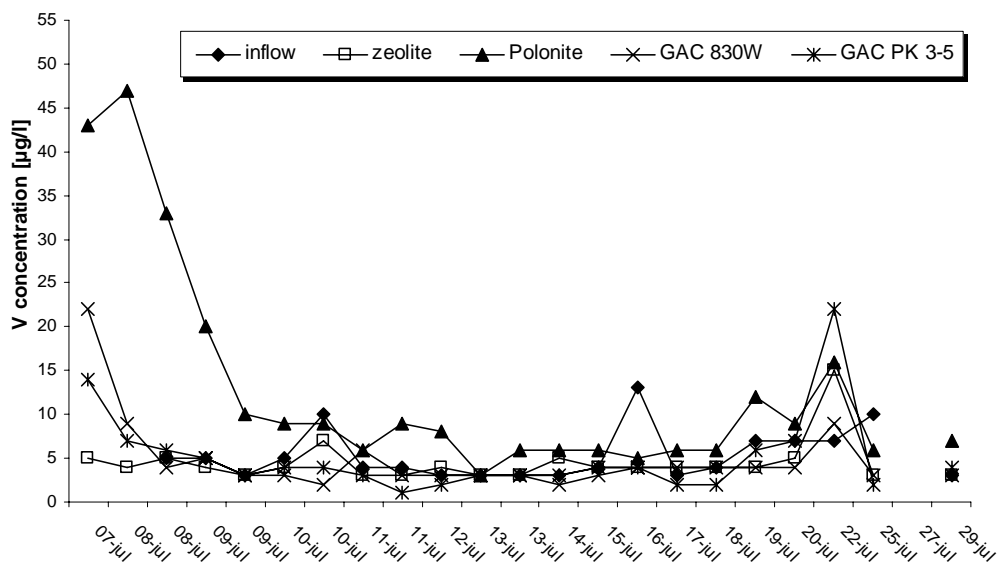
Figure 19. Total V concentration values in influent and effluent from filter selection, un-saturated conditions

Estimation of the total metal amount that has been captured by a particular medium was also carried out. The calculations were performed by using the data of daily concentrations (influent and effluent) and the volume of treated stormwater between each sampling. The overall load of a singular metal removed by material in mg/kg is presented in Table 13. The data indicate the quantity of removed species without differentiation between particulate-bound and colloidal forms for each tested filter material. The calculated sorption based only

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on data acquired from the sampling period and does not show total sorption capacity of the materials.

Table 15. Values for sorption by four selected media [mg/kg], unsaturated conditions (data from sampling period 2005/07/07-29)

Element	ZEOLITE [mg/kg]	POLONITE [mg/kg]	GAC 830W [mg/kg]	GAC PK 3-5 [mg/kg]
Fe	429.75	307.42	956.56	946.94
Al.	158.01	125.44	334.29	351.32
Mn	56.85	37.10	115.23	136.44
Zn	17.86	15.10	44.48	18.85
Cu	5.47	3.63	27.82	19.39
V	1.62	-6.71	6.07	2.76
Cr	0.21	-4.03	1.38	0.17
Pb	1.28	0.85	3.25	2.01
Ni	1.35	2.46	-2.32	4.47
Cd	0.011	0.013	0.041	0.011

It is clearly seen that the highest quantity of iron, aluminium, manganese and zinc has been reduced in the case of all examined filter substrates. Probably due to already mentioned fact that those elements are predominantly bound to the suspended organic compounds, they are mechanically removed with suspended solids from water. Other authors recognised also the importance of Mn, Fe, Al and Zn removal, since such a complexants as hydrous iron oxides, hydrous manganese oxides, sulphides or natural organic matter play fundamental role in transport of trace elements in aquatic environments (Taillefert M., Gaillard J. F., 2001). Trace metals are scavenged by particulate or colloidal forms of the complexants. Colloids, whose specific surface areas are very reactive towards trace elements, can capture metals and thereafter aggregate them into particulate hydrous oxides. Thus, potentially threatening dissolved form of heavy metals is transformed to the particulate phase. Filters performing mechanical treatment effectively remove this fraction.

This experiment has proved the highest efficiency of the activated carbon performance. Some previous studies on activated carbons, mainly batch experiments and fixed-bed columns using synthetic wastewater, showed encouraging results. The studies highlighted such main factors that affect the adsorption efficiency as pH value of influent, ionic strength and filtration rate (Chen and Xiaoyuan, 1999; Corapcioglu and Huang, 1987). Chen and Xiaoyuan (1999) performed fixed-bed column experiments for single-species (Cu, Zn and Pb) and for multi-species metal ions using synthetic solution to assess competitive ions' addition effect on adsorption process. They reported that metal ion adsorption increases along with increasing pH of influent, ionic strength and decreasing flow rate. An increase of ionic strength slightly

improved copper removal but did not significantly affect zinc's uptake. Studies on competitive adsorption indicated that the removal of single metal ions was decreased when other metals were added to the solution. Especially on addition of Cu showed drastic decrease in the Zn uptake due to much higher affinity of copper ions to the carbon functional groups. The activated carbon performance showed descending order in competitive metal adsorption: Cu > Pb > Zn. Since in storm water many different metal ion species occur, thus, their competitiveness affects its adsorption. Therefore, the results and findings of this study can be referred to above stated conclusion. In this study, the activated carbon column performance also showed selective removal. However, better removal efficiency for some of metals was observed if their initial concentrations were elevated. Thus, activated carbon removed significant amount of copper and zinc with mean efficiency rates 51 and 49 per cent respectively (Table 12). This percentage rates increased into circa 60 – 90 for Cu when initial concentrations were much above 10 µg/l (in the range of 30 – 40 µg/l) and 50 - 65 per cent for Zn also when initial concentration was lifted above 10 µg/l (up to 28 µg/l). Thus, one can conclude that in this case the pre-concentration was the main factor that affected the selective removal, quantity of metals but also the occurrence of other chemical compounds that constitute strong complexants is of importance. Chen and Xiaoyuan (1999) reported also that an addition of such strong complexant as EDTA caused a significant increase in metals' adsorption. This is related by the presence of four carboxylic groups that can bind more free metal ions and as metal-organic compound complex can be attracted to the filter's free sites. In the real conditions, the chemical speciation of metals also affects the relative degree of adsorption or binding to particles in natural waters (Schnoor, 1996). Still the quality and quantity of organic compounds can also decide about the amount of metals removed by the attraction of metal complexes onto the filter surface. This phenomenon is possibly responsible for such a good removal of total Cu, Zn, but also Fe, Mn, and Al by activated carbon. This is probably the main removal mechanism due to the fact that in this field experiments the rain-water contained non-organic and organic matter, which binds metal ions. The metals present mainly as bound to the particles or in colloidal form can be removed through the electrostatic attraction of filter particles. Also, due to much larger surface area of reactive filters characterised by small grain diameter the higher adsorption can be expected. This phenomenon was noticed in this study by once comparing the sorption efficiency for both forms of the tested activated carbon. Courser GAC PK 3-5 achieved poorer results than finer GAC 830W for all monitored parameters except nickel (see Table 12). Analyses of the daily effluent concentrations profile showed that some of the single maximum removal rates were

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higher for courser carbon. However, such a situation was rather very exceptional and appeared seldom. The maximum and minimum obtained values are presented in Table 16.

Table 16. Maximum and minimum metal removal efficiency by both types of granulated activated carbon

Element	Finer GAC 830W		Courses GAC PK 3-5	
	Maximum [%]	**Minimum [%]**	**Maximum [%]**	**Minimum [%]**
Mn	98.2	59.4	89.3	47.4
Al	88.4	5.5	92.6	-60
Fe	78.4	29.5	63	19.9
Zn	65.6	19.2	57.4	25
Pb	75	0	60	0
Cu	95.2	28.6	86.4	7.1
Cr	80	0	70	0
V	80	0	80	0
Ni	77.8	-325	85.7	-250
Cd	66.7	0	66.7	0

Corapcioglu and Huang (1987) examined different types of activated carbon by performing batch experiments. They demonstrated that the percentage of removal decreases with increasing initial concentrations in the range of 0.63 ppm to 18 ppm which is contradictory to the results in this field trial. However, such results were obtained at the acidic conditions of the pH value in the range of 3 - 7. At the alkaline conditions (pH > 8), that was also in the case of this study, the removal rates achieved good results between 80 and 100% of removal and was not affected by surface loading. This fact can be considered in deciding on relatively good results of activated carbons used in this study. The pH value remained in the range of 9 - 7 during the whole trial.

Estimation of the total amount of metals that has been removed by the activated carbon showed also encouraging results (Table 15). Nevertheless, considering single metal species one can conclude that the maximum adsorption capacity has not been reached. For instance, the sorption of Fe and Mn amounted to 956.56 mg/kg and 115.23 mg/kg, respectively (GAC 830W). To compare, some batch tests showed that the adsorption capacity can reach 3,601 mg/kg (Fe) and 2,545.1 mg/kg (Mn) (Ahmad bin Jusoh *et al.,* 2005). The adsorption capacity of iron is higher than that of manganese as a result of the differences in the ionic radius that is smaller in the case of Fe. Electronegativity is also of importance and decides of iron's higher strength to attach to GAC's negatively charged surface. Still, in storm water the variability of appearing organic and inorganic compounds that create complexes with metals and alkaline

conditions affect the appearance of free ions and modify its adsorption onto the adsorbent surface.

3.2.2. Saturated conditions

The selection of substrates (GAC W830, GAC PK3-5, Polonite®, zeolite) in this field trial was applied as in the former one. The difference, however, was in operating conditions. The aim was to compare how the complete exposure of a filter bed in contact with solution affects metals' removal. This experiment was carried out during approximately four weeks with the desired hydraulic load value as in the test with un-saturated conditions test. However, the measured everyday load was somewhat raised comparing to the previous trial. This higher flow rate could not be avoided for the technical reasons and ranged from 1.4 to 2.0 m/l (desired load value 1m/h), which corresponds to the load of 1l/h = 0.11m/h.

The diminishing of bed's permeability was observed only in the case of finer carbon GAC 830W tests, despite the application of the same preparation procedure as at the former trial (fine fraction removal through sieving and washing away fine fraction of each material before installation). After approximately 15 hours, the overflow was observed in the column. Therefore, the operation of finer activated carbon (GAC 830W) column was ended as the effect of hydraulic resistivity caused by settling of the suspension from the influent that blocked the void space of the filter bed.

3.2.2.1. Field measurement (turbidity, electrical conductivity, and pH)

The performance of this experiment with changed hydraulic conditions brought comparable result on the efficiency of all examined materials. As in the case of the former trial, each substrate reduced turbidity to the level of value below 4 NTU. However, the fluctuation of influent clarity was higher during the whole August due to the constant rain events (Figure 20). Thus, higher turbidity occurred more often, which affected substrates efficiency.
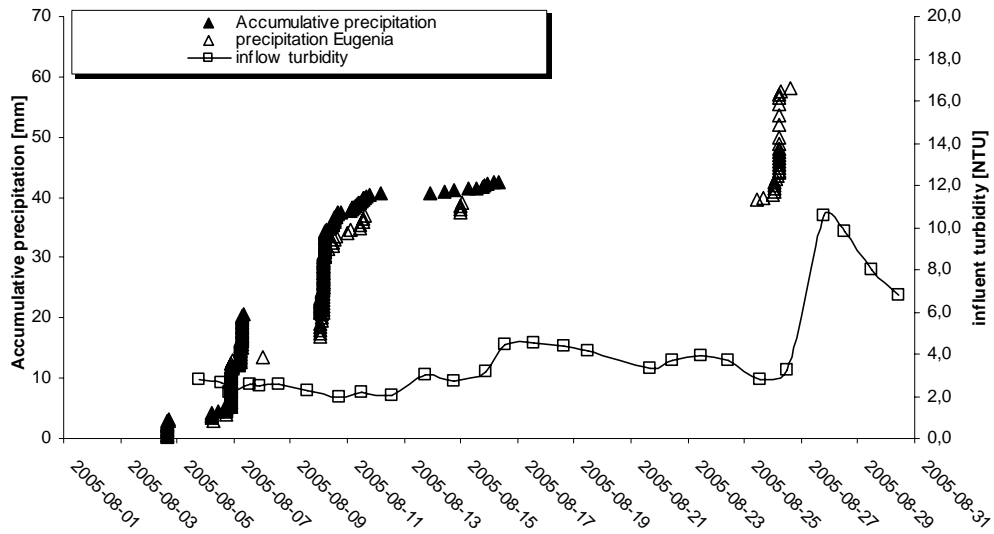
Figure 20. Accumulated Precipitation (Fredhäll and Eugenia tunnel Rain Gauge) and turbidity values of influent measured between 2005-08-04 and 2005-08-27 in Lilla Essingen.

At the first part of trial between August 4th and 12th the precipitation was rather intensive; 40.6 mm of accumulated precipitation. However, the inflow turbidity upheld on low level of up to 2.8 NTU. With the occurrence of successive rain clarity was diminished to the value of 4 NTU. The inflow turbidity declined till the August 25th, after which it rapidly increased to the value of 10.6 NTU as a result of intensive rain occurrence. The highest efficiency can be attributed to finer activated carbon (GAC 830W), which effluent reached value bellow 2 NTU and during storm event even below 1 NTU. These values are classified among slight and moderate extent of turbidity according to the SEPA environmental quality criteria for lakes and watercourses. Clinoptilolite that reduced turbidity to value oscillating 1 – 3.5 NTU during the whole time of operation can be assessed as effective in reduction of suspension in stormwater. Moreover, zeolite maintained the turbidity value of 3.6 NTU despite drastic increase of suspension in influent to the value of 10.6 NTU (Figure 21). Such a result of GAC and clinoptilolite performance can be explained by the smaller void size. The lowest efficiency was recorded for Polonite[®] and courser GAC PK3-5; both materials reduced turbidity to the value ranged from 1 to 2.5 NTU at lower influent values. Although its effluents' suspension rose up to 5.9 NTU, which is classified as significant extent of turbidity into the recipient. Again, such results can be probably related with the size of material granules that are too course and do not capture sufficient amount of suspended solids from the solution
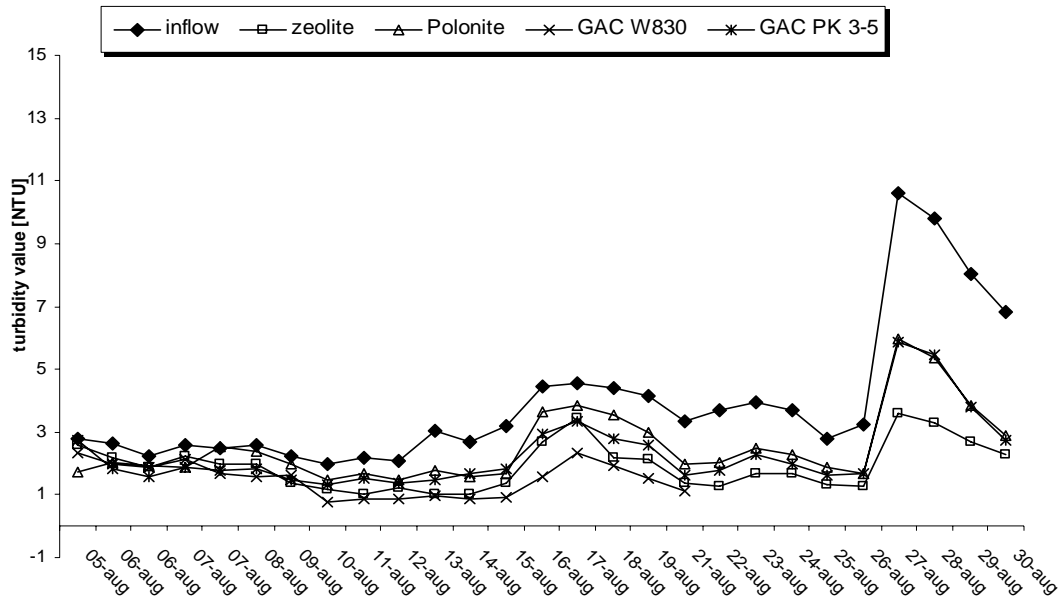
Figure 21. Turbidity reduction of all tested material under downward flow saturated conditions, data from 2005-08-05/30)

The conductivity of influent and effluents was decreasing constantly during the whole period of trial. The parameter values of each material effluent followed values of influent with the exception in Polonite® performance. This material released calcium oxide due to its content at the initial phase of experiment, thus conductivity of its outflow water after approximately 8 hours of constant operation reached value of 101.5 mS/m (Figure 22). This phenomenon was reported by Kietlińska and Renman (2004) and also twice confirmed by herein experiment. However, such high value decreased rapidly to the level of influent and stabilized during the majority of trial period. Still, it is worthy to notice that constant decrease of electric conductivity was upholding despite intensive run-off from the catchment area. Along with each rainfall and accumulation of stormwater in pond, declining tendency of conductivity was slower. Similarly as in the case of experiment conducted in un-saturated conditions, values of influent and effluents during the whole period of experiment remained on the same level. Therefore, it can possibly indicate that the contaminants in dissolved form were not adsorbed onto substrate surface.

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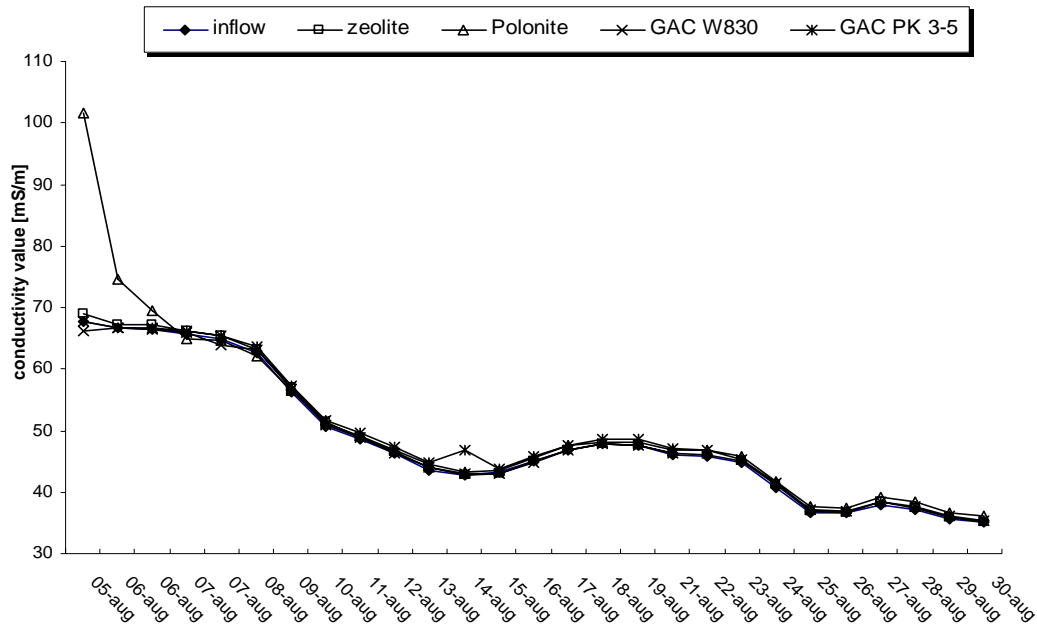
Figure 22. Conductivity values during the period of second field trial (2005-07-07/08-03), saturated conditions

The profile of pH values measured everyday showed that inflow values ranged from 7.5 to 7.0, therefore remained rather stable during the experiment. Polonite® effluent pH values showed decreasing tendency from value approximately 11.4 to 7.9. Both types of activated carbon also kept alkaline pH value of 9.7 – 9.6 at initial part of experiment, afterwards constantly decreased to the value of 7.3. The pH of clinoptilolite effluent at the beginning of trial was slightly increased. However, it rather followed the pH values of influent.

Figure 23. A variation in pH value in filters effluent and inflow (2005-08-05/30), saturated conditions

3.2.2.2. Laboratory analysis results

The same parameters, as in the case of experiment performed under un-saturated conditions, were analysed. Again, the results of the analysis showed low influent concentrations of cadmium (Cd; <0.01 – 0.03 µg/l), also low concentration of chromium (Cr; 0.8 – 3 µg/l), nickel (Ni; 1 – 3 µg/l) and lead (Pb; 0.8 – 5 µg/l). Ac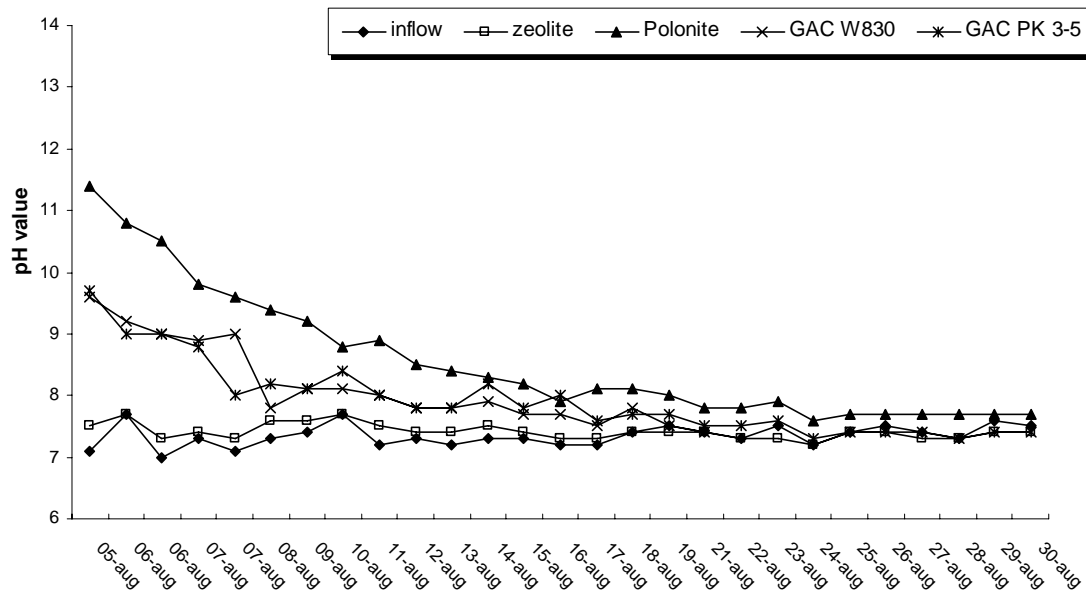cording to the water quality standards of the Swedish Environmental Protection Agency, such concentrations cause none or little biological risk in surface waters. The exception is however total concentrations of lead higher than 3 µg/l that represent the increased risk of biological processes disruption. In the case of all tested materials the removal efficiency of those elements was consequently very low, which is presented in Table 17 below. It is shown as the mean value of reduction calculated from daily concentrations.

Such metal as manganese, iron, aluminium, and zinc again were removed in the highest amounts by all substrates. However, those metals appeared also in analysed storm water at the highest concentrations during whole period of sampling. Still the highest removal efficiency was observed for the activated carbon with smaller grain size (GAC 830W) and clinoptilolite.

Table 17. Values in percentage of removal efficiencies by four selected filter media (negative values indicate release of particular metal); n=19, SD = standard deviation

Element	ZEOLITE		POLONITE		GAC 830W		GAC PK 3-5	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Mn	77.4	15.1	57.1	21.4	72.3	31.7	53.2	37.5
Al	66.5	4.8	-42.1	107.0	40.0	36.5	-43.8	82.9
Fe	51.0	15.5	30.0	14.2	54.0	18.2	34.5	16.2
Zn	31.5	10.5	24.9	14.4	34.6	22.1	33.5	21.7
Pb	-27.9	111.7	11.6	35.8	-26.9	162.6	-32.8	99.8
Cu	15.8	8.8	8.5	8.5	49.5	10.8	35.9	22.0
Cr	12.8	34.7	-254.7	472.0	52.1	12.6	4.9	52.8
V	11.8	19.3	-232.0	413.5	18.0	52.9	-14.0	43.1
Ni	21.1	25.4	18.4	24.8	-34.2	47.3	35.5	30.2
Cd	19.7	31.5	14.5	41.7	35.1	37.6	32.5	39.0

Also important is to notice that aluminium was released constantly by Polonite® and courser GAC PK3-5 material during the initial period of approximately one week. This

phenomenon is illustrated on the Figure 23. The raised concentrations of this element were reported for GAC PK3-5 effluent and they remained on the level of 80 – 100 µg/l, whereas influent concentrations were recorded in the range of 30 – 60 µg/l. Still, such values do not exceed the limits for concentration in drinking water (100 µg/l; Swedish regulations SLV FS 1999:35). Also, the constant increase of concentrations of the influent was recorded and possibly caused by the appearance of rain events. Polonite® effluent also contained elevated concentrations of aluminium compound. However, its concentration decreased rapidly from the initial value of 160 µg/l (first sampling) to 78 µg/l (second sampling) during ca 19 hours of the column operation. Thereafter, the effluent value stabilised slightly above influent concentrations on the same level of 50 – 60 µg/l. However, after the intensive rain occurrence August 26th the concentration of Polonite® effluent raised to the value of 150 µg/l, while the incoming water reached the value of 210 µg/l (Figure 24).

Figure 24. Total Al concentration values in influent and effluent from filter selection, saturated conditions

Again Polonite® removal of Fe, Mn and Zn achieved the highest results with the mean daily removal percentage of 30 %, 57% and 25 % respectively. The variation in time of metals uptake by Polonite® was however significant also under complete hydraulic saturation of the material. Thus, Polonite® highest removal efficiency for manganese ranged from 80.8 % to the minimum of 20% based on everyday effluent concentrations (Figure 25).
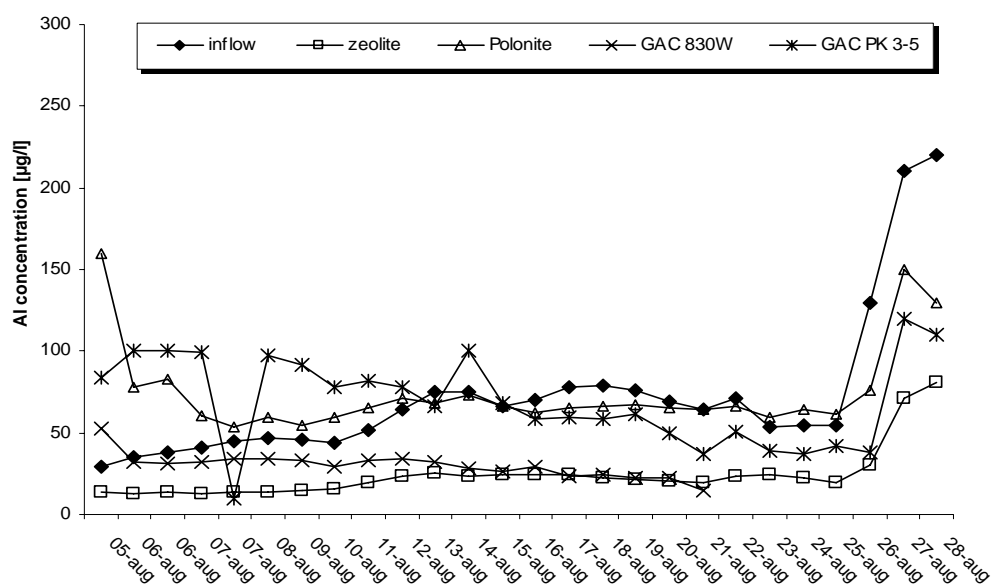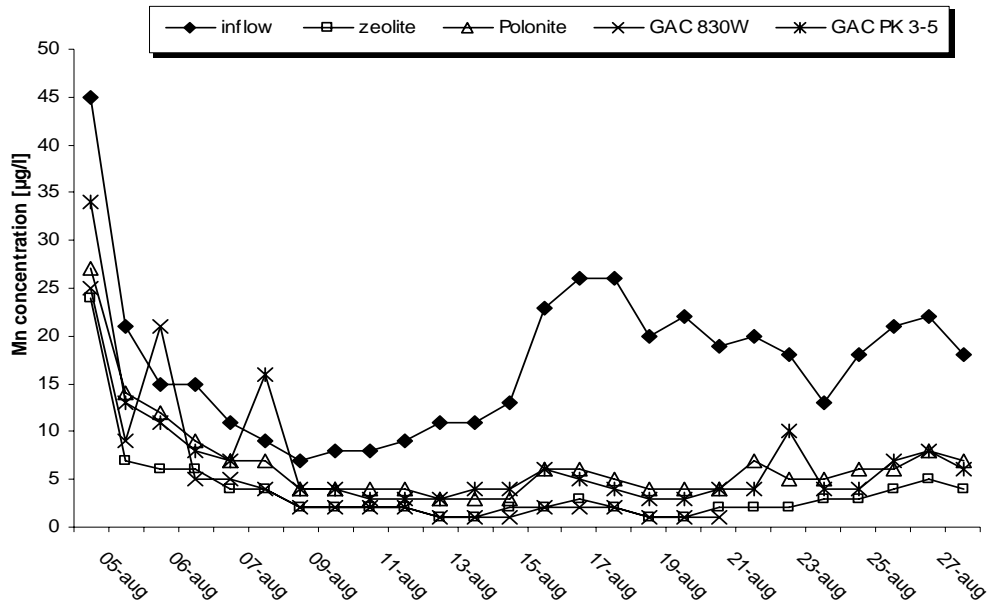
Figure 25. Total Mn concentration values in influent and effluent from filters selection, saturated conditions

Zinc was removed by Polonite® with maximum efficiency 51.6 % and minimum merely 6.3 %, for iron maximum 54.1 % and minimum 6.3 %. For such metals as nickel, and copper Polonite® performed poorly during the whole period of experiment independently on the changes in influent concentrations. It is also important to mention that Polonite® achieved better overall results of cadmium (maximum 67 %) and lead (up to 57 %) removal under hydraulic saturation. This was caused possibly due to the higher concentrations of influent. Still, the uptake was very unequal and e.g. despite elevated initial concentration of lead after storm event that reached 10 µg/l, the uptake of this element by Polonite® increased only to the 40 % (Figure 26).
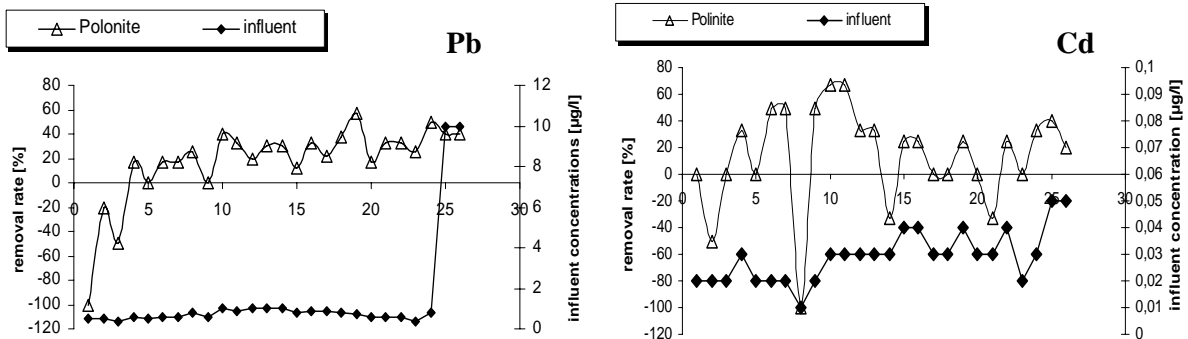
Figure 26. The fluctuations in metals uptake by Polonite® and its dependence on initial concentrations

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Therefore, the results from this trial also proved that such low removal efficiency of Polonite® is caused by low concentrations of influent. Thus, it indicates dependence on level of initial concentrations in water introduced into the column. Additionally, such poor uptake can be explained again by short contact time of solution with medium due to the high filtration velocity set up in this experiment. Assuming already discussed precipitation of metals hydroxide as the suggested removal mechanism for Polonite® (Kietlińska and Renman, 2004), again one can conclude the decrease of pH as the factor that could inhibit this process of dissolved fraction uptake.

This field trial confirmed again the release of vanadium and chromium from Polonite® material that was recorded at the initial period of the column operation. The concentrations of Cr and V in Polonite® effluent significantly exceeded values recorded for the influent. Thus, the effluent concentration constantly decreased from value of 54 µg/l in case of vanadium and 20 µg/l of chromium to the level of influent during approximately one week. This initial release of considered metals remained for a short time, however prompted high concentrations in effluent. They are classified to the fourth class of surface waters and assessed to caused the increased risk of negative biological effects according to the SEPA criterion. It is illustrated on the Figure 27 below.
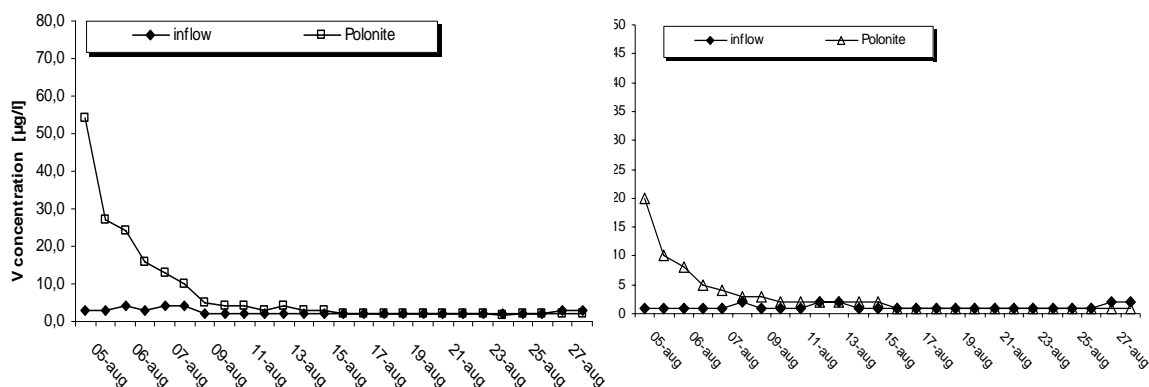
Figure 27. The release of vanadium (V) and chromium (Cr) from Polonite® material.

This experiment performed under hydraulic saturation also showed better results of clinoptilolite performance than of Polonite®. The uptake of manganese by zeolite was

amounted with the highest average of 77.4 %, while the finer GAC 830W, used as the reference material, achieved 72.3 %. On Figure 25 that illustrates manganese removal, one can see that the best and comparable performance was recorded for zeolite and finer GAC 830W throughout the whole time of experiment.

Iron, zinc and aluminium were again similarly removed by zeolite and activated carbon and again both achieved the best results of all examined materials (Figure 24, 28, and 29).
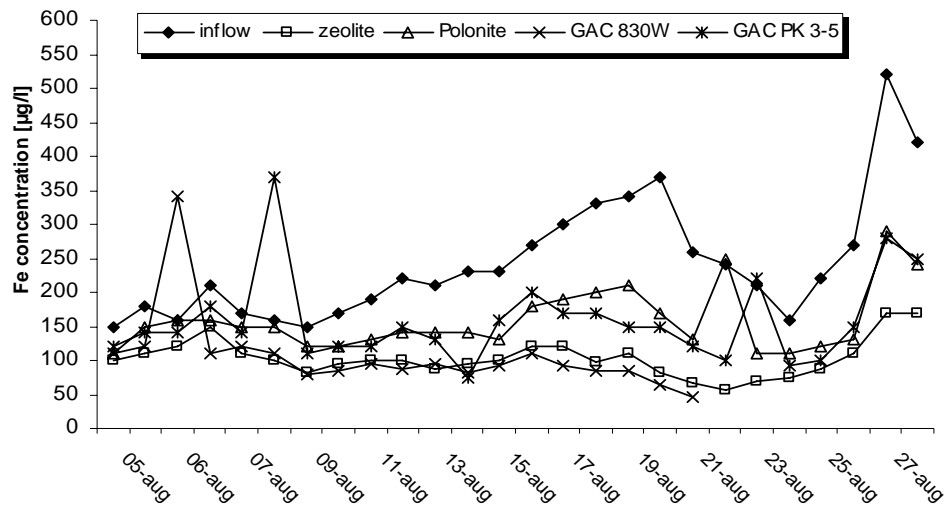
Figure 28. *Total Fe concentration values in influent and effluent from filters selection, saturated conditions*
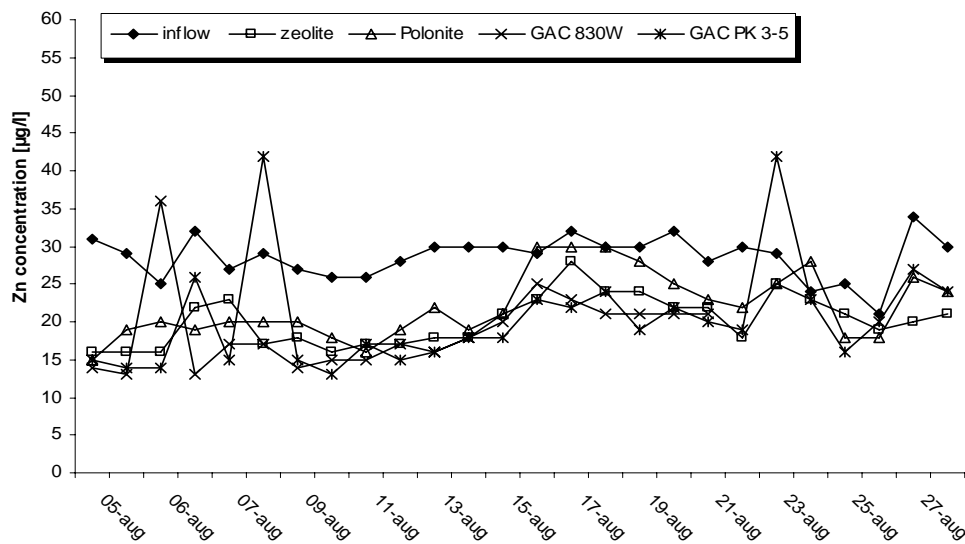
Figure 29. Total Zn concentration values in influent and effluent from filters selection, saturated conditions

Copper and chromium uptake by clinoptilolite was however much lower on the average level of 20 – 12 %, but still reduction achieved (Table 17). As already mentioned, the concentrations of chromium in incoming water were very low thus it was possibly responsible

for such poor reduction. Though copper concentrations of influent reached high values generating increased risk for the environment, which were decreased by the material to the level of moderately high concentrations and less hazardous. In case of lead, zeolite effluent contained its lifted concentrations during the first week of sampling, which were still low but affected the average value of this metal removal efficiency. The difference from the previous experiment conducted under un-saturated conditions was that at hydraulic saturation nickel, cadmium and vanadium were removed with higher efficiency. The average removal rate reached 21 % for nickel, 20 % for cadmium and 12 % for vanadium. Such results can be assessed as only slightly better. However, it can indicate that the complete hydraulic saturation of filter bed thus presumably larger surface area was utilised to treat incoming stormwater.

Daily monitored concentrations in the clinoptilolite column effluent expressed in percentage of reduction revealed maximum efficiency of manganese (Mn) removal 95.5% and minimum 46.7 %, for iron (Fe) maximum was amounted as 78 %, while minimum 25 % also zinc (Zn) maximum reached 48 % and minimum 4 %.
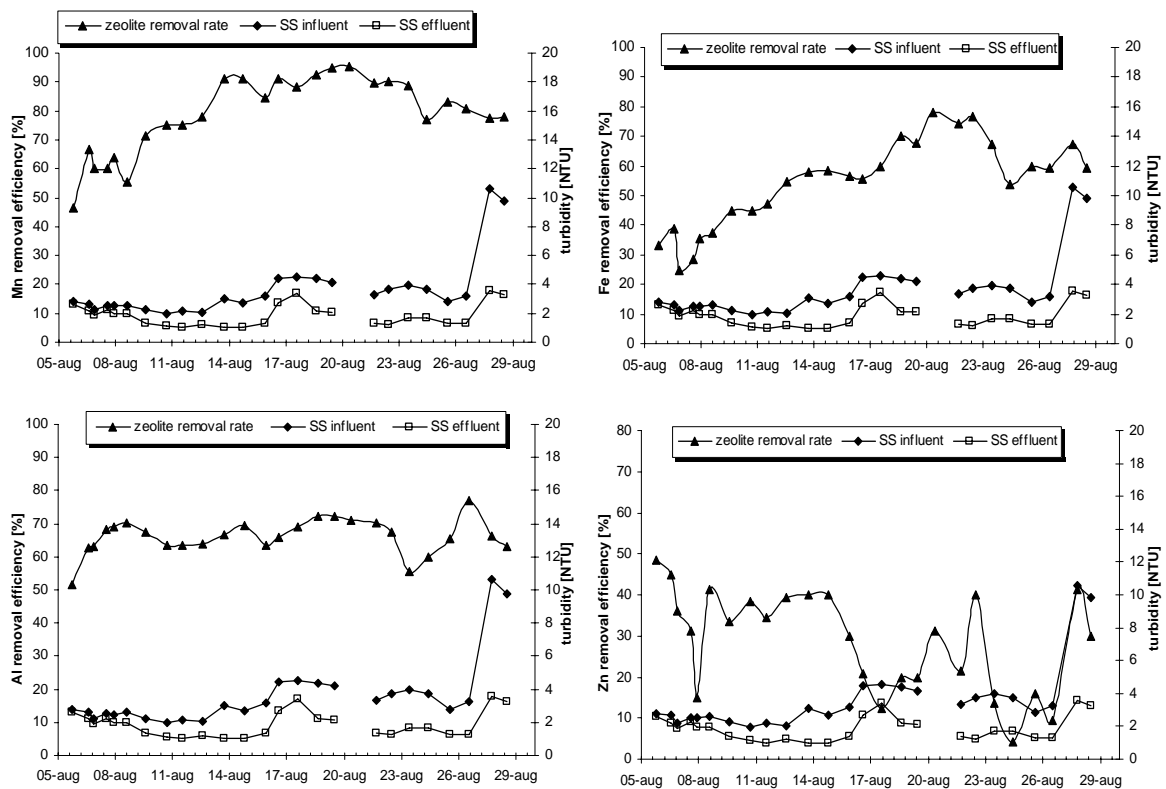
Figure 30. Increasing uptake of Mn, Fe, Al, and Zn by clinoptilolite at higher reduction of suspended solids (left axis shows percentage of metal uptake, right axis refers to the turbidity value [NTU]), saturated conditions

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Thus, the removal efficiency was found to be a very diverse and affected primarily by initial concentration of pollutants. The percentage of metal uptake increased with increase of concentration in influent. The effect of initial concentration on removal efficiency was already found in former trial and also confirmed by previous studies (Athanasiadis and Helmreich, 2005, Inglezakis and Grigoropoulou, 2004). Additionally, the enhanced removal percentage of Mn, Fe, Al and Zn by clinoptilolite was found again to be related with the increase of suspended solids in incoming water and its higher reduction, which is demonstrated on Figure 29. As it can be observed, the increased removal of suspension from incoming stormwater especially manganese and iron investigation showed such relation. This possibly indicates the removal of those metals mainly by mechanical filtration. Such results are probably related with high filtration velocity and consequently low contact time, which could be insufficient to achieve equilibrium of ion exchange by clinoptilolite. However, during the initial period of the trial recorded reduction of turbidity by the material was much lower but the uptake of Mn, Al and Zn was above 50 %. Only Fe removal rate increased with turbidity reduction. Thus, one can see that also the dissolved and colloidal form of those metals was possibly captured by clinoptilolite through ion exchange process. Still, it resulted in lower removal rates when less amount of suspension was kept by this material. The graph displayed Zn removal however showed much higher fluctuations independently on concentrations of the suspension. Yet, the tendency to uptake higher amount of the metal with increased reduction of suspension can be recognized (Figure 30).

The overall load of all monitored metals removed by material in mg/kg is presented in Table 18. Data indicate the amount of removed metals in particulate bound, colloidal and dissolved form for each tested filter material. Still, calculated sorption based only on limited data obtained from the sampling period 2005-08-05 and 2005-08-21and thus does not show total sorption capacity of materials. In order to estimate sorption from this particular period data of daily concentrations (influent and effluent) and volume of treated stormwater between each sampling were used again.

Table 18. Values for sorption by four selected media [mg/kg], saturated conditions (data from sampling period 2005-08-05/08-21)

Element	ZEOLITE reduction [mg/kg]	POLONITE reduction [mg/kg]	GAC 830W reduction [mg/kg]	GAC PK 3-5 reduction [mg/kg]
Fe	202.47	181.84	462.35	456.67
Al	61.09	-13.33	103.68	-43.69
Mn	19.46	22.31	40.83	49.04
Zn	13.36	15.08	34.15	46.84
Cu	1.92	1.36	12.91	14.02
V	0.38	-9.25	1.76	-1.17
Cr	0.35	-3.40	2.09	0.98
Pb	0.11	0.41	0.56	0.21
Ni	0.69	0.85	-1.70	3.62
Cd	0.010	0.014	0.039	0.052

The highest quantity of iron, aluminium, manganese and zinc has been reduced by the each examined filter material. The highest concentrations of those elements were, however, recognised in storm water incoming to the pilot plant. Therefore, those were competitive in sorption by the materials comparing to the other monitored elements. This could be explained also by the fact that those elements are bound to the particles of the solution and therefore are removed with suspended solids from water mechanically. The importance of those elements removal has been documented (Taillefert and Gaillard ,2001, Balistrier et al., 1992), since Their compounds such as hydrous oxides, sulphides or natural organic matter play fundamental role in scavenging and transport of trace elements in aquatic system.

The experiment conducted in hydraulic saturation also confirmed again the highest efficiency of finer activated carbon sorption. Thus, the difference in material performance was recognised as the effect of granules size. The courser GAC PK3-5 sorption was poorer that finer GAC 830W in case of all investigated metals (Table 17). The importance of grain size is know due to much larger surface area of reactive filters characterised by small grain diameter and thus the higher adsorption can be expected. Both forms of GAC however performed also with broad range in removal rate. Table 19 presents the highest daily-recorded reduction of metals and the lowest values, of removal efficiency achieved by the materials. The negative values indicate a release of element by the particular substrate.

Table 19. Maximum and minimum metal removal efficiency by both types of granulated activated carbon

Element	Finer GAC 830W		Courses GAC PK 3-5	
	Maximum [%]	**Minimum [%]**	**Maximum [%]**	**Minimum [%]**
Mn	95.5	44.4	86.4	24.4
Al	76.6	8.6	77.8	-189.7
Fe	82.7	26.7	67.4	12.5
Zn	59.4	13.8	51.7	20.7
Pb	75	-650	50	-300
Cu	77.8	37.5	77.8	11.1
Cr	80	40	50	0
V	66.7	-166	50	-150
Ni	0	-100	70	0
Cd	66.7	0	66.7	0

3.2.3. Comparison of materials efficiency under different hydraulic conditions

In both experiments the atmospheric conditions and mainly the intensity and frequency of rain events were similar. This favourably affected the obtained results and therefore they could be assumed as analogous. As a result of this, it is possible to compare the efficiency of the materials that were examined in two different hydraulic conditions, un-saturated and saturated. Daily concentrations of the investigated metals were also comparable in the case of lead, chromium, vanadium, nickel, and zinc. However, some particular daily monitored concentrations were much higher at the period trial in un-saturated conditions in the case of zinc, vanadium and nickel. Such elements as iron, aluminium, manganese and copper appeared generally in increased amounts during the whole period of the experiment in un-saturated conditions (Table 20). There was also the general tendency in both cases to occur significantly increased concentration of inflow after the most intensive rain events that appear randomly at the end of each trial period.

Table 20. Comparison of daily influent concentrations monitored during experiment (un-saturated 2005/07/07-29 and saturated conditions 2005/08/05-28), n.d. – no data

Element	The range of inflow concentrations (un-saturated conditions) [µg/l]	The range of inflow concentrations (saturated conditions) [µg/l]	Class*	Risk of biological effects *
Fe	440 – 1000 [1]	150 – 520	n.d.	n.d.
Al	32 – 450	29 – 220	n.d.	n.d.
Mn	15 – 95	8 – 45	n.d.	n.d.
Zn	22 – 47	24 – 34	III	Increased risk
Cu	9 – 42	7 – 11	III and IV	Increased risk
V	3 – 13	2 – 4	n.d.	n.d.
Ni	1 – 9	1 – 3	II	Little risk
Pb	0.8 – 5	0.5 – 10 [2]	II to IV	Little to increased risk
Cr	0.8 – 3	0.8 – 2	II	Little risk
Cd	<0.01 – 0.03	0.01 – 0.03	II	Little risk

* Classification according to the Swedish Environmental Protection Agency quality criteria for surface waters
[1] Singular concentration of Fe = 150 µg/ occurred at the end of trial
[2] Higher concentrations of Pb = 10 µg/l occurred only at the end of trial after intensive precipitation

From all monitored metals only nickel, chromium and cadmium occurred in low concentrations in stormwater that was supplied into the pilot plant. The other screened elements were found in high concentrations causing increased risk for the biological processes. All tested materials decreased the amount of metals to the level of low or moderately high concentrations, which refer to the little or increased risk of biological effects respectively. This was valid for both field trials; therefore the results obtained were reported as comparable in terms of the media performance and overall amount of the pollutants release with the effluents to the environment. The difference, however, appeared in case of copper concentrations in effluent of the clinoptilolite material that were higher at un-saturated conditions (Table 21). Still, also the influent concentrations were comparatively higher and because clinoptilolite performance of copper uptake was poor in both experiments, the increased concentrations in outflow solution were found as well.

Table 21. Comparison of daily concentrations in effluent from clinoptilolite column monitored during experiment (un-saturated 2005/07/07-29 and saturated conditions 2005/08/05-28), n.d. – no data

Element	The range of clinoptilolite effluent concentrations (un-saturated conditions) [µg/l]	Class*	The range of clinoptilolite effluent concentrations (saturated conditions) [µg/l]	Class*	Risk of biological effects *
Fe	120 – 380	n.d.	56 – 170	n.d.	n.d.
Al	20 – 100	n.d.	13 – 81	n.d.	n.d.
Mn	2 -42	n.d.	1 -24	n.d.	n.d.
Zn	12 – 25	II – III	16 – 28	II – III	Little to increased risk
Cu	7 – 28	III – IV	6 – 9	III	Increased risk
V	3 – 7		1 – 3		
Ni	2 – 6	II	1 – 2	II	Little risk
Pb	0.4 – 3	III	0.2 – 3	III	Increased risk
Cr	0.6 – 3	II	0.5 – 2	II	Little risk
Cd	<0.01 – 0.05	I – II	0.01 – 0.04	I – II	None to little risk

The case study also revealed no significant differences between each field trial of Polonite® and GAC material performance efficiency. Also, in terms of metals discharge into the environment by all tested substrates the obtained results were similar which can be observed from data presented in Tables 22 and 23 below. The tables show the range of effluent concentrations and related classes of surface water quality that were comparable for both experiments in un-saturated and saturated conditions.

Table 22. Comparison of daily concentrations in effluent from Polonite® column monitored during experiment (un-saturated 2005/07/07-29 and saturated conditions 2005/08/05-28), n.d. – no data

Element	The range of Polonite effluent concentrations (un-saturated conditions) [µg/l]	Class*	The range of Polonite effluent concentrations (saturated conditions) [µg/l]	Class*	Risk of biological effects *
Fe	260 – 780	n.d.	110 – 290	n.d.	n.d.
Al	35 – 290	n.d.	55 – 160	n.d.	n.d.
Mn	4 – 42	n.d.	3 – 27	n.d.	n.d.
Zn	12 – 33	II – III	15 – 30	II – III	Little to increased risk
Cu	7 – 13	III – IV	6 – 9	III – IV	Increased risk
V	6 – 47	n.d.	2 – 54	n.d.	n.d.
Ni	2 – 3	II	1 – 2	II	Little risk
Pb	0.7 – 4	II – IV	0.3 – 6	II – IV	Little to increased risk
Cr	0.8 – 28	II – IV	0.9 – 20	II – IV	Little to increased risk
Cd	<0.01 – 0.03	II	0.01 – 0.04	II	Little risk

Table 23. Comparison of daily concentrations in effluent from GAC 830W column, monitored during experiment (un-saturated 2005/07/07-29 and saturated conditions 2005/08/05-28), n.d. – no data

Element	The range of GAC effluent concentrations (un-saturated conditions) [µg/l]	Class*	The range of GAC effluent concentrations (saturated conditions) [µg/l]	Class*	Risk of biological effects *
Fe	86 – 350	n.d.	47 – 120	n.d.	n.d.
Al	12 – 120	n.d.	15 – 53	n.d.	n.d.
Mn	1 – 29	n.d.	1 – 25	n.d.	n.d.
Zn	8 – 21	II – III	13 – 25	II - III	Little Increased risk
Cu	2 – 7	II – III	2 – 5	II – III	Little Increased risk
V	3 – 22	n.d.	1 – 8	n.d.	n.d.
Ni	1 – 4	II	1 – 4	II	Little risk
Pb	0.4 – 3	II – III	0.4 – 3	II – III	Little Increased risk
Cr	0.4 – 3	II	0.4 – 0.6	II	Little risk
Cd	<0.01 – 0.02	I – II	<0.01 – 0.04	I - II	None to little risk

The fact that the efficiencies of the materials were analogous in the case of experiment conducted in un-saturated and saturated conditions can be explained by the hydraulic performance of the columns. During the period when the columns were set to operate in the aeration, for most of the time complete saturation arose as the result of high hydraulic load. Thus, the aim to create two experiments with different hydraulic conditions can be assumed as unsuccessful.

Apart from monitored metals also the total organic carbon (TOC) parameter indicating the amount of organic matter was measured. With the aim to assess the efficiency of organic matter removal by the materials the daily concentrations were displayed on the Figure 31. It can be seen that the concentration in incoming stormwater were low or moderately high often below 10 mg/l, according to the Swedish Environmental Protection Agency criteria for lakes and watercourses (Table 24). Similar concentrations were recorded for both experiments.
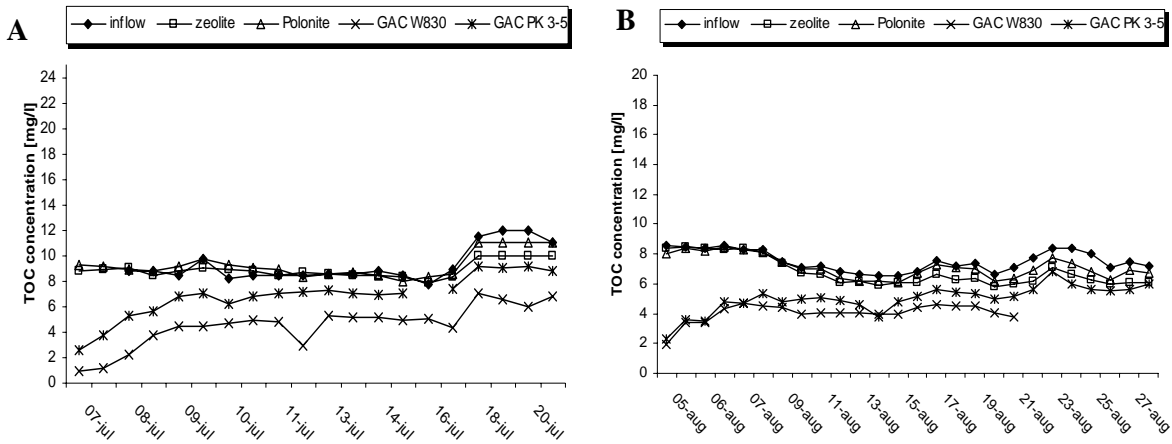
Figure 31. TOC reduction by filter selection in un-saturated (A) and saturated (B) conditions (the singular value of 24 mg/l of GAC PK3-5 was excluded from the graph as assumed error)

Table 24. Classification of organic metter concentration in lakes and watercourses according to the Swedish Environmental Protection Agency criteria, TOC – total organic carbon

Class	Level	Level of TOC (mg/l)
1	Very low	< 4
2	Low	4-8
3	Moderately high	8-12
4	High	12-16
5	Very high	< 16

In both cases the same results on the removal efficiency were obtained. Thus, Polonite® and clinoptilolite materials performed poorly while both forms of activated carbon showed expected reduction of organic matter. TOC removal was also observed to have a decreasing tendency in time due to the clogging phenomenon. Yet, finer GAC 830W decreased TOC concentration to the values of around 4 mg/l, which is defined as very low or low concentrations according to the SEPA criterion. Courser GAC PK3-5 achieved the concentrations level approximately 7 – 9 mg/l in un-saturated conditions and up to 5 mg/l in constant hydraulic saturation. Thus, the difference can not be found either in the removal of organic matter in both trials, since the effluent concentrations were rather related to the level of TOC in aqueous solution distributed into the pilot plant. However, the main part of organic carbon concentrations in the influent was the dissolved part, which shows Figure 32. Thus, the removal of those substances by activated carbons was the most efficient. Also it was confirmed that such nutrients as nitrogen and phosphorus appeared in the storm water in very

low concentrations, and therefore was very poorly removed by all tested materials (Figure 33, 34).
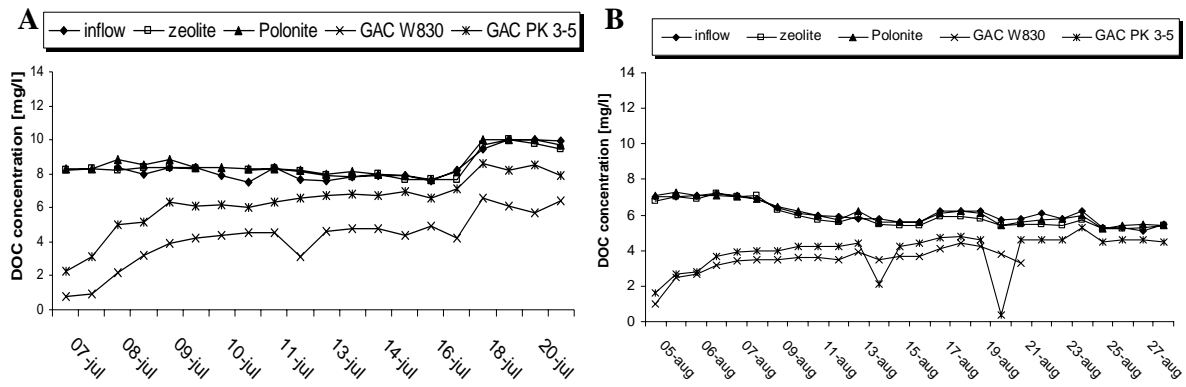

Figure 32. DOC reduction by filter selection in un-saturated (A) and saturated (B) conditions experiment
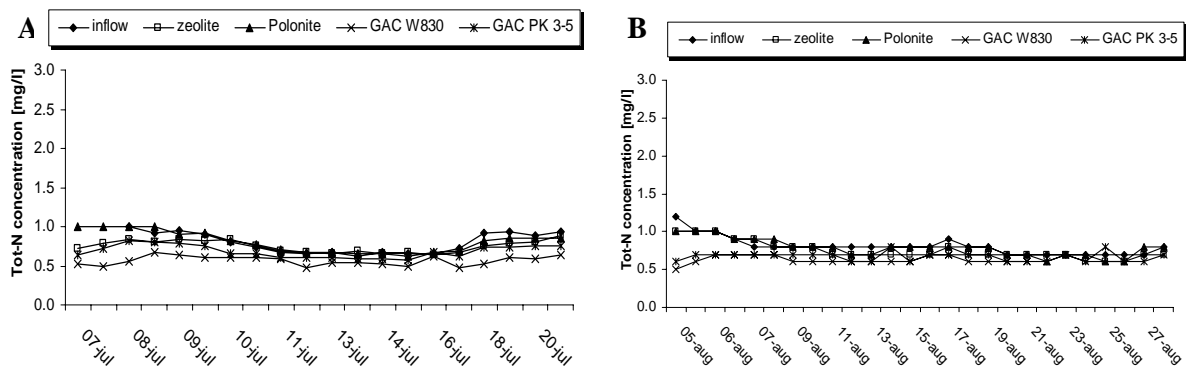

Figure 33. TOT – N reduction by filter selection in un-saturated (A) and saturated (B) conditions experiment
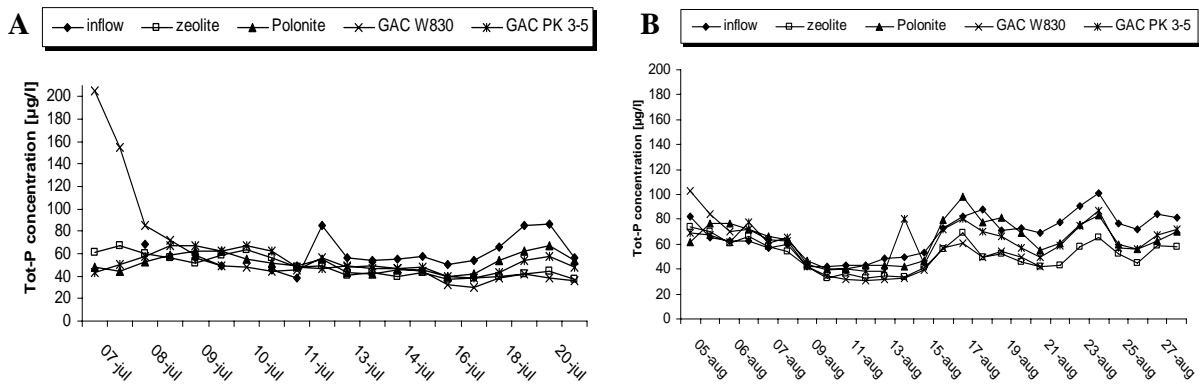

Figure 34. TOT – P reduction by filter selection in un-saturated (A) and saturated (B) conditions experiment

4. Conclusions

The most important question in this study concerned the investigations of different filter materials that could be used for pollution control with special regard to the metals uptake. All the experiments were conducted in real environment using the stormwater as the treated solution within pilot plant at Lilla Essingen. Selection of substrate was investigated to indicate the material that achieved the best results in sorption and hydraulic performance.

The most important findings were:

- The first column experiment brought an immediate knowledge concerning mostly hydraulic properties of the materials. All the substrates showed a tendency of rapid hydraulic clogging if were installed as a raw material without cleaning and sieving and thus with wide range in grain's size.

- The reduction efficiency of such metals as Cd, Pb, Cr and Ni was found to be very low for all tested materials as the results of low concentrations in influent, which was distributed to the pilot plant. Thus it was assumed that competitive role of those metals was rather less in the adsorption process in all conducted experiments.

- All examined materials were recognised to be efficient in the case of manganese, iron, aluminium and zinc removal which was related to the mechanical filtration and reduction of suspension containing complexes of Fe, Mn, Zn and Al.

- All screened metals showed large differences in their removal by all tested substrates, which was mainly depended on the concentrations in the influent.

- The removal efficiency differed also for each filter material, still it remained rather low for all media comparing to the other reviewed studies as the possible effect of high hydraulic load. Thus it was found that higher contact time could increase the efficiency of metals sorption.

- The clinoptilolite material and the finer GAC 830W were found to be the most efficient in metals uptake in the column experiments and in the particular conditions. However, cleaned and sieved Polonite® material achieved the best results in terms of hydraulic performance.

- It can be finally concluded that the pre-concentration of metals was the main factor that affected the selective removal, but also the occurrence of other chemical compounds that constitute strong complexants was of importance.

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Appendix 1

Table 1. Field measurements and sampling for field trials – 2.5 m/h

Date	Time	pH, Conductivity, Turbidity, Temperature, flow	Water sampling for heavy metals analysis	Water sampling for TOC, DOC, COD, Tot-N, Tot-P analysis
2005-06-23	09:58	X	X	X
2005-06-23	16:45	X	X	X
2005-06-24	11:53	X	X	X
2005-06-24	15:40	X	X	X
2005-06-25	14:30	X	X	X

Table 2. Field measurements and sampling for field trials - 1 m/h, un-saturated conditions

Date	Time	pH, Conductivity, Turbidity, Temperature, flow	Water sampling for heavy metals analysis	Water sampling for TOC, DOC, Tot-N, Tot-P analysis
2005-07-07	18:30	X	X	X
2005-07-08	11:30	X	X	X
2005-07-08	19:50	X	X	X
2005-07-09	09:50	X	X	X
2005-07-09	20:30	X	X	X
2005-07-10	10:50	X	X	X
2005-07-10	19:00	X	X	X
2005-07-11	11:00	X	X	X
2005-07-11	20:00	X	X	X
2005-07-12	10:30	X	X	X
2005-07-12	19:30	X		
2005-07-13	11:00	X	X	X
2005-07-13	19:00	X	X	X
2005-07-14	11:00	X	X	X
2005-07-15	11:00	X	X	X
2005-07-16	12:00	X	X	X
2005-07-17	13:00	X	X	X
2005-07-18	12:00	X	X	X
2005-07-19	16:30	X	X	X
2005-07-20	11:00	X	X	X
2005-07-21	19:30	X		
2005-07-22	11:00	X	X	X
2005-07-23	11:30	X		
2005-07-23	20:00	X		
2005-07-24	12:30	X		
2005-07-25	10:00	X	X	
2005-07-26	07:00	X		
2005-07-27	11:00	X	X	
2005-07-29	10:00	X	X	
2005-07-31	12:00	X		
2005-08-01	17:00	X		
2005-08-02	19:00	X		
2005-08-03	16:00	X		

Table 3. Field measurements and sampling for field trials - 1 m/h, saturated conditions

Date	Time	pH, Conductivity, Turbidity, Temperature, flow	Water sampling for heavy metals analysis	Water sampling for TOC, DOC, Tot-N, Tot-P analysis
2005-08-05	18:00	X	X	X
2005-08-06	13:30	X	X	X
2005-08-06	20:30	X	X	X
2005-08-07	13:30	X	X	X
2005-08-07	22:00	X	X	X
2005-08-08	14:00	X	X	X
2005-08-09	14:30	X	X	X
2005-08-10	16:45	X	X	X
2005-08-11	12:00	X	X	X
2005-08-12	14:00	X	X	X
2005-08-13	17:30	X	X	X
2005-08-14	18:00	X	X	X
2005-08-15	21:00	X	X	X
2005-08-16	14:00	X	X	X
2005-08-17	13:30	X	X	X
2005-08-18	15:00	X	X	X
2005-08-19	11:00	X	X	X
2005-08-20	08:00		X	X
2005-08-21	16:30	X	X	X
2005-08-22	11:00	X	X	X
2005-08-23	10:45	X	X	X
2005-08-24	10:45	X	X	X
2005-08-25	13:30	X	X	X
2005-08-26	12:45	X	X	X
2005-07-27	18:30	X	X	X
2005-07-28	12:30	X	X	X
2005-07-29	11:00	X		
2005-07-30	10:30	X		

Table 4. Classification of metals concentration in lakes and watercourses according to the
Swedish Environmental Protection Agency criteria

Concentration	Class 1 Very low	Class 2 Low	Class 3 Moderately high	Class 4 High	Class 5 Very high
µg/l					
Arsenic	< 0.4	0.4-5	5-15	15-75	> 75
Cadmium	< 0.01	0.01-0.1	0.1-0.3	0.3-1.5	> 1.5
Chromium	< 0.3	0.3-5	5-15	15-75	> 75
Copper	< 0.5	0.5-3	3-9	9-45	> 45
Nickel	< 0.7	0.7-15	15-45	45-225	> 225
Lead	< 0.2	0.2-1	1-3	3-15	> 15
Zinc	< 5	5-20	20-60	60-300	> 300
Risk of biological effects					
	None or very little	Little	Primarily in acidic water and in soft water with low concentrations of humus and nutrients	Increased risk	High risk even with brief exposure