THE INFLUENCE OF DE-ICING SALT ON THE REMOBILIZATION OF HEAVY METALS AND PAH IN AN ARTIFICIAL WETLAND

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FOREWORD

The last step to become a Civil Engineer from Delft Technical University is finishing a graduation research. This thesis is now in front of you. This result wouldn't be achieved without the support of a lot of people.
First I want to thank Floris Boogaard and Frans van de Ven for supporting me during the whole process. As members of my graduation committee you were responsible for the regular support.
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ABSTRACT

1 PREFACE

Runoff from highways is often of poor quality. Pollutants in runoff can influence the water quality of adjacent water courses or the quality of the groundwater. Since July first, the Resolution discharging outside devices (Besluit lozen buiten inrichtingen) became active in the Netherlands. This resolution imposes a general duty of care (algemene zorgplicht). For road maintainers this resolution means that they have to prevent pollution of the soil, groundwater and surface water by (road)runoff. Further this resolution provides general rules which state that road runoff preferably should be infiltrated in the roadside.

Rijkswaterstaat, responsible for highways, shapes the resolution by Good Housekeeping. This comprehends different measures like ZOAB cleaning, scraping roadsides, construct and maintain discharge facilities like artificial wetlands. Rijkswaterstaat is using several artificial wetlands to purify runoff from highways before it is discharged to a water course or before infiltration to the groundwater (Muiswinkel, Berendsen, & Grinsven, 2010). Six of them are located at traffic junction Raasdorp where highways A5 and A9 cross. One of these is used to do research at in this study, see Figure 1. Advantage of purifying road runoff in the artificial wetland before water is infiltrated, compared to direct infiltration in roadsides is that the pollutants are located at one location. Namely, in the artificial wetland.

Sewer systems are constructed to transport the road runoff of an particular road surface to the artificial wetland. This water is the whole year, in varying concentrations, polluted by copper, zinc, oil, polycyclic aromatic hydrocarbons (PAH) and other pollutants. In wintertime de-icing salts are used to prevent vehicles skidding the road when road surface becomes slippery when ice is formed on top because of frost and precipitation. The main components of de-icing salts are Sodium (Na) and Chlorine (Cl). After a precipitation event, de-icing salt will enter the artificial wetland together with other pollutants. In 2005 a report states that de-icing salts are a reason for remobilization of heavy metals in an artificial wetland so that they will flush out again. Because of this situation one of the recommendations is to bypass the artificial wetland in wintertime to avoid de-icing salt in the artificial wetland and thus keep the mobilized pollutants inside (Tromp, 2005). Since the total influence of de-icing salt in an artificial wetland is not clear, this research aims to deepen the insight. The main question for this report is: What is the influence of de-icing salts on the remobilization of heavy metals and PAH in an artificial wetland? It is essential to realize that a pollutant is effectively removed from solution when it is appropriate immobilized.

FIGURE 1 TRAFFIC JUNCTION RAASDORP WITH SIX ARTIFICIAL WETLANDS. THE ONE WITH A DOTTED CIRCLE IS USED FOR TAKING MEASUREMENTS IN THIS RESEARCH.

2 INTRODUCTION

2.1 STRUCTURE

This research can roughly be divided into three main parts: literature studies, research methods and discussion.
The literature studies focusses in the first place on available articles regarding the use of de-icing salts on highways and the influence on artificial wetlands or other similar infiltration facilities like road sides. Also the processes and conditions which can cause mobilization of heavy metals and PAH will be studied. This is important to get insight into major and minor processes involved with remobilization. Preliminary a field visit will take place in order to identify the current situation and to describe the condition of the artificial wetlands. This field visit is also important to get known with the current situation, state and surroundings which can have influence on the performance.
The research in this graduation thesis focusses on gathering samples to give an quantitative review on the presence and availability of de-icing salts, metals and PAH in one of the artificial wetlands located at traffic junction Raasdorp. Secondly a leaching test in a column will take place. A soil sample of the artificial wetland will be flushed with known concentrations of de-icing salts. The effluent of the leaching test will be analysed in laboratory.
The discussion in the last place reflects on the research results in relation to circumstances during measuring and connections found in literature. The result of the discussion will be the conclusion in which an answer will be given on the main question: “What is the influence of de-icing salt on the remobilization of heavy metals and PAH in an artificial wetland?”.

2.2 CURRENT STATE

A field visit did take place to identify the condition of the artificial wetlands. Also the possible measurement locations are determined. Depending on whether or not work the artificial wetlands, these locations will be used for measurement. During the first field visit it became clear that the not all artificial wetlands function properly. The following deficiencies and defects are visually noticed:

- Willows are growing in the artificial wetland
- Plants in the filter died because of suffocation
- Holes in the plastic sheeting
- Plants are growing in the sedimentation basin / wrong location inflow pipe
- Large quantity of water under the plastic sheeting

Basically all deficiencies of the artificial wetland are a result of deferred maintenance. Due to the problems most filters are not suitable to take measurements. The defects and deficiencies cause among others extra pollution and leakage. An elaboration on the deficiencies named above can be found in Annex 1 It is known that a contractor is responsible for the maintenance of the artificial wetland but at Rijkswaterstaat is lack of clarity about who is responsible for the control of the performance of the artificial wetland. In practice this led to the earlier named deficiencies.
Due to the deficiencies it was not possible to directly use an artificial wetland to take measurements in. A proper working artificial wetland had to be determined before by checking the through flow. In other words, does road runoff which enters the sedimentation basin flow through the actual artificial wetland so that it can be purified? The way in which this additional research is carried out is described in paragraph 5.1.
The artificial wetlands located at traffic junction Raasdorp are according to RWS constructed following the example of the artificial wetland constructed near highway A1. The final documents related to the artificial wetlands located at traffic junction Raasdorp were not available anymore at RWS. Part of the documents is obtained from the contractor who designed the artificial wetlands,

namely Dura Vermeer. The obtained documents are added in Annex 2. Since the design is taken from the artificial wetland located at highway A1 near 't Gooi, no large differences were expected between artificial wetlands on the different locations. However, a difference is found between the two artificial wetlands what can possibly be of influence on the performance. The substrate of the artificial wetland located near the A1 consists of sand where that of the wetlands at traffic junction Raasdorp consist of Eifellith Lava. The reason for choosing a lava fill instead of filter sand did not became clear during this research. To get insight in possible difference in performance the results of this research can be partially compared with the research of Tromp which is published in 2005. This comparison will be described in the discussion at the end of this report.

2.3 HEAVY METALS

The term "heavy metals" has been widely used worldwide. The term represents a collection of metals with a relative high density. However there is no definition which is commonly used for this term. As a result, different collections can be meant by the term heavy metals. Some of them are stated below.

- Heavy metals are the group of elements with a density greater than 6 g/cm^3 (Alloway, et al., 1995).
- Heavy metals are the group of elements with a density greater than 3 g/cm^3 (Evangelou, 1998).
- All metals with atom numbers 23 till 83, except the alkaline (earth) metals, though barium plus non-metals arsenic, selenium, tellurium are included (Steketee, 2009).

Definitions of heavy metal can be made on 6 different properties, density, atomic weight, atomic number, chemical properties, toxicity and non-chemical use. This leads to an extensive list of different definitions for heavy metal which is made by Duffus (Duffus, 2002).

Heavy metals do occur on highways because of several occasions. The combustion process of gasoline is the major source of lead in road soils, while diesel oil (Cd), tire attrition (Zn and Cd), steel parts attrition (Ni, Cr, V, W, Mo) and the wear of bearings and bushing (Cu) all contribute trace metals to roadside soils (Amrhein, Strong, & Mosher, 1992). Other sources of pollution are leaking of oil and coolants even as corrosion of the guardrail. (Bohemen & Janssen - Van de Laak, 2003). Heavy metals are not biodegradable and have become an eco-toxicological hazard of prime interest and increasing significance owing to their harmful effect on biological systems when they exceed the tolerance levels.
The appearance of heavy metals next to highways are on the one hand because of polluted runoff and transport by air of heavy metals from the highway and on the other hand because of natural presence. The presence of heavy metals does not imply quality problems for soil of water and thus indirectly on living species. The point where heavy metals get toxic depend on a lot of factors like the nature of the metal, speciation, the concentration and the time of exposure. Acute poisoning of humans as a result of contact with water or soil polluted by heavy metals is negligible, chronic problems are not. For example cadmium can cause kidney problems, lead disturbs production of blood and lead and mercury can cause problems with the nerve system(Steketee, 2009).
In the Netherlands are quality standards set like the "streefwaarden" (target levels) and "interventiewaarden" (intervention levels). The intervention levels for soils and groundwater are targets with a signal value. If this level is exceeded it is called a heavy pollution, the functional properties of the soil are (possibly) severely diminished for human and wildlife.

Target levels represent the level where there is a sustainable soil quality. At this level the functional properties of the soil are for human, wildlife and vegetation restored. Therefore the target levels are used for preventive policy (RIVM, 2011).

TABLE 1 TARGET AND INTERVENTION LEVELS FOR AN SELECTION OF METALS

Element	Target levels shallow groundwater (µg/l)	Groundwater intervention levels (µg/l)
Cr	1	30
Ni	15	75
Cu	15	75
Zn	65	800
Cd	0,4	6
Pb	15	75

3 ARTIFICIAL WETLAND

Natural wetlands are areas where the soil is either permanent or temporally saturated with water. They can be found all over the world and have been used for wastewater treatment in a lot of occasions. For example they are used to treat domestic and industrial wastewater or to treat mine wastewater drainage. It is showed that in most cases, improvement of the water quality of the wastewater is realized as a result of flow through a wetland.

Artificial or constructed wetlands are manmade wetlands which do have the main purpose to treat wastewater consisting different pollutants. Among others Shutes and Verhoeven and Meuleman showed that artificial wetlands can reach high levels of COD, BOD, P and N removal.

3.1 LAY-OUT

Artificial wetlands do occur in various dimensions and types. We can distinguish the artificial wetlands with subsurface flow into horizontal subsurface flow, vertical flow and hybrid artificial wetlands. Here the hybrid artificial wetlands do consist of a combination of horizontal subsurface flow and vertical flow. The artificial wetland which is studied can be seen as a horizontal subsurface flow type. It consists of two compartments. First compartment is the sedimentation basin. It is used to collect the highway runoff water which is collected by the sewer. The sewer transports the water to the sedimentation basin where suspended solids can settle before the water is discharged to the second compartment, the actual artificial wetland. By a drain which is constructed between the sedimentation basin and the artificial wetland the water is led into the artificial wetland. At the end of the artificial another drain is present which transports the water to the infiltration ditch where the purified water can infiltrate to the groundwater. The water level is maintained on a fixed depth by a tube which is constructed at the end. The maintained water level in the artificial wetland is 50 centimeter according to the technical drawings, see Annex 2.

The filtration media which is used for an artificial wetland should provide three main properties: facilitate macrophytes growth, provide a high and sustainable filtration effect and maintain high hydraulic conductivity. The early systems built in 1970s and early 1980s used mostly soil materials which fulfilled the first two requirements but failed to maintain high hydraulic conductivity. Now in most cases coarser materials are used where the most common fraction size is 4/8 and 8/16 millimeter. These fractions provide a sufficient hydraulic conductivity and are depending on the material supporting a healthy macrophytes growth and good treatment efficiency (Vymazal, The use of sub-surface constructed wetlands for wastewater treatment in the Czech Republic: 10 years experience, 2002).

The artificial wetlands at traffic junction Raasdorp dig out next to the highway. The ground is covered with a plastic sheeting which is covered again with coarse material to prevent floating on groundwater. An overview of the layout of the artificial wetland can be found in Figure 2. To prevent water spilling to the adjacent field overflow gates are constructed. These are located between the sedimentation basin and the artificial wetland and again between the wetland and the infiltration ditch. If the water level is as high as the inflow of these overflow gates, water spills to the next compartment.

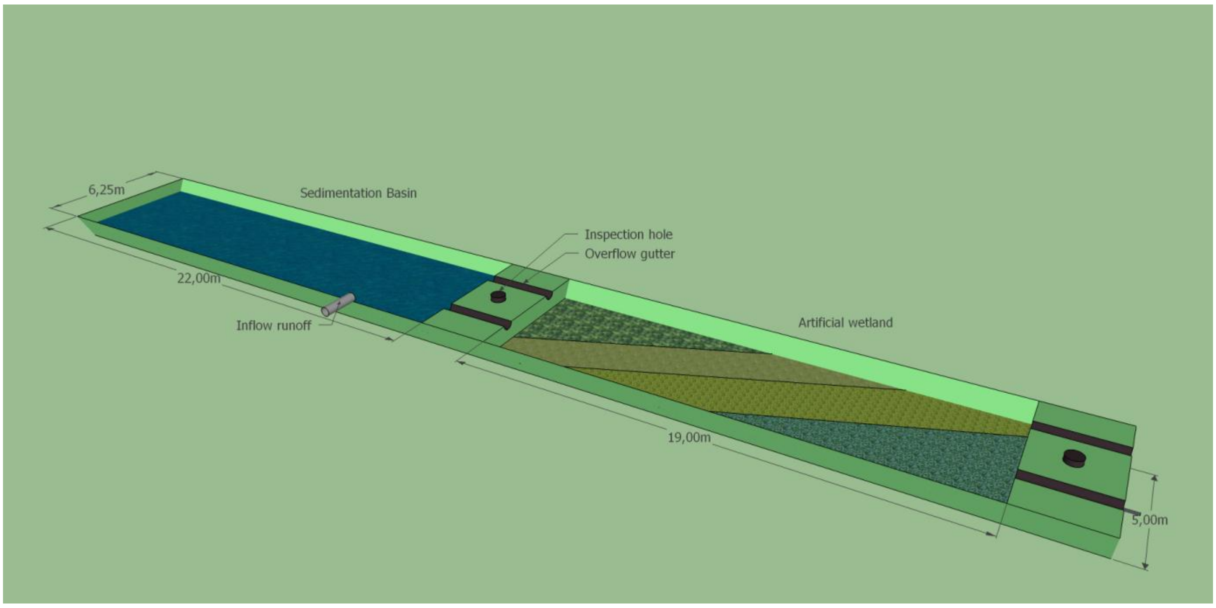


FIGURE 2 OVERVIEW OF THE ARTIFICIAL WETLAND

3.1.1 VEGETATION

In what is known as the clean water act of the US government, wetlands are defined as “areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support, and that under normal circumstances do support a prevalence of vegetation typically adapted for life in saturated soil conditions” (Brix H., 1997). Vegetation is thus an integral part of an artificial wetland.

The role of vegetation in an artificial wetland is versatile. The key reason why they are present is their ability to improve or to enlarge the water quality improvement. Next to the treatment functions, all kinds of other reasons can be mentioned to use vegetation. In artificial wetlands it does provide shelter and habitat for different animals. The different types of vegetation which can be used in an artificial wetland can also serve to aesthetical purposes. In wintertime the vegetation insulates the filter bed if it is not mown. Further does vegetation stabilize the filter bed and it reduces the risk of erosion and resuspension. The vegetation cover does also function as sort of wetland climate control system. In wintertime, the vegetation cover provides insulation and as a result it keeps the soil free of frost (for a while). On the other hand the cover prevents the soil in times of higher temperatures so the soil keeps a lower temperature (Brix H. , 1994).


FIGURE 3 IN WINTERTIME THE VEGETATION PROVIDES INSULATION AND KEEPS THE SOIL PARTLY FREE OF FROST

The approach of using plant biomass for removing contaminants, primarily toxic metals, from polluted water is called phytoremediation. Phytoremediation is an emerging biological technique which uses plants and their associated rhizospheric zone to extract or inactivate heavy metals located in soil and/or water with the least environmental effects (Yadav, Siebel, & Bruggen, 2011). Also the term biosorption is of the used in literature. This appoints the sorption and/or complexation of dissolved metals based on the chemical activity of microbial biomass (Volesky & Holan, 1995). In general there are three key processes in phytoremediation are: adsorption, biofiltration and biological uptake (Revitt, Shutes, Jones, Forshaw, & Winter, 2004).

Adsorption

Biofiltration
First, a chemical in the gas phase crosses the interface between gas flowing in the pore space and the aqueous biofilm surrounding the solid medium. Then, the chemical diffuses through the biofilm to a consortium of acclimated microorganisms. Finally, the microorganisms obtain energy from oxidation of the chemical as a primary substrate, or they cometabolize the chemical via nonspecific enzymes. Simultaneously, there is diffusion and uptake of nutrients, such as nitrogen and phosphorous in available forms, and oxygen within the biofilm (Swanson & Loehr, 1997).

Biological uptake
Aquatic plants contribute to the nutrient transformation by abetting in the physical, chemical and microbial processes besides removing nutrients for their own growth. Important is also that vegetation do add organic matter into the water and provide surface area for microbial growth. Many aquatic plants actively transport oxygen to the anaerobic layers of the soil and help in oxidation and precipitation of heavy metals on the root surfaces (Gopal, 1999).

Biosorption
Sorption or complexation of dissolved metals based on the chemical activity of microbial biomass is known as biosorption. Strong biosorbent behaviour of certain types of microbial toward metallic ions is a function of the chemical makeup of the microbial cells of which it consists. This type of active biomass consists of dead and metabolically inactive cells. It is concluded that from all three groups of easily available biomass types, algae, fungi, and bacteria, there are potent biosorbent materials.

- Movement of metallic contaminant toward the sorbing root surface
- Transport of metal flux through the root cell membranes into root biomass

The artificial wetland at traffic junction Raasdorp is initially planted with four different Carex species, see Table 2.

TABLE 2 VEGETATION TYPES ON ARTIFICIAL WETLAND

Vegetation type	Dutch translation	Amount (pieces)
Carex Muskingumensis	Palmzegge	130
Carex Panicea	Blauwe zegge	130
Carex Pendula	Oeverzegge	130
Cared Riparia	Hangende zegge	130

Another important aspect of macrophytes in wetlands is the transport of oxygen to the root zone. In wetlands with subsurface flow this is important for aerobic degradation of oxygen-consuming substances and nitrification.

Carex pendula

The results presented here demonstrate that C. pendula accumulates considerable amounts of lead, particularly in root biomass if exposed to wastewater containing varying concentrations of this heavy metal pollutant. The Pb accumulation is higher in roots compared to shoot biomass, however, its content in the shoots is also significant; particularly at higher Pb feed concentrations. Therefore, a complete harvesting of the C. pendula would need significantly less time for the remediation of a lead containing wastewater.

3.2 PERFORMANCES OF ARTIFICIAL WETLANDS

Artificial wetlands are a well-known measure to improve water quality in various cases. Initially they were used to remove nutrients from residential and municipal sewage, storm water and agricultural runoff. However results show a wide range of removal efficiencies.

In Santo Tomé, Argentina, a small scale artificial wetland with dimensions of 6 m length, 3 m width and 0,4 m depth, is used to treat wastewater from a tool manufacturing plant. A soil layer of 0,3 m is transplanted with eight different emergent macrophytes. The residence time was seven day. Here it is showed that the artificial wetland removed 81%, 66% and 59% of incoming Cr, Ni and Zn, respectively, and 84% and 75% of inorganic N and soluble reactive P from the incoming wastewater (Maine, Suñe, Hadad, Sánchez, & Bonetto, 2006).

Due to short-circuiting, short detention and contact times, pollutant remobilisation and seasonal vegetation effects.

TABLE 3 MAXIMUM MEASURED METAL CONCENTRATIONS IN (UG/L) PER LOCATION AT THE ARTIFICIAL WETLAND NEAR THE A1 (TROMP, 2005)

Metal	Road runoff	Influent	Effluent
Cadmium	5,5	1,3	4,3
Chrome	11	6,1	2,2
Copper	445	405	980
Lead	72	20	15
Nickel	12	5,1	16
Zinc	602	256	379

3.3 IMPORTANT ADDITIONAL FACTORS

Artificial wetlands do consist of a couple of main components which are necessary to provide a situation where polluted water can be purified. In the first place the artificial wetland should work properly regarding hydraulic conductivity, macrophytes growth and filtration media. If this is the case, the influence of de-icing salt and road cover is assessed.

3.3.1 DE-ICING SALT

In wintertime when roads can become slippery, de-icing salt is used to prevent roads to become slippery. The most used form of de-icing salt is NaCl however other forms like $CaCl_2$ and $MgCl_2$ can also be used. On roads covered with DAB (dicht asfaltbeton) approximately a dose of 3.4 g chloride per square meter is used. In the case of roads covered with ZOAB (zeer open asfaltbeton) this dose is approximately twice as high. The open structure of ZOAB compared to DAB is the reason that more de-icing salt is needed to prevent slippery situations (Werkgroep 4: water en milieu, 2002). In **ANNEX Winterzout** the different mixtures of de-icing salts used by RWS are clarified.

Get insight in the influence of de-icing salts on the performance of an artificial wetland is the aim of this research. De-icing salt is held responsible for remobilization of heavy metals in the artificial wetland which has the consequence that metals will flush out. Due to this it is recommend to bypass

the wetland in wintertime (Tromp, 2005). Another option is not to use an artificial wetland to treat road runoff what is heavily polluted with heavy metals (Scholz, 2004). Scholz showed that there is a high correlation between the conductivity and the breakthrough of nickel. For his research road runoff water is taken from gully pots on the campus of The University of Edinburg, Scotland. Instead of other findings where the breakthrough of copper is predominantly, in this case copper did not show high correlation with conductivity.
Two CTD divers are placed into the artificial wetland to obtain the variation in conductivity of the influent of the sedimentation basin and the effluent of the artificial wetland. Further the total concentrations of Na^+ and Cl^- is determined in several water samples on different locations in the artificial wetland. The relation between chloride concentration and the conductivity is quantified by the Swedish environmental protection agency as can be seen in Table 4. This table is obtained in absence of other ions in solution. If other ions are in the solution. Since in the artificial wetland also the presence of other ions is expected, the conductivity is only used to see if and when peaks in concentrations do occur.

TABLE 4 RELATION BETWEEN CHLORIDE CONCENTRATION AND CONDUCTIVITY IN ABSENCE OF OTHER IONS (SEPA, 2000)

Chloride concentration (mg/L)	Conductivity (mS/cm)
20	0,30
50	0,50
100	0,70
300	1,00

3.3.2 ASPHALT

Two main types of asphalt used as road cover can be distinguished, DAB and ZOAB. DAB is asphalt with a dense surface opposed to ZOAB. The top layer of a surface covered with ZOAB does contain pores. For the drainage of precipitation and water quality on the road section, this means substantial differences. Precipitation on DAB does flow on the surface to road sides. Precipitation on DAB flows off the surface to the sides of the road. In the runoff pollutants are directly transported to the roadside.
Precipitation on ZOAB flows in the pores. Pollutants which are transported by the precipitation remain to a certain extent in the pores. This results in a better water quality of road runoff when discharged in road sides or other constructions.

4 PROCESSES IN A WETLAND

It is clear that wetlands are used all over the world to treat wastewater. The processes which are responsible for the improvement for the water quality are stated below (USDA-Natural Resources Conservation Service and the US Environmental Protection Agency-Region III, 1994).

- Settling of suspended particulate matter
- Filtration and chemical precipitation through contact of the water with the substrate and litter
- Chemical transformation
- Adsorption and ion exchange on the surface of plants, substrate, sediment and litter (primary fallen plant material)
- Breakdown and transformation of pollutants by microorganisms and plants
- Uptake and transformation of nutrients by microorganisms and plants
- Predation and natural die-off of pathogens

4.1 PROCESSES IN SOIL

In an artificial wetland the soil is used as a highly complex, highly variable bio-molecular sieve. Depending on the composition and type of soil processes like adsorption, transformation and release behaviour of chemical constituents to water or soil take place. The physical properties which are fulfilled by the soil as a sieve are:

- Macroporosity (composed of pores with diameter greater than 200 µm)
- Microporosity (composed of pores with diameter less than 200 µm)
- Physical stability (refers to bonding strength between soil particles forming aggregates)
- External/internal surface and its geometry (defined as magnitude of soil's specific surface in square meters per gram and depth or width of clay's internal surface in nanometers)

Transport of metals bound to colloid particles can be of interest in course substrates where in cases of finer textured substrates it can cause clogging.

The chemical properties include:

- Permanent charge (defined as cation exchange capacity, CEC, which is independent of pH)
- Variable charge (defined as pH-dependent CEC)
- Point of zero charge, PZC (defined as the pH at which the net surface charge is zero or CEC minus anion exchange capacity, AEC, equals zero)
- Inner-sphere/outer-sphere surface complexes (defined as strong surface complexes or inner-sphere complexes, as opposed to weak surface complexes or outer-sphere complexes)
- Hydrophobic-hydrophilic potential (defined as the potential of soil to adsorb water)
- pH buffering (defined as the potential of soil to resist pH changes)

Composition and structure of soil minerals

Clay mineral surface charge

Sorption processes

Adsorption and sorption are both terms which denote the removal of solution chemical species from water by mineral surfaces. The distinction between both terms is based on the mechanisms responsible for this removal. In adsorption, a chemical species may be adsorbed by a surface either electrostatically or chemically. In sorption, a chemical species may accumulate on a mineral's surface either through adsorption, hydrophobic interactions and/or precipitation.

4.2 SPECIATION

The collection of all different physicochemical bonding of metals at a certain location is called speciation. Metals can be present as stable, slightly soluble bonds or as good soluble or even volatile compounds.

TABLE 5 OVERVIEW OF SOLID STATE BINDINGS IN THE SOIL (STEKETEE, 2009)

Binding form	Stability / Solubility
Part of sand or clay particles (silicates)	Very stable, not soluble
(Co-)precipitates of salts (E.g. carbonates, sulphites); (hydro)oxides	Varying sability, from very stable and slightly soluble (sulphites) to good solvable (some hydroxides)
Bond at surfaces of clay, organic matter, oxides	Varying bond strength, potentially soluble
Metallic particles	Stable, not soluble

In the aquatic phase there are also different bonds of metals. The most important ones are stated in Table 6. In the aquatic phase the binding type is important for adsorption as for transport through the soil. When adsorption takes place in the aquatic phase, it is often in the form of the free ion. The transport time is often higher for ions with less charge or neutral complexes as for ions with a higher charge.

TABLE 6 OVERVIEW OF BINDINGS IN AQUATIC PHASE OF SOIL (STEKETEE, 2009)

Binding form	Example
Free ion (Cat ion)	Zn^{2+}
Inorganic complexes	$Zn(OH)^+$, $Zn(SO_4)_2^{2-}$
Organic complexes	Zn-fulvaat, Zn-acetate
Bond to colloidal particles (<0.45 µm)	Humus particles, iron-oxide particles

4.3 ACCELERATING AND INHIBITING FACTORS

An environment involving solution/solid interactions contains accelerating and inhibiting factors and processes on the speciation. Accelerating factors and processes comprise effects of varying pH, redox changes, inorganic and organic complexation, microbially mediated species transformations such as biomehylation. On the other hand the inhibiting factors and processes are physical processes as adsorption, sedimentation and filtration; chemical processes as complexation and precipitation; biological processes as membrane processes. Compexation in its various forms can both accelerate and inhibit metal fluxes (Förstner, 1993).

4.3.1 PH

The degree of acidity of a solution is called acidity and is expressed in unit pH. The pH is defined as the negative logarithm of the concentration of H_3O^+ ions. The dimension of the concentration is mole/L. In formula form: $pH = -\log[H_3O^+]$. The pH is a measure which gives insight in the question whether a solution is an acid or a base. The pH of water varies approximately between 0 and 14 where an acid is indicated by an pH which is lower than 7 and a base by an pH which is higher than 7. The pH of pure water is approximately 7. Under certain values of pH, processes can take place or oppositely doesn't take place. The pH value can also influence the growth of several bacteria in a wetland.

A problem of clay soils related to pH is that for a varying pH, adsorbed pollutants can be released more easily (Tromp, 2005).
Read: (Mayes, et al., 2009)
Heavy metal ions sorb onto non-living biomass surfaces and the sorption is greatest at a pH value that is just slightly more acidic than the pH at which there is bulk precipitation of metal hydroxide. As pH is further raised, once the bulk solubility limit is reached, the sorption is greatly reduced because the metal ion is removed from solution by the bulk precipitation. Thus the maximum bio-sorption of metal ions is always attained at the optimum pH value. (Shaker, 2007)

4.3.2 REDOX

When in a reaction electrons are donated by the one substances and are accepted by another substance, it is called a redox reaction. There is a tension difference with the aqueous solution containing the substances of interest and a standardised hydrogen gas electrode. The tension difference is the driving force for the reaction and is termed redox potential – Eh (SEPA, 2000). An element which donates an electron is called a reducer or electron donor where an element which accepts an electron is called an oxidant or an electron acceptor. The most important oxidants are: O_2, NO_3^-, SO_4^{2-}, Cl_2 and O_3. Important reducers are Fe^{2+}, H_2S, NH_3 and Pb (Moel, Verberk, & Dijk, 2005).
A redox reaction is often reversible and, depending on whether the redox potential is above or below the equilibrium, either the oxidising or the reducing form will be stable.
Figure 4 shows

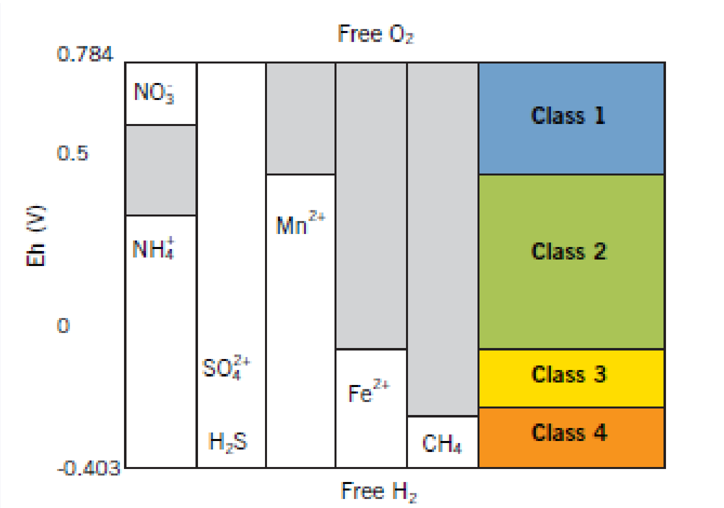


FIGURE 4 FORMS IN WHICH CERTAIN REDOX-SENSITIVE SUBSTANCES OCCUR IN RELATION TO REDOX (SEPA, 2000)

5 METHODS

To investigate the influence of de-icing salts on the remobilization of heavy metals and PAH the research is roughly split up in four parts. First the artificial wetland which is supposed to be used as the object to study will be tested if road runoff water will actually flow through the filter. Secondly water and soil samples will be taken of the artificial wetland to get insight in the main parameters which are present in the soil and the road runoff water in the different compartments of the filter. Thirdly research in the laboratory will be done. Fourthly, parallel to the other three parts, a literature study will be carried out to get insight in the key processes and obtain results an recommendations from earlier research. The results of this study are mainly described in the previous chapters.

5.1 THROUGHFLOW CHECK ARTIFICIAL WETLAND

To determine an artificial wetland which is suitable to take the needed measurements the water level is monitored for a longer period by use of divers. The diver is particularly used to determine water level fluctuations. Also a visual inspection of the artificial wetland is carried out. For the same period precipitation data will be obtained from the KNMI for station 240 – Schiphol.

5.1.1 RESULTS

The water level fluctuations of the sedimentation basin and the precipitation data is merged as shown in Figure 5. Also the water level fluctuations of the filter basin merged with the precipitation data is shown in Figure 6.

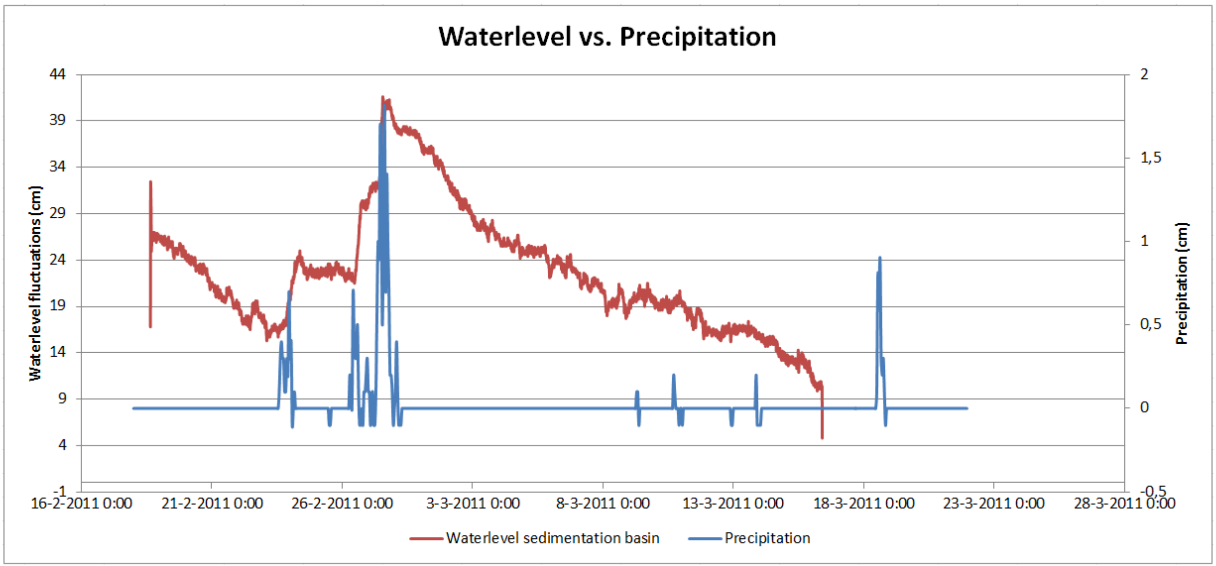


FIGURE 5 WATER LEVEL FLUCTUATIONSIN SEDIMENTATION BASIN VS PRECIPITATION

Figure 5 shows that the water level increases during a precipitation event. In times of drought the water level decreases until a new precipitation event occurs. Water from the sedimentation basin is likely discharged to the filter basin. By determine the slope of the water level fluctuations the rate in which water is discharged into or out the sedimentation basin can be determined.

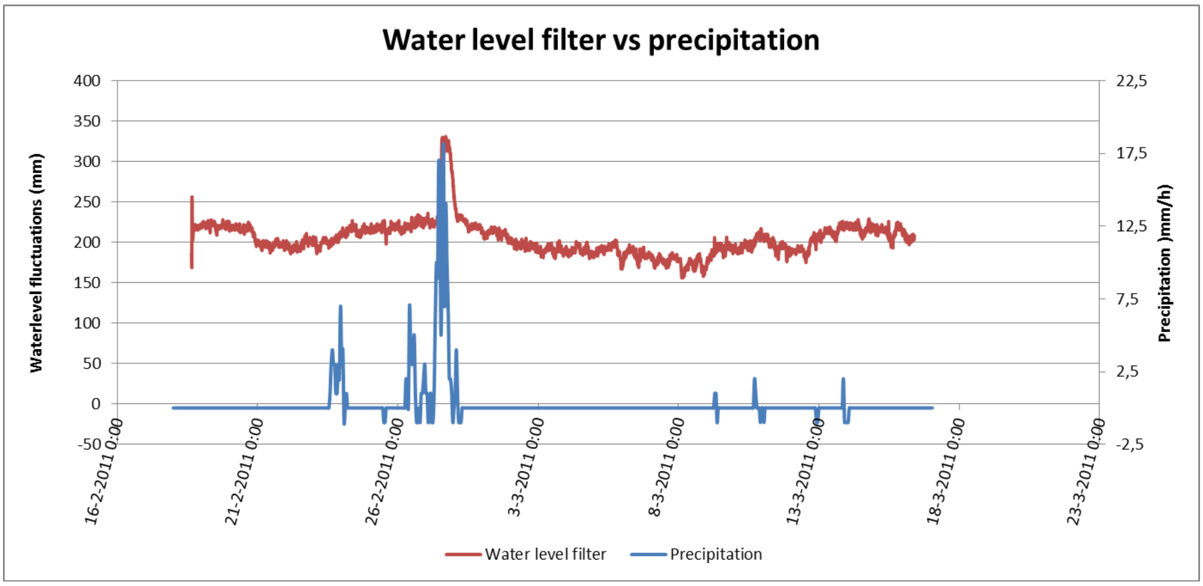


FIGURE 6 WATER LEVEL FLUCTUATIONS IN FILTER VS PRECIPITATION

The water level in the filter part of the artificial wetland is more or less constant except directly after the large precipitation event. The water level in the filter is maintained on a minimum level due to the outflow pipe which is designed 40 centimeter above the bottom of the filter compartment. This explains the small variation in water level which is present in the filter compartment. The discharge of water to the infiltration ditch is also visible looking at the discharge pipe. This pipe is located in the manhole between filter compartment and infiltration ditch, see Figure 7. Several times this pipe is inspected and most of the times it is noticed that water discharges out the pipe.

FIGURE 7 DISCHARGE PIPE OF THE ARTIFICIAL WETLAND

5.1.2 FLUXES

From the obtained results also an estimate of the amount of inflow, through flow and discharge can be made. To obtain an estimate of the discharge of the sedimentation basin into the artificial wetland a trend line is plotted in the water level fluctuation data. The data used are the water level fluctuations in the sedimentation basin following a precipitation event. A useful range is obtained from the data in march. The data is plotted in a graph, showed in Figure 8. The graph shows the water level decrease in the sedimentation basin directly after a precipitation event. This can also be seen in Figure 5 as the data used now is part of that series. The formula displayed in Figure 8 belongs to the trend line. This trend line gives information about the velocity of the water level decrease. Together with the dimensions of the sedimentation basin an estimate of the discharge to the artificial wetland can be made.

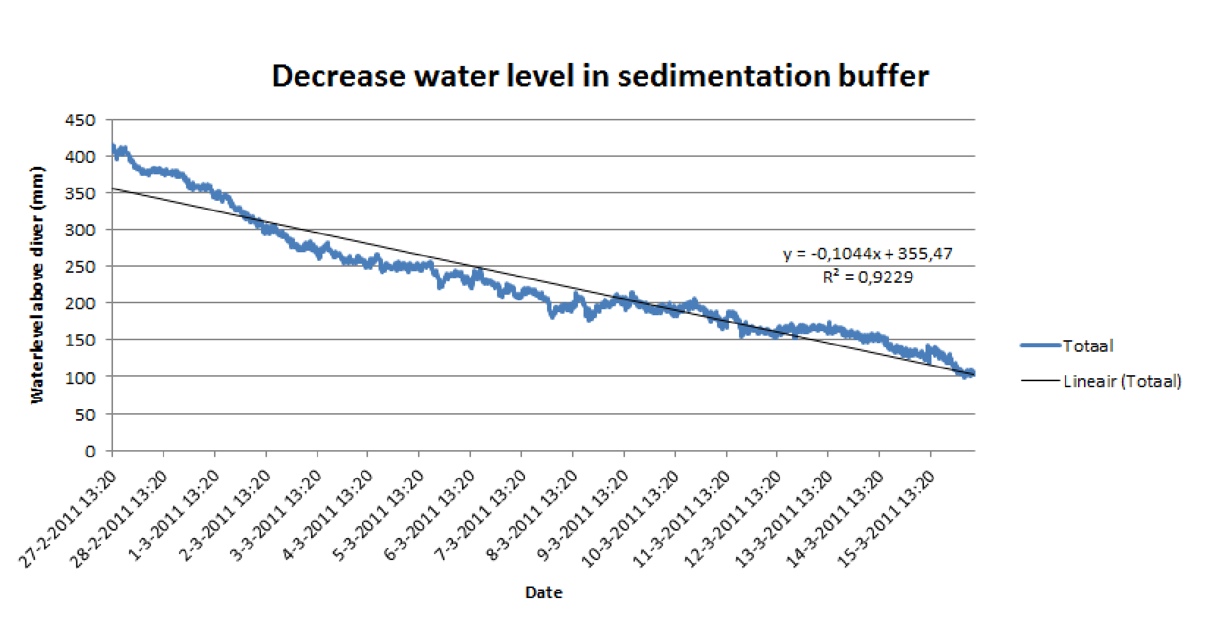


FIGURE 8 DECREASE WATER LEVEL IN SEDIMENTATION BUFFER WITH TREND LINE TO DETERMINE THE DISCHARGE

5.1.3 CONCLUSION

Based on the obtained results, it is plausible that the sedimentation basin discharges the water through the drain into the filter, and the filter discharges its water into the infiltration ditch. Side note is that it is not possible to check if the textile cover of the filter compartment contains holes beneath the water level. If this is the case, in the filter compartment there could be an interaction with groundwater.

5.2 WATER AND SOIL SAMPLES

To get insight into the key parameters which are present in road runoff water or sedimentation basin influent, filter basin influent and filter basin effluent several water samples are taken. The samples are taken in a period of precipitation at the inflow of the sedimentation basin, the sedimentation basin itself and the effluent pipe of the filter basin.

5.2.1 RESULTS

The results of the ions which are measures in water at different locations are displayed in Figure 9**.**

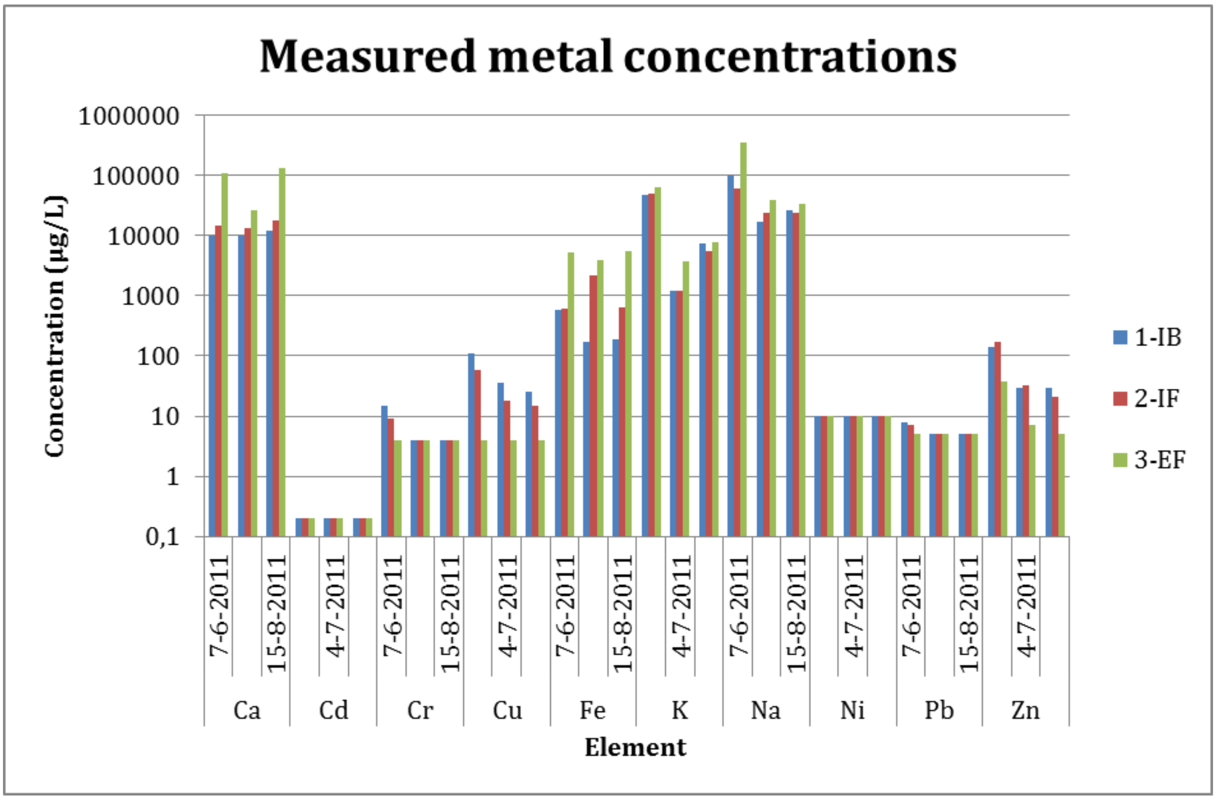
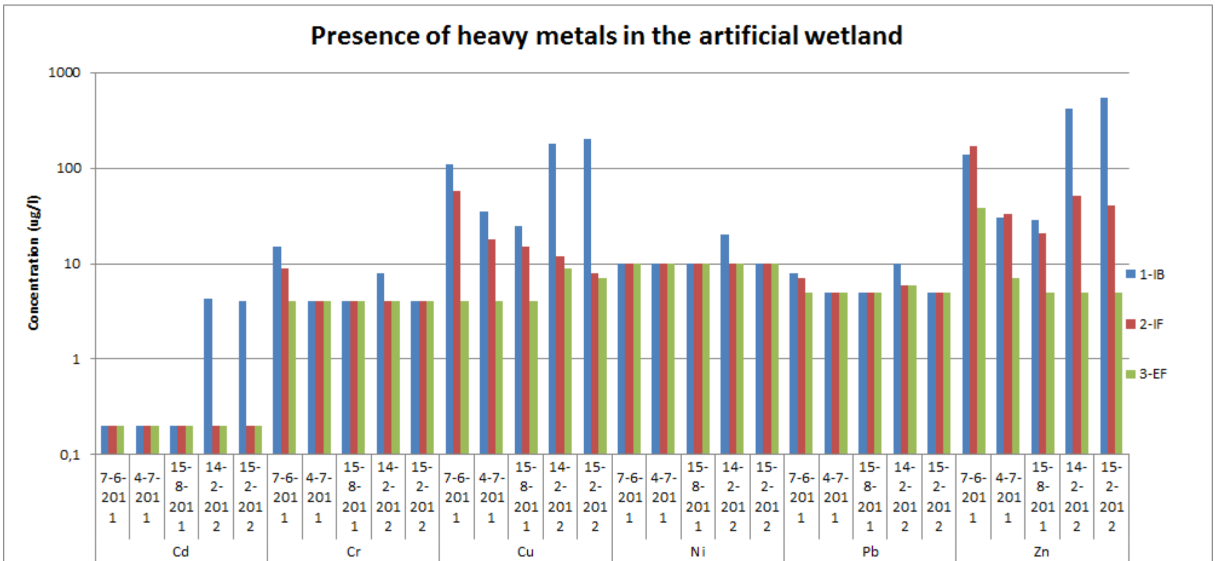


FIGURE 9 MEASURED METAL CONCENTRATIONS IN THE INFLUENT AND EFFLUENT OF THE ARTIFICIAL WETLAND COMPARTMENTS



	Cd 7-6-2011	Cd 4-7-2011	Cd 15-8-2011	Cd 14-2-2012	Cd 15-2-2012	Cr 7-6-2011	Cr 4-7-2011	Cr 15-8-2011	Cr 14-2-2012	Cr 15-2-2012
1-IB	0,2	0,2	0,2	4,3	4	15	4	4	8	4
2-IF	0,2	0,2	0,2	0,2	0,2	9	4	4	4	4
3-EF	0,2	0,2	0,2	0,2	0,2	4	4	4	4	4

	Cu 7-6-2011	Cu 4-7-2011	Cu 15-8-2011	Cu 14-2-2012	Cu 15-2-2012	Ni 7-6-2011	Ni 4-7-2011	Ni 15-8-2011	Ni 14-2-2012	Ni 15-2-2012
1-IB	110	35	25	180	200	10	10	10	20	10
2-IF	58	18	15	12	8	10	10	10	10	10
3-EF	4	4	4	9	7	10	10	10	10	10

	Pb 7-6-2011	Pb 4-7-2011	Pb 15-8-2011	Pb 14-2-2012	Pb 15-2-2012	Zn 7-6-2011	Zn 4-7-2011	Zn 15-8-2011	Zn 14-2-2012	Zn 15-2-2012
1-IB	8	5	5	10	5	140	30	29	420	550
2-IF	7	5	5	6	5	170	33	21	51	41
3-EF	5	5	5	6	5	38	7	5	5	5

This graph contains the highest possible values which are measured. For example the shaded values of Cd were all below the detection boundary of 0,200 micrograms per liter. To obtain the graph these values are set to the detection boundary. These values cannot be used to evaluate specific performance of the artificial wetland on this element. The reason they are in is to compare the concentrations of the different metals to obtain an indication of the key elements and to compare them with the intervention values. Since these are 0,4 ug/l for cadmium, these boundary is not exceeded in the effluent water.

The smallest concentrations of Cr, Cu, Ni and Zn are all measured in the effluent of the filter which suggested that somewhere in the artificial wetland these metals stay behind. On the other hand higher concentration of metals Ca, Fe, Ka and Na are measured in the effluent of the artificial wetland discharge. It seems like these metals will be released somewhere in the artificial wetland.

A grab monster is taken of soil in the buffer and of the filter. In the buffer, soil is taken from the sides where sedimentation took part and emergent macrophytes are growing. The bottom of the sedimentation basin is filled up with larger stones. In the filter the soil is collected on four different locations equally spread over the bed. The sampling depth was approximately 20 centimeter. The water level was located approximately 12 cm below the surface. The lava stones visually dominates the sample. The presence of dry matter (DS), particles with a diameter of respectively 2 and 16 micrometer (KGF2 and KGF16) and organic matter (OS) is presented in Figure 10**.**
The result of KGF16 in the filter is set to -1 because these value was not determined in the results.

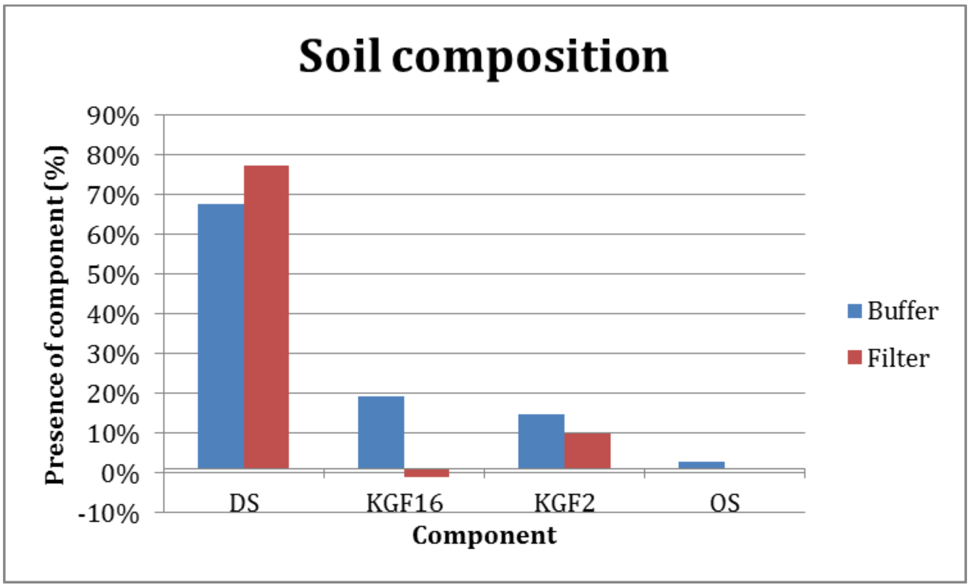


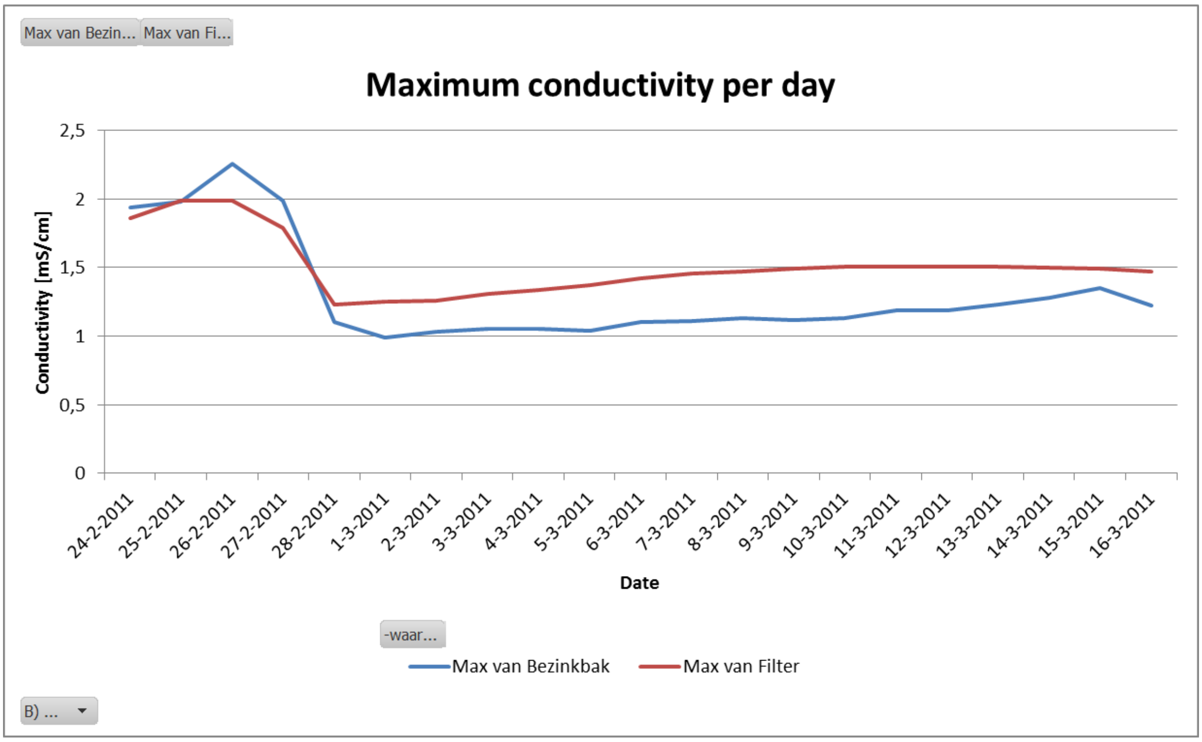
FIGURE 10 ARTIFICIAL WETLAND SOIL COMPOSITION OF BOTH COMPARTMENTS

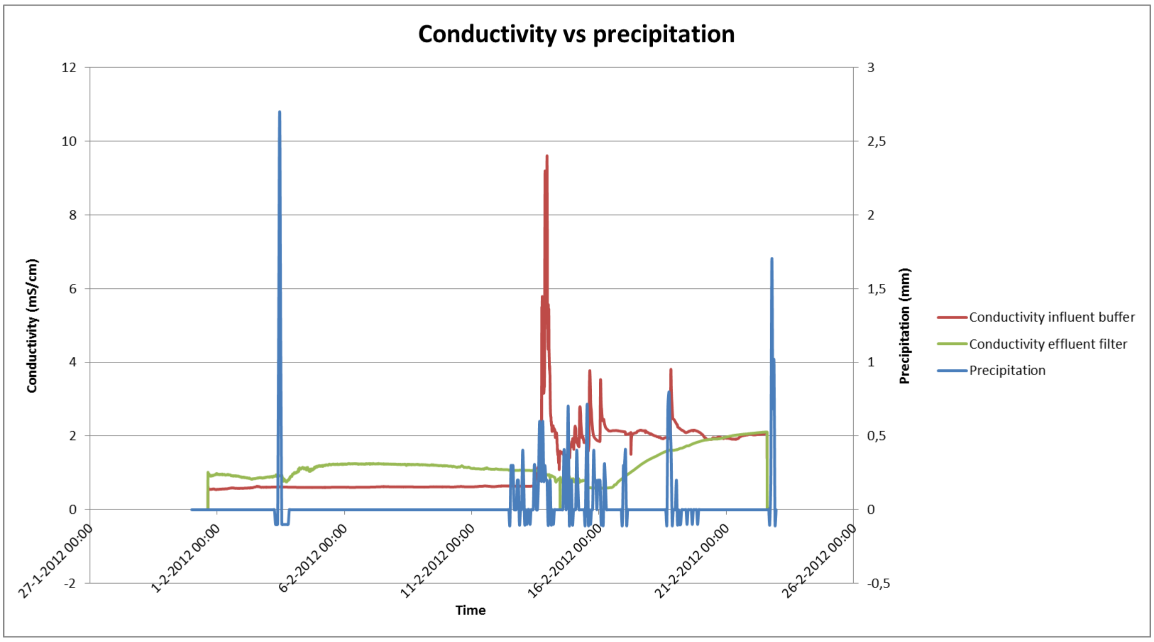
5.2.2 DISCUSSION

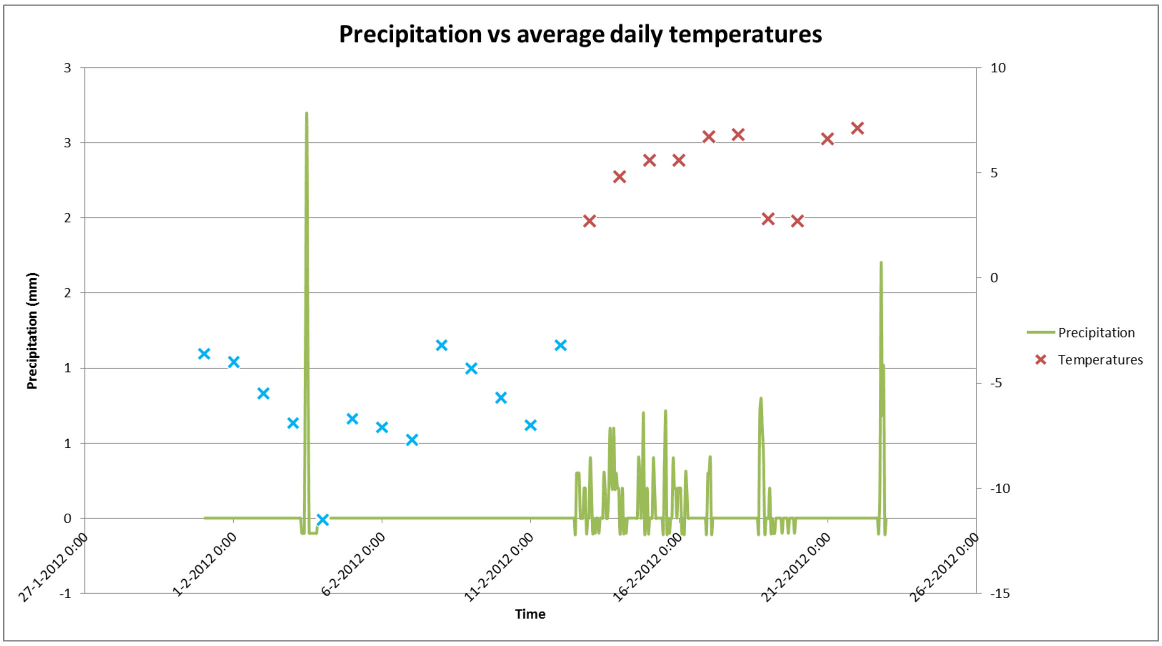
All the measurements are random samples. Since the concentrations of different elements do change over time it is not possible to quantify if a measurement is taken before, right onto or just after a peak concentration of a certain element. On the other hand, the more measurements taken, the more reliable the pattern which can be found in concentrations will be.

5.3 CONDUCTIVITY

The conductivity is measured to see when deicing salt does enter the artificial wetland.


Max van Bezin...
Max van Fi...
Maximum conductivity per day
Conductivity [mS/cm]
2,5
2
1,5
1
0,5
0
24-2-2011
25-2-2011
26-2-2011
27-2-2011
28-2-2011
1-3-2011
2-3-2011
3-3-2011
4-3-2011
5-3-2011
6-3-2011
7-3-2011
8-3-2011
9-3-2011
10-3-2011
11-3-2011
12-3-2011
13-3-2011
14-3-2011
15-3-2011
16-3-2011
Date
-waar...
Max van Bezinkbak
Max van Filter
B) ...


Conductivity vs precipitation
Conductivity (mS/cm)
Precipitation (mm)
12
10
8
6
4
2
0
-2
3
2,5
2
1,5
1
0,5
0
-0,5
27-1-2012 00:00
1-2-2012 00:00
6-2-2012 00:00
11-2-2012 00:00
16-2-2012 00:00
21-2-2012 00:00
26-2-2012 00:00
Time
Conductivity influent buffer
Conductivity effluent filter
Precipitation


Precipitation vs average daily temperatures
Precipitation (mm)
Time
Precipitation
Temperatures
27-1-2012 0:00
1-2-2012 0:00
6-2-2012 0:00
11-2-2012 0:00
16-2-2012 0:00
21-2-2012 0:00
26-2-2012 0:00
10
5
0
-5
-10
-15

6 DISCUSSION

In the growing season vegetation is present in the artificial wetland. The vegetation is responsible for the uptake of part of the heavy metals by storing it into biomass. This manner of removal of the heavy metals can only contribute efficiently if vegetation is mown after the growing season. By removal of the biomass, the stored heavy metals will be removed also. If the vegetation remains in the artificial wetland it will decompose again. This results again in a release of the previously adsorbed heavy metals. To get the best performance of an artificial wetland it is important to have a good maintenance contract. Only a contract can't do the job which became clear in practice. From the side of the clients it is recommended to assign a supervisor. This person has to check whether the artificial wetland is maintained properly or not. If not, he can directly take measures to prevent the artificial wetland of poor performance.

Vegetation

The role of vegetation does have different roles according to literature. On the one hand vegetation is important because of the uptake of pollutants and thus has to be harvested before it dies which results in an release of the pollutants which were taken up. On the other hand vegetation should not be harvested in winter time, when most species die, because of the insulation by vegetation of the surface of vegetated beds. An option in which both advantages of vegetation are represented is desirable. In this case a vegetation type which does not decompose in wintertime should be used. Fallen leaves or other plant residues which are present in the filter have to be removed from time to time. This can be done on schedule but good monitoring of the state of the artificial wetland is crucial to avoid pollution in the meantime.

Metal analysis

The metals which are present in the artificial wetland are partly available for remobilization. Metals bound by an ion exchange process are still available when other ions are available in solution. The general rule is that trivalent ions are preferred over divalent ions. Divalent ions are on their place preferred over monovalent ions. At high concentrations, the differences in exchange potentials of ions of different valence diminish and, in some cases, the ion of lower valence has the higher exchange potential (Wachinski & Etzel, 1997).

7 CONCLUSIONS

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9 APPENDIX

1. Review on maintenance
2. Construction documents Dura Vermeer
3. Graduation research proposal
4. Measurement plan initial description
5. Sample locations
6. Measurement plan column test

10 OVERIG

10.1 COPPER

Two natural isotopes of copper are known, Cu-63 (69, 17%) and Cu-65 (31, 83%). In the environment copper is present as free (hydrated) ion but more frequently in complexed form (carbonates, cyanides, amino acids, chlorides and humus acids). The speciation pattern of copper depends on pH, redox potential and of the local concentrations of ligands, like the amount of organic material (Slooff, Cleven, Janus, & Ros, 1987).

Copper and its alloys, like brass, are widely used. It is used for electrical wiring, machine components, catalysts and more.

Speciation

Behaviour in water

When a physical/chemical equilibrium is reached, the distribution of copper over several species can be calculated. To do this, the stability constant K of all present equilibrium reactions should be present even as nature and concentration of all reaction partners. Important ligands for copper to form complexes with are: OH^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, colloidal iron- and manganese hydroxides and macromolecular organic matter. (Slooff, Cleven, Janus, & Ros, 1987)

Behaviour in soil

The behaviour of copper in the soil depends on different variables. Important are clay content, type of clay, acidity (pH), redox potential (pE), organic matter content, nature of all other components in groundwater and the nature and content of manganese compound.