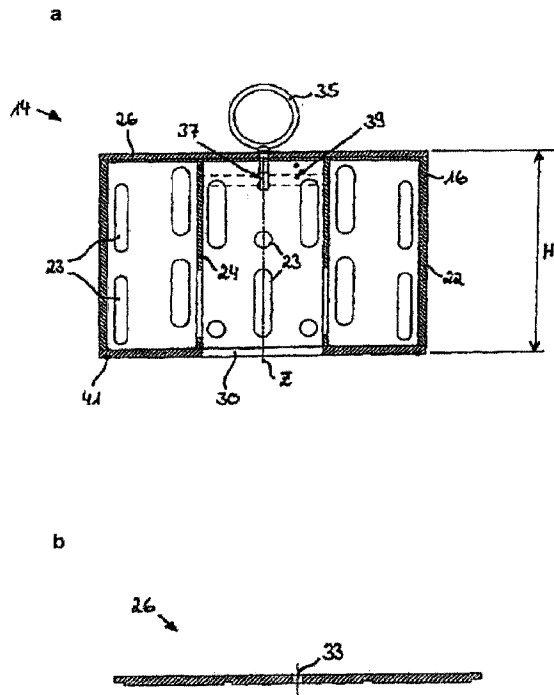




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(57) Abrégé/Abstract:

The present invention relates to a composition, in particular for immobilising metal ions, comprising at least one iron hydroxide and at least one porous carrier material, to a filter apparatus or a wastewater treatment device, comprising said composition, and to the use thereof for treating wastewater.

Abstract

The present invention relates to a composition, in particular for immobilising metal ions, comprising at least one iron hydroxide and at least one porous carrier material, to a filter apparatus or a wastewater treatment device, comprising said composition, and to the use thereof for treating wastewater.

Composition for immobilising metal ions

Description

The present invention relates to a composition, in particular for immobilising metal ions, comprising at least one iron hydroxide and at least one porous carrier material, to a filter apparatus or a wastewater treatment device, comprising said composition, and to the use thereof for treating wastewater.

Precipitation that in particular runs off road surfaces is often contaminated with a plurality of substances (e.g. heavy metals, polycyclic aromatic hydrocarbons and de-icing salts) and requires treatment before seeping or discharging into water systems.

In recent years, numerous decentralised treatment systems have been developed as alternatives to central systems, such as rain sedimentation tanks or retention soil filters, for traffic area drains. Usually, the contaminants from traffic area drains are adsorbed on suitable filter media in the decentralised systems.

Conventional wastewater treatment devices are supplied by the applicant under the name "SediSubstrator®", for example. Wastewater treatment devices of this type are disclosed in DE 10 2010 040 645 or DE 10 2008 007 227, for example. While sedimentable solids are first separated in the first purification stage of the system, the pre-treated wastewater is then fed into a filter apparatus in a second purification stage, in which filter apparatus the impurities remaining in the wastewater, for example dissolved metal ions, in particular heavy metal ions, oil particles etc., are separated. The purified wastewater is largely free of substances that are harmful to the environment, and after treatment can be discharged into the environment without any concerns.

The filter apparatuses are in particular designed to immobilise metal ions remaining in the wastewater, especially heavy metal ions. Filter apparatuses or filter media are replaced and professionally disposed of in a specific cycle (after which almost complete loading is assumed). The cycle should not be less than three years in order to be able to ensure economical operation of the systems. For this reason, the loading capacity of the filter media

for metal ions should be as high as possible. Materials based on carbonates, coal, coke or aluminium oxide are currently used as suitable filter media.

However, it has been found that wastewater that contains de-icing salts (gritting salt), which are usually used in winter maintenance operations for preventing the formation of ice, causes the impurities, in particular metal ions, already immobilised in the filter medium to be remobilised (desorbed). Solid gritting salts, such as sodium chloride, are used as de-icing salt. Recently, so-called wet salts have also been used, in which case the gritting salt is applied to the street already in liquid form or as an aqueous suspension. Wet salts of this type dampen better and can be applied more sparingly in comparison with "dry" gritting salt. Salts or salt mixtures that ensure a longer-lasting de-icing effect and can lower the freezing point more effectively are preferably used as wet salts. In particular, mixtures of sodium chloride and calcium chloride or sodium chloride and magnesium chloride are used as wet salts. Hilliges et al. (J. Environ. Man., Volume 128, 2013, pages 306-312) investigated the contaminant remobilisation from treatment systems for traffic area drains by exposure to gritting salt. In the study, the remobilisation of heavy metals already immobilised on filter media (e.g. brown coal coke or hard coal) under the influence of wastewater containing de-icing salts was scientifically proven for the first time.

The object of the present invention is therefore to provide filter media that have reduced remobilising (desorption) of immobilised contaminants under the influence of wastewater containing salt.

This object is achieved according to the invention by a composition, comprising (i) at least one iron hydroxide and (ii) at least one porous carrier material. The composition is particularly suitable for immobilising metal ions and also demonstrates a reduced tendency of remobilisation or desorption in the presence of gritting salt (in particular sodium chloride, magnesium chloride, calcium chloride and mixtures thereof).

In a preferred embodiment, the composition further comprises (iii) calcium carbonate and optionally (iv) at least one manganese oxide.

In a preferred embodiment, the composition comprises (i) at least one iron hydroxide, (ii) at least one porous carrier material, (iii) calcium carbonate and (iv) at least one manganese oxide.

At least one iron(III) hydroxide ($\text{Fe}(\text{OH})_3$) or iron(III) oxide-hydroxide is preferably used as component (i), more preferably selected from bog iron ore ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $2\text{FeO}(\text{OH}) \cdot 2\text{H}_2\text{O}$), limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $4\text{FeO}(\text{OH}) \cdot \text{H}_2\text{O}$), jarosite ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ or $2\text{FeO}(\text{OH}) \cdot \text{H}_2\text{O}$) and goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{FeO}(\text{OH})$).

The composition preferably contains approximately 30-80 wt.%, more preferably 40-70 wt.%, component (i), based on the total composition.

The porous carrier material (ii) may be an organic or inorganic, preferably an inorganic, material. Preferably, the porous carrier material is an alkaline material. An alkaline carrier material within the meaning of the present invention has a pH of > 7 , preferably > 7.5 , more preferably > 8 and most preferably between 8 and 9, in an aqueous suspension (20 wt.%) at 20°C .

The porous carrier material (ii) preferably has a pore volume of at least 20-80%, preferably 40-60%. The specific surface area of the porous carrier material (ii) is preferably in the range of $100\text{-}400\text{ m}^2/\text{g}$, more preferably $250\text{-}350\text{ m}^2/\text{g}$ (measured according to BET, DIN ISO 9277:2003-05). Component (ii) is preferably in the form of a granulate. In this case, the mean particle size is preferably approximately 0.5-10 mm, more preferably 1.0-6 mm and even more preferably 1.0-4.5 mm. The bulk density of the porous carrier material (ii) is preferably between $300\text{ and }600\text{ kg/m}^3$, more preferably between $400\text{ and }500\text{ kg/m}^3$.

In a preferred embodiment, the porous carrier material (ii) is based on coal or carbonate, e.g. alkaline earth carbonate (magnesium carbonate, calcium carbonate and mixtures thereof, in particular calcium carbonate), more preferably on coal. Preferably, component (ii) is a coke material that is optionally modified. Brown coal coke or hard coal coke, more preferably brown coal coke, are particularly suitable. In a preferred embodiment, the coke can be modified by sulphur and/or sulphur compounds, in particular by at least one polysulphide. In this case, the coke material preferably contains 0.3-0.8 wt.%, more preferably 0.4-0.6 wt.%, sulphur, based on the total weight of the coke material. The modification of the coke material by sulphur and/or sulphur compounds can take place by methods known to a person skilled in the art. Preferably, the coke materials are modified according to the method disclosed in DE 10 2006 050 987, to which reference is made herein. In a particularly preferred

embodiment, the porous carrier material (ii) is a brown coal coke modified by at least one polysulphide.

The porous carrier material (ii) is preferably present in a proportion of approximately 20-50 wt.%, preferably 20-30 wt.%, based on the total composition.

In a preferred embodiment, the composition contains calcium carbonate, in particular in a proportion of approximately 0-30 wt.%, preferably 5-30 wt.% and more preferably 7-25 wt.%, based on the total composition.

The composition according to the invention may further contain at least one manganese oxide, preferably manganese(III) oxide or manganese(IV) oxide, in particular MnO_2 .

The proportion of component (iv) in the total composition is preferably approximately 0-10 wt.%, more preferably 0.05-8 wt.%, even more preferably 0.5-5 wt.%.

In a preferred embodiment, component (i) and optionally component (iii) and optionally component (iv) are in the form of a granulate. A granulate within the meaning of the present invention consists of many small, solid particles, such as grains or spheres. The granulate preferably has a mean particle size (e.g. d_{50} measured according to DIN 18123) of 0.2-5 mm, more preferably 1.0-3.0 mm. Values of at least 50%, preferably 70-95%, in particular have proven to be a suitable granulate porosity.

The granulate containing components (i) and optionally (iii) and optionally (iv) preferably has a specific surface area (according to BET) of 100-500 m^2/g , more preferably 200-350 m^2/g . Further, the granulate preferably has a bulk density of 400-800 kg/m^3 , more preferably 500-700 kg/m^3 .

Preferably, the composition comprises

- (a) at least one granulate made up of components (i) and optionally (iii) and optionally (iv), and
- (b) at least one porous carrier material (ii).

In a more preferred embodiment, the composition comprises

(A) at least one granulate made up of components (i) and optionally (iii) and optionally (iv), and

(B) at least one porous carrier material in the form of a granulate as defined above.

Components (a) or (A) to (b) or (B), respectively, are preferably in a weight ratio of from 80:20 to 65:35, more preferably from 80:20 to 70:30, even more preferably from 78:22 to 70.4:29.6.

In another embodiment, the volume ratio of components (a) or (A) to (b) or (B), respectively, is in the range of from 2:1 (i.e. one part by volume (a) or (A) to one part by volume (b) or (B), respectively) to 5:1 (i.e. four parts by volume (a) or (A) to one part by volume (b) or (B), respectively), preferably 3:1 to 4:1.

In a preferred embodiment, the composition comprises: (i) at least one iron hydroxide, (ii) at least one porous carrier material, in particular coke modified by sulphur and/or sulphur compounds, and (iii) calcium carbonate.

In a further preferred embodiment, the composition comprises: (i) at least one iron hydroxide, (ii) at least one porous carrier material, in particular coke modified by sulphur and/or sulphur compounds, (iii) calcium carbonate and (iv) at least one manganese oxide.

In a further preferred embodiment, the composition comprises: (i) at least one iron hydroxide, (ii) at least one porous carrier material, in particular coke modified by sulphur and/or sulphur compounds, and (iv) at least one manganese oxide.

In a preferred embodiment, the components (i)-(iv) are present in the composition as homogenous mixture, as mixture having a gradient, or in separate layers.

In a further preferred embodiment, the at least one porous carrier material (b) or (B) and the granulate (a) or (A), respectively, are present in the composition as homogenous mixture, as mixture having a gradient, or in separate layers. A homogenous mixture that can be obtained by mixing components (a) or (A) and (b) or (B), respectively, is preferred. During mixing, abrasion of the materials should be avoided. Components (a) or (A) and (b) or (B), respectively, may be in separate layers, e.g. inside a container. The separate layers may have different thicknesses. Preferably, the layers (a) or (A) and (b) or (B), respectively,

alternate. In a preferred embodiment, layering occurs in such a way that the wastewater to be purified flows first through the layer (a) or (A) and then through the layer (b) or (B), respectively, in the direction of flow.

A further aspect of the present invention relates to a filter apparatus, in particular for treating wastewater, comprising a composition according to the invention as a filter medium. The filter apparatus preferably comprises a housing having a plurality of openings, optionally a mesh layer and optionally a drain layer. The housing is advantageously formed such that the filter medium can be received by the housing.

The housing of the filter apparatus may be substantially cylindrical. According to the general definition of a cylinder, said cylinder is produced by a self-contained curve that is in a plane being displaced along a straight line that is not in said plane. In order to allow the wastewater to be filtered to flow in as uniformly as possible, it is advantageous for the housing to be substantially in the shape of a straight cylinder. In principle, however, other shapes, such as a cuboid shape, are conceivable. In a preferred embodiment, the wastewater flows against the housing of the filter apparatus horizontally, i.e. the longitudinal axis of the housing is perpendicular to the expected wastewater flow. In another embodiment, the flow encounters the closed curve vertically, i.e. the direction of flow and the longitudinal axis of the housing extend mutually parallel.

In an advantageous development of the invention, it is proposed that the housing of the filter apparatus comprise an outer peripheral wall that extends around a substantially vertical axis (longitudinal axis) and an inner peripheral wall that extends around a substantially vertical axis, which walls form a receiving space therebetween for the filter medium and are each formed in such a way that wastewater can flow therethrough. Furthermore, the housing may have an upper boundary wall that seals the housing at the top in a completely fluid-tight manner, while a lower boundary wall that is also sealed against wastewater seals merely the receiving space in a fluid-tight manner at the bottom. The filter medium can be inserted into the receiving space of the filter apparatus from above, the inner and outer peripheral wall of the filter housing that are formed in such a way that wastewater can flow therethrough enclosing the filter medium. In order to prevent unfiltered wastewater being able to flow into the inner region of the filter apparatus that does not contain a filter medium, said apparatus comprises the upper boundary wall, which seals the housing at the top in a completely fluid-tight manner. It is therefore ensured that only wastewater that is filtered by the filter medium

enters the inner region of the filter apparatus that does not contain a filter medium. From this inner region, the filtered wastewater can then flow out through one or more apertures provided in the lower boundary wall.

The upper boundary wall may furthermore comprise a hooking device, such as a ring, for lifting or lowering at least one portion of the filter apparatus.

In a development of the invention, it is further proposed that the outer peripheral wall and the inner peripheral wall of the housing each have a plurality of openings through which wastewater can flow, a drain layer being arranged in each case between the filter medium on one side and the outer peripheral wall and/or the inner peripheral wall on the other side, and a mesh layer being arranged preferably between the outer peripheral wall or the inner peripheral wall and the drain layer associated with said wall in each case, which mesh layer has a mesh size that is smaller than the smallest particle size of the filter medium used.

The mesh layer, which is also known by the term "gauze layer", can securely seal the filter medium inside the filter housing virtually as a "pack", the mesh size of the mesh layer having to be matched to the particle size of the filter medium used. In this way, it is possible to take the filter medium in its entirety out of the filter housing or insert it therein. In this case, the drain layer may be arranged in the manner of a spacer between the mesh layer on one side and the outer peripheral wall or the inner peripheral wall of the filter housing on the other side in each case. The drain layer is used to distribute the wastewater flowing into the receiving space for the filter medium over the entire outer lateral surface of the filter medium as uniformly as possible or to collect the wastewater flowing out of the receiving space for the filter medium over the entire inner lateral surface of the filter medium and feed said wastewater to the openings. The efficiency of the filter medium can therefore be utilised in the best possible manner. The drain layer may be, for example, a three-dimensional, mat-like plastics product. The mesh layer is preferably made of natural or synthetic non-woven material.

A preferred filter apparatus is disclosed in DE 10 2010 040 645, to which reference will be explicitly made herein.

In the filter apparatus, the filter medium is, as described above, preferably a homogenous mixture, a mixture having a gradient, or in separate layers. A homogenous mixture that can

be obtained by mixing components (i)-(iv), or (a) or (A) and (b) or (B), respectively, is preferred. If the components are in separate layers, the layers are preferably arranged in such a way that the wastewater to be purified flows first through the layer of component (i) and optionally (iii) and optionally (iv), or (a) or (A), respectively, and then through the layer of component (ii), or (b) or (B), respectively, in the direction of flow.

In a further aspect, the present invention is directed to a wastewater treatment device, comprising a wastewater inlet, a wastewater outlet and a composition or filter apparatus according to the invention. Preferably, the wastewater treatment device comprises a wastewater inlet, a wastewater outlet and at least one filter apparatus, as described above, that is fluidically arranged between the wastewater inlet and the wastewater outlet. In a preferred embodiment, systems for rain water management, as disclosed in DE 10 2008 007 227, or wastewater treatment devices, as disclosed in DE 10 2010 040 645, are used. Reference is explicitly made herein to the system or the device in the patent applications, respectively.

A further aspect of the invention is the use of the composition according to the invention as a filter medium.

A further aspect of the invention is the use of the composition according to the invention or of the filter apparatus according to the invention or of the wastewater treatment device according to the invention for treating wastewater, in particular rain water. The composition, filter apparatus and/or wastewater treatment device is used in particular to immobilise, in particular adsorb, metal ions, in particular heavy metal ions, from the wastewater, in particular rain water. The composition, filter apparatus and/or wastewater treatment device is in particular suitable for immobilising copper, zinc, nickel, cadmium and/or lead, in particular copper and zinc, from the wastewater at the filter medium.

It has been found that the compositions described above have a high absorption capacity, i.e. can immobilise, in particular adsorb, large amounts of metal ions. Surprisingly, it has been found that the immobilised contaminants, in particular metal ions, cannot be released or can hardly be released from the composition according to the invention even under the impact of de-icing salts, which are used in winter maintenance operations for de-icing roads, for example. Changing the composition or filter apparatus according to the invention

preferably in a cycle of 3-5 years ensures that the treated wastewater is substantially not contaminated by metal ions, even in the winter when gritting salts are used.

A further aspect of the invention is directed to a method for treating wastewater, the wastewater being brought into contact with the composition according to the invention or the filter device according to the invention. In another aspect of the invention, the method for treating wastewater comprises wastewater flowing through the wastewater treatment device according to the invention.

The invention is explained in the following by way of example.

Drawings

Fig. 1a is a detailed illustration of the housing of the filter apparatus;

Fig. 1b is a detailed illustration of a cover of the housing illustrated in Fig. 1a;

Fig. 2 is a detailed sectional view of the housing illustrated in Fig. 1a, which encloses a filter medium;

Fig. 3 shows the design of the measuring cylinder for the remobilisation experiments;

Fig. 4 shows the experiment set-up for the remobilisation experiments;

Fig. 5 shows measurement results for the filter medium according to the invention (volume ratio 4:1);

Fig. 6 shows measurement results for the filter medium according to the invention (volume ratio 3:1);

Fig. 7 shows measurement results for the filter medium of the prior art (left-hand column); and

Fig. 8 shows measurement results for the filter medium of the prior art (right-hand column).

Examples

Example 1 – Design of a filter apparatus according to the invention

A preferred embodiment of the filter apparatus is shown in Fig. 1 and 2. The filter device (14) comprises a housing (16), which is designed to receive a filter medium (18) (see Fig. 2). In this case, the filter housing (16) substantially has the form of a straight, hollow circular cylinder, the cylinder axis Z being oriented vertically. The filter housing (16) comprises a

radially outer peripheral wall (22) that is formed such that the wastewater can flow therethrough in the horizontal direction substantially on all sides thereof, and a radially inner peripheral wall (24) that is formed such that the wastewater can flow therethrough in the horizontal direction substantially on all sides thereof, each of said walls having a plurality of substantially evenly distributed openings (23) through which the wastewater can flow through the walls. The radially outer peripheral wall (22) forms, together with the radially inner peripheral wall (24), a receiving space for the filter medium (18). It should be noted here that only the empty filter housing (16), i.e. the filter housing (16) without the filter medium (18), is shown in Fig. 1a, whereas Fig. 2 shows a section perpendicular to the cylinder axis Z of the filter housing (16) having the filter medium (18).

As is merely implied in Fig. 2, the filter medium (18) can be securely enclosed by a mesh layer (31), which is also known as a gauze layer, virtually as a pack inside the hollow-cylinder-shaped filter housing (16), the mesh size of the mesh layer (31) having to be matched to the particle size of the filter medium (18) used. The mesh size of the mesh layer can therefore be 0.5 mm if the filter substrate has a particle size of 1-2 mm, for example.

A drain layer (29) is also merely implied in Fig. 2, which drain layer can be arranged between the mesh layer (31) on one side and the outer peripheral wall (24) or the inner peripheral wall (22) on the other side in the manner of a spacer. The drain layer (29) is used to distribute the wastewater flowing into the receiving space for the filter medium (18) over the entire outer lateral surface of the filter medium (18) as uniformly as possible or to collect the wastewater flowing out of the receiving space for the filter medium (18) over the entire inner lateral surface of the filter medium (18) and feed said wastewater to the openings (23). The efficiency of the filter medium (18) can therefore be utilised in the best possible manner. The drain layer (29) is, for example, a three-dimensional, mat-like plastics product.

The housing (16) is delimited at the bottom by a lower boundary wall, which seals only the receiving space for the filter medium (18) at the bottom in a fluid-tight manner, but has an aperture (30) in the centre, through which aperture the wastewater purified by the filter medium (18) can flow out.

At the top, the housing (16) is sealed over its entire surface in a fluid-tight manner by an upper boundary wall (26) in the form of a cover that can be removed from the rest of the housing (16). The upper boundary wall (26) is shown again separately in Fig. 1b. In the

present embodiment, the wall comprises a through-hole (33) in the centre, through which a pin having a ring (35) at the upper longitudinal end thereof can be guided, as a result of which the through-hole (33) is sealed in a fluid-tight manner. The pin comprising the ring (35) comprises a thread (37) at the lower longitudinal end thereof. As shown by the dashed line in Fig. 1a, a flat bar (39) comprising a threaded hole can be rigidly connected to the rest of the filter housing (16). In this case, the thread (37) on the pin comprising the ring (35) can mesh with the threaded hole in the flat bar (39). In order to change the filter medium (18), the entire filter apparatus (14) can therefore be lifted or lowered by means of a hoist, which is usually provided on cleaning vehicles, and which can be meshed with the ring (35) in a simple manner.

Example 2 – Impact of de-icing salts on remobilising metal ions retained by filter media

Materials and analysis methods

For the entire test, the drinking water from the research campus of the Technical University of Munich in Garching was used as feed water having an electrical conductivity (EC) of approximately 580 $\mu\text{S}/\text{cm}$, which drinking water was artificially enriched with the de-icing salts sodium chloride, calcium chloride and magnesium chloride. The chemicals used for the de-icing salts were sodium chloride (25 kg PE bag, esco – european salt company GmbH & Co. KG), calcium chloride dried, pulverised, ultra-pure (5 kg, APPCA1426.5000, AppliChem GmbH) and magnesium chloride hexahydrate, ultra-pure (5 kg, APPCA1447.5000, AppliChem GmbH). The pH of the solution was not changed in the storage container, and was therefore in the range between 6.7 and 8.9. No buffer was added, so that the pH of the water in the system could change rapidly according to the conditions prevailing therein.

SediSorp® (HeGo Biotec) on one hand and a mixture of SediSorp® and Herdofenkoks (rotary-hearth furnace coke) HOK® granulate (RWE Power AG) made of brown coal coke on the other hand were used as the filter medium in a ratio of 74.2:25.8 wt.% (volume ratio 3:1) and 77.9:22.1 wt.% (volume ratio 4:1), respectively. SediSorp® is a granulated filter material based on iron(III) oxide hydrate (particle size range 1-2 mm). SediSorp® contains approximately 1-10 wt.% MnO_2 , 10-30 wt.% CaCO_3 and 60-90 wt.% iron(III) oxide hydrate.

250 ml PE-LD bottles (VWR Collection) were used for sampling. For each water sample taken, the pH according to EN ISO 10523:2012, the EC according to DIN EN 27888-C8 and

the temperature according to DIN 38404-C4 were measured, in addition to the zinc and copper concentrations being measured by means of atom absorption spectroscopy (AAS) according to DIN 38406-E8 and DIN 38406-E7, respectively. All the samples were preserved with nitric acid 65% for analysis (EMSURE® ISO 2.5 I, 1.00456.2500, Merck KGaA).

In numerous samples, the concentrations of sodium, calcium and magnesium were additionally determined according to DIN 38406-E14 (sodium) or DIN 38406-E3-1 (calcium and magnesium) by means of AAS. Additionally, additional samples were taken for determining the chloride in 50 ml Greiner test tubes (VWR Collection) at the same time as the other samplings. These samples were not acidified and were analysed by means of ion chromatography according to EN ISO 10304-1:2009-D19. In the case of the outflow composite samples, rapid photometric cuvette tests by the company HACH LANGE GmbH were used for determining purposes (LCK 329, limits of determination 0.1-8.0 mg/l for Cu; LCK 360, limits of determination 0.2-6.0 mg/l for Zn).

Experiment set-up

Two identically constructed measuring cylinders were used as experimental equipment, the design of which cylinders is shown in appendix 12 of the test report 7312218-01 by the LGA dated 28.03.2012 and therefore was also used during the test by the LGA. A drawing of the cylinder design used is shown in the following in Fig. 3, each cylinder being filled up to 144 mm with the substrate SediSorp® or the mixture according to the invention.

Correspondingly, the model factor of these tests was 1:82, as at the LGA, and the calculated connecting surface area was therefore 9.15 m² for each column. The two identically constructed columns are shown together with the sample bottles used in Fig. 4 while the experiment is being conducted.

Conducting the experiment

In part 1 of conducting the experiment, a preload of contamination was applied to the filter medium with a charge of three years. For this purpose, 3729 mg zinc and 430 mg copper were dissolved in 35 l water and a sample was taken from the storage container, in order to check the desired concentrations. The feed water was applied to the system together with a quantity of rain water of 10 l/(s·ha). All of the outflow was collected in a container of

appropriate size. After one pass, the outflow composite concentrations of zinc and copper contained therein were determined using the rapid photometric test. Subsequently, the feed water was pumped through the system in a circuit until at least 90% of each of the two heavy metal charges in the system were retained. Two outflow composite samples were then taken.

In part 2, the heavy metal charges of the fourth year were applied. The procedure was carried out analogously to the DIBt (Deutsches Institut für Bautechnik) method using the filter element having the *preload of contamination of three years*. The *calculated one-year charge* was dissolved in three identical charge portions to 413 mg zinc and 48 mg copper in 65.9 l water in each case. In each case, 65.9 l were applied to the system together with the heavy metal ions in one of the three quantities of rain water. The amounts of the three quantities of rain water were 2.5 l/(s·ha), 6.0 l/(s·ha) and 25 l/(s·ha) at the corresponding durations of 480 min, 200 min and 48 min, respectively. The heavy metal concentrations in the inflow water should therefore always be 6.35 mg/l zinc and 0.72 mg/l copper. Before the start of each experiment, an inflow sample was taken in order to check, in turn, the desired concentrations. In the outflow, there were four samplings per quantity of rain water using two sample bottles in each case after each quarter of the test duration.

After the three partial quantities of rain water from part 2 were applied, the experiment set-up was rinsed with drinking water in order to completely remove the feed water contaminated with heavy metals from the experiment model. The amount of water used corresponded to the one partial quantity of rain water from part 2 and therefore was 65.9 l. An inflow sample was also taken in order to analyse the drinking water composition and two samples were taken after each half of the rinsing duration in order to determine the heavy metal concentrations.

Part 3 of the test began 17 hours after rinsing, which concerned the retention of the heavy metals under the impact of salt. The same contaminated model was used that had also been used in the experiment parts 1 and 2.

In the first salt experiment in the example according to the invention (mixture of SediSorp and HOK), a de-icing salt solution was produced using drinking water, which solution had a concentration of 10 g NaCl/l. The water volume corresponded to the amount of water used in part 2 per partial quantity of rain water. Analogously to the DIBt, 6.0 l/(s·ha) at a duration of

200 min was used as quantity of rain water. In the outflow, four samples were taken using two sample bottles in each case after each quarter of the experiment duration.

Subsequently, the two columns were rinsed again with drinking water, in order to completely remove the feed water contaminated with salt from the experiment model.

In the second salt test in the example according to the invention or in the first salt test in the comparative example, a de-icing salt solution was produced using drinking water having concentrations of 10 g NaCl/l and 2.5 g CaCl₂/l. The water volume corresponded to the amount of water used in part 2 per partial quantity of rain water. 6.0 l/(s·ha) at a duration of 200 min was used in part 3 as quantity of rain water. In the outflow, four samples were taken using two or three sample bottles in each case after each quarter of the test duration.

Subsequently, in both the comparative test and the test according to the invention, the two columns were rinsed again with drinking water in order to completely remove the feed water contaminated with the two salts from the test model.

The second (comparative example) or third (example according to the invention) salt experiment took place analogously to the previous salt experiments, the de-icing salt solution having a concentration of 10 g NaCl/l and 2.5 g MgCl₂/l.

Results of the experiments according to the invention

In Tables 1 and 2, the outflow concentrations measured in each test from part 3, separated according to zinc and copper, are shown individually as mean values for each column (= mixture), together with the desired outflow concentrations, which can be found in the requirements put on the system by the BBodSchV (Federal Soil Protection and Contaminated Sites Ordinance). All of the analysis results used to calculate the mean values are shown in Fig. 5 (volume ratio 4:1) and 6 (volume ratio 3:1) for the two columns together with the temperature, pH, value and EC measurement results.

Table 1: results of the water samples with regard to zinc

	Inflow [µg/l]	Sample	Outflow [µg/l]	Outflow desired [µg/l]
Rinse 1	< 20	Column 1:4	113	
	< 20	Column 1:3	90.7	

Salt 1 (NaCl)	21.4	Column 1:4	59.3	
	21.4	Column 1:3	82.2	
		Mean value	70.8	< 500
Rinse 2	< 20	Column 1:4	34.0	
	< 20	Column 1:3	61.1	
Salt 2 (NaCl/CaCl ₂)	< 20	Column 1:4	488	
	< 20	Column 1:3	508	
		Mean value	498	< 500
Rinse 3	< 20	Column 1:4	44.1	
	< 20	Column 1:3	43.0	
Salt 3 (NaCl/MgCl ₂)	< 20	Column 1:4	149	
	< 20	Column 1:3	166	
		Mean value	158	< 500

Overall, all of the measured copper outflow concentrations meet the requirements of the BBodSchV, and therefore a very minimal impact of the three de-icing salts tested on copper remobilisation can be assumed. On the other hand, higher zinc outflow concentrations have been measured compared with the inflow, and therefore an impact of the salt on the filter medium according to the invention could be established. However, in the outflow, the requirements of the BBodSchV for all three of the de-icing salts tested were also complied with on average for zinc.

Table 2: results of the water samples with regard to copper

	Inflow [µg/l]	Sample	Outflow [µg/l]	Outflow desired [µg/l]
Rinse 1	< 50	Column 1:4	< 50	
	< 50	Column 1:3	< 50	
Salt 1 (NaCl)	< 50	Column 1:4	< 50	
	< 50	Column 1:3	< 50	
		Mean value	< 50	< 50
Rinse 2	< 50	Column 1:4	< 50	
	< 50	Column 1:3	< 50	
Salt 2 (NaCl/CaCl ₂)	< 50	Column 1:4	< 50	
	< 50	Column 1:3	< 50	
		Mean value	< 50	< 50
Rinse 3	< 50	Column 1:4	< 50	
	< 50	Column 1:3	< 50	
Salt 3 (NaCl/MgCl ₂)	< 50	Column 1:4	< 50	
	< 50	Column 1:3	< 50	

		Mean value	< 50	< 50
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In summary, it should be noted that long-lasting consistency of the contaminant retention at the filter medium according to the invention under the impact of de-icing salt (sodium chloride, calcium chloride and magnesium chloride) could be established under the stated experiment conditions, taking the BBodSchV into consideration.

Results of the comparative experiments

In Tables 3 and 4, the outflow concentrations measured in each test from part 3, separated according to zinc and copper, are shown individually for each column as mean values, together with the desired outflow concentrations, which can be found in the requirements on the system and the inflow concentrations analogously to the DIBt method. All of the analysis results used for calculating the mean values are shown in Fig. 7 and 8 for the two columns, together with the temperature, pH and EC measurement results and the results for the chloride, sodium, calcium and magnesium concentrations.

Overall, all of the measured copper outflow concentrations are only slightly higher than the inflow concentrations, and therefore a very minimal impact of the two de-icing salt mixtures tested on the copper remobilisation can be assumed. On the other hand, significantly higher zinc outflow concentrations have been measured in comparison with the inflow, and therefore in particular a very significant impact of the second salt mixture and a lower impact of the third salt mixture on the zinc remobilisation can be established.

Table 3: results of the water samples with regard to zinc. The retention in all four partial tests was calculated according to the DIBt approval policies (permissible Zn total discharge (500 + measured value of de-icing salt solution) µg/l).

	Inflow [µg/l]	Sample	Outflow [µg/l]	Outflow desired [µg/l]
Rinse 1	598	Left-hand column	843	
	992	Right-hand column	1170	
Salt 2 (NaCl/CaCl₂)	692	Left-hand column	1710	< 1190
	809	Right-hand column	2000	< 1300
Rinse 2	546	Left-hand column	524	
	806	Right-hand column	555	
Salt 3 (NaCl/MgCl₂)	816	Left-hand column	822	< 1310

	995	Right-hand column	841	< 1490
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Table 4: results of the water samples with regard to copper. The retention in all four partial tests was calculated according to the DIBt approval policies (permissible Cu total discharge (50 + measured value of de-icing salt solution) µg/l).

	Inflow [µg/l]	Sample	Outflow [µg/l]	Outflow desired [µg/l]
Rinse 1	9.71	Left-hand column	63.8	
	20.4	Right-hand column	84.5	
Salt 2 (NaCl/CaCl₂)	9.96	Left-hand column	32.0	< 59.9
	25.8	Right-hand column	40.1	< 75.8
Rinse 2	8.38	Left-hand column	32.0	
	10.2	Right-hand column	42.8	
Salt 3 (NaCl/MgCl₂)	10.6	Left-hand column	25.2	< 60.6
	35.4	Right-hand column	25.4	< 85.4

In summary, it can be established that using the composition according to the invention can significantly reduce the remobilisation of heavy metal ions, in particular zinc, under the impact of salt.

The present invention is described in more detail by the following points:

1. Composition, in particular for immobilising metal ions, comprising
 - (i) at least one iron hydroxide and
 - (ii) at least one porous carrier material.
2. Composition according to point 1, further comprising
 - (iii) calcium carbonate and optionally
 - (iv) at least one manganese oxide.
3. Composition according to either of the preceding points, wherein component (i) comprises at least one iron(III) hydroxide or iron(III) oxide-hydroxide, preferably selected from bog iron ore (Fe₂O₃·3H₂O), limonite (2Fe₂O₃·3H₂O), jarosite (Fe₂O₃·2H₂O) and goethite (Fe₂O₃·H₂O).

4. Composition according to any of the preceding points, wherein component (ii) is an organic or inorganic, preferably inorganic, carrier material.
5. Composition according to any of the preceding points, wherein the porous carrier material (ii) has a pore volume of at least 20-80%, preferably of 40-60%.
6. Composition according to any of the preceding points, wherein the porous carrier material (ii) has a specific surface area (according to BET) of 100-400 m²/g, preferably 250-350 m²/g.
7. Composition according to any of the preceding points, wherein the porous carrier material (ii) is in the form of a granulate, preferably having a mean particle size of 0.5-10 mm, more preferably 1.0-6 mm.
8. Composition according to any of the preceding points, wherein the porous carrier material (ii) is coal-based or is a carbonate.
9. Composition according to any of the preceding points, wherein the porous carrier material (ii) comprises optionally modified coke, preferably optionally modified brown coal coke.
10. Composition according to point 9, wherein the porous carrier material (ii) is modified by sulphur and/or sulphur compounds, preferably by at least one polysulphide.
11. Composition according to any of the preceding points, wherein the porous carrier material (ii) is a brown coal coke modified by at least one polysulphide.
12. Composition according to any of the preceding points, wherein component (iv) is Mn(III) oxide or Mn(IV) oxide, preferably MnO₂.
13. Composition according to any of the preceding points, wherein components (i), optionally (iii) and optionally (iv) are in the form of a granulate, preferably having a mean particle size of 0.2-5 mm, more preferably 1.0-3.0 mm.

14. Composition according to point 13, wherein the granulate has a porosity of at least 50%, preferably 70%-95%.
15. Composition according to point 13 or point 14, wherein the granulate has a specific surface area (according to BET) of 100-500 m²/g, preferably 200-350 m²/g.
16. Composition according to any of points 13-15, wherein the granulate has a bulk density of 400-800 kg/m³, preferably 500-700 kg/m³.
17. Composition according to any of the preceding points, wherein the porous carrier material (ii) and the granulate according to points 13-16 are in the composition as homogenous mixture, as mixture having a gradient, or in separate layers.
18. Composition according to any of the preceding points, wherein the proportion of component (ii) to the entire composition is approximately 20-50 wt.%, preferably 20-30 wt.%.
19. Composition according to any of the preceding points, wherein the proportion of component (i) to the entire composition is approximately 30-80 wt.%, preferably 40-70 wt.%.
20. Composition according to any of the preceding points, wherein the proportion of component (iii) to the entire composition is approximately 0-30 wt.%, preferably 5-30 wt.%, more preferably 7-25 wt.%.
21. Composition according to any of the preceding points, wherein the proportion of component (iv) to the entire composition is approximately 0-10 wt.%, preferably 0.05-8 wt.%.
22. Filter apparatus, in particular for treating wastewater, comprising a composition according to any of points 1-21 as the filter medium.
23. Filter apparatus according to point 22, further comprising a housing having a plurality of openings, optionally a mesh layer and optionally a drain layer.
24. Filter apparatus according to point 23, wherein the housing is formed such that it can receive the filter medium.

25. Wastewater treatment device, comprising a wastewater inlet, a wastewater outlet and a composition according to any of points 1-21 or a filter apparatus according to any of points 22-24.

26. Use of the composition according to any of points 1-21 or of the filter apparatus according to any of points 22-24 or of the wastewater treatment device according to point 25 for treating wastewater, in particular rain water.

27. Use according to point 26 for removing metal ions from wastewater.

28. Method for treating wastewater, comprising bringing the wastewater into contact with the composition according to any of points 1-21 or with the filter apparatus according to any of points 22-24 or wastewater flowing through the wastewater treatment device according to point 25.

CLAIMS:

1. Composition, for the immobilization of metal ions, comprising
 - (i) at least one iron hydroxide, and
 - (ii) at least one porous carrier material,
 wherein the porous carrier material (ii) comprises coke modified with sulfur and/or sulfur compounds.
2. Composition according to claim 1, wherein the iron hydroxide is in an amount of 30-80 wt.-% based on the total composition.
3. Composition according to claim 1, wherein the porous carrier material is in a proportion of 20-50 wt.-% based on the total composition.
4. Composition according to any one of claims 1 to 3, further comprising
 - (iii) calcium carbonate, and optionally
 - (iv) at least one manganese oxide.
5. Composition according to claim 4, wherein the calcium carbonate is in a proportion of less than 30 wt.-% based on the total composition.
6. Composition according to claim 4 or 5, wherein the manganese oxide is Mn(III) oxide or Mn(IV) oxide.
7. Composition according to claim 4 or 6, wherein the manganese oxide is in a proportion of 0-10 wt.-% based on the total composition.
8. Composition according to any one of claims 1 to 7, wherein component (i) comprises at least one iron (III) hydroxide or iron (III) oxide hydroxide.
9. Composition according to claim 8, wherein the component is from bog iron ore ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), jarosite ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) and goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$).

10. Composition according to any one of claims 1 to 9, wherein the porous carrier material (ii) is in the form of a granular material.
11. Composition according to claim 10, wherein the granular material is having an average grain size of 0.5-10 mm.
12. Composition according to claim 10, wherein the granular material is having an average grain size of 1.0-6 mm.
13. Composition according to any one of claims 1 to 12, wherein the porous carrier material (ii) comprises modified lignite coke.
14. Composition according to any one of claims 1 to 13, wherein the porous carrier material (ii) is modified with at least one polysulfide.
15. Composition according to any one of claims 1-9, wherein the component (i) is in the form of granular material.
16. Composition according to claim 15, wherein the component (iii) is in the form of granular material.
17. Composition according to claim 15, wherein the component (iv) is in the form of granular material.
18. Composition according to any one of claims 15 to 17, wherein the granular material is having an average particle size of 0.2-5 mm.
19. Composition according to any one of claims 15 to 18, wherein the granular material is having an average particle size of 1.0-3.0 mm.
20. Composition according to any one of claims 1 to 19, wherein the porous carrier material (ii) and the granular material according to claim 15 are present in the composition as a homogeneous mixture, as a mixture having a gradient or in separate layers.

21. Filter device, for wastewater treatment, comprising a composition according to any one of claims 1 to 20 as a filter medium.
22. Filter device according to claim 21, further comprising a housing having a plurality of openings.
23. Filter device according to claim 22, further comprising a mesh layer.
24. Filter device according to claim 22 or 23, further comprising a drainage layer.
25. Wastewater treatment apparatus comprising a wastewater inlet, a wastewater outlet and a composition according to any one of claims 1 to 20 or a filter device according to any one of claims 21 to 24.
26. Use of the composition according to any one of claims 1 to 20 or the filter device according to any one of claims 21-24 or the wastewater treatment apparatus according to claim 25 for the treatment of wastewater.
27. Use according to claim 26, wherein the wastewater is rainwater.
28. Use according to claim 26 for the removal of metal ions from wastewater.
29. Method for the treatment of wastewater, comprising bringing the wastewater into contact with the composition according to any one of claims 1 to 20 or the filter device according to any one of claims 21 to 24 or flowing wastewater through the wastewater treatment apparatus according to claim 25.

Fig 1a

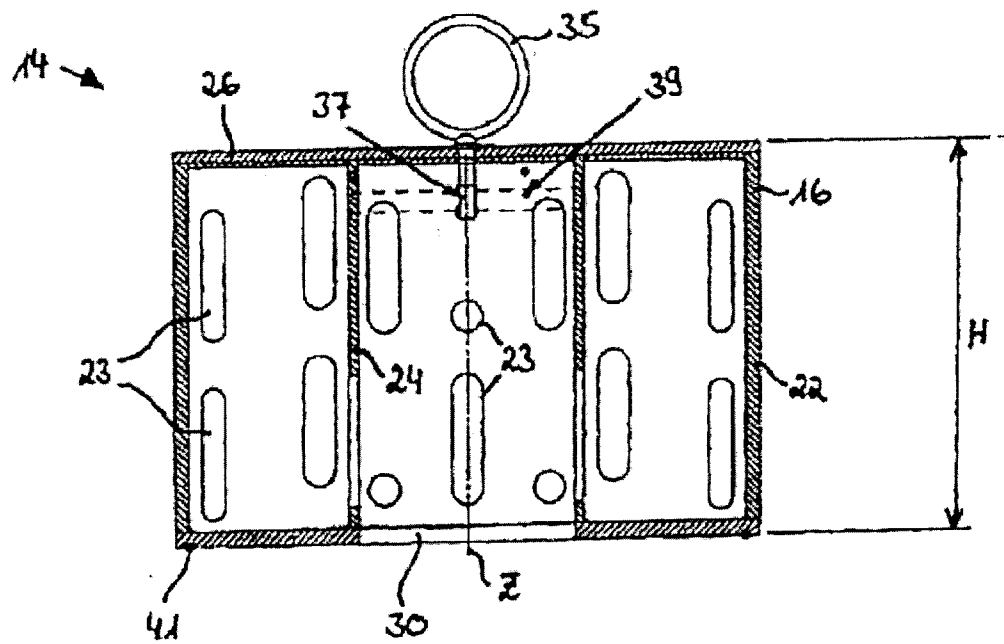


Fig 1b

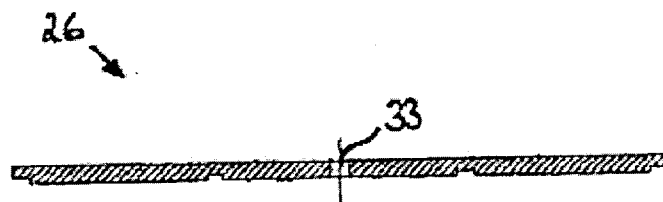


Fig 2

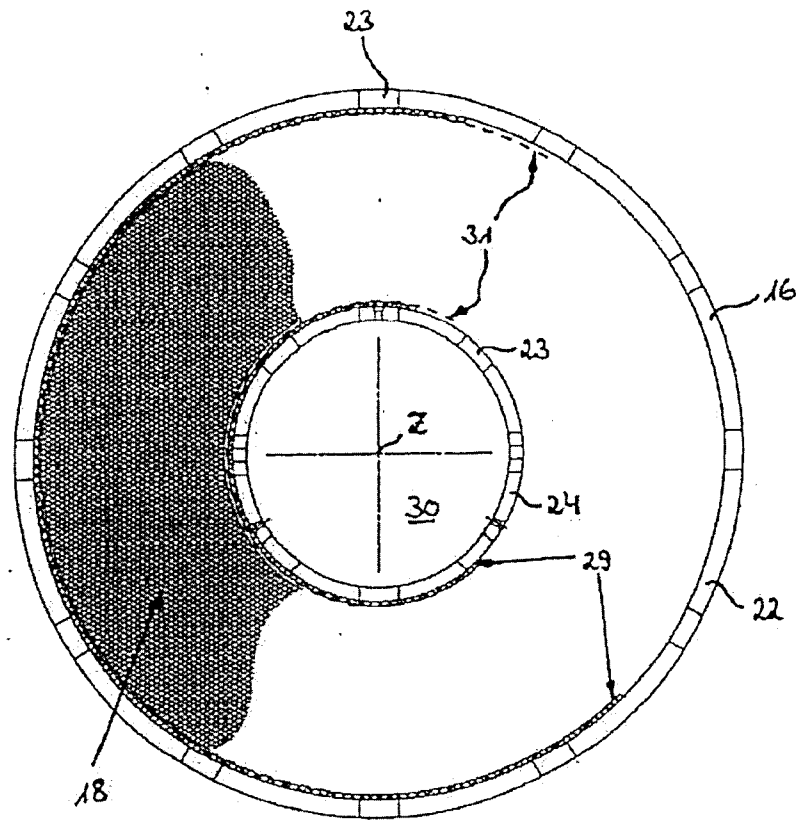


Fig 3

Design of the measuring cylinder

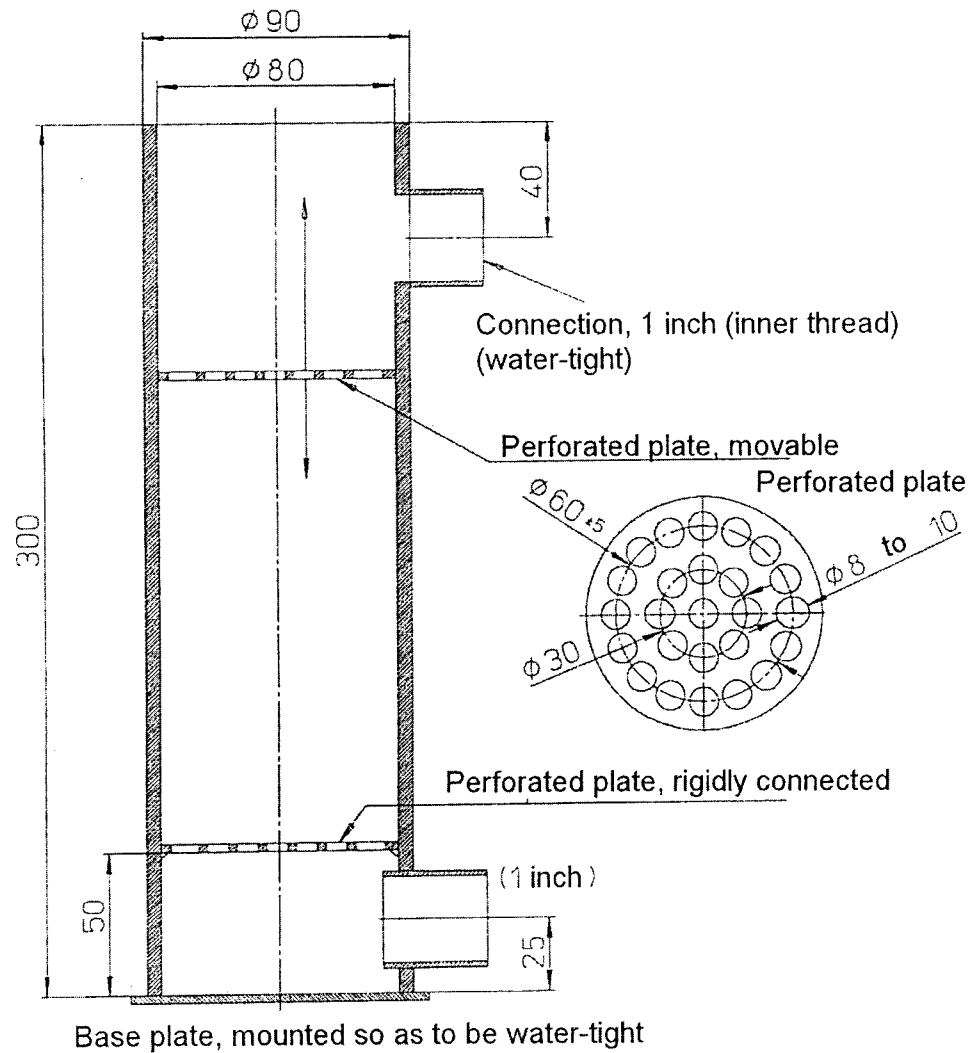


Fig 4

Experiment set-up
“Left-hand column” (left) and “right-hand column” (right)

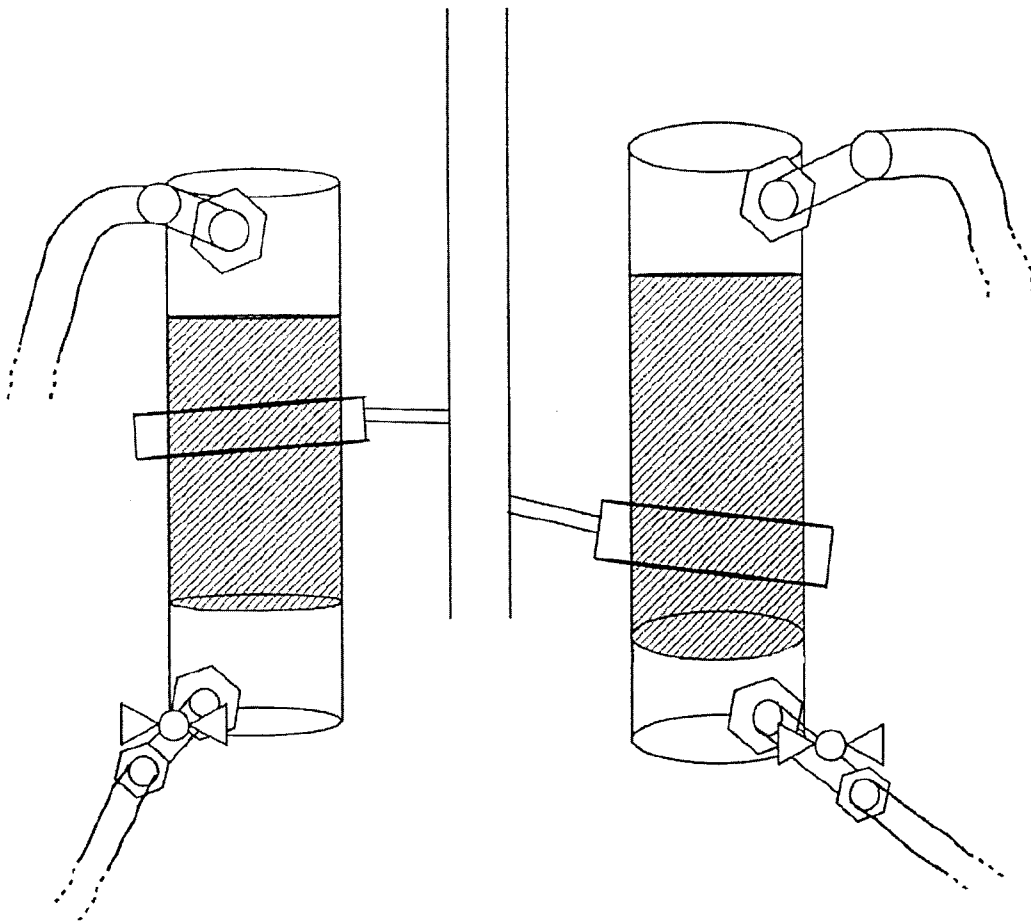


Fig. 5a

Measurement results for "column 4:1" – part 1

17.08.2015	Zero sample: after rinsing, clear as far as outlet						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Outflow	< 20	—	< 5	—	—	—	99
17.08.2015	Part 1: pre-loading - deionised water with heavy metals						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	99800	—	11900	—	22.8	5.2	365
Composite sample	6250	—	167	—	21.2	6.8	623
18.08.2015	Part 2: quantity of rain water 1 - deionised water with heavy metals						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	6020	—	721	—	22.2	5.1	29
Outflow 1	69.3	71.1	12.8	12.0	21.4	8.5	95
Outflow 2	70.5	61.1	11.8	7.81	21.7	8.6	84
Outflow 3	53.5	54.0	6.35	5.43	21.8	8.6	73
Outflow 4	103	78.1	6.73	< 5	21.7	8.5	66
19.08.2015	Part 2: quantity of rain water 2 - deionised water with heavy metals						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	6720	—	689	—	21.9	5.1	27
Outflow 1	185	186	10.6	10.2	21.5	8.3	54
Outflow 2	262	269	11.8	11.3	21.3	8.3	51
Outflow 3	322	336	12.1	11.9	21.1	8.3	49
Outflow 4	357	372	13.5	13.3	20.8	8.3	49
19.08.2015	Part 2: quantity of rain water 3 - deionised water with heavy metals						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	6000	—	713	—	22.1	5.2	27
Outflow 1	1760	1760	89.9	88.4	22.2	7.8	47
Outflow 2	2370	2430	134	140	22.0	7.4	54
Outflow 3	3940	3050	153	153	21.9	7.4	42
Outflow 4	2810	3030	154	169	21.6	7.1	46

Fig. 5b

Measurement results for "column 4:1" – part 2

19.08.2015	Rinsing quantity of rain water - drinking water without additives						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	22.8	6.9	0.8
Outflow 1	100	111	< 50	—	22.5	8.7	28.3
Outflow 2	125	112	< 50	—	22.0	8.7	20.6
20.08.2015	Part 3: quantity of rain water - drinking water with salt (NaCl)						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	21.4	—	< 50	—	20.8	6.8	17700
Outflow 1	74.1	74.7	< 50	< 50	21.0	8.9	17600
Outflow 2	60.6	62.4	< 50	< 50	20.9	9.1	17800
Outflow 3	52.4	51.2	< 50	< 50	21.1	9.1	17800
Outflow 4	48.3	50.9	< 50	< 50	20.8	9.1	17800
20.08.2015	Rinsing quantity of rain water - drinking water without additives						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	22.6	7.2	2.8
Outflow 1	44.8	—	< 50	—	22.7	10.0	978
Outflow 2	23.1	—	< 50	—	22.0	9.8	143

Fig. 5c

Measurement results for "column 4:1" – part 3

20.08.2015	Part 3: quantity of rain water - drinking water with salts (NaCl and CaCl ₂)						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	22.9	8.9	21100
Outflow 1	605	612	< 50	< 50	22.3	7.8	21200
Outflow 2	515	500	< 50	< 50	22.2	7.7	21200
Outflow 3	430	430	< 50	< 50	22.0	7.7	21300
Outflow 4	401	413	< 50	< 50	21.5	7.7	21400
20.08.2015	Rinsing quantity of rain water - drinking water without additives						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	22.8	7.1	0.7
Outflow 1	66.5	—	< 50	—	22.1	8.4	1400
Outflow 2	21.7	—	< 50	—	21.8	9.4	34.2
21.08.2015	Part 3: quantity of rain water - drinking water with salts (NaCl and MgCl ₂)						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	21.7	6.7	19800
Outflow 1	165	172	< 50	< 50	20.5	8.4	19700
Outflow 2	143	195	< 50	< 50	20.6	8.4	19800
Outflow 3	129	128	< 50	< 50	20.5	8.5	19800
Outflow 4	139	121	< 50	< 50	20.6	8.4	19800

Fig. 6a

Measurement results for "column 3:1" – part 1

17.08.2015	Zero sample: after rinsing, clear as far as outlet						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Outflow	< 20	—	< 5	—	—	—	117
17.08.2015	Part 1: pre-loading - deionised water with heavy metals						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	99800	—	11900	—	22.8	5.2	365
Composite sample	7520	—	201	—	21.2	6.8	593
18.08.2015	Part 2: test quantity of rain water 1 - deionised water with heavy metals						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	6020	—	721	—	22.2	5.1	29
Outflow 1	92.2	82.2	12.2	10.8	21.5	8.6	84
Outflow 2	95.7	91.0	8.77	7.81	21.6	8.7	74
Outflow 3	103	104	7.92	6.71	21.9	8.6	66
Outflow 4	110	124	6.98	6.89	21.6	8.6	63
19.08.2015	Part 2: quantity of rain water 2 - deionised water with heavy metals						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	6720	—	689	—	21.9	5.1	27
Outflow 1	282	289	14.7	5.41	21.5	8.4	51
Outflow 2	383	393	15.9	15.5	21.3	8.3	48
Outflow 3	519	543	19.3	21.6	21.2	8.3	47
Outflow 4	673	684	22.5	23.3	20.8	8.2	44
19.08.2015	Part 2: quantity of rain water 3 - deionised water with heavy metals						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	6000	—	713	—	22.1	5.2	27
Outflow 1	2860	2870	124	125	21.7	7.3	35
Outflow 2	3160	3430	150	151	22.0	7.3	33
Outflow 3	3700	3590	170	169	21.9	7.2	34
Outflow 4	3700	3810	183	182	21.6	7.1	32

Fig. 6b

Measurement results for "column 3:1" – part 2

19.08.2015	Rinsing quantity of rain water - drinking water without additives						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	22.8	6.9	0.8
Outflow 1	119	126	< 50	—	22.4	8.5	17.6
Outflow 2	62.4	62.9	< 50	—	21.9	8.7	18.7
20.08.2015	Part 3: quantity of rain water - drinking water with salt (NaCl)						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	21.4	—	< 50	—	20.8	6.8	17700
Outflow 1	93.4	85.5	< 50	< 50	20.9	9.1	17700
Outflow 2	88.1	100	< 50	< 50	21.2	9.1	17500
Outflow 3	79.0	79.3	< 50	< 50	21.2	9.1	17700
Outflow 4	67.0	65.6	< 50	< 50	21.0	9.1	17600
20.08.2015	Rinsing quantity of rain water - drinking water without additives						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	22.6	7.2	2.8
Outflow 1	77.0	—	< 50	—	22.2	10.0	532
Outflow 2	45.1	—	< 50	—	22.0	9.9	51.4

Fig. 6c

Measurement results for "column 3:1" – part 3

20.08.2015	Part 3: quantity of rain water - drinking water with salts (NaCl and CaCl ₂)						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	22.9	8.9	21100
Outflow 1	658	655	< 50	< 50	22.4	7.8	21100
Outflow 2	531	523	< 50	< 50	22.1	7.7	21300
Outflow 3	462	445	< 50	< 50	22.0	7.7	21200
Outflow 4	394	392	< 50	< 50	21.7	7.8	21400
20.08.2015	Rinsing quantity of rain water - drinking water without additives						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	22.8	7.1	0.7
Outflow 1	46.8	—	< 50	—	22.3	8.6	700
Outflow 2	39.2	—	< 50	—	22.1	9.4	21.0
21.08.2015	Part 3: quantity of rain water - drinking water with salts (NaCl and MgCl ₂)						
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	< 20	—	< 50	—	21.7	6.7	19800
Outflow 1	193	197	< 50	< 50	20.6	8.6	19600
Outflow 2	173	169	< 50	< 50	20.6	8.6	19700
Outflow 3	150	151	< 50	< 50	20.4	8.6	19800
Outflow 4	151	146	< 50	< 50	20.6	8.6	19700

Fig. 7a

Measurement results for "left-hand column" – part 1

28.11.2013											
Zero sample: after rinsing, clear as far as outlet											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Outflow	1.94	—	< 5	—	—	0.46	16.0	4.43	16.1	8.4	58.2
29.11.2013											
Zero sample: stagnant water, murky, taken at the very start of part 1											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Outflow	7.69	—	< 5	—	—	1.29	20.7	6.48	15.9	8.3	154
29.11.2013											
Part 1: pre-loading - deionised water with heavy metals											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	117000	—	12900	—	—	< 0.1	< 0.2	< 0.1	15.5	4.8	425
Composite sample	5070	5160	81.0	77.1	—	2.54	86.2	11.0	14.7	7.4	608
02.12.2013											
Part 2: quantity of rain water 1 - deionised water with heavy metals											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	6970	—	778	—	—	—	—	—	16.7	5.0	28.8
Outflow 1	57.1	28.2	7.85	5.81	—	—	—	—	17.2	8.0	101
Outflow 2	26.2	x	< 5	x	—	—	—	—	16.2	8.2	91.4
Outflow 3	21.1	9.73	< 5	< 5	—	—	—	—	16.1	8.2	89.6
Outflow 4	21.1	10.7	< 5	< 5	—	—	—	—	15.9	8.2	82.2

Fig. 7a (continued)

03.12.2013	Part 2: quantity of rain water 2 - deionised water with heavy metals										
	Zn [$\mu\text{g/l}$]	Zn [$\mu\text{g/l}$]	Cu [$\mu\text{g/l}$]	Cu [$\mu\text{g/l}$]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [$^{\circ}\text{C}$]	pH	EC [$\mu\text{S/cm}$]
Inflow	7190	—	745	—	—	1.91	< 0.2	< 0.1	16.1	5.2	27.5
Outflow 1	59.1	59.1	5.14	< 5	—	—	—	—	16.5	8.2	63.9
Outflow 2	77.5	68.5	< 5	< 5	—	< 0.1	19.0	1.53	16.8	8.0	59.6
Outflow 3	83.4	83.4	< 5	< 5	—	—	—	—	16.5	8.1	56.9
Outflow 4	127	119	7.8	< 5	—	—	—	—	16.6	7.9	55.5
03.12.2013	Part 2: quantity of rain water 3 - deionised water with heavy metals										
	Zn [$\mu\text{g/l}$]	Zn [$\mu\text{g/l}$]	Cu [$\mu\text{g/l}$]	Cu [$\mu\text{g/l}$]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [$^{\circ}\text{C}$]	pH	EC [$\mu\text{S/cm}$]
Inflow	7190	—	745	—	—	1.91	< 0.2	< 0.1	16.1	5.2	27.5
Outflow 1	1850	1780	92.3	95.7	—	—	—	—	16.4	6.9	37.0
Outflow 2	2110	2030	107	109	—	—	—	—	16.4	6.8	36.4
Outflow 3	2250	2290	116	118	—	—	—	—	16.2	6.8	35.9
Outflow 4	2500	2360	113	119	—	< 0.1	8.94	0.45	16.1	6.7	35.9

Fig. 7b

Measurement results for "left-hand column" – part 2

03.12.2013 Rinsing quantity of rain water - drinking water without additives											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	598	—	9.71	—	—	—	—	—	17.5	7.6	603
Outflow 1	844	922	67.2	71.3	—	—	—	—	17.7	7.7	584
Outflow 2	805	799	59.5	57.2	—	—	—	—	17.8	7.7	590
04.12.2013 Part 3: quantity of rain water - drinking water with salts (NaCl and CaCl ₂) (17-hour break beforehand)											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	692	—	9.96	—	10400	3820	926	26.6	16.4	7.6	21900
Outflow 1	1630	1530	32.4	32.7	10000	3610	908	30.5	16.6	7.7	21900
Outflow 2	1760	1760	33.3	34.4	8860	3760	964	28.6	16.4	7.7	21900
Outflow 3	1800	1800	34.4	32.7	8550	3750	953	28.5	16.2	7.7	21900
Outflow 4	1670	1690	29.4	26.9	9380	3800	921	27.8	15.6	7.7	22000
04.12.2013 Rinsing quantity of rain water - drinking water without additives											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	546	—	8.38	—	18.3	27.4	64.9	25.3	15.8	7.6	612
Outflow 1	450	467	21.4	26.0	18.4	31.3	68.3	25.6	16.2	7.8	624
Outflow 2	461	718	23.8	56.8	16.8	28.0	68.7	25.6	16.0	7.7	617
05.12.2013 Part 3: quantity of rain water - drinking water with salts (NaCl and MgCl ₂) (20.5-hour break beforehand)											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	816	—	10.6	—	7920	3760	75.3	313	16.3	7.4	20100
Outflow 1	823	791	26.4	24.8	11900	3730	113	306	16.3	7.8	20200
Outflow 2	855	781	30.2	22.1	7380	3670	99.2	315	16.3	7.8	20100
Outflow 3	780	791	22.4	22.9	8810	3780	91.3	318	15.9	7.8	20100
Outflow 4	960	795	31.1	21.5	8730	3700	90.8	320	15.6	7.8	20200

Fig. 8a

Measurement results for "right-hand column" – part 1

28.11.2013	Zero sample: after rinsing, clear as far as outlet										
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Outflow	2.64	—	< 5	—	—	0.80	17.0	5.28	16.0	8.3	68.9
29.11.2013	Zero sample: stagnant water, murky, taken at the very start of part 1										
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Outflow	1.81	—	< 5	—	—	1.42	18.6	6.22	16.0	8.3	148
29.11.2013	Part 1: pre-loading - deionised water with heavy metals										
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	11600 0	—	1280 0	—	—	0.12	3.64	< 0.1	16.1	5.0	424
Composite sample	5350	5310	71.5	71.5	—	0.65	83.4	11.5	15.2	7.3	617

Fig. 8a (continued)

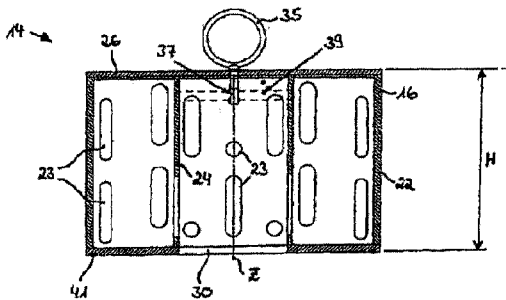
02.12.2013 Part 2: test quantity of rain water 1 - deionised water with heavy metals											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	7340	—	735	—	—	—	—	—	16.0	4.6	34.5
Outflow 1	34.4	29.0	6.68	5.21	—	—	—	—	16.8	8.0	114
Outflow 2	24.3	22.3	< 5	< 5	—	—	—	—	16.3	8.0	99.1
Outflow 3	21.1	11.0	< 5	< 5	—	—	—	—	16.1	8.1	90.5
Outflow 4	12.5	9.14	< 5	< 5	—	—	—	—	16.0	8.1	87.5
03.12.2013 Part 2: quantity of rain water 3 - deionised water with heavy metals											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	7350	—	751	—	—	0.35	< 0.2	< 0.1	16.1	4.8	29.9
Outflow 1	121	129	7.63	9.80	—	—	—	—	16.1	8.1	62.7
Outflow 2	158	158	8.29	6.98	—	0.61	18.8	1.44	16.7	7.9	59.2
Outflow 3	194	200	8.31	11.5	—	—	—	—	16.6	7.9	56.8
Outflow 4	239	224	7.89	8.05	—	—	—	—	16.4	7.8	55.8
03.12.2013 Part 2: quantity of rain water 3 - deionised water with heavy metals											
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	7350	—	751	—	—	0.35	< 0.2	< 0.1	16.1	4.8	29.9
Outflow 1	1820	1860	91.0	105	—	—	—	—	16.4	6.9	38.5
Outflow 2	2100	2040	112	113	—	—	—	—	16.5	6.8	37.6
Outflow 3	2380	2370	113	106	—	—	—	—	16.4	6.8	37.5
Outflow 4	2330	2400	124	123	—	0.13	9.24	0.44	16.4	6.7	37.0

Fig. 8b

Measurement results for "right-hand column" – part 2

03.12.2013	Rinsing quantity of rain water - drinking water without additives										
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	992	—	20.4	—	—	—	—	—	18.9	7.5	582
Outflow 1	963	1070	67.8	66.3	—	—	—	—	18.4	7.7	553
Outflow 2	1600	1060	142	61.9	—	—	—	—	18.3	7.7	570
04.12.2013	Part 3: quantity of rain water - drinking water with salts (NaCl and CaCl₂) (17-hour break beforehand)										
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	809	—	25.8	—	8900	3690	947	26.2	17.8	7.5	22200
Outflow 1	2080	2070	41.5	47.8	8240	3790	927	30.1	16.5	7.7	22200
Outflow 2	1990	2070	40.5	44.5	10100	3810	972	27.3	16.5	7.7	22200
Outflow 3	2050	2030	38.2	38.8	8850	3820	925	26.7	16.1	7.7	22200
Outflow 4	1890	1840	32.7	36.6	8610	3820	938	27.7	15.7	7.7	22300
04.12.2013	Rinsing quantity of rain water - drinking water without additives										
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	806	—	10.2	—	17.3	28.7	66.3	25.4	16.5	7.6	610
Outflow 1	510	566	36.4	54.2	18.0	32.6	67.4	24.0	16.6	7.8	621
Outflow 2	570	574	39.4	41.2	17.3	30.0	69.2	25.4	16.5	7.7	617
05.12.2013	Part 3: quantity of rain water - drinking water with salts (NaCl and MgCl₂) (20.5-hour break beforehand)										
	Zn [µg/l]	Zn [µg/l]	Cu [µg/l]	Cu [µg/l]	Cl [mg/l]	Na [mg/l]	Ca [mg/l]	Mg [mg/l]	Temp. [°C]	pH	EC [µS/cm]
Inflow	995	—	35.4	—	8790	3800	74.1	320	17.3	7.4	20100
Outflow 1	835	835	30.8	26.4	8040	3810	110	299	16.5	7.8	20200
Outflow 2	839	x	31.3	x	8070	3660	197	312	16.6	7.8	20200
Outflow 3	849	835	23.1	23.8	8690	3760	91.2	309	16.4	7.8	20200
Outflow 4	845	847	21.1	21.6	7740	3800	90.4	317	16.1	7.8	20300

a



b

