CHALMERS

Järnbrott Stormwater Pond

Evolution of the Pollutant Removal Efficiency and Release from Sediments

Master's Thesis in the International Master's Programme, Applied Environmental MeasurementTechniques

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Cover page: Views of Järnbrott stormwater pond

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ABSTRACT

Stormwater ponds have often been used in monitoring urban stormwater pollution. They provide quiescent conditions for particles to settle. By this way, pollutants are removed from the water phase. Indeed, pollutants like heavy metals, polycyclic aromatic hydrocarbons (PAH), oxygen demanding compounds and nutrients are, to a large extent, attached to particles. However, other mechanisms such as uptake from living organisms, photoreactions, decaying vegetation, and release from the sediments to the overlying water can have an effect on the removal mechanisms. Thus pollutant removal efficiency in stormwater ponds will be affected by the changes in pond morphology (vegetation growth and increased sediment layer), catchment area, and amount of sediments accumulated on the pond's bottom.

The Järnbrott pond, situated in Göteborg, Sweden, was studied for the first time in 1997. According to the results recorded in this study, in 2004, suspended solids, some of the heavy metals studied (Cd and Pb) and phosphorus compounds are removed to a large extent and their removal efficiencies are comparable to the one measured in 1997. During the time of this study nitrogen compounds have been produced in the pond probably by decaying vegetation and release from the sediments. This potential release from the pond's sediments has been shown during a laboratory experiment. An additional study on heavy metals that were not considered in 1997 (Co, Cr and Ni), as well as PAH and oxygen demanding compounds shows that the Järnbrott pond is able to remove most of these compounds: PAH, Co and Cr are highly removed whereas Ni show negative removal efficiency. Oxygen demanding compounds are less removed than expected but no values from 1997 are available for comparison.

From the results it is concluded that the changes in pond's morphology between 1997 and 2004 affected nitrogen compounds, Cu and Zn removal efficiency negatively. Concerning phosphorus compounds, it seems that they haven't been affected by changes in and around the pond.

Keywords: stormwater pond, removal efficiency, suspended solids, heavy metals, nutrients, PAH, sediments, pollutant release.

Järnbrotts dagvattendamm
Effektivitet i föroreningsavskiljning och utlösning av föroreningar från sediment
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SAMMANFATTNING

Dagvattendammar används ofta till att behandla föroreningar i dagvatten. Dammar skapar lugna flödesförhållanden vilket möjliggör sedimentering av partiklar, vilket innebär att föroreningar associerade till dessa såsom tungmetaller, polycykliska aromatiska kolväten (PAH), syreförbrukande ämnen och näringsämnen avskiljs från vattenfasen. Dock kan andra mekanismer såsom upptag från levande organismer, fotosyntesreaktioner, nedbrytning av vegetation och utlösning av föroreningar från sedimenten till omgivande vattenfas påverka avskiljningsmekanismerna. Således kommer föroreningsavskiljningens effektivitet i dagvattendammar att påverkas av förändringar inom avrinningsområdet samt förändringar i dammorfologi, d.v.s. vegetationstillväxt och ökning av sedimentlagret ackumulerat på dammbotten.

Järnbrottsdammen som är belägen i Göteborg studerades på motsvarande sätt, som i denna studien, första gången 1997. Resultaten från denna studie 2004 visar på god avskiljningsförmåga för suspenderat material, vissa tungmetaller (Cd och Pb) och fosforföreningar, vilka är jämförbara med resultaten från mätningarna 1997. Resultaten visar också att halterna av kväveföreningar ökar när dagvattnet passerar genom dammen vilket troligtvis beror på att nedbrytning av vegetation bildar kväveföreningar samt att processer i bottensedimenten orsakar att bundet kväve går i lösning. Det sistnämnda har också påvisats från laboratorieexperiment i denna studie. Ytterligare föroreningar, som inte tidigare studerats, såsom tungmetallerna Co, Cr, och Ni, PAH och syreförbrukande ämnen visar sig avskiljas väl i Järnbrottsdammen. PAH, Co och Cr avskiljs mycket väl medan Ni visar en negativ avskiljning. Syreförbrukande ämnen visar sig ha en sämre avskiljningsförmåga än förväntat, dock finns inga resultat från 1997 att jämföra med.

Från resultaten i denna studie kan man dra slutsatsen att dammens förändrade morfologi mellan 1997 och 2004 påverkat avskiljningsförmågan av kväveföreningar, Cu och Zn negativt. Dock verkar det som avskiljningen av fosforföreningar inte har påverkats av förändringarna i dammen.

Nyckelord: dagvattendamm, avskiljningseffektivitet, suspenderat material, tungmetaller, näringsämnen, PAH, sediment, föroreningsspridning

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LIST OF ABBREVIATIONS

BCF: bioconcentration factor
BOD_5: biological oxygen demand measured for a 5 days period
DOC: dissolved organic carbon
EMC: event mean concentration
EPA: environmental protection agency
K_{ow}[1]: distribution coefficient between octanol and water
PAH: polycyclic aromatic hydrocarbons
SMC: site mean concentration
TOC: total organic carbon
TSS: total suspended solid
VSS: volatile suspended solid

The following chemicals will be further on denominated by their formula:
Heavy metals:
Al: aluminium
Cd: cadmium
Cr: chromium
Cu: copper
Fe: iron
Mn: manganese
Ni: nickel
Rh: rhodium
Zn: zinc

Nutrients:
NH_4^+: ammonia
NO_3^-: nitrate
NO_2^-: nitrite
Total-N: total nitrogen
PO_4^{3-}: orthophosphate
Total-P: total phosphorus

Reagents used:
HNO_3: nitric acid

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[1] $K_{ow} = \frac{[C]_{octanol}}{[C]_{water}}$

TABLE OF CONTENT

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF EQUATIONS

1. Introduction

1.1. Stormwater management

For more than thousand years, men are familiarized with drainage, primarily used for irrigation purpose. However, stormwater drainage is a rather new technology since comprehensive approach for the simulation of flow quantities, indispensable for the conception of stormwater drainage and detention systems only began in the late 1950's. (Mays, 2001). Storm drainage systems developed with the urbanization. Indeed, the impervious cover used for roads, parking lots construction increases all together the volume of water available for runoff and the amount and the harmfulness of pollutants. Storm drainage systems are a combination of a number of hydraulic elements, interrelated: gutters, pipes, and manholes. Two kinds of sewer network are used to collect rainwater: combined and separated sewers. The first one mixes urban wastewater and stormwater and ends up in wastewater treatment plants. The second one collects stormwater separately and ends up, normally untreated, into the closest receiving waters, e.g. rivers, lakes and seas. Sometimes stormwater is treated by using ponds, wetlands or other facilities. Detention facilities such as detention ponds have been first constructed to smoothen the flow peaks generated by rainfalls in urban areas and diverted into receiving waters (watercourses, lakes and oceans). Moreover, if the pond's characteristics are adequate, it also serves water quality improvement purposes, mainly by settling of particles and attached pollutants, such as heavy metals, nutrients and polycyclic aromatic hydrocarbons for instance.

1.2. Aims and goals

Two different studies, both related to the study of pollutants in the Järnbrott pond (Göteborg, Sweden) were carried out during this thesis work. The first study focuses on the pollutant removal efficiency in the Järnbrott pond and the second one deals with the driving mechanisms for release of pollutants from the sediments to the water column.

The goal of the first part of the project was to calculate the removal efficiency of the pond for different pollutants: suspended solids, heavy metals, PAH, oxygen demanding compounds, nutrients and some of the microorganisms present in stormwater. In this part of the project, water samples have been taken at the inlet and outlet of the treatment facility for several storm events. Analyses have been carried out in the laboratory for the parameters quoted above and the removal efficiency calculated from the measured concentrations. The values will be compared with the removal efficiency determined during a similar work done seven years ago in the same pond, in order to assess the development of the pond efficiency over the years.

The aim of the second part of the work was to study the potential release of toxic compounds from the sediments to the water column under different conditions :anoxic conditions, high conductivity and turbulences. For example, low oxygen content can be recorded during winter period, due to ice cover. What is the influence of these conditions on the pond's water quality, consider whether sludge has to be removed or not? Removal of sediments is an expensive process and no efficient treatment is nowadays available. The second part of the project will be focused on nutrients, nitrogen and phosphorus compounds, and heavy metals.

1.3. Litterature review

In the literature review, different stormwater treatment facilities, their advantages and disadvantages will be reviewed. Then, the literature concerning each pollutant studied in this thesis work will be summarized, focusing on the sources, the removal efficiencies and mechanisms for each pollutant in stormwater. For metals and nutrients, an additional part on their behavior in the sediments will be added in order to give a background for the lab work that has been made on the mechanisms release from the sediments.

1.3.1. Stormwater management

Storm sewers are crucial in canalisation of urban runoff. Separate or combined sewer systems, which gather stormwater and wastewater, can be found. Both are designed to connect stormwater inlets points (road gullies, roof downpipes) to a discharge point, by using a serie of pipes (with an additional pipes bringing wastewater from household in the case of combined sewers) (David and John, 2000). This was made to decrease the local flooding problems. However, nowadays the goal of stormwater management is not only drainage of stormwater but also treatment and possible reuse. For this, stormwater management options have been developed. In Table 1 below, different stormwater treatment facilities are presented (Butler and Davies, 2000).

Table 1: Stormwater management options, their advantages and disadvantages (Based on Butler and Davies, 2000)

Options	Examples	Advantages	Disadvantages
Local disposal	Infiltration devices (e.g. soakaways, infiltration trenches)	• Runoff reduction of minor storms • Groundwater recharge • Pollution reduction	• Capital cost • Clogging • Groundwater pollution
	Vegetated surfaces (e.g. swales)	• Runoff decay • Aesthetics • Pollution reduction • Capital cost	• Maintenance cost • Groundwater pollution
	Porous pavement	• Runoff reduction of minor storms • Groundwater recharge • Pollution reduction	• Capital and maintenance costs • Clogging • Groundwater pollution
Inlet control	Rooftop pounding	• Runoff delay • Cooling effect on building • Possible fire protection	• Stuctural loading • Roof leakage • Outlet blockage
	Downpipe storage (e.g. water butts)	• Runoff delay • Reuse opportunities • Small size	• Small capacity • Access difficulties
	Paved area ponding (e.g. gully throttles)	• Runoff delay • Pollution reduction • Possible retrofitting	• Restricts other uses when raining • Damage to surface

On-site storage	Surface ponds (e.g. water meadows, detention ponds)	• Large capacity • Runoff reduction of major storms • Aesthetics • Multipurpose use • Pollution reduction	• Capital and maintenance cost • Large footprint • Pollution and eutrophication • Pest breeding potential • Aesthetics • Safety hazards
	Underground tanks	• Runoff reduction of storms • Pollution reduction • No visual intrusion • Capital cost	• Maintenance cost • Access difficulties
	Oversized sewers	• Runoff reduction of storms • Pollution reduction • No visual intrusion • Capital cost	• Maintenance cost • Access difficulties
Other devices	Oil trap	• Flow rate reduced	• Small catchment area where heavy oil or petrol spills are expected • Maintenance
	Constructed wetlands	• Simple and inexpensive to build • Reduction of runoff flows • Important pollution reduction • Multipurpose use (recreational, wildlife habitat)	• Large area needed • Long term program of maintenance • High sensitivity

The principal advantages and disadvantages of each facility are discussed above. The classification of on-site storage systems, in which detention ponds are included, is built on several parameters: the storage time (retention or detention), the configuration (on-stream or off-stream), the standing water (wet, dry or wet/dry), the location (surface or underground) and the function (flow balancing/flow storage or water quality) (Butler and Davies, 2000).

Complementing non-structural measures can be added to reinforce the effectiveness of the structural measures listed above. Street cleaning performed with new techniques available showed that street sweeping could be an effective technique to reduce stormwater pollution (German, 2001). Gully pot cleaning allows the removal of coarse particles and some highly insoluble compounds like oils. The removal efficiency of cleaning can raise 70% for these pollutants (Butler and Davies, 2000).

Several other obvious but not easily set up methods should be included in the stormwater management like: control of illicit discharges, pesticides and fertilizers management, careful chemical storage and usage, and the last but not least, the education of the public and their role in stormwater pollution.

1.3.2. Stormwater pollutants: removal mechanisms and fate in the sediments

A complex mixture of organic and inorganic pollutants can be found in stormwater, resulting from both natural and anthropogenic sources. The most common pollutants in urban stomwater runoff are suspended solids, heavy metals, nutrients, hydrocarbons (mainly originating from petroleum products), pesticides and fertilizers (Karouna-Renier and Sparling, 2000). Two mechanisms prevail in urban stormwater pollution: the dissolution or wet deposition of atmospheric compounds washed by rainfall, and the erosion of urban surfaces (Butler and Davies, 2000).

1.3.2.1. Suspended solids

Suspended solids in stormwater runoff are of great importance because they increase the turbidity in the receiving waters, decreasing the visibility and thus creating unfavorable conditions for living organisms. However, their main impact on ecosystem is due to their high specific area that makes them the main vector of pollution (Chebbo and Bachoc, 1992).

Sources and characteristics

Urban runoff and especially paved surface runoff contains significant concentrations of colloidal and volatile fractions of both inorganic and organic particulates (Sansalone et al., 1995) ranging from the sub microns to the gravel size (Schroeter and Watt, 1989). Indeed, sand (from 0,062 to 2,0mm), silt (from 0,004 to 0,062mm) and clay fractions (smaller than 0,004mm) are present in urban dirt and road dust (Greb and Bannerman, 1997) on which biodegradable organics, phosphorus, heavy metals and polycyclic aromatic hydrocarbons are bound (Schroeter and Watt, 1989, Greb and Bannerman, 1997). Indeed, smaller particles, which have the highest specific surface will have more affinity with pollutants like heavy metals, whereas solids with size greater than 100µm have a much higher organic content and thus a high concentration of oxygen demanding compounds (Chebbo and Bachoc, 1992). A study on a storm sewer, in France showed very high particulate concentrations for certain pollutants (Table 2) (Chebbo and Bachoc, 1992).

Table 2: Pollution load attached to particles (as a % of the total pollution) (Chebbo and Bachoc, 1992)

Pollutants	COD	BOD	Total-N	Hydrocarbon	Pb
Pollution load attached to particles	84-89%	>77-95%	57-82%	>86%	79-96%

More details are found for each pollutant and its affinity to particulate matter in the following sections.

The fine particles are the main ones that can be transferred in suspension in the down stream sections of the sewer network and thus to the treatment facility (Chebbo and Bachoc, 1992) whereas the coarser ones are more subjected to sedimentation in the pipes (Perrusquia, 1991). Particles with a size under 10µm have a tendency to agglomerate before flocculation followed by sedimentation (see Figure 1).

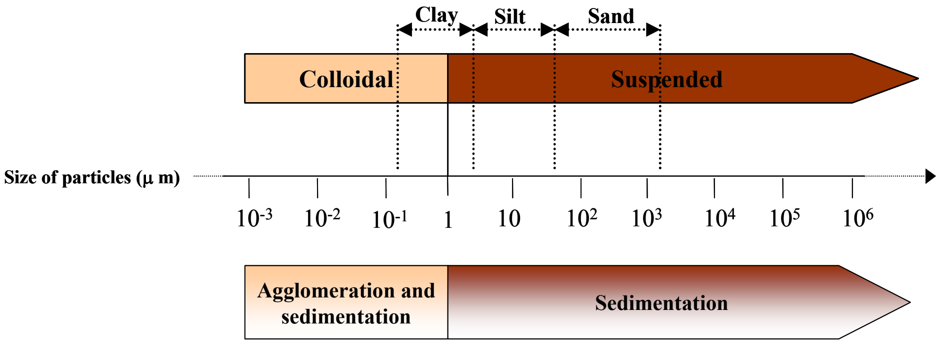

Figure 1: Particle size and their chemical and physical properties (Based on Nix, S.J. and al., 1988)

Suspended solids and removal efficiency

Stormwater detention ponds provide quiescent conditions and thus time promoting particles settling. Sedimentation is often based on Stoke's law (Equation 1) for calculation of particle removal (Greb and Bannerman, 1997, Nix et al., 1988).

Equation 1: Stoke's law

$$V = \frac{g * \left(\rho_{liquid} - \rho_{particle}\right) * D_{particle}{}^{2}}{18 * \mu}$$

V: particle settling velocity (m/s)
g: gravitational constant (m/s^2)
ρ_{liquid}: liquid density (kg/m^3)
$\rho_{particle}$: particle density (kg/m^3)
$D_{particle}$: particle diameter (m)
µ: solvent viscosity (kg/ms)

From Equation 1, we can see that many parameters influence the settling velocity such as size and density of the particles as well as viscosity and density of the fluid, which in this case is water whose density mainly varies with temperature (Nix et al., 1988) but can also vary greatly with salt concentration. Stoke's law is defined for spherical particles, a condition that is never obtained in nature, why the shape of the particle will influence the settling velocity as well. In addition, impaction of particulate matter with the vegetation in the pond contributes to increase the removal efficiency (Figure 2) (Palmer et al., 2004).

Pond design and specific pond area are important factors influencing the removal of suspended solids. It has been shown that increasing the specific pond area up to $250m^2/ha$ lead to improvement in particulate removal efficiency (Pettersson, 1999).

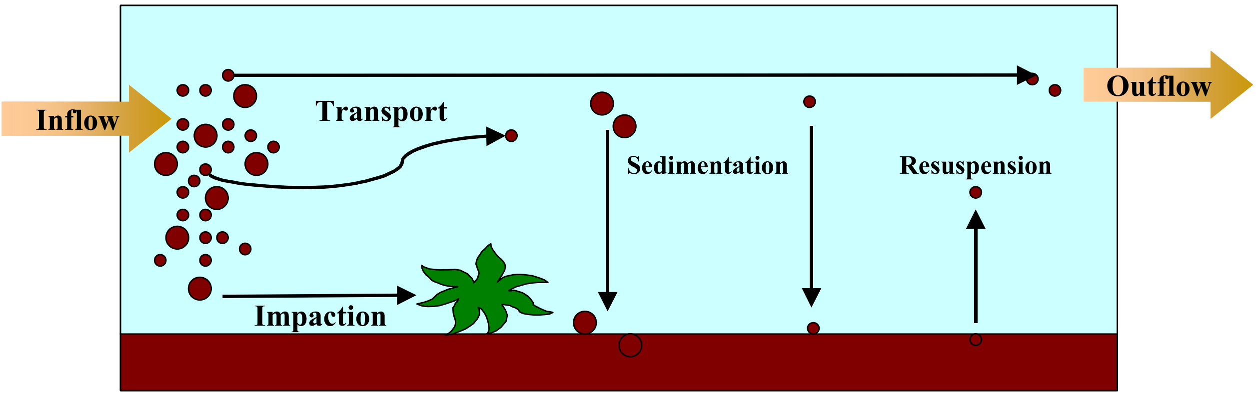

Figure 2: Removal mechanisms for suspended solids (Based on Nix, S.J. and al., 1988)

Table 3: Removal efficiency for TSS and VSS for two ponds in Sweden (Pettersson et al. 1999)

	Pollutant removal efficiency (%)	
	TSS	VSS
Krubban pond	85	75
Järnbrott pond[2]	70	60

Stormwater wet detention ponds are not likely to remove colloidal sized particles to a great extent (Sansalone et al. 1995) but have shown very good removal efficiency for suspended solids (Pettersson, 1999). As an example, the results collected from two stormwater ponds in Sweden are shown in Table 3.

The results on the Järnbrott pond obtained in 1997 are particularly important because they will be compared in the discussion with results obtained in the present study.

Suspended solids concentration and particle-size distribution show very large variations between storms (Greb and Bannerman, 1997, Pettersson, 1998), and pond design, dry periods and rain depths will affect the removal efficiency (Pettersson et al. 1999). Indeed, dry periods between storms will affect the accumulation rate of particles on urban surfaces and thus the amount of TSS (and attached pollutants) washed off during the next rain event. In the same time, high rain frequency will decrease the removal efficiency of the pond by decreasing the residence time (Pettersson and Svensson, 1998); more than 90% of the removal process takes place during dry the inter-event period (Pettersson and Svensson, 1998).

1.3.2.2. Heavy metals

Characteristics and sources

The term heavy metal is used for chemical compounds with metallic character, which have a relative density of $5 g/m^3$. All heavy metals occur naturally in varying concentrations in soil, water, air, plants and animals (Malmqvist, 1983). The term systematically associated with heavy metals nowadays is toxicity. However, some metals are essential for survival and health of humans and animals: Se, Fe, Mn, Zn and Cu. For these five metals, both deficiency and excess can have bad effects on health. The body does not need the others and even in low quantity they can affect the cycle of essential metals that is why they are also of concern (Vernet, 1991). This study is only focused on 7 of the metals present in stormwater: Cd, Cu, Co, Cr, Pb, Zn, Ni, among which the main ones, usually studied in stormwater are Cd, Pb, Cu and Zn. Indications on chemical characteristics are important because the bioavailability and thus the toxicity of heavy metals, are directly related to the soluble compounds of these metals. Moreover, metal elements are not degraded in the environment and thus are accumulated in sediments or living bodies and constitutes an important class of persistent pollutants (Sanalone and Buchberger, 1997). They can thus be bioaccumulated and biomagnificated. Health effects on both humans and aquatic life, due to this accumulation are mentioned as well in the Table 4, complementary to the sources of these metals:

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[2] This removal efficiency is calculated for the pond only. The overflowed untreated stormwater is not taken into account.

Table 4: Anthropogenic sources, main compounds and health effects of the studied heavy metals

(Based on Butler and Davies, 2000; Malmqvist, 1983; Vernet, 1991, Ellis et al., 1987, Sansalone and Buchberger, 1997, Lenntech.)

Metals	Sources	Important chemical characteristics	Health effects on humans, animals and plants
Cd	• Mining, smelting, • Fossil fuel combustion, • Industrial use, • Fertilizers.	• Major compounds in water bodies: free ion (Cd^{2+}), carbonate ($CdCO_3$), chloride ($CdCl_2$), sulphate ($CdSO_4$), and complex with acetate. All these compounds are highly soluble. • Cd is often associated with Zn. • Low-solubility compounds: oxides, sulfides. • Present essentially in the dissolved phase in highway runoff.	• Toxicity to humans: bone fracture, reproductive failure, damage to the brain and the immune system, possibility of cancer development. • Toxicity to animals: lethal for soil organisms even at low concentrations, liver and brain damages for other animals.
Co	• Coal combustion, • Mining.	• Major compounds in water bodies: free ion (Co^{2+}) and carbonate ($CoCO_3$), • Strongly organically complexed.	• Toxicity to humans: vomiting and nausea, vision problems, heart problems, thyroid damage, possibly carcinogenic, breathing problems. • Toxicity to plants and animals: bioaccumulation by plants and animals.
Cr	• Coal combustion, • Textile manufacturing.	• Major compounds in water bodies: free ion of Co(III) (Co^{3+}) and oxyde of Co(VI) (CrO_4^{2-}),	• Toxicity to humans: skin problems, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer. • Toxicity to animals: respiratory problems, infertility, birth defects.
Cu	• Atmospheric pollutant (metal works and mining, other industries, oil and coal combustion, refuse incineration, car exhaust) • Vehicles: wear of clutch and brake lining • Roofs and buildings corrosion • Asphalt paving and vehicle exhausts.	• Major compounds in water bodies: carbonate ($CuCO_3$), hydroxides ($Cu(OH)_2$),	• Toxicity to humans (in high concentration): hepatic cirrhosis, brain damage, renal disease, and copper deposition in the cornea. • Toxicity to plants: algaecide in high concentration.
Ni	• Power plants, • Trash incinerators.	• Major compounds in water bodies: free ion (Ni^{2+}), carbonate ($NiCO_3$), chloride ($NiCl_2$).	• Toxicity to humans: respiratory failure, birth defects, asthma and chronic bronchitis, allergic reactions,

			heart disorders. • Toxicity to plants and animals: bioaccumulation in plants and animals.
Pb	• Car exhausts (petrol additive), • Vehicles corrosion, • Oil and coal combustion, • Solid waste combustion, • Lead-containing paints, • Roof runoff, • Pesticides.	• Major compounds in water bodies: carbonate ($PbCO_3$), chloride ($PbCl^+$), • Present in stormwater essentially bound to particles.	• Toxicity to humans: anaemia, kidney damage, disruption of nervous systems, declined fertility of men, behavioural disruptions of children. • Toxicity to animals: disruption of water organisms' metabolisms even at low concentrations.
Zn	• Car exhaust, • Vehicles corrosion, • Mining, • Industrial use • Oil and coal combustion, • Tyre wear, • Spilling of motor oils, • Building corrosion (roof runoff).	• Major compounds in water bodies: free ion (Zn^{2+}), carbonate ($ZnCO_3$), chloride ($ZnCl_2$), • Present essentially in the dissolved phase.	• Toxicity to humans: skin irritations, nausea and anaemia, pancreas damages, arteriosclerosis, respiratory disorders. • Toxicity to plants: in high quantity decrease the growth of plants.

Heavy metals in urban runoff and detention pond: partitioning and removal efficiency

The metal concentration in stormwater differs from country to country as well as from site to site. In stormwater runoff from urban areas in the Nordic countries, a study carried out in 1983 shows an average concentration in the range of 60 to 920µg/L for Zn, 50 to 460µg/L for Pb, 18 to 330µg/L for Cu (Malmqvist, 1983). The values given by the study made in 1997-98 for the Järnbrott pond fit to these intervals except for lead which has been prohibited in fuel in Sweden at the end of the 70's and thus gave a lower value (2,11µg/L). This has been followed by a decrease of 70% of the deposition of lead during the last 20 years (Swedish EPA).
In the literature, the heavy metals studied in stormwater are always the same: Zn, Cd, Cu and Pb. The two first are chosen because they are significantly dissolved in highway runoffs, Cu is also mainly in dissolved phase. Usually Pb is highly bounded with fine sediment particles, 79% to 100% (Nascimento et al., 1999) and has a concentration exceeding the water quality standard for surface water, at least before the prohibition of lead petrol (Sansalone and Buchberger, 1997). Three other metals have been additionally added in recent stormwater studies: Cr, Co and Ni because of their anthropogenic sources and their potential toxic effects on water bodies and living organisms.

The location, the catchment's area and the precipitations affect, among other things, the metal concentration runoff. The major emitter of heavy metals is known to be road traffic. Thus, a pond with a catchments area including a road's portion is more likely to receive high metal's concentration even if elevated heavy metal concentrations from industrial, commercial and residential areas have been recorded (Toet et al., 1990). As the dissolved heavy metals are mainly removed by adsorption on suspended particles, followed by settling, the design of the pond is crucial to achieve high removal efficiency (Pettersson, 1999). It has to be noted that seasonal variations can occur, especially between rain and snow event, the last usually showing higher metal concentration (except for cadmium) (Sansalone, 1995).

Table 5: Removal efficiency for metals in Järnbrott pond (Pettersson et al., 1999)

Metal analysed	Removal efficiency for the Järnbrott pond	Removal efficiency for the system (pond + overflow[3])
Zn	30%	25%
Cu	30%	25%
Pb	50%	30%
Cd	10%	10%

High removal efficiency is dependent on the pond geometry, which should be designed so that turbulences, short cuts, velocity gradients, and anoxic conditions are avoided. Moreover, for high removal efficiency, an optimal specific pond area of $250m^2$/ha of impervious soil has been determined as an optimal size for efficient pollutant removal (Pettersson et al., 1999). The specific area of the Järnbrott pond is only $40m^2$/ha and it has been shown that the removal efficiency varies greatly between storm events, from negative values up to 80% (Pettersson, 2004). This is mainly due to rain characteristics such as the duration of the dry period preceding the storm event, rain depth, rain intensity and rain duration (Pettersson, 1998). Thus, a removal efficiency based on two series of storm events, covering a one-year period has been calculated for the Järnbrott pond (Pettersson et al., 1999), and the results are presented in Table 5:

The removal efficiency of a pond for heavy metals is strongly related to the metal partitioning. It has been shown that there is a strong correlation between heavy metals and particles concentration (except for cadmium), especially for the fraction with a size inferior to 15µm that have a high specific area (Sansalone, 1995). Indeed, Zn, Cu and Pb masses increase with decreasing particle size whereas Cd doesn't exhibit the same trend (Sansalone, 1995).

Heavy metals in sediments

Once heavy metals have been removed from pond water by sedimentation, the fate of metals trapped in the sediments is controlled by other mechanisms like absorption, precipitation, deposition and solubilization processes (Ellis et al., 1987). Pond sediments are known to have an elevated metal concentration and even if only a minor part is present in the pore water (German, 2001), 70 to 90% of the total metal are in potentially mobile forms (Marsalek and Marsalek, 1997). These are divided in five particulate metal fractions: exchangeable (fraction 1), bounded to carbonates (fraction 2), bonded to iron and manganese oxides (fraction 3) and bounded to organic matter (fraction 4). They can be released from the sediments under different conditions, like changes in water ionic composition, pH, reducing and oxidizing conditions that can affect all the four fractions of the particulate metals respectively (Marsalek and Marsalek, 1997). To a lesser extent, the presence of organic matter as well as plant and animal intake also influences the sediment metal level. These mechanisms occur in the surface layer (first 2 or 3cm (Karouna-Renier and Sparling, 2000)) of the sediments exhibiting a high concentration. This is due to the upward migration of metals previously released from diagenesis processes (for instance the dissolution of manganese and iron oxyhydroxides) occurring in the deepest layers (German, 2001). This phenomenon is enhanced by biological processes, using bacteria that exchange materials from the sediments with the overlying water column. The mobility sequence for the four most important metals present in urban runoff was found to be: Cd>Zn>Pb>Cu (German, 2001). A release of heavy metals from the sediment to the pond water would have as a final effect the pollution of the receiving waters.

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[3] The overflow is located upstream the pond and is diverting untreated stormwater directly to the river at heavy stroms.

The metal content of the Järnbrott pond, measured in 2001 gives high concentration for Cu (424 mg/kg of dried sediments), followed by Zn (672 mg/kg) and Pb (152 mg/kg) (German, J. 2001). Copper was mostly bounded to organic matter, whereas lead was preferably bounded to Fe- and Mn- oxides and Zn uniformly distributed between bound to carbonate and bound to organic matter. In 1979, the release of metals from sediments was tested under different conditions of pH and redox potential. It was shown that the influence from pH was greater than the influence from redox potential which was negligible at the tested pH (7,5-8,5) except for cadmium (Tessier et al., 1979). However, different mechanisms control the solubility of heavy metals under different redox potential: in oxic and suboxic conditions, organic matter, iron and manganese hydroxides are considered important adsorbent whereas under anoxic conditions, sulphide minerals are the most important components (Van den Berg et al., 1998).
Finally it has to be noticed that seasonal variations in sediment metal concentration has been recorded (Karouna-Renier and Sparling, 2000), especially during winter months when the pond is covered with ice, leading to anoxic conditions (Marsalek and Marsalek, 1997).

1.3.2.3. Nutrients

Less interest has been put on nutrients as important stormwater pollutants compared to heavy metals for instance. However, nitrate and phosphate are essential nutrients for plant growth both on earth and under water and nowadays we are sometimes facing too high concentrations of nutrients in water bodies that may lead to eutrophication. This stage is characterized by an excess of biomass production not compensated by grazing of higher organisms. The decay of the dead biomass leads to oxygen depletion and high turbidity in water, creating unfavorable conditions for living organisms.
The natural sources of nutrients, which are soil erosion and animal droppings, are nowadays also enhanced by anthropogenic emissions. Table 6 lists the different sources for both nitrogen and phosphorus compounds in stormwater runoff:

In addition, the loss of natural wetlands during the last century, due to anthropogenic activities like construction of dams, irrigation, emission of greenhouse gases leading to global warming, enhance the nutrients load in water bodies. Indeed, wetlands are considered as good natural nitrate and phosphate removers.

An increase of nutrients ending up in natural water bodies leads to an overgrowth of vegetation (algae and plants) and will later lead to increased decay of organic matter causing decrease in dissolved oxygen.

Table 6: Nutrient sources in stormwater (Malmqvist, 1983)

Nutrients	Sources
Nitrogen compounds	✓ Atmospheric pollutant ✓ Animal droppings ✓ Fertilizers ✓ Decay of vegetation
Phosphorus compounds	✓ Atmospheric pollutant ✓ Animal droppings ✓ Traffic ✓ Fertilizers ✓ Vegetation

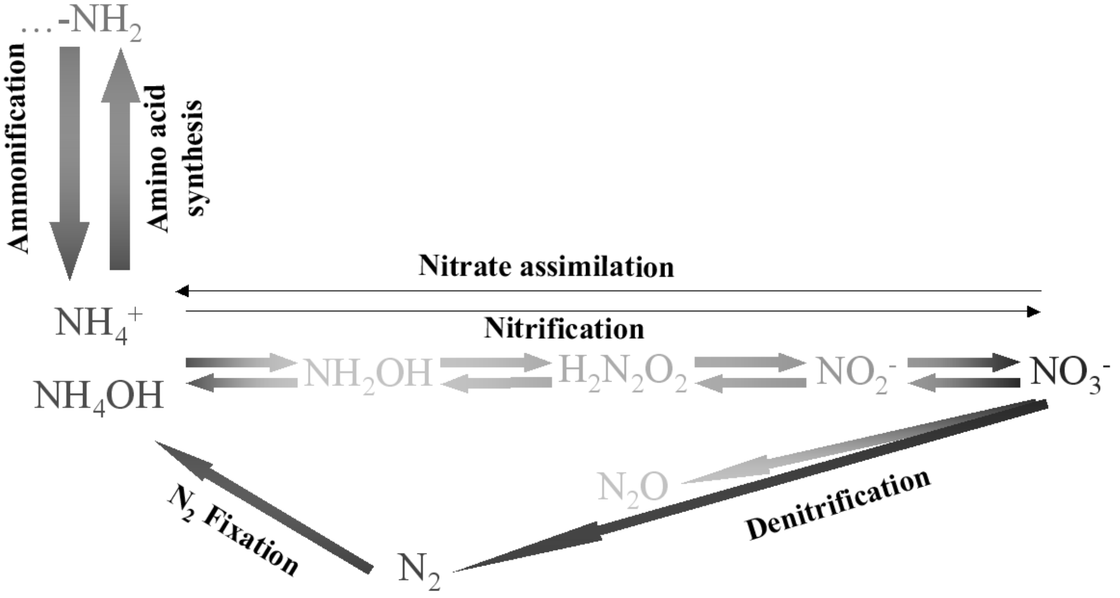


Figure 3: Nitrogen cycle (Based on Wetzel, 2001)

Nitrogen compounds

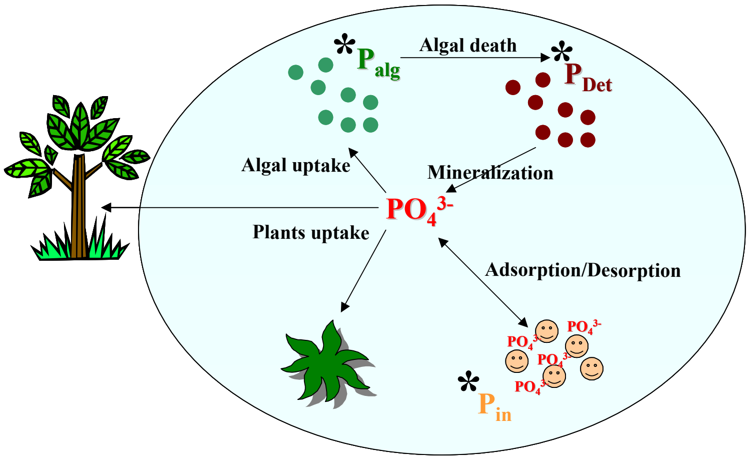
The main sources of nitrogen compounds in stormwater are atmospheric outfalls and leakage of farmland fertilizers, leading to the introduction of different chemicals in water bodies. Reactive nitrogen is present in the form of N bounded to carbon, oxygen and hydrogen as in NO_x (NO_3^- and NO_2^- for instance), NH_4^+ and organic N (amines and amino-acids) (Wetzel, 2001). All these compounds are part of the natural nitrogen cycle (Figure 3) and excesses are likely to disrupt this cycle.

This nitrogen cycle taking place in every water bodies is highly influenced by biological activities. Indeed, plants and algae are using nitrate, ammonia and even dissolved N_2, from the atmosphere, during their life cycle and release many simple and complex organic carbon and nitrogen compounds.

As seen in Figure 3, the nitrogen cycle shows complex and reversible oxidation-reduction reactions including different kinds of nitrogen compounds. NH_4^+ and NH_4OH considered by the US EPA as very toxic substances for aquatic organisms yielded from the decomposition of organic matter such as deamination of proteins, amino acids, urea and other nitrogenous organic compounds (Wetzel, 2001). The further steps of oxidation leading to the nitrification process require renewal of oxygen present in the environment; thus, nitrification is greatly reduced in undisturbed sediments because the oxygen concentration is very low. The loss of nitrogen compounds by volatilisation of N_2 (Figure 3) requires a denitrification step achieved by bacteria and with concomitant oxidation of organic matter. It has to be noted that the denitrification is decreased at for low temperature (<2ºC) (Wetzel, 2001).

Phosphorus compounds

The main source of phosphorus present in urban stormwater comes from atmospheric fallout and animal droppings (Malmqvist, 1983). Despite the decrease in phosphorus emissions since 1980's, mainly by controlling the wastewater runoff and the use of fertilizers, the phosphorus pollution is still a problem in Sweden. In natural freshwater systems, phosphorus is the limiting essential nutrient and therefore it is important to limit the loads in natural water



P_{alg}: phosphorus in algae
P_{det}: phosphorus in decaying organisms
P_{in}: inorganic particulate phosphorus
*: compounds that can settle

Figure 4: Dissolved and particulate phosphorus in water phase (Based on Toet et al., 1990)

bodies in order to efficiently limit the over growth of algae. In contrast to nitrogen compounds, there is mainly one significant form of inorganic reactive soluble phosphorus: PO_4^{3-} (Wetzel, 2001). A very large proportion of phosphorus compounds occurs as organic phosphate (in vitamins, DNA, enzymes) or adsorbed to inorganic particles (clays, carbonates, ferric, manganese and aluminum hydroxides) and dead organic materials (Wetzel, 2001; Kisand, Noges, 2003).

Nutrient partitioning and removal efficiency in stormwater ponds

Nitrogen may enter a drainage area in its different stable forms: dissolved N_2, HNO_3, NH_4^+, NO_3^-, and organic compounds that can occur in either dissolved or particulate phase. Phosphorus from runoffs is mainly in the colloidal phase or adsorbed to particles smaller than 0,1mm.

Normally nutrients are not efficiently removed by stormwater ponds, and also differ highly for different ponds, compared to metals and suspended solids (Pettersson, 1999). As seen for heavy metals, the partitioning of elements in the ponds is essential for the removal mechanisms. Nutrients are not an exception to this rule and their removal limit is a function of their partitioning between particulate and dissolved form, as only particulate fraction is subjected to settling. This is the case for NH_4^+, which is known to be strongly adsorbed on particulate and colloidal particles especially in presence of humic dissolved organic matter (Wetzel, 2001). However, this chemical process is not the unique removal process.

Indeed, it has been shown that dry ponds generally have negative removal for nitrogen and poor removal efficiency for phosphorus compounds. This fact shows the importance of biological processes in the removal of nutrients, which is thus more likely to happen in wet ponds (Randall, 1982) and in wetlands (Martin, 1988). The nutrients' bioavailability and partitioning between reactive and inactive species, is crucial: biological uptake or conversion of active forms of nutrients account for a great part of their removal from the water phase. This is the case of orthophosphate, whose main removal mechanism depends on algal and bacteria uptake followed by sedimentation (Toet et al., 1990; Wetzel, 2001). The use of dissolved phosphate by terrestrial vegetation surrounding the pond accounts for the phosphorus removal as well (Martin, 1988). The coprecipitation with and the adsorption on calcium carbonate compounds also take a part in the removal of phosphorus and are enhanced by high concentration of calcium and magnesium in water (Wetzel, 2001). On the contrary, dissolved organic matter tends to destabilize the colloidal particles, slowing the aggregation process and thus the sedimentation rate.

Nitrification, denitrification, volatilisation, uptake of NO_3^- and NH_4^+ by microorganisms, algae, bacteria as well as mineralisation of organic nitrogen (Figure 3) are the possible routes of biological and chemical transformations in a pond (Senzia et al., 2002). It has to be noted that a very low number of N_2 fixing bacteria occurs in rainwater (Wetzel, 2001) limiting the production of NH_4^+ from the transformation of dissolved N_2 in stormwater runoff. The nitrification process ($NH_4^+ \rightarrow NO_3^-$) accounts for the high removal efficiency for total ammonia and the negative efficiency for nitrate (Martin, 1988).

In order to profit from natural removal mechanisms, the pond has to be properly designed. The importance of the residence time of runoff water in the pond, ruled by the pond volume, is crucial for pollutants removal and eutrophication. Indeed, unlike metals, for which a higher residence time is synonym to higher removal efficiency, an extended residence time in a pond for nutrients might lead to high eutrophication level, with a growth of algae harmful towards receiving waters (Toet et al., 1990). It has been determined that a pond volume of 200 to 250m^3/ha is sufficient to remove 50% of the total phosphorus, however, as shown in the results below (Table 7), nitrogen compounds are more difficult to remove. Indeed, the study on two different detention ponds in Sweden showed the following results for nutrients removal:

Table 7: Ponds' characteristics and removal efficiencies for nutrients (Pettersson et al., 1999)

Pond's name	Pond's volume (m^3)	Specific pond area (m^2/ha)	Removal efficiency (%)	
			Nitrogen	Phosphorus
Järnbrott	6000	200	7	40
Krubban	11300	700	33	74

In addition, the amount of rain and the length of the inter-event dry period between successive storm events as well as the composition of the drainage area, also play an important role in the amount of nutrient reaching the pond (Toet et al., 1990).

Nutrients in sediments and mobilisation processes

Once particle-associated nutrients settled down in the pond, they are not removed from the cycle. Particles can be resuspended and nutrients dissolved in the water column by physical, chemical or biological processes.

The main physical processes are: high runoff flows entering the pond, wind-induced circulation and pressurized flows under ice cover (Mayer et al., 1996) which is likely to suspend the sediments and thus favour the migration of absorbed nutrients from the particulate to the water phase.

Concerning chemical conditions susceptible to lead to nutrients release from the sediments, the most commonly studied is the oxygen free environment (Mayer et al., 1996; German, 2003). Usually, the ponds are shallow enough not to allow anoxic conditions at the bottom. However, during wintertime, the ice cover is an important factor for oxygen free conditions in the pond water, especially in Nordic countries where the winter last for several months.

A lot more information is available on the equilibrium of phosphorus between the sediments and the water phase compared to nitrogen compounds.

The main nitrogen compound interacting with sediments is ammonia. Under anaerobic conditions ammonia stored in the sediment phase can be released in the water column (Mayer et al., 1996). This is achieved by bacterial metabolism in the sediments (Wetzel, 2001). The resulting NH_4^+ is then accumulated in water because the nitrification process (Figure 3) cannot occur anymore in the absence of oxygen. In addition, increasing concentrations of NO_2^- have also been recorded when anoxic conditions are achieved (Wetzel, 2001).

Concerning phosphorus compounds, the exchange between sediments and the overlying water is a major component of the phosphorus cycle (Figure 5). Indeed, the phosphorus content of sediments can be several orders of magnitude greater than that of the water. Some mechanisms leading to adsorption and sedimentation, using iron and aluminium ions are reversible and can be the source of release from the sediments as well (Equations 2, 3, 4 and 6).

$$Al_2O_3\,part + PO_4^{\;3-} \Leftrightarrow Al_2O_3 - PO_{4\,absorbed}$$

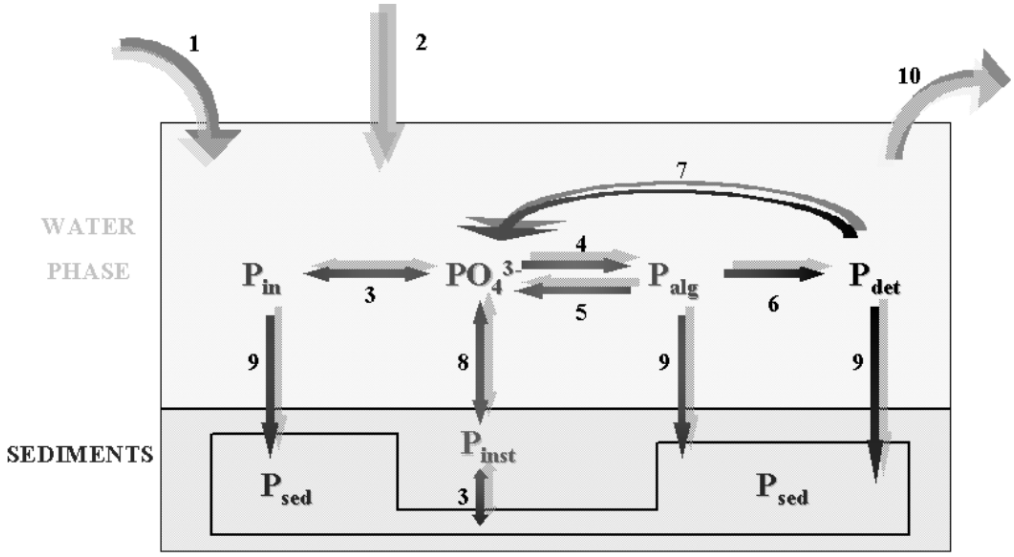
Equation 2: Adsorption/desorption mechanisms for phosphate on aluminium oxides (Wetzel, 2001)

$$Al^{3+} + PO_4^{\;3-} + 2H_2O \Leftrightarrow AlPO_4, H_2O(s)$$

Equation 3: Precipitation of orthophosphate and aluminium ions (Wetzel, 2001)

$$Fe^{3+} + PO_4^{\;3-} \Leftrightarrow FePO_4(s)$$

Equation 4: Precipitation of orthophosphate and iron ions (Wetzel, 2001)



P_{in}=inorganic particulate phosphorus
P_{alg}=phosphorus in algae
P_{det}=phosphorus in decaying organisms
P_{inst}=phosphorus in pore water
P_{sed}=phosphorus adsorbed on the solid phase of the sediments
1: Input from urban catchment
2: Precipitation
3: Adsorption/desorption
4: Algal uptake
5: Autolysis
6: Algal death
7: Mineralization
8: Diffusion
9: Sedimentation
10: Output to receiving water

Figure 5: Phophorus processes (Based on Toet et al., 1990)

Particles containing phosphate can be found in the sediments and orthophosphate can possibly be released in the water under anoxic reducing conditions (German, 2003). In addition to anoxic conditions, the presence of sulphate leads to a major release process well know in lake limnology: the reduction of Fe(III) and the concomitant desorption of orthophosphate (Equation 5 and 6).

Equation 5: Action of a sulfate reducing bacteria (SRB) (Wetzel, 2001)

$$SO_4^{2-} \xrightarrow{SRB} H_2S$$

Equation 6: Reduction of iron and release of reactive phosphate (Wetzel, 2001)

$$H_2S + Fe(OH)_3 - PO_4 \rightarrow \underrightarrow{H_2S} + Fe^{2+} + PO_4^{3-}$$

Remark: These equations are not chemically balanced because they include enzymatic reactions.

It has to be noted that the rate of phosphorus release from the sediments increases markedly if the sediments are disturbed by agitation from turbulences (Wetzel, 2001).

1.3.2.4. Polycyclic aromatic hydrocarbons

Chemical and physical characteristics

PAHs are of concern when it comes to environmental pollution because they are ubiquitous in urban environment and many of them are mutagens and carcinogenic and listed as priority pollutants by several national environmental protections agencies (Durand et al., 2004; Tsapakis and Stephanou, 2004) and are quoted in the EU water directives. These compounds belong to the organic compounds containing only carbon and hydrogen associated in benzene rings. Because of the high stability of the benzene rings, these compounds are persistent pollutant, which means that they are not easily degraded in the environment where they remain for months or years depending on the number of benzene rings contained in the compound. Indeed, the higher the ring number, the more persistent the compound is (Hutzinger et al., 1998). In addition, some of these compounds or their metabolized by-products have a structure similar to hormones, which can cause adverse effects on living organisms.

The lightest PAHs can be destroyed by photoreaction (Figure 6) that is the most important pathway for degradation in the environment. It occurs when PAHs are exposed to air and light. The second pathway is the oxidation of these compounds by ozone or iron (III) in the sediments (Hutzinger et al., 1998). A microbial degradation under both aerobic and anaerobic conditions has been shown driving to the mineralisation of the PAHs (Talley et al., 2002). Moreover, they are semi-volatile compounds so they might be easily transported on long distances (Hutzinger et al., 1998). In the atmosphere and water bodies, they are condensed or adsorbed on sub-microns particles because of their semi-volatile and hydrophobic characteristics (Appendix 1) (Sheu et al., 1997; Kiss et al., 2000).

Sources and sinks of polyaromatic hydrocarbons

The primary sources of PAHs in the environment can be categorised as follow: domestic, industrial, mobile, agricultural and natural sources (forest fires and volcano eruptions) (Prevedouros et al., 2003). The main sources are the combustion processes which account for 90% of the environmental concentration and include vehicles engines as well as coal burning

Table 8: Sources of PAH in the environment (Hutzinger et al., 1998; Baird, 1999)

Sources	Compounds emitted[4]
Coal combustion	Anthracene, phenanthrene, fluoranthene, pyrene and benz[*a*]anthracene, benzo[*a*]pyrene
Coke production	Anthracene, phenanthrene, benz[*a*]pyrene, benz[*ghi*]perylene
Incineration	Phenanthrene, fluoranthene and especially pyrene
Wood combustion	Anthracene, phenanthrene, fluoranthene, pyrene, benzo[*a*]pyrene
Oil burning	Fluoranthene, pyrene
Petrol-powered cars	Fluoranthene, pyrene and especially benz[*ghi*]perylene, coronene
Diesel-powered vehicles	Fluoranthene, pyrene and especially benz[*ghi*]perylene, coronene, benz[*b*]fluoranthene, benz[*k*]fluoranthene

for residential heating, industrial processes, power generation (Hutzinger et al., 1998). Since the 1960s, the sources of PAHs have been shifted from mainly home heating and industrial sources to vehicles sources, which are nowadays the main source of PAHs in the environment (Van Metre et al. 2000). This is due to more efficient power plants, regulation on industrial emissions and decrease in coal burning use for household heating. Exhaust pipe's emission is not the only car-related source of PAHs; asphalt wears, tire wears as well as leaks and spills of engine oil have to be taken into account (Van Metre et al. 2000), each of these sources emitting a complex mixture of these persistent pollutants (Table 8). Combustion processes result predominantly in emission of four and five ringed compounds whereas the other sources emit mainly two and three ringed PAHs (Van Metre et al. 2000).

In urban environment, PAHs concentrations are driven by primary sources, however, different kind of processes like volatilization from water, soil, vegetation, urban surfaces contribute to secondary emissions in the atmosphere (Prevedouros, et al., 2003). Then, other processes take place, removing PAHs from the atmosphere, such as wet deposition, reactions with OH radicals, scavenging by vegetation, etc The lifetime of a PAH in a given media differs from medium to medium and from compounds to compounds. As seen before, some PAHs will have more affinity with water than others, some will be more volatile. However, soils and sediments are considered as sinks for PAHs since their residence time in these media can reach several years. Elevated concentrations have been found in urban soils with a number of compounds exceeding 20 PAHs (Krauss and Wilcke, 2002). However, it has to be noted that the soils' concentrations vary greatly from sites to sites even for the soils under the same land use except for road sites, which always show particularly high concentrations. Typical topsoils of European industrialized countries are dominated by fluoranthene, benzofluoranthene, pyrene and chrysene (Krauss and Wilcke, 2002).

Polycyclic aromatic hydrocarbons, partitioning and removal efficiency

Until recently, studies on PAHs mainly focused on the air phase, whereas the fate of these substances in water bodies and aquatic sediments lead to less interests (Van Metre, et al., 2000). Despite the fact that PAHs are recognized to come from vehicle related sources to a large extent (Van Metre et al., 2000), the literature is poor in study of PAHs in road runoff or stormwater contamination.

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[4] The compounds written in green are the compounds analysed in this work

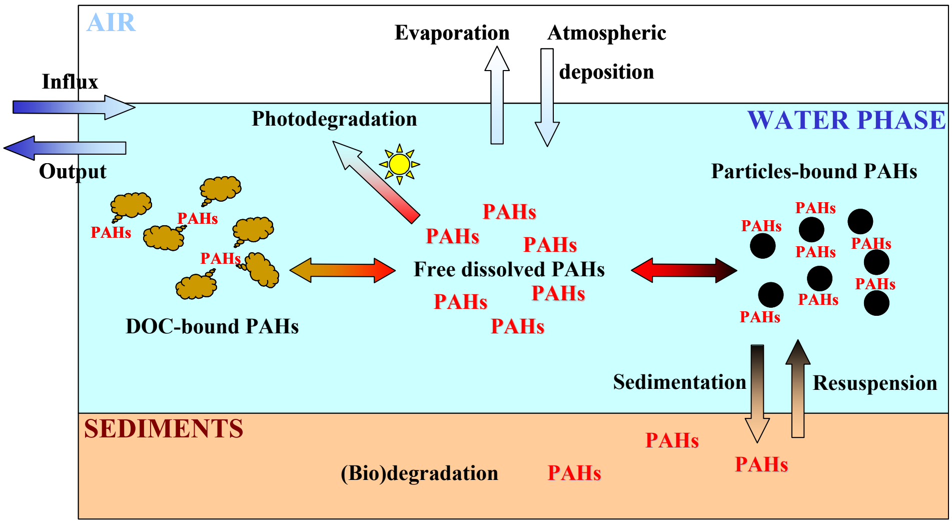

Figure 6: PAHs in the environment (Based on Hutzinger et al., 1998)

Biological effects of PAHs are function of their bioavailability[5] in water bodies. The partitioning between dissolved and bound PAHs is one of the major factor influencing bioavailability. Only the free dissolved PAHs are available, once these compounds are bound to dissolved organic carbon, particulate or colloidal matters (Figure 6), the bio concentration factor (BCF) for aquatic organisms is significantly reduced (Hutzinger et al., 1998). Almost 100% of the super hydrophobic compounds (log $K_{ow}>7$) tend to be bound to particles or organic carbon. This bounding is also high for five- and six-ringed compounds whereas the highest free dissolved PAHs concentration have been recorded for two- and three- ringed compounds (Hutzinger et al., 1998). The settling of particles-bound PAHs is the main removal mechanism for these compounds in water bodies and is used to remove these organic compounds from stormwater runoff. From what is written above, the higher molecular weights PAHs are expected to predominate in sediments (Hutzinger et al., 1998). A study on PAHs distribution in river sediments and road dust showed that two- and three- ringed compounds are more likely to adsorb coarser particles (from 60 to 600µm), whereas five- and six- ringed compounds show higher concentration for fine particles (from 2 to 12µm)) (Krein and Schorer, 2000). PAHs are less correlated within the 15 to 50µm range (Sansalone et al., 1995).

Once in the sediments, if adequate bacteria and favourable conditions are gathered, biodegradation can take place (Figure 6). As mentioned above, the degradation rate and the residence time in water and in sediments are correlated with the number of benzene rings of the compound. Naphtalene, phenanthrene and fluorene, that contain three, three, and two benzene rings respectively are quite abundant in the environment but are not considered as mutagenics and don't have a structure similar to hormones. In addition, they are susceptible to biodegradation (Hutzinger et al., 1998).
Under certain conditions like turbulences, the suspension of particulate matter followed by desorption can lead to the release of free dissolved PAHs in the water phase (Figure 6).

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[5] Bioavailability: fraction of the chemical present in soil/sediment and (interstitial) water which can potentially be taken up during the organisms life-time into the organism tissue.

1.3.2.5. Microorganisms

In addition to chemical contaminants, microorganisms are found in various amounts in stormwater. Bacteria from faecal origin present in stormwater find their sources in septic tank seepage, sewer leakage and overflow (Davies et Bavor, 2000), and domestic animal faeces (pets and native animals) especially after heavy rains (Leeming et al., 1998). The bacterial groups, which are usually used as indicators of faecal contamination, are total coliforms, faecal coliforms (including *Escherichia coli*) and faecal enterococci (Noble et al., 2004). Figure 7 shows the repartition of coliform bacteria.

Bacteriophages are bacteria viruses that share a lot of features with human viruses, e.g. the composition, morphology, size, structure and multiplication mechanisms. Since bacteriophages naturally are present in faeces they are suitable models or substitutes for judging behaviour of viruses in water environments and their sensitivity to different water treatment methods, e.g. pond storage.

Following parameters were analysed in this work:
The coliform group (Figure 8) gathers anaerobic, gram-negative, non-spore-forming, rod-shaped bacteria from faecal or non-faecal origin.
Escherichia coli (Figure 9) is a normal inhabitant of the digestive tract of warm-blooded animals, including humans. It is considered as a specific indicator of faecal contamination. There are different groups of *E. coli*, some of them are pathogenic and can cause diarrhoeal diseases in humans.
Clostridium perfringens (Figure 10) is a sporulated bacterium, known to be an origin of food poisoning. However, it has been reported that *C. perfringens* could be a good indicator for the presence of pathogens of faecal origin in surface water (Araujo et al., 2004). Its development occurs under anaerobic conditions leading to the apparition of grey and black colonies when grown on substrate (Davies and Bavor, 2000).

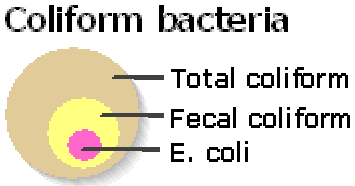

Figure 7: Repartition of the coliform bacteria

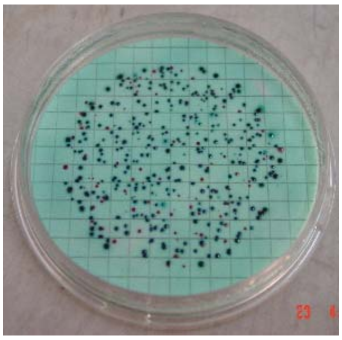

Figure 8: Colonies of coliforms

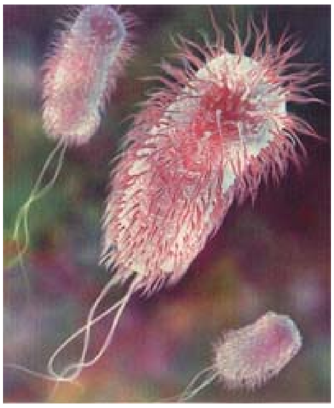

Figure 9: *E. coli*

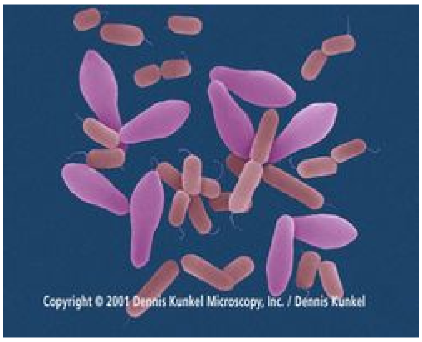

Figure 10: *Clostridium perfringens*

Furthermore, *Somatic coliphages*, *F-specific RNA bacteriophages* and *Intestinal enterococci* have been studied as well.

Removal efficiency by ponds and wetlands

The evaluation of removal efficiency in stormwater treatment systems has been mainly focused on physical and chemical contaminants (suspended solids, nutrients, heavy metals and organic compounds). Only little information is available on the removal of microbial pathogens (Kurz, 1999). However, a few studies on the removal efficiency of bacteria by ponds and wetlands for stormwater treatment in Australia and United States have been carried out.

As for other pollutants studied, the removal of bacteria from the water column is dependent on the settling velocity. Indeed, bacteria are associated to particles present in stormwater and predominantly within the finest fraction (Davies and Bavor, 2000) i.e., less than 2 µm in size on which nutrients are as well preferentially adsorbed (Bavor et al., 2001).

It has been clearly shown that the removal efficiency is much higher in constructed wetlands than in pond systems (Davies and Bavor, 2000). Two stormwater treatment systems (one constructed wetland and one detention pond) situated in the same area in Australia showed a removal efficiency of 79% and –2,5% respectively for faecal bacteria (Bavor et al., 2001). This result can be explained by several removal processes occurring in wetlands such as predation, filtration, solar radiation, sedimentation enhanced by the extensive vegetation (Bavor et al., 2001), aggregation, oxidation, antibiosis, and competition (Davies and Bavor, 2000). In constructed ponds, the association of bacteria with fine particles protects them from predation. A study carried out in Florida (Kurz, 1999) on a wet stormwater detention pond showed the effect of pond depth and residence time on the removal efficiency of total coliforms and faecal coliforms. A strong correlation with suspended solid removal is also shown by the results (Appendix 6). A low depth and a 5 days residence time lead to the highest removal efficiency (64% for total coliforms and 98% for faecal coliforms) (Kurz, 1999).

A study carried out in Australia (Bavor et al., 2001) showed that the concentration of bacteria in sediments, for both ponds and wetlands is higher than the concentration in the water column by several orders of magnitude. The greatest difference was observed for *Clostridium perfringens* (Davies and Bavor, 2000). In addition, the bacteria's mortality rate is dependent on the particle size in the sediments: the rate will be lower for clay-sized particles than in coarser sediments (Howell et al., 1996). In particular, *E. coli* survives longer in sediments containing a proportion of at least 25% of clay (Burton et al. 1987). Then, the pond and wetland sediments act like a reservoir: bacteria can be released from the sediments under stormy conditions leading to deterioration of the quality of the overlying water (Davies and Bavor, 2000).

2. Stormwater analysis and removal efficiency of the detention pond

2.1. Experimental part

2.1.1. Pond location and characteristics

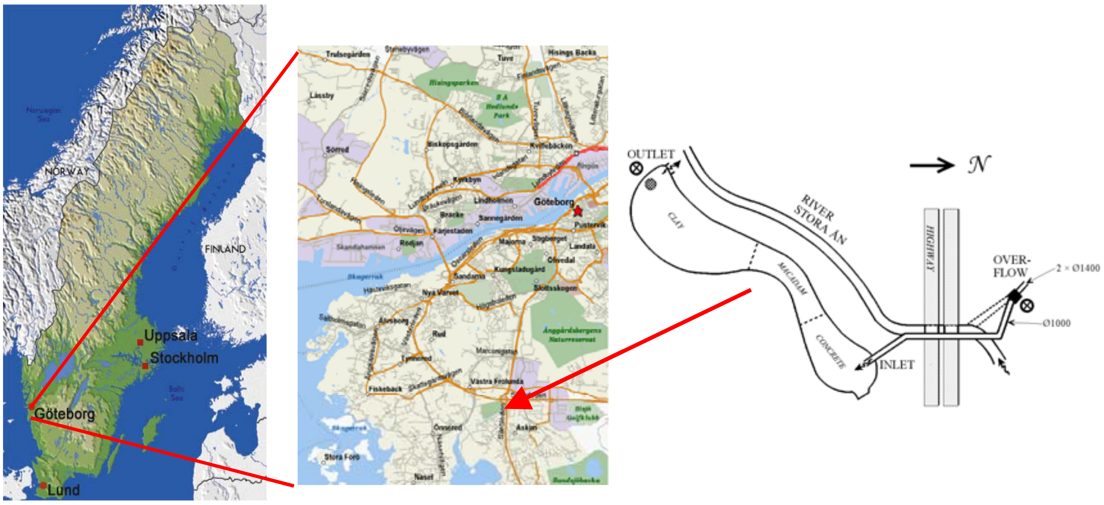

Figure 11: Location of the Järnbrott pond

The city of Göteborg in Sweden owns several stormwater ponds situated in different areas and with different catchments leading to the input of different pollutants in different concentrations.

The Järnbrott pond (Figure 11), situated 5km from the city of Göteborg in Sweden, was constructed in 1996. It is a surface wet pond, opened to the atmosphere and permanently filled with water. It is used for quality improvement purposes: the water is stored temporarily and released slowly at the outlet. It is an off-stream pond because during dry weather, only a small input from groundwater infiltration to the stormwater pipe system is observed. Finally, this pond was built to reduce stormwater pollution (Pettersson, 1999). The catchment (Figure 12) has a total area of 480 ha with 160 ha covered by impervious surfaces such as highways, industrial, commercial and residential areas. Up to 6000 cars a day use the highway situated in this catchment area, making it one of the largest contaminating factor.

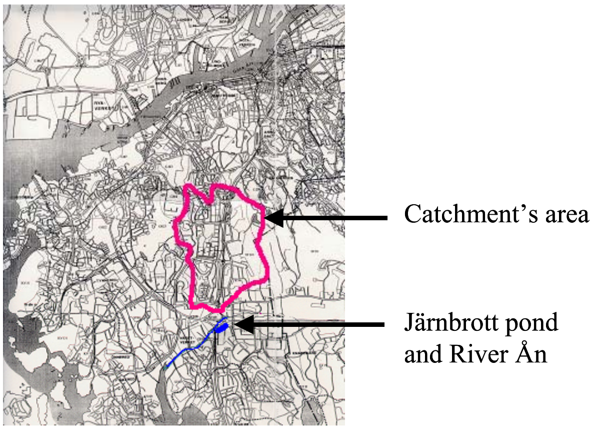

Figure 12: Catchment's area of the Järnbrott pond

The Järnbrott pond (Figure 11) has, during dry weather conditions, a surface of 6200m^2, a volume of 6000m^3 and a specific pond area of 40m^2 per hectare of impervious area: this specific pond area is small compared to the optimum value of 250m^2/ha. This reference value is based on the study of long term TSS removal efficiency determined for several ponds with different catchment's area. (Pettersson, 1999).

The pond inlet consists in a ∅1000mm steel pipe coming from an overflow chamber (Figure 13) with a limited volume. This overflow chamber is connected to the stormwater sewer system and when the inflow intensity exceeds 700l/s, the exceeding part is directly discharged to the River Stora Ån (Figure 13). Thus, the part of untreated stormwater modellled to be 20% of the total inflow per year. On the other hand, the outlet of the pond is an 8 meters broad concrete crest (Figure 13), over which output water is flowing to the River Stora Ån (Pettersson, 1999).

The bottom of the pond has been constructed with three different materials due to the necessity to adapt to local variation in soil strength. At the inlet, a concrete bottom slab was made, in order to be able to remove the excess of sediments, using a wheel-mounted loader. The depth reaches 1,5m during dry weather. At the middle section, the corresponding depth is only 0,6m and consists of penetration macadam (Figure 13). Finally, the outlet bottom section consists of clay and the depth is about 1,6m. The pond slope consists of clay with a gradient of 30%.

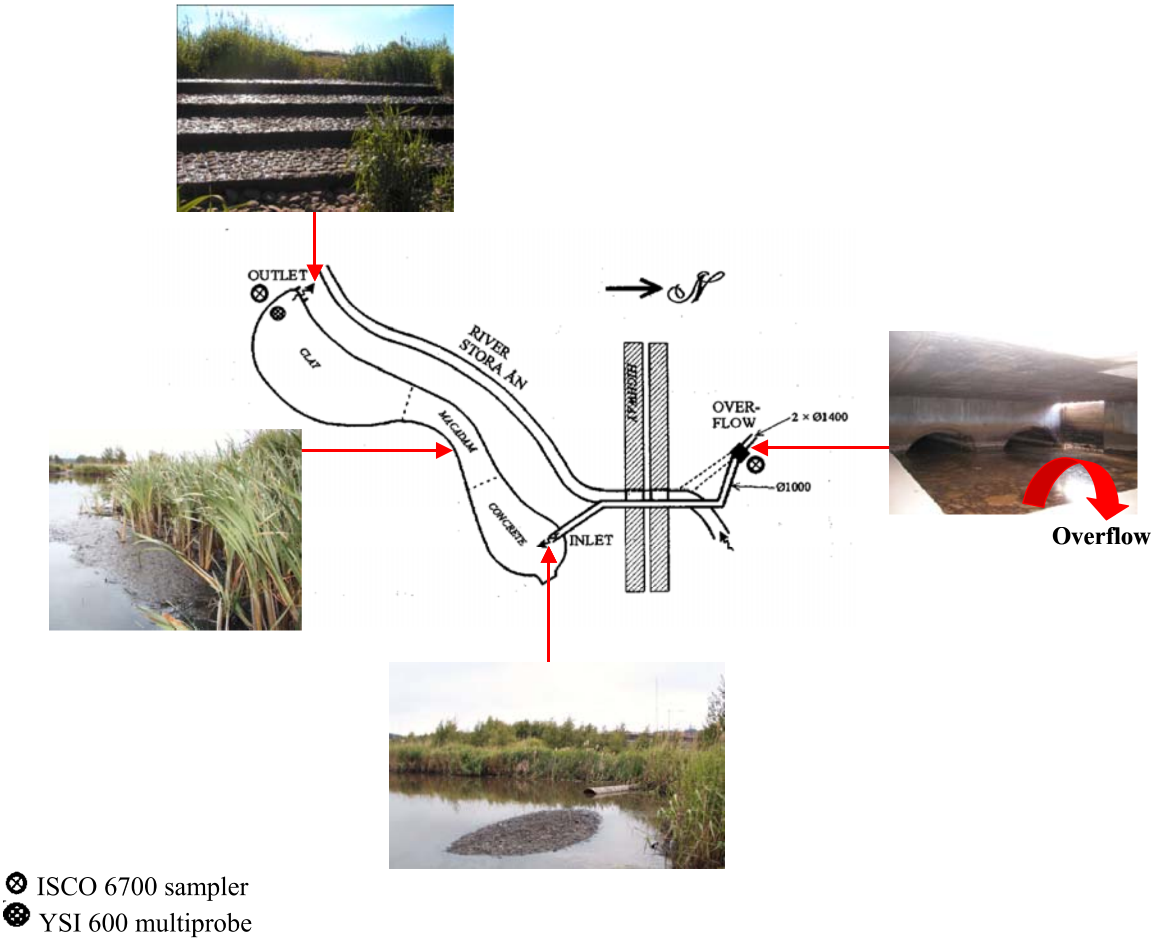

Figure 13: Järnbrott pond, bottom material and samplers' position

2.1.2. Sampling and on site measurement equipment

The inlet and outlet of the pond were equipped with portable automatic stormwater samplers, ISCO 6700 model (Figure 14). The same samplers were used five years ago during the first measurement campaign on this pond. Each sampler has a capacity of 12 bottles: six were made of polyethylene and six were glass bottles (Figure 15). They were filled by a peristaltic pump that pumped the stormwater through a PVC (Chlorinated PolyVinyl Chloride) (Figure 14) tube. At the end a propylene strainer was adapted to prevent the intake of leafs and other materials that would clog the tubing.

At the inlet of the pond, the strainer is placed 10cm above the bottom of the pipe. The suction length and the suction height of the vinyl tubing were 5,5m and 2m respectively (Pettersson, 1999). In order to take flow-weighted samples, the inlet sampler was equipped with a V-H probe (ISCO 750 Area Velocity Module) (Figure 16) fixed at the bottom of the inlet pipe. The probe is able to detect water pressure, converted to water level, in the pipe. The sensor also measures average velocity by using ultrasonic sound waves and the Doppler Effect. The reception of sound waves reflected by both particles and air bubbles in the water, gives the water velocity in the inlet pipe. By using velocity and water level measurements, combined with the inlet pipe characteristics, the flow was calculated.

The outlet sampler was placed in a manhole (Figure 17). The strainer was placed 2m upstream the outlet weir and 0,3m below the dry weather water level. A pipe, connecting the pond and the manhole, ends up in a bucket in which the strainer was placed and the samples taken. The suction length and the height of the vinyl tubing were 4m and 1m respectively (Pettersson, 1999). Here, a pressure probe (ISCO 720 Submerged Probe Module) was connected to the sampler. It was mounted in the pipe, linking the pond and the sampling well, and calculates the outflow from the measurement of the water level above the outlet weir, and it forces the intake of flow-weighted samples.
In addition, a multiprobe (YSI 600 Multi Parameter Water Quality Monitor) (Figure 18) was connected to the outlet sampler, monitoring different parameters: dissolved oxygen, pH, conductivity and water temperature.

Figure 14: ISCO 6700 inlet sampler

Figure 15: Polyethylene and glass bottles

Figure 16: ISCO 750 Area Velocity module

Figure 17: ISCO 6700 outlet sampler

Figure 18: YSI 600 multiprobe

Figure 19: ISCO 720 submerged probe module

Figure 20: Data downloading

All these field data, from flow meters and multi probe, were stored in the sampler data loggers and then downloaded after each rain event by a laptop computer (Figure 20).

2.1.3. Analyses

For most of the storm events, the compounds concentration has been determined in a composite sample. At the end of the storm events, the bottles were collected and the water in the glass bottles was mixed together and used for PAH analysis. Another composite sample made from water samples in the plastic bottles was used for the other parameters. The analyses performed gave an event mean concentration (EMC) representative for the storm event studied.

For each parameter measured, a short description of the analytical method, detection limit and precision will be given when these data are available.

2.1.3.1. Suspended solids

Both total and volatile suspended solids have been analyzed for each storm event. The Swedish Standard method and the detection limit for these analyses are presented in Table 9.

Table 9: Methods for analysis of suspended solids

Parameters analysed	Analytical method	Detection limit
TSS (total suspended solids)	SS 02 81 12	5 mg/l
VSS (volatile suspended solids)		

The TSS concentration was determined by filtration of a known volume of sample in a glass fiber filter (MGC; pore size: 1,2µm). The filter was weighted before and after filtration, once dried at 105°C for one hour. The mass of VSS was determined by weighing after one additional hour at 550°C. A blank filter, in which nanopure water was filtered, was run in parallel in order to compensate for the mass loss of the filter itself.

2.1.3.2. Heavy metals

Both dissolved and total metal concentrations have been determined for each storm event. Detection limits and precision of the ICP-MS method can be found in Table 10.

Table 10: Method for analysis of metals

Parameters analysed	Analytical method	Detection limit (ppb)	Precision
Cd	Inductively coupled plasma – mass spectrometry (ICP-MS)	0,007	The equipment has been conditioned in order to have a precision higher than 1%
Co		0,002	
Cr		0,04	
Cu		0,01	
Pb		0,003	
Zn		0,06	
Ni		0,06	

In order to analyze total metals, water samples have been digested at 120°C in 20% of HNO_3 (for ultra trace analysis) during 2 hours and then diluted ten times with milli-Q water. The internal standard (Rh) was added before introducing the sample to the ICP-MS.

For the determination of the dissolved concentration, the sample was filtered in a 0,45µm pores cellulose acetate filter, acidified with 1% of HNO_3. The internal standard (Rh) was then added and the sample analyzed on the ICP-MS.

ICP-MS stands for inductively coupled plasma – mass spectrometry. Once introduced in the instrument, the sample is converted into a fine aerosol by a nebulizer. The aerosol is ionized by a high temperature plasma (10000K). This plasma is formed by the interaction of an intense magnetic field and high voltage sparks in a flow of argon. Once ionized, the sample is directed to the mass spectrometer via an interface region. Each ion is separated according to its m/z ratio, where m is the atom's mass and z the ion's charge, and then detected.

2.1.3.3. Nutrients

The stormwater samples have been sent to a certified laboratory, Lackarebäck Water Laboratory; Göteborg, for analyses of nutrients. The standard methods used are quickly described below. The detection limit and precision are presented in Table 11.

The European standard procedure for the analysis of NO_2^- + NO_3^- uses flow injection analysis and a spectrometric detection. Once the sample injected in the instrument, metallic cadmium reduces NO_3^- into NO_2^-. Thereafter, organic compounds are introduced to the solution and their reaction with NO_2^- produces a dye, detectable by spectrometry.

Table 11: Methods for analysis of nutrients

Compound analysed	Analysis method	Detection limit	Precision
$NO_2^-+NO_3^-$	SS-EN ISO 13395	0,2 mg/l	
NO_2^-	SS-EN 26777-1	2 µg/l	
NH_4^+	SS-EN ISO 11732		
Total-N	SS-EN ISO 11905-1	0,02 mg/l	
PO_4^{3-}	SS 028126-2	2 µg/l	0,5 µg/l
Total-P	SS 028127-2	2 µg/l	0,5 µg/l

The procedure for the analysis of NO_2^- uses the formation of a pink dye by reaction of NO_2^- with organic compounds. The color intensity of the dye's solution, which is determined by spectrometry, is proportional to NO_2^- concentration in the solution.

The European standard procedure for the analysis of NH_4^+ also uses flow injection analysis and spectrometric detection. The sample is mixed to an alkaline solution in order to convert NH_4^+ into NH_3, which is the base associated to NH_4^+. A spectrometer recording the change in color of a pH indicator solution monitors the detection.

The first step for total-N measurement is the oxidation of NH_4^+, NO_2^- and many other organic nitrogen-containing compounds to NO_3^- at high temperature. The next step is the reduction of all NO_3^- into NO_2^-, followed by the same procedure used for NO_2^- analysis.

The European standard procedure for the analysis of PO_4^{3-} uses a spectrometric method. PO_4^{3-} reacts with molybdate (Mo), forming a complex, which is then reduced by ascorbic acid, producing an intense blue color, detected by spectrometry.

The first step in the analysis of total-P is the oxidation of inorganic and organic bound phosphate into PO_4^{3-}. The analysis of the PO_4^{3-} formed follows the procedure explained above for the determination of PO_4^{3-}.

2.1.3.4. Polycyclic aromatic hydrocarbons

A number of 16 PAH (Appendix 1) including 7 compounds known to be carcinogenic and 9 non-carcinogenic have been measured on composite samples for the rain events studied. A certified laboratory (Analytica AB, Täby) performed the analyses. The analytical method and the detection limit are shown in Table 12.

The NEN 6524 procedure uses HPLC as measurement technique. HPLC stands for high performance liquid chromatography. The main component of this instrument is the chromatographic column composed by fine spherical modified-silica particles, which form the stationary phase. The mobile phase carries the analytes into the column. The separation of the

Table 12: Method for analysis of PAH

Compound analysed	Analytical method	Detection limit (µg/l)
Naphtalene	NEN 6524	0,06
Acenaphthylene		0,08
Acenaphthene		0,05
Fluorene		0,05
Phenanthrene		
Anthracene		0,01
Fluoranthene		
Pyrene		
☠Benz[a]anthracene		0,01
☠Chrysene		0,01
☠Benzo[b]fluoranthene		0,02
☠Benzo[k]fluoranthene		0,01
☠Benzo[a]pyrene		0,01
☠Dibenzo[ah]anthracene		0,01
Benzo[ghi]perylene		0,02
☠Indeno[123cd]pyrene		0,02

different PAHs is done according to their affinity with the stationary phase. The PAH compound which has the lowest affinity with the stationary phase will be the first to leave and be detected.

Prior to the analysis procedure, the first step is to extract the analytes from the water phase to an organic solvent, in order to be further injected onto the HPLC column. In the NEN 6524 hexan is used as extraction solvent for PAH. The extraction is carried out at two different pH. Thereafter, the hexane extract is dried with sodium sulfate and the extract is purified, then diluted with methanol and injected in the column. The detector used is a combined UV/fluorescence detector.

2.1.3.5. Oxygen demand

Both biological and chemical oxygen demands have been determined. A certified laboratory (Lackarebäck) determined the chemical oxygen demand (COD), whereas the biological oxygen demand (BOD) has been a part of my laboratory work. It is important to notice that the biological demand is included in COD.

Table 13: Analytical methods for oxygen demand

Parameters	Analytical method	Detection limit
COD_{Mn}	SS 028118-1	1 mg/l
BOD_5		

The chemical oxygen demand is the total amount of oxygen consumed in the transformation of organic constituents into inorganic compounds in the samples. However, the measurement does not include the oxidation of PAH, which occurs in relatively low concentrations compared to natural organic matter and are also volatile enough to escape from the samples during the analysis. COD can be determined with permanganate (MnO_4^-) or with chromate ($Cr_2O_4^{2-}$) as oxidizers. In the case of the study, potassium permanganate ($KMnO_4$) was added to the sample and heated during 20 minutes. Thereafter, the permanganate which did not react was mixed with iodine (I^-). From the amount of iodine necessary to react on permanganate, COD was calculated.

The biological oxygen demand reflects the amount of dissolved oxygen required for the biological degradation of organic and inorganic matter present in the water sample. This test has been carried out on a five days period, hence the name BOD_5. This measurement is more representative of what can happen in the natural environment. The determination consists of measurement of dissolved oxygen in the sample at the initial time, and measurement after 5 days incubation in the dark and at room temperature. The difference between these two values gives the BOD_5 value.

2.1.3.6. Microorganisms

The Göteborg Sewage and Water Works laboratory at Lackarebäck's drinking water treatment plant has analysed the microbiological parameters, *E. coli* and Total Coliforms (method Colilert-18 ver1 040401) and *Cl. perfringens* (method ISO/CD 6461-2:1986) in stormwater from three storm events. The *somatic coliphages* (method ISO 10705-2), *F-specific RNA bacteriophages* (method ISO 10705-1) and *Intestinal enterococci* (method S-EN ISO 7899-2) were analysed in stormwater from two storm events by the Swedish Institute for Infectious

Disease Control (SMI), Stockholm. All samples were stored in the fridge after the sampling event until analysed. Membrane filtration was applied for the determination of *Intestinal enterococci* and presumptive colonies were verified by darken spots when grown on esculine substrate. For the determination of the *bacteriphages* 25 mL of sample were analysed. The samples were sterile-filtrated (45 µm high-flow filter) prior to the analyses of bacteriophages in order to remove debris and bacteria.

2.1.4. Data processing

In order to get removal efficiencies from the concentration measured, several calculation steps are necessary: the calculation of the stormwater volume at the inlet and outlet for each event, the calculation of pollutant mass load entering and leaving the pond, leads to the calculation of the site mean concentration (SMC).

Determination of the stormwater volume

Flow data from the inlet and outlet samplers have been downloaded from the loggers processed with the software Flowlink 4 and exported to Excel. From the flow curve, Figure 23 shows an example, the stormwater volume is calculated by integration of the area below the curve.

Determination of the removal efficiency for a single storm event

For a single storm event, the removal efficiency was calculated from the event mean concentration (EMC) of each pollutant, determined from composite samples both at the inlet (EMC_{in}) and outlet (EMC_{out}). The removal efficiency is given by Equation 7.

Equation 7: Calculation of the removal efficiency for a single storm event

$$R(\%) = \frac{(EMC_{in} - EMC_{out})}{EMC_{in}} * 100$$

Determination of the long-term removal efficiency

The long-term removal efficiency is calculated using the pollutant concentrations determined during all the storm events studied. Thus, it gives a global overview of the pond efficiency, which can vary greatly from one storm event to another. First, a site mean concentration (SMC) was calculated from the total mass of each pollutant reaching and leaving the pond for all the storm events studied, both at the inlet and outlet of the pond, see Equation 9. The long-term removal efficiency was then calculated with this SMC.

Equation 8: Calculation of the pollutant mass for one storm event

$$M_i = C_i * V_i$$

Equation 9: Calculation of the SMC for a series of storm events

$$SMC_{inlet} = \frac{\sum_i M_{i\ inlet}}{\sum_i V_{i\ inlet}} \qquad SMC_{outlet} = \frac{\sum_i M_{i\ outlet}}{\sum_i V_{i\ outlet}}$$

Equation 10: Calculation of the long-term removal efficiency

$$R(\%) = \frac{(SMC_{in} - SMC_{out})}{SMC_{in}} * 100$$

2.2. *Results and discussion*

2.2.1. Observation program

A total of seven storm events have been monitored in order to calculate the pollutant removal efficiency in the Järnbrott pond and to compare any changes that occurred since 1997-98. The measurement period lasted for six weeks, from mid-October (16th) until the end of November (24th). Due to problems linked to the sampling equipment, the study has been divided in two observation periods. The first one gathered three successive storm events from the 16th until the 22nd October 2004 (Figure 21). The second period gathers four individual storm events, the first one collected 29th of October 2004 (Figure 21), the second, the third and the fourth ones 12th, 18th and 24th of November 2004 respectively (Figure 22). The very small amount of water collected during the rain event number 4 only allowed the analysis of metals and suspended solids (see Table 14). For the three last storm events (number 5, 6 and 7), the precipitations were a mixture of rain and snow. At the end of these events, the runoff mainly came from snowmelt.

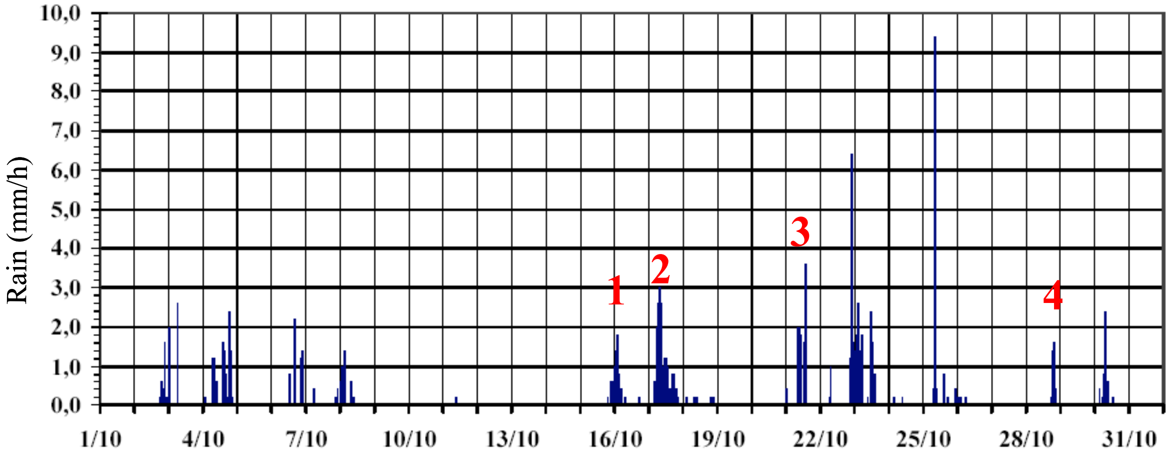

Figure 21: Precipitation in October 2004

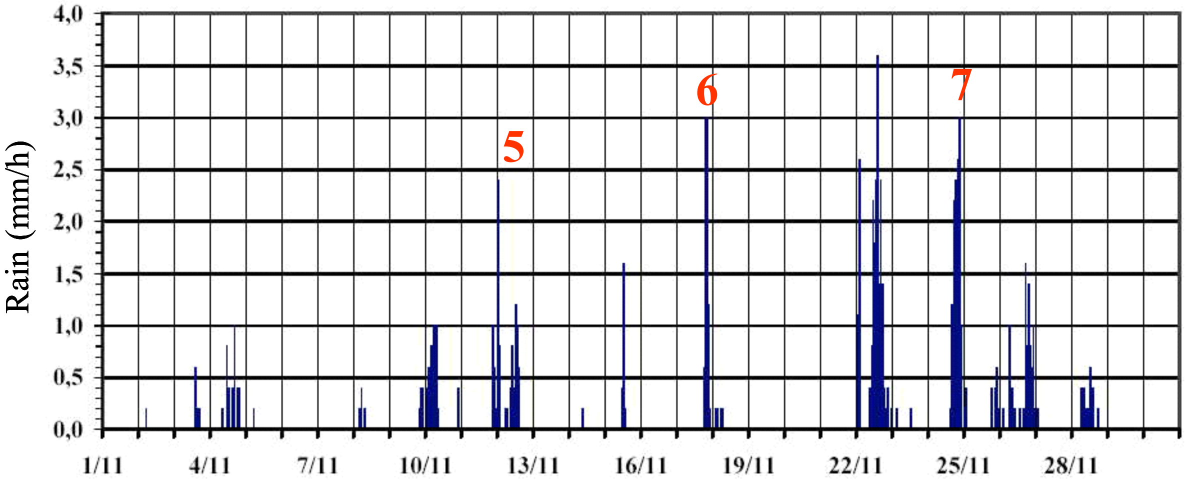

Figure 22: Precipitation in November 2004

Table 14: Dry periods and parameters monitored for each rain event

Rain event	Dry period (days)	Rain depth (mm)[6]	Stormwater volumes (m^3)	Parameters monitored
1 (16/10/2004)	7,5	8	6000	BOD_5, COD, TSS, VSS, nutrients, heavy metals, PAHs
2 (18/10/2004)	0,8	20	30000	BOD_5, COD, TSS, VSS, nutrients, heavy metals, PAHs
3 (22/10/2004)	3	11	15000	BOD_5, COD, TSS, VSS, nutrients, heavy metals, PAHs, bacteria
4 (28/10/2004)	2	4	5500	TSS, VSS, PAHs
5 (12/11/2004)	1,5	8	11000	BOD_5, COD, TSS, VSS, nutrients, heavy metals, PAHs
6 (18/11/2004)	2	9	12000	BOD_5, COD, TSS, VSS, nutrients, heavy metals, PAHs, bacteria
7 (24/11/2004)	1	12	16000	BOD_5, COD, TSS, VSS, nutrients, heavy metals, PAHs, bacteria

In addition to the studied stormwater parameters (Table 14), during the first measurement period, from 16th to 22nd of October 2004, dissolved oxygen, conductivity, pH and temperature were continuously measured at the outlet by the ISCO 6700 multiprobe. After the 22nd October 2004, due to maintenance problems, the multiprobe readings were not available.

For the sixth storm event, individual samples taken from each of the filled bottles, have been analyzed for suspended solids, heavy metals and nutrients. The rest of the parameters have been determined in the composite sample.

2.2.2. Changes in pond morphology

In order to be able to interpret possible differences in the removal efficiency from the 1997-98 monitored period and the one measured in 2004, changes in pond morphology and catchment's area have to be considered.

No changes have been noticed in the catchment's area since 1998; therefore, the main differences appeared in the pond and its surroundings. A high amount of vegetation grew in six years all around and in the pond. In addition, the thickness of the sediments was higher than in 1998. These two changes have probably decreased the volume of the pond available for exchanges. In addition, higher vegetation content certainly has an effect on the nutrients' cycle and probably increases the seasonal variation of the nutrients' removal efficiency. Indeed, the nutrient cycle is highly subjected to seasonal variation; for instance, algal utilization of NO_3^- during summer time is a factor for decreasing concentration of nutrients in water (Wetzel, 2001). On the other hand, the increasing vegetation may promote a higher impaction probability for the particles (see Figure 2 in section 1.3.2.1.) and their attached pollutants. This might have an effect on the pollutant removal efficiency as well.

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[6] These values are estimated from the monthly report given by the environmental protection agency measurements in Göteborg. These rain depths have been measured in the city center.

2.2.3. Study of the results from the seven rain events

The results obtained for each pollutant will be studied separately; their outlet concentration, removal efficiencies both in a long term and for single storms will be given and discussed. Before that, general information on flow patterns and outlet parameters will be highlighted.

The curves of the inflow and outflow always follow the same trend. However, the outflow is delayed compared to the inflow, as the example seen in Figure 23. This is due to the slight increase in the pond storage volume at the beginning of the rain event.

For the three first rain events, during which the dissolved oxygen, pH, conductivity and temperature have been monitored, the evolution of these parameters was similar for each storm event. In Figure 23 an example shows the trends observed for the rain event from 17th to 18th of October 2004.

At the beginning of a rain event, the dissolved oxygen at the outlet increases whereas the conductivity decreases first before slightly increasing during the flowing period, see Figure 23. Concerning the temperature and pH measurements, the values are constant during the whole storm event.

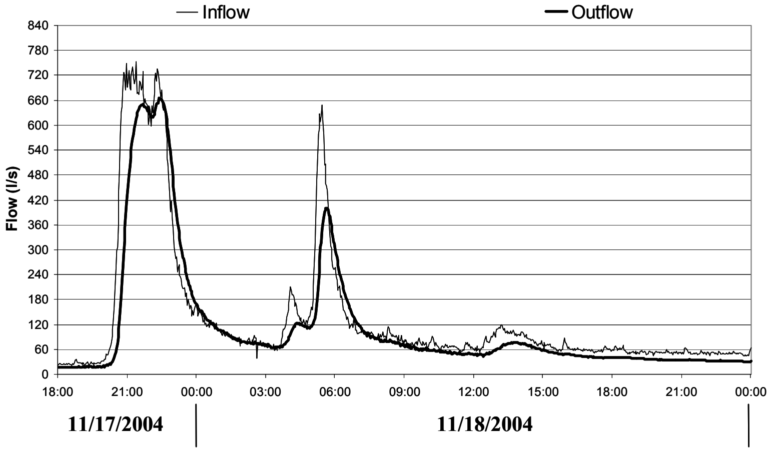

Figure 23: Inflow and outflow for the rain event 18th of November

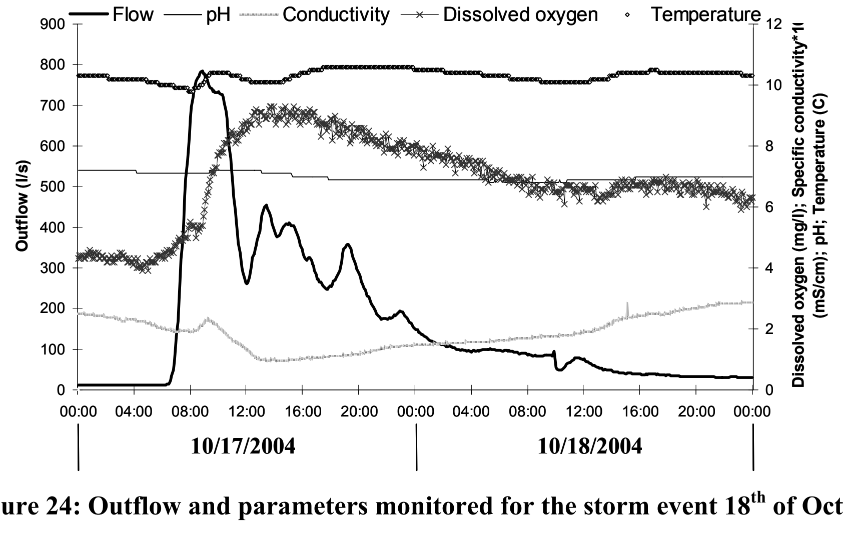

Figure 24: Outflow and parameters monitored for the storm event 18th of October

Table 15: SMCs and removal efficiencies for the measured parameters for the studied storm events[7].

Parameters	**SMC$_{\text{inlet (mg/l or µg/l)}}$**	**SMC$_{\text{outlet (mg/l or µg/l)}}$**	**Removal efficiency (%)**
SUSPENDED SOLIDS (mg/l)			
TSS	38	14	60
VSS	14	7	50
NUTRIENTS (mg/l)			
NO_2^--N	0,014	0,023	*-60*
NO_3^--N	0,77	1,70	*-125*
NH_4^+-N	0,13	0,12	10
Tot-N	1,70	2,60	*-50*
PO_4^{3-}-P	0,06	0,05	15
Tot-P	0,14	0,09	30
HEAVY METALS (µg/l)			
Tot-Cd	0,35	0,31	10
Tot-Co	1,50	0,80	45
Tot-Cr	9,50	7,40	20
Tot-Cu	190	210	*-10*
Tot-Pb	8,30	4,50	45
Tot-Zn	200	170	15
Tot-Ni	12	14	*-15*
Diss-Cd	0,13	0,10	25
Diss-Co	0,44	0,34	25
Diss-Cr	4,20	3,60	15
Diss-Cu	16	13	25
Diss-Pb	0,83	0,74	10
Diss-Zn	69	43	40
Diss-Ni	4,70	7,00	*-50*
PAHs (µg/l)[8]			
Naphtalene			
Acenaphthylene			
Acenaphthene			
Fluorene			
Phenanthrene	0,08	<0,05	>30
Anthracene			
Fluoranthene	0,13	0,05	60
Pyrene	0,14	0,06	60
Benz[a]anthracene☠	0,04	<0,02	>55
Chrysene☠	0,06	<0,02	>65
Benzo[b]fluoranthene☠	0,06	<0,03	>55
Benzo[k]fluoranthene☠	0,03	<0,01	>55
Benzo[a]pyrene☠	0,05	<0,02	>65
Dibenz[ah]anthracene☠			
Benzo[ghi]perylene			
Indeno[1,2,3-cd]pyrene			
∑ 16 EPA-PAHs	0,70	0,20	70
∑ cancerogen PAHs☠	0,30	<0,08	>70
∑ non cancerogen PAHs	0,45	0,15	65

The removal efficiencies presented in the Table 15, show great disparity in the results between pollutants. Some of them have high removal efficiency, like suspended solids

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[7] The values for SMC$_{inlet}$, SMC$_{outlet}$ and removal efficiency are round off. The real values were kept for the calculation, which is why the removal efficiency might not exactly fit to the site mean concentrations. The true values are shown in appendix.

[8] The shadowed cells stands for PAHs whose inlet and outlet concentrations are lower than the detection limit. Thus, long-term removal efficiencies cant be calculated.

whereas some others show negative removal efficiency, like total Ni, total Cu or NO_3^- for instance (Table 15). These results will be deeper studied in the following sections.

In the following sections, for each of these parameters, the comparison between the EMC's interval at the outlet and the guideline values issued by the Swedish EPA will give an indication of the potential impact of the outflow on the receiving water. In addition, the removal efficiency will be commented and compared to the removal efficiencies calculated in 1997 for metals, suspended solids and nutrients. In order to draw more reliable conclusions, the removal efficiency in 2004 will be compared to, both the one calculated for the period 1997/1998 and the one calculated in autumn 1997 (during the same season as the one studied in this work). Finally, the removal efficiencies calculated for single storm event will be presented and analyzed.

2.2.3.1. Suspended solids

Table 16: Outlet concentrations and long-term removal efficiencies for suspended matter

	Interval of EMC_{out} (mg/l)	Removal efficiency in 2004 (%)	Removal efficiency in 1997/1998 (%)	Removal efficiency autumn 1997 (%)
TSS	5-25	**60**	70	60
VSS	3-14	**50**	60	70

The removal efficiency for suspended solids (Table 16) is high and comparable to the literature. In addition, removal efficiencies obtained in autumn 1997 as well as on the period 1997/1998 are similar to the ones calculated in 2004, meaning that the Järnbrott pond is still efficient in removing particles. The changes in the morphology did not appear to affect this parameter.

Table 17: Single storm removal efficiencies for suspended solids (in %)

	Event 1 (16/10/2004)	Event 2 (18/10/2004)	Event 3 (22/10/2004)	Event 4 (29/10/2004)	Event 5 (12/11/2004)	Event 6 (18/11/2004)	Event 7 (24/11/2004)
TSS	70	70	80	45	50	60	45
VSS	50	50	75	45	0,5	65	-2

The study of the removal efficiency for single storm events shows disparity in values calculated from different storms ranging from 45 to 80% for TSS and from –2 to 75% for VSS, see Table 17.

Since the removal efficiency for suspended matter is high, the attached pollutants should also be removed to a large extent.

2.2.3.2. Heavy metals

The results obtained for heavy metals will be split in two parts, the first part will deal with Cd, Cu, Pb and Zn, which were analyzed in 1997/1998, and the second part will evaluate the results obtained for the other metals: Co, Cr and Ni. For all of them, the dissolved and total fraction will be presented.

Analysis of the results obtained for Cd, Cu, Pb and Zn

- Outlet concentrations and long term removal efficiencies

The outlet concentration are considered by the Swedish EPA as moderately high to very high for lakes and water courses, see Table 18. The risk of biological effects associated ranges from "increased risks" to "high risks even with brief exposure" (Swedish EPA). Therefore, it is sensible to consider that these outlet concentrations may have an impact on the receiving waters. In addition, the dissolved concentrations, accounting for the most available and thus most harmful metal fraction is not negligible.

However, the removal efficiency of total Cd, Pb and Zn are comparable to the results found in the literature, ranging from 45% for Pb to 10% for Cd (Table 18). The high removal efficiency recorded for Pb can be explained by its high affinity for particulate matter (Nascimento et al., 1999) easily removed by settlement in the pond (Pettersson, 1998). It has to be noted that the removal efficiency for the dissolved fraction for these three metals is quite good. It can be explained by two reasons: the uptake from organisms living in the pond (for Zn which is an essential metal) and the migration of dissolved metals from the water phase to the particles followed by settling.

Concerning Cu, the negative removal efficiency (-10%) for the total fraction can be correlated with the positive removal efficiency measured for the dissolved fraction. The values obtained for the long-term removal efficiency can lead to the following hypothesis: the adsorption of the free metal fraction on particles or the aggregation of colloidal particles through the pond can explain the removal of dissolved Cu and the "production" of adsorbed Cu counted in the total fraction. This mechanism will thus lead to negative removal efficiency for total Cu. In order to confirm or infirm this hypothesis, single removal efficiencies have to be considered. This transformation can also be positive for risks reduction because the bounded fraction is less available for living organisms than the dissolved fraction and thus less harmful.

The comparison of the total metals' removal efficiencies in 2004 and 1998 shows comparable results for Pb and decreasing removal for Cu and Zn. Concerning Cd, the value obtained in 2004 is comparable to the one obtained during autumn 1997 and lower than the one obtained for the whole period 1997/1998. Cd seems to be more affected by seasonal variations than Pb, Cu and Zn.

Table 18: Outlet concentrations, EPA guidelines and long-term removal efficiency for Cd, Cu, Pb and Zn

		Interval of EMC_{out} (µg/l)	**EPA guidelines[9]**	**Removal efficiency in 2004 (%)**	**Removal efficiency in 1997/1998 (%)**	**Removal efficiency autumn 1997 (%)**
Cd	Total	0,1-0,5	moderately high - high	**10**	10	20
	Dissolved	0,1-0,2		**25**	*-15*	15
Cu	Total	18-530	high - very high	***-10***	30	35
	Dissolved	9-19		**25**	0	10
Pb	Total	2-8	high	**45**	50	45
	Dissolved	0,4-1,2		**10**	5	10
Zn	Total	70-310	high - very high	**15**	30	35
	Dissolved	27-82		**40**	10	25

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[9] These guidelines are issued for lakes and watercourses.

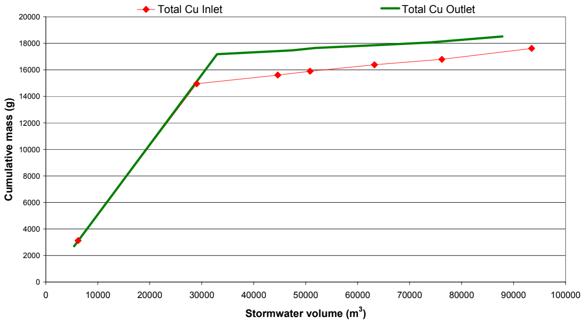

Figure 25: Cumulative amount of total Cu in outflow

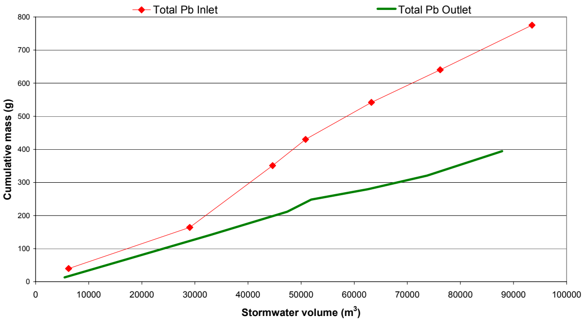

Figure 26: Cumulative amount of total Pb in outflow

- Removal efficiency for single storm events

The removal efficiency for single storm events shows the disparity of the results from one storm event to another. The biggest differences have been recorded for the total and the dissolved fraction of Cd respectively, whose highest removal is 70% for the event 4, 40% for the event 7 respectively, whereas the lowest is -40% for the event 2, -70% for the storm event 6 respectively.

The study of the removal efficiency for single storm events for Cu (Table 19) gives a good tool to understand the negative long-term removal efficiency (-10%) for this metal (Table 18). Given the section 2.1.4., the calculation of the long-term removal efficiency is based on the inlet and outlet concentrations and volumes. In the case of the second storm event, the stormwater volume (23000m^3) is much bigger than the other storms' volumes (from 6000m^3 for events 1 and 4 up to 17000m^3 for the last one). If the conclusion is based on single storm event's removal efficiency, we can see that the Cu removal varies a lot but show good removal efficiencies for the last 4 storms, ranging from 20 to 50%.

The low removal efficiency values obtained for the total concentration during the second storm event can be explained by the very short dry period between the two first storms (0,8 days) and the high stormwater volume for this event (23000m^3). Indeed, a short dry period does not promote enough time for the particles and attached pollutants to settle. Moreover, the high flow engendered during the second storm event may have created pollutants' resuspension leading to very low removal efficiency for total-Zn and total-Pb and negative removal efficiency for total-Cd and total-Cu.
The conclusion of the Cu behavior in the pond from single storm removal efficiencies shows the importance of considering long-term removal efficiency for stormwater ponds.

Table 19: Single storm removal efficiencies (in %) for Cd, Cu, Pb and Zn

		Event 1 (16/10/2004)	Event 2 (18/10/2004)	Event 3 (22/10/2004)	Event 4 (29/10/2004)	Event 5 (12/11/2004)	Event 6 (18/11/2004)	Event 7 (24/11/2004)
Cd	Total	15	*-40*	45	70	35	-5	30
	Dissolved	-5	15	15	25	30	*-70*	40
Cu	Total	2	*-2*	50	20	50	40	35
	Dissolved	50	10	10	40	20	35	15
Pb	Total	60	15	60	35	70	50	35
	Dissolved	55	10	*-15*	2	*-20*	25	20
Zn	Total	20	4	45	20	50	35	30
	Dissolved	20	15	*-2*	30	10	15	60

Table 20: Outlet concentrations, EPA guidelines and long-term removal efficiency for Co, Cr and Ni

		Interval of EMC_{out} (µg/l)	**EPA guidelines[10]**	**Removal efficiency in 2004 (%)**
Co	Total	0,03-1,6		**45**
	Dissolved	0,2-0,7		**25**
Cr	Total	3-18	moderately high - high	**20**
	Dissolved	1-12		**15**
Ni	Total	4-29	low – moderately high	***-15***
	Dissolved	4-14		***-50***

Analysis of the results obtained for Cr, Co and Ni

o Outlet concentrations and long term removal efficiencies

No guideline values are available for cobalt concentration in lakes and watercourses. Both Cr and Ni show less alarming situation than for the previous metals with moderately high to high concentrations recorded for Cr and low to moderately high for Ni (Table 20). According to the Swedish EPA, the risk of biological effects ranges from little to increased risks. Nevertheless, even if these results confirm that the most important metals to consider in urban runoff are Cd, Cu, Pb and Zn, the others should not be neglected.

For total Co and Cr, the results show high long-term removal efficiencies (Figure 27 and Table 20) whereas low values have been recorded for the dissolved fraction as expected (Table 20). Indeed, the colloids and free fractions of metals are not easily removed because they cannot be settled, as attached metals.

On the contrary, Ni shows negative removal efficiency (Table 20 and Figure 28), but fortunately, according to the EPA guidelines, the outlet concentration is not too alarming (Table 20).

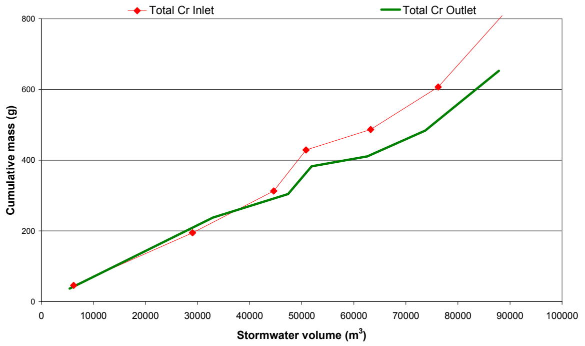

Figure 27: Cumulative amount of total Cr in outflow

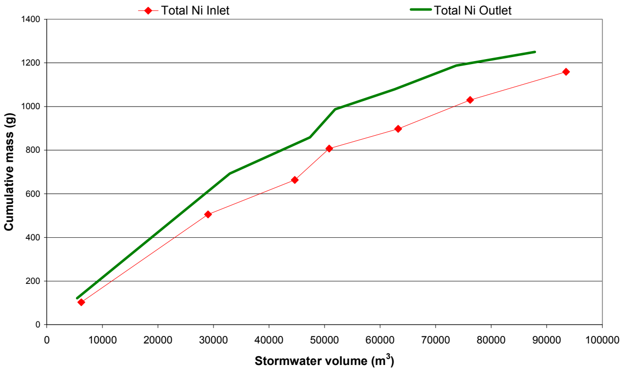

Figure 28: Cumulative amount of total Ni in outflow

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[10] These guidelines are issued for lakes and watercourses.

Table 21: Single storm removal efficiencies (in %) for Co, Cr and Ni

		Event 1 (16/10/2004)	Event 2 (18/10/2004)	Event 3 (22/10/2004)	Event 4 (29/10/2004)	Event 5 (12/11/2004)	Event 6 (18/11/2004)	Event 7 (24/11/2004)
Co	Total	100	10	60	5	60	45	40
	Dissolved	*-20*	20	*-10*	*-5*	*-5*	2	40
Cr	Total	10	*-10*	40	5	45	30	25
	Dissolved	*-45*	0,5	10	*-5*	*-10*	*-5*	15
Ni	Total	*-35*	*-20*	*-15*	*-25*	*-20*	5	40
	Dissolved	*-190*	40	120	*-80*	*-100*	*-25*	*-20*

- Removal efficiency for single storm events

Once more, the removal efficiency for single storm events shows the disparity of the results from one storm event to another (Table 21) ranging from 5 to 100% for total Co; -10 to 45% for total Cr and –35 to 40% for total Ni. The removal efficiency of Cr shows the same anomaly as the one mentioned for Cu (Tables 18 and 19) for the second storm event. The low removal efficiency can thus be explained once more by the short dry period between the two first storm events. The negative removal efficiency recorded for the dissolved fraction of these metals suggests the possibility of desorption from the sediments or/and from the particles present in the water phase. Indeed, the sediment experiment (see section 3.2.) proved the release of dissolved Cr and Ni from the sediments under anoxic and turbulent conditions. As Co has not been studied previously no conclusion can be drawn for this metal. In addition negative removal efficiency for total Ni have been recorded for all the storm events studied except for the two last ones (Table 21).

2.2.3.3. Nutrients

As nitrogen and phosphorus compounds show very different behaviours (Table 22), the interpretation of the results will be done separately.

Table 22: Outlet concentrations, EPA guidelines and long-term removal efficiencies for nutrients

	Interval of EMC_{out} (mg/l)	**EPA guidelines[11]**	**Removal efficiency in 2004 (%)**	**Removal efficiency in 1997/1998 (%)**	**Removal efficiency autumn 1997 (%)**
NO_2^--N	0,01-0,05		***-60***		
NO_3^--N	0,08-2		***-130***		
NH_4^+-N	0,7-3		**10**		
Total-N	1-3	very high	***-50***	10	*-10*
PO_4^{3-}-P	0,04-0,1		**15**	40	30
Total-P	0,08-0,1	very high – extremely high	**30**		

Table 23: Single storm removal efficiencies (in %) for nutrients

	Event 1 (16/10/2004)	Event 2 (18/10/2004)	Event 3 (22/10/2004)	Event 5 (12/11/2004)	Event 6 (18/11/2004)	Event 7 (24/11/2004)
NO_2-N	*-150*	*-30*	*-80*	*-70*	*-30*	*-95*
NO_3-N	*-180*	*-65*	*-3000*	*-100*	*-30*	*-150*
NH_4^+-N	*-550*	*-25*	80	30	20	*-35*
Total-N	*-80*	*-10*	*-90*	*-80*	*-20*	*-100*
PO_4-P	50	30	0	40	40	*-80*
Total-P	50	25	50	40	40	*-10*

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[11] These guidelines are issued for lakes.

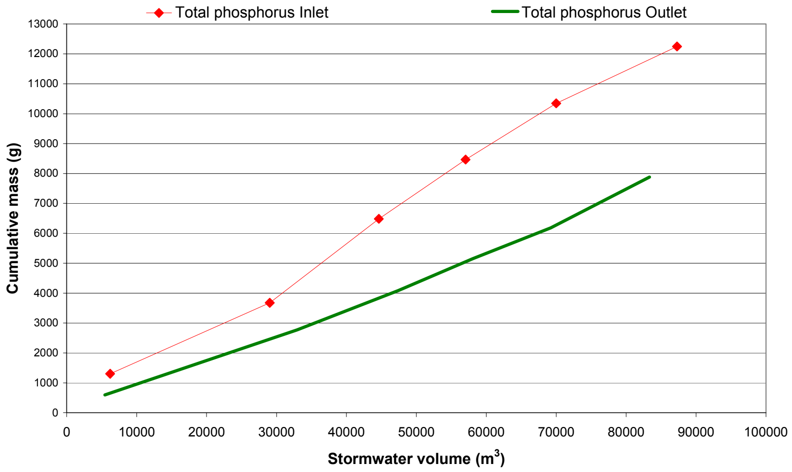

Figure 29: Cumulative amount of total phosphorus in outflow

o Phosphorus compounds

Environmental quality criteria values from the Swedish environmental protection agency are only available for total phosphorus. At the pond outlet, the concentration recorded for total phosphorus is considered as very high to extremely high (Table 22) and even much higher than the concentration measured in autumn 1997 for total P (0,06mg/l). It has to be noticed that these guideline values are issued for lakes and it is not possible to draw direct conclusions regarding the effect of this outflow on the receiving watercourse. However, in the case of these extreme values, the lake is considered as eutrophic or hypertrophic, it is sensible to expect damaging effect on the receiving water.

The removal efficiency for total phosphorus and PO_4^{3-} is positive (30% and 15% respectively (Table 22 and Figure 29)). For total-P, the value is comparable to the different results given in the literature for stormwater ponds. However, the removal efficiency for PO_4^{3-} is quite low (only 15%). In addition, the removal of PO_4^{3-} is lower than the removal efficiency obtained during the autumn 1997. In this case vegetation influenced the phosphorus removal even if the Järnbrott pond is still able to remove phosphorus. This might be due to the decaying vegetation surrounding the pond, which leads to an input of PO_4^{3-} and total-P in the water phase. As well, the hypothesis of release of PO_4^{3-} from the sediments is conceivable as shown during the sediment experiment (see section 3.1.2.2.).

For these compounds, removal efficiencies are quite constant for all storms (Table 23), except for the event 3 and 7 for PO_4^{3-}. This is probably due to the rain depth which is high in both cases (11mm and 12mm respectively) giving less time for the particles to settle and thus creating low removal efficiencies. Concerning total-P, the removal efficiency is low for the last rain event, probably for the same reason. In addition, during days before the last rain event, the pond was frozen creating anoxic conditions in the water phase. In this case, phosphorus compounds might have been released from the sediments, leading to a higher outlet concentration than inlet concentration.

o Nitrogen compounds

Concerning the nitrogen compounds, the long-term removal efficiency is surprisingly low except for NH_4^+ (Table 23).

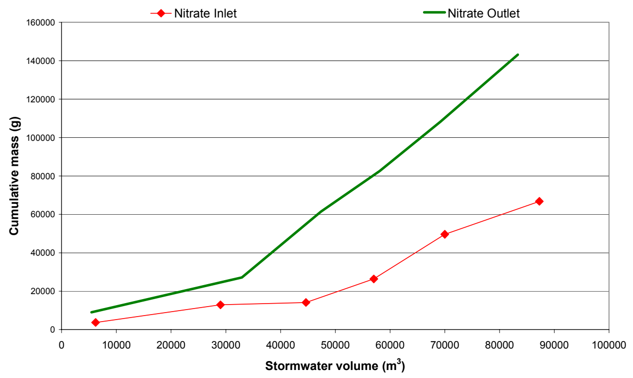

Figure 30: Cumulative amount of nitrate (NO_3^-) in outflow

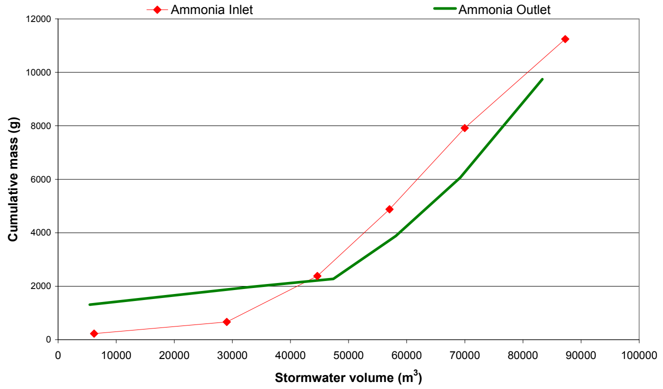

Figure 31: Cumulative amount of ammonium (NH_4^+) in outflow

The removal efficiencies calculated for each single storm event (Table 23) show the same trend, with negative values for NO_3^-, NO_2^- and total-N for every storm event, suggesting the production of these compounds in the pond. However, despite the negative removal efficiency of NO_2^-, the concentration is very low, ranging from 9 to 50µg/l. The measurement campaign was carried out in autumn and early winter. During this period, the vegetation around the pond is decaying leading to an additional input of nitrogen substances into the pond water. As well, birds have been observed on the pond, and they can also be a source of nitrogen. The nitrogen cycle (Figure 3 section 1.3.2.3.) suggests that these substances coming from the life cycle of living beings, should be transformed in NH_4^+ and then being nitrified and thus accumulated in the water phase as NO_2^- and NO_3^- before the denitrification step. However, presence of bacteria is needed to achieve the denitrification, and during this period of the year, all biological activities are reduced. These two factors would explain both, the production and the accumulation of NO_3^- in the pond (Figure 30) by suppression of the denitrification process, leading to negative removal efficiency.

Comparison between nitrogen and phosphorus compounds' removal efficiencies, showing higher removal for phosphorus compounds and negative removal for most of the nitrogen compounds, leads to the conclusion that phosphorus is more adsorbed to particles than nitrogen compounds in urban stormwater runoff.

2.2.3.4. PAH

Studies of PAH include 16 compounds that have been analysed for each rain event, including 9 non-carcinogenic PAHs and 7 carcinogenic ones (Appendix 1). However, for some of these compound both inlet and outlet concentrations are below the detection limit, it is impossible to calculate the removal efficiency. For the compounds whose outlet concentrations are below the detection limit the removal efficiency could only be estimated as superior to a certain value. However, the removal efficiency for the sum of the 16 PAHs, considered as primary pollutants by the EPA all around the world could be calculated for all storm events and gives a global overview.

Table 24: Outlet concentrations, EPA guidelines and long-term removal efficiencies for some PAH

		Interval of EMC$_{out}$ (µg/l)	EPA guidelines[12]	Removal efficiency in 2004 (%)
PAHs	Phenanthrene	<0,03-0,09		**>30**
	Fluoranthene	0,03-0,09		**60**
	Pyrene	0,03-0,1		**60**
	Benz[a]anthracene☠	<0,01-0,03		**>55**
	Chrysene☠	<0,01-0,04		**>65**
	Benzo[b]fluoranthene☠	<0,02-0,04		**>55**
	Benzo[k]fluoranthene☠	<0,01-0,02		**>55**
	Benzo[a]pyrene☠	<0,01-0,03		**>65**
	∑ 16 EPA-PAHs	0,07-0,5		**70**
	∑ cancerogen PAHs☠	<0,03-0,2	Not very serious – moderately serious	**>70**
	∑ non cancerogen PAHs	0,07-0,3	Not very serious	**70**

The Swedish EPA gives guideline values only for the sum of the 9 non-carcinogenic PAHs and for the sum of the 7 carcinogenic ones. As seen in the Table 24, the outlet event mean concentration for the sum of the 9 non-carcinogenic PAH is relatively low (from 0,07 to 0,30µg/l). As the reaction's mechanisms of these PAH in living bodies are still not well characterized it is not easy to draw conclusions. Indeed, as seen in the section 1.3.2.4., even the non-carcinogenic PAH or their metabolites can cause damages in organisms.

Removal efficiencies for these parameters are high (Table 24), ranging from superior to 30 to higher than 70%. This means that the Järnbrott pond is efficient in removing PAHs. This is confirmed by the removal efficiency calculated for each storm event, presented in Table 25.

Table 25: Single storm removal efficiencies (in%) for PAHs

	Event 1 (16/10/2004)	Event 2 (18/10/2004)	Event 3 (22/10/2004)	Event 4 (29/10/2004)	Event 5 (12/11/2004)	Event 6 (18/11/2004)	Event 7 (24/11/2004)
Naphtalene	■	■	■	■	■	■	80
Acenaphthylene	■	■	■	■	■	■	■
Acenaphthene	■	■	■	■	■	■	■
Fluorene	■	■	■	■	■	■	■
Phenanthrene	70	*-100*	45	40	>50	>20	30
Anthracene	■	■	■	■	0	■	5
Fluoranthene	80	35	60	40	85	60	35
Pyrene	80	50	60	40	80	45	45
☠Benz[a]anthracene	>80	>0	70	*-200*	>80	>50	45
☠Chrysene	>85	>65	55	60	>85	50	55
☠Benzo[b]fluoranthene	>65	>30	70	20	>75	>30	45
☠Benzo[k]fluoranthene	>50	>0	60	0	>75	>50	>65
☠Benzo[a]pyrene	>65	>50	65	25	>85	65	70
☠Dibenzo[ah]anthracene	■	■	>0	■	>50	■	■
Benzo[ghi]perylene	>65	■	60	35	>75	>30	>85
☠Indeno[123cd]pyrene	>50	■	40	0	>65	>0	>85
Σ 16 EPA-PAH	**85**	**55**	**60**	**30**	**95**	**70**	**70**
☠**Σ 7 carcinogenic PAHs**	**80**	**50**	**60**	**5**	**>85**	**80**	**70**
Σ 9 non carcinogenic PAHs	**80**	**20**	**60**	**40**	**90**	**65**	**75**

■	Both inlet and outlet concentration were under the detection limit
🟦	The outlet concentration was under the detection limit and the concentration used for the calculation is the value of the detection limit. The removal efficiency was then estimated as superior to this value.

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[12] These guidelines are issued for groundwater contamination.

For most of the PAH, the removal efficiencies are high, reaching 85% for some individual PAHs (fluoranthene, chrysene, benzo[a]pyrene, benzo[ghi]perylene and indeno[123cd]pyrene). However, once more, it is possible to notice the high differences between storms. For example the removal efficiency for benz[a]anthracene goes from -200% for the fourth storm up to >80% for the events 1 and 5. Nevertheless, most of the storm events, the outlet concentrations were very low and even lower than the detection limit. These values suggest that PAH are, to a large extent attached to particles in storm water runoff. Indeed, the main removal process occurring in ponds is the settling of particles and their attached pollutants.

Phenanthrene and benz[a]anthracene are the only PAHs presenting negative removal efficiency (for the second and the fourth event respectively). However, in the case of phenanthrene, it has to be noticed that the inlet and outlet concentrations are very low for this second storm event: 0,02 and 0,04µg/l respectively, compared to the concentration recorded for example for the third storm event for the same compounds: 0,16 and 0,09µg/l for the inlet and outlet respectively. Considering the second compound (benz[a]anthracene) the inlet concentration for the fourth event is the lowest recorded whereas the outlet concentration is the highest recorded. Therefore, it is important to consider both the removal efficiency and the outlet concentrations of the pollutants in order to draw reliable conclusions on the potential effect on the receiving water.

2.2.3.5. Oxygen demand

For the events 1 and 4, BOD_5 has not been measured; therefore, the removal efficiency on a long term, for this parameter is based on the results obtained for five rain events (rain event 2, 3, 5, 6 and 7 that occurred 18th and 22nd October and 12th, 18th and 24th November respectively). In order to compare BOD_5 and COD, the removal efficiency for COD will here be calculated in the same period of time (Table 26).

Table 26: Outlet concentrations, EPA guidelines and long-term removal efficiencies for COD and BOD_5

	Interval of EMC_{out} (mg/l)	**EPA guidelines[13]**	**Removal efficiency in 2004 (%)**
COD	4-9	Low – moderately high	**25**
BOD_5	0,5-7,5		**20**

The EPA guidelines are only available for the chemical oxygen demand. When compared to the outlet concentration, they give a level of contamination considered as low to moderately high.

The removal efficiency for COD and BOD_5 is medium and inferior to the literature values. This was not expected because oxygen-demanding compounds are known to be attached to particles with a size superior to 100µm (Chebbo and Bachoc, 1992). Thus BOD_5 and COD compounds should be easily removed by settling. This low removal efficiency, compared to the literature can be explained by the relatively low value obtained for total-N (Table 22 section 2.2.3.3.), which gather, for a part nitrogen compounds that can be further oxidized (like for instance NO_2^- that can be oxidized into NO_3^-). As BOD_5 and reduced form of nitrogen are included in COD, the poor removal efficiency for these parameters will influence the removal efficiency for COD. No value is available to compare with 1997 but given the results for Total-N, it may be expected that the vegetation play a role in this low removal efficiency.

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[13] These guidelines are issued for lakes and watercourses.

Table 27: Single-event removal efficiencies (in %) for oxygen demand

	Event 1 (16/10/2004)	Event 2 (18/10/2004)	Event 3 (22/10/2004)	Event 5 (12/11/2004)	Event 6 (18/11/2004)	Event 7 (24/11/2004)
COD	20	20	30	40	40	*-35*
BOD_5		*-0,5*	65	*-40*	*-70*	*-5*

Table 27 shows a great disparity in the results for single storm removal efficiency for COD and BOD_5, whose removal efficiency ranges from -35% to 40% and -70 to 65% respectively. The low removal efficiency can be explained by the decay of vegetation taking place at this time of the year, leading to the production of suspended organic matter in the pond discharged in the outlet. However, this kind of natural pollution is not harmful for the environment and is a part of the natural life cycle. Therefore, despite the poor removal efficiency for BOD_5, the situation is not alarming.

2.2.3.6. Microorganisms

The analysis of the amount of bacteria in stormwater has not been done for all storm events. The amount of water collected during the third, the sixth and the last storm events allowed the determination of these parameters. In addition, another limitation for this analysis is the delay between the collection of the sample and the analysis that has to be as short as possible. Table 28 shows the concentrations and removal efficiency of microbiological parameters for the three storm events studied.

The measurement period is too short to draw any conclusion on the pond removal efficiency for these parameters. Indeed, the removal efficiencies are fluctuating a lot from one rain to another for each of these parameters. For Coliforms, the removal efficiency values range from

Table 28: Concentrations and removal efficiencies (in %) for the studied microbiological parameters for the events studied.

	Event 3 (22/10/2004)		Event 6 (18/11/2004)		Event 7 (24/11/2004)	
Concentrations (PFU / 100 mL)	In	Out	In	Out	In	Out
Coliforms	120 000	57 000	37 000	73 000	23 000	37 000
E. Coli	9 000	9 000	9 300	4 100	4 100	7 500
Cl. perfringens	140	210	450	280	320	270
Somatic coliphages	n.a. [2]	n.a.	176 [1]	428 [1]	268	688
F-specific RNA bacteriophages	n.a.	n.a.	300 [1]	212 [1]	132	724
Intestinal enterococci	n.a.	n.a.	730 [1]	390 [1]	764	927
Removal efficiency (%)						
Coliforms	55		-100		-60	
E. Coli	0		55		-85	
Cl. perfringens	-50		40		15	
Somatic coliphages	-		-145		-160	
F-specific RNA bacteriophages	-		30		-450	
Intestinal enterococci	-		45		-20	

[1] seven days fridge storage before analysis

[2] n.a. = not analyzed

-100% to 55% for event 6 and event 3 respectively, meaning that the pond is sometimes removing bacteria to a large extent and sometimes increasing them. Birds and other animals living on and around the pond may function as sources of faecal contaminants, leading to higher outlet than inlet microbiological levels and thus a negative removal. The sediments can also be a source for these organisms: the sediments' concentration is much higher than the water concentration, and in clay dominating sediments (which is the case for the sediments present at the Järnbrott pond outlet), these bacteria have a high life expectancy (Davies and Bavor, 2000). Moreover, these organisms are associated with the finest particle fraction, inferior to 2µm diameter (Davies and Bavor, 2000). Consequently turbulent conditions can significantly increase the outlet concentration.

The bacteriphages at the two precipitation events were not reduced in the pond. The levels of somatic coliphages at event 6 were higher in the outlet of the pond, though the opposite was observed for the F-specific RNA bacteriophages. At event 7 the occurrence of each virus indicator was significantly higher in the outlet water compared to the inlet. This may be explained by a release of particles stored within the pond, possibly resulting from the higher flows of water during the precipitation. The intestinal enterococci were reduced within the pond at event 6, but higher levels were found in the outlet at event 7. Parasites and bacteria are several times larger and may therefore have a higher potential to sediment within the pond. The survival of viruses may also be higher within water environments compared to the bacteria. Current results shows that the reduction of virus within Järnbrott pond was weak.

Generally, the concentrations of all these microbiological parameters (Table 28) varied greatly from one rain to another, especially at the inlet of the pond. The results clearly show that additional studies are needed to confirm these observations and to further assess the effect of stormwater ponds on the reduction (or the increase) of bacteria and virus present in urban runoff and to discover the sources of these pollutants in stormwater.

2.2.4. Single rain event

The storm event 18th November has been studied in details, i.e. several individual samples were analysed (in and out) in order to understand the variations and mechanisms of the pollutants' concentration at the inlet and at the outlet during a storm event. Total metals, suspended solids and nutrients have been monitored this way. The other parameters (Table 13) have been measured only from a composite sample.

2.2.4.1. Variation of TSS, VSS, heavy metals and nutrients at the inlet

This particular storm event exhibited three flow peaks at the inlet (centred 10pm 17th, 6am and 2pm 18th respectively) (Figure 32). The total suspended solids (Figure 32), the heavy metals (Figure 33) (except Cd and Ni) and phosphorus compounds concentrations (Figure 34) follow the flow peaks, whereas nitrate and ammonia concentrations variations are less easy to explain. The highest concentration is registered at the beginning of the storm event for metals (except Cd and Ni), suspended solids and phosphorus compounds. This is usually explained by the high amount of particles deposited on impervious surfaces during dry period easily washed off at the beginning of the runoff. The good correlation between suspended solids and total metal concentration (except Cd and Ni) is a proof that metals in stormwater runoff are highly adsorbed on particles. The same conclusion can also be drawn for orthophosphate and

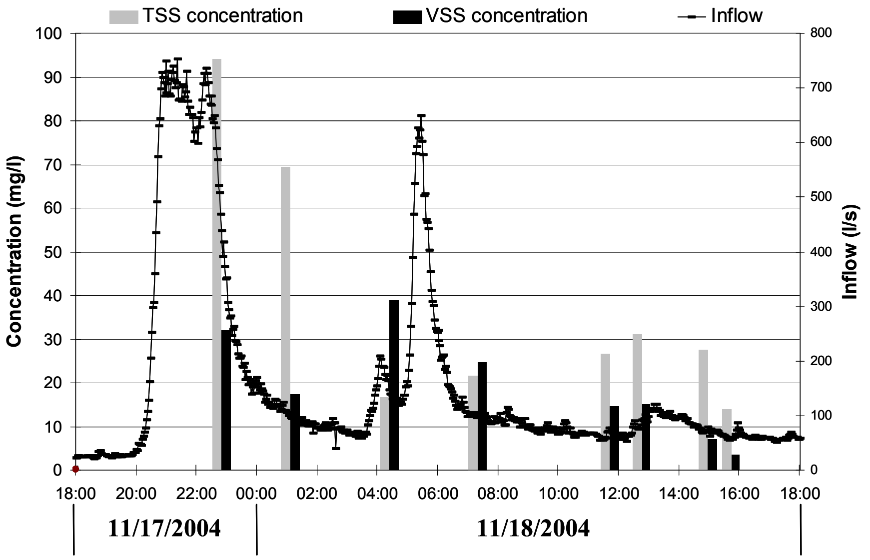


Figure 32: TSS and VSS concentrations during the storm event 17th November 2004

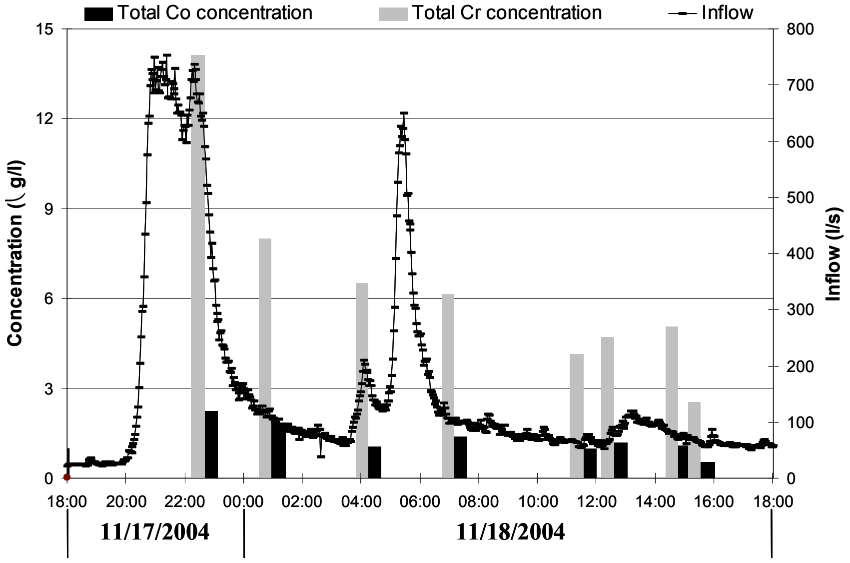


Figure 33: Co and Cr concentrations during the storm event 17th November 2004

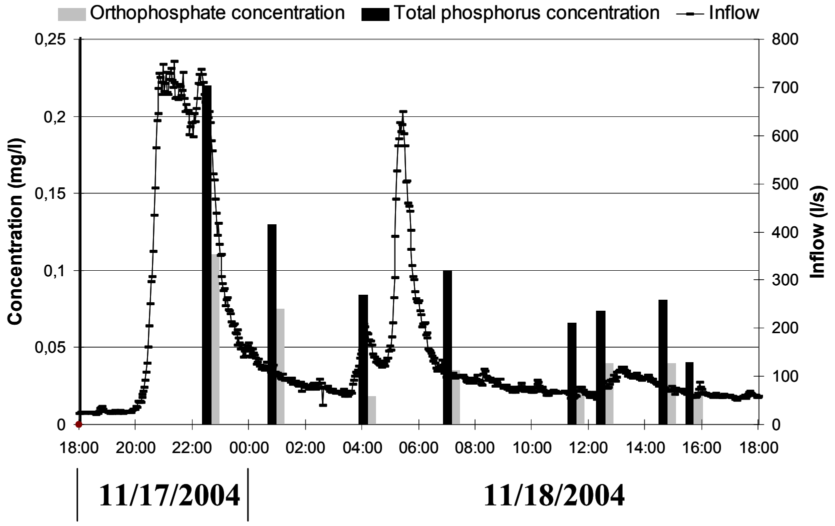


Figure 34: PO_4^{3-} and total-P concentrations during the storm event 17th November 2004

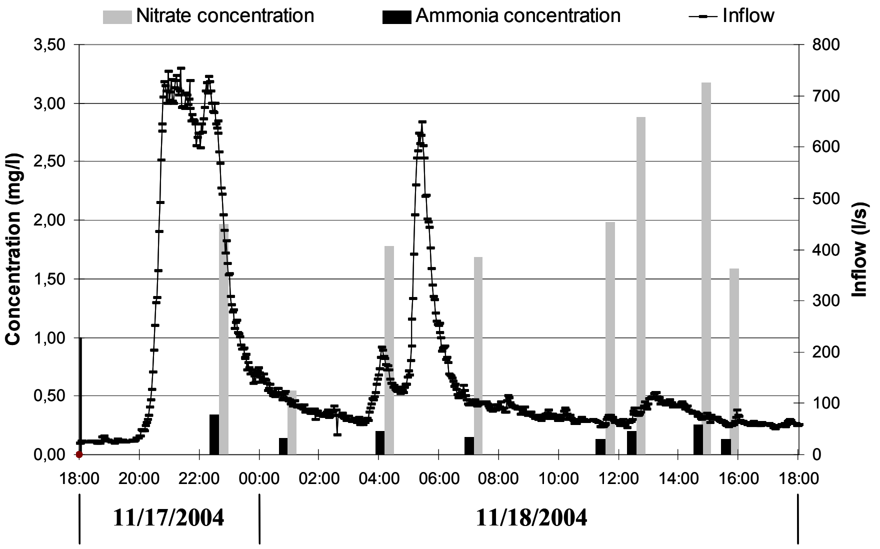


Figure 35: NO_3^- and NH_4^+ concentrations during the storm event 17th November 2004

total phosphorus concentrations whose evolution during the storm event is clearly correlated with suspended solid concentrations.

Figure 33 illustrating the results obtained for Co and Cr at the inlet can be generalised to the other metals, except Cd, whose concentration evolution is more unpredictable and doesn't show any specific trend. It can be explained by the characteristics of Cd, which is the most soluble of the metal studied. Therefore, there is less correlation between TSS and Cd than between TSS and other metals. Concerning Ni, its concentration is increasing during the last flow peak at the end of the storm, as is the concentration of NO_3^- and NH_4^+ (Figure 35) and the intensity of the flow peak is not intense enough to justify a so high concentration.

2.2.4.2. TSS, VSS, heavy metals and nutrients at the outlet

At the beginning of the rain event, the suspended solid concentrations are low (Figure 36). Indeed, at the outlet, the water flowing first comes from the water stored in the pond since the previous rain event. It is expected to be much cleaner than the water entering the pond at the same time and thus contain fewer particles and other pollutants. After that, both TSS and VSS concentrations increase; the suspended solids present at the inlet are flowing at the outlet. Then, Figure 36 shows a divergence in the TSS and VSS behaviour: TSS concentration decreases with the flow whereas VSS continues to increase. Considering the TSS fraction, this might be due to the settling properties of different particles' fractions. Indeed, once the flow decreases in the pond, the heaviest particles will settle rapidly, leading to a rapid decrease in the TSS concentration. However, the evolution of the VSS concentration is expected to follow the same trend because solids with size greater than 100µm have a higher organic content (Chebbo and Bachoc, 1992).

The trend highlighted for TSS concentration is followed by PO_4^{3-}, total-P, NH_3 and Cr whose concentrations are first increasing and then decreasing slightly at the end of the storm event (Figures 2, 4 and 5 in Appendix 5). From these observations, it is possible to conclude that Cr, PO_4^{3-}, total-P and NH_3 are probably associated with a heavy fraction of particles. On the contrary, the other metals' concentrations decrease only slightly at the end of the storm event

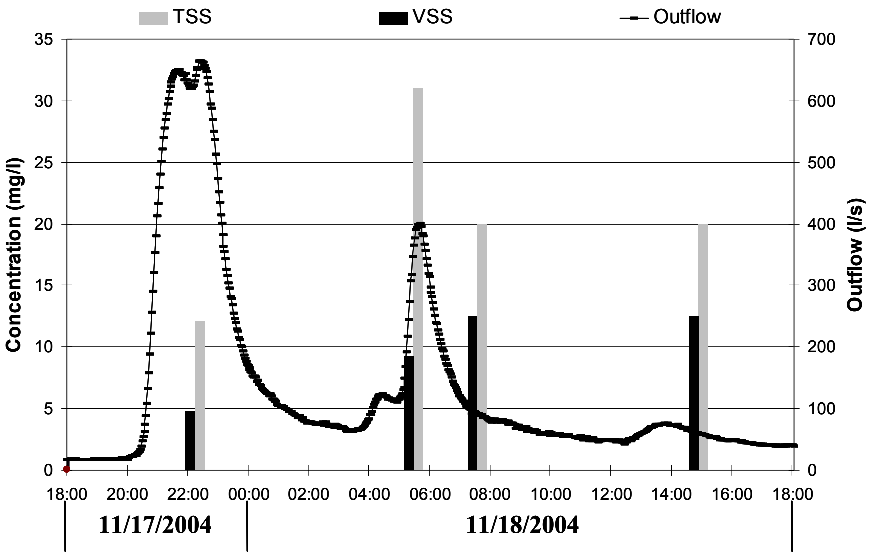


Figure 36: TSS and VSS concentrations during the storm event 17th November 2004

(Figures 1, 2 and 3 in Appendix 5). A possible explanation would be to consider that a portion of these metals is attached to the finest particles' fraction. This would explain the non-significant decrease in metal concentration during the storm event. Indeed, even during dry periods, the finest particles are not always able to settle down and thus appear at the outlet at the beginning of the next storm event.

The behaviour of NO_3^- at the outlet is also very interesting (Figure 5 in Appendix 5). At the beginning of the storm event the concentration is very high and then constantly decreases. This behaviour suggests the production of NO_3^- in the pond as discussed above in section 2.2.3. Indeed, as said earlier, the first water leaving the pond comes from the water stored in the pond between two storms and is supposed to be representative of the water quality in the pond. This is a proof that the vegetation and life around and in the pond are affecting the nitrogen cycle and thus the pond removal efficiency for nutrients.

2.2.5. Conclusions

Several conclusions can be drawn from the study of pollutants removal efficiencies and outlet concentrations.

First, high disparity between the removal efficiencies of the different pollutants is observed leading to the conclusion that the Järnbrott pond is not able to remove all pollutants to the same extent.

Secondly, despite the high outlet concentration of heavy metals and phosphorus compounds, the Järnbrott pond is efficient in removing them from the water phase. As shown in the detailed study of the event 6, this might be due to the high correlation between particles and heavy metals and between particles and phosphorus compounds. Suspended solids and PAHs equally show rather high removal efficiencies. However, the results discussed above show lower removal efficiencies than expected for oxygen demanding compounds and for of the nitrogen compounds (except NH_4^+). The detailed study of a single storm event even highlights the production of nitrogen compounds in the pond, by oxidation of NH_4^+ and other mechanisms, leading to high outlet concentrations.

From the comparison between the removal efficiency calculated in 2004 and the one measured 7 years ago, it is possible to confirm that the changes in pond's morphology (increasing surrounding vegetation, increase in the sediments' thickness) affected the pollutant removal efficiency in different ways. The removal of Cu, Zn and total-N is negatively affected whereas Cd, Pb and total-P are not affected by the changes.

Thirdly, for all pollutants without exception, removal efficiencies for single storm event vary greatly, especially for metals and some PAHs (benzo[k]fluoranthene, benz[a]anthracene and phenanthrene).

Then, what is important to consider to assess the risks to the receiving water is not only the long-term removal efficiency but also the outlet concentrations and the partitioning of the pollutants (it is mainly relevant for heavy metals).

Finally, some improvement could be done to strengthen this work. The microorganisms' removal has to be deeper studied in order to establish if stormwater ponds are able to remove bacteria and to which extent. The long-term removal efficiency has been determined for only a one-month period. A longer monitoring period would highlight the seasonal variations and thus lead to more reliable results. A study of pollutant partitioning would give a good tool to assess the threat of the outlet concentrations on the receiving waters.

3. Release of heavy metals and nutrients from the sediments in the water column under different conditions

As written in the goals of this master thesis work, the aim of the study is to understand the mechanisms that can affect the release of nutrients and heavy metals from pond sediments to the water column. For this, different water conditions were applied to experimental beakers in which the water-sediment interface was reproduced. The effect of salinity and turbulences were studied for the nutrients whereas oxygen depletion and turbulences were applied for the study of the release of heavy metal from sediments. At the same time, for the nutrient part, conclusions from the effect of water microorganisms were drawn by comparing the release of nutrients in water pond and in nanopure water.

These two experiments were conducted separately and differently. The first release simulation has been first set for the study of nutrients and metals release from sediments. Unfortunately, because of contamination from unknown sources, the results for heavy metals, which were present in low quantities (except iron and aluminium), and thus vulnerable to contamination, were not possible to evaluate. However, mistakes made, helped to set the second experiment in which more care were taken concerning possible contamination of the water during sampling, filtration and analysis.

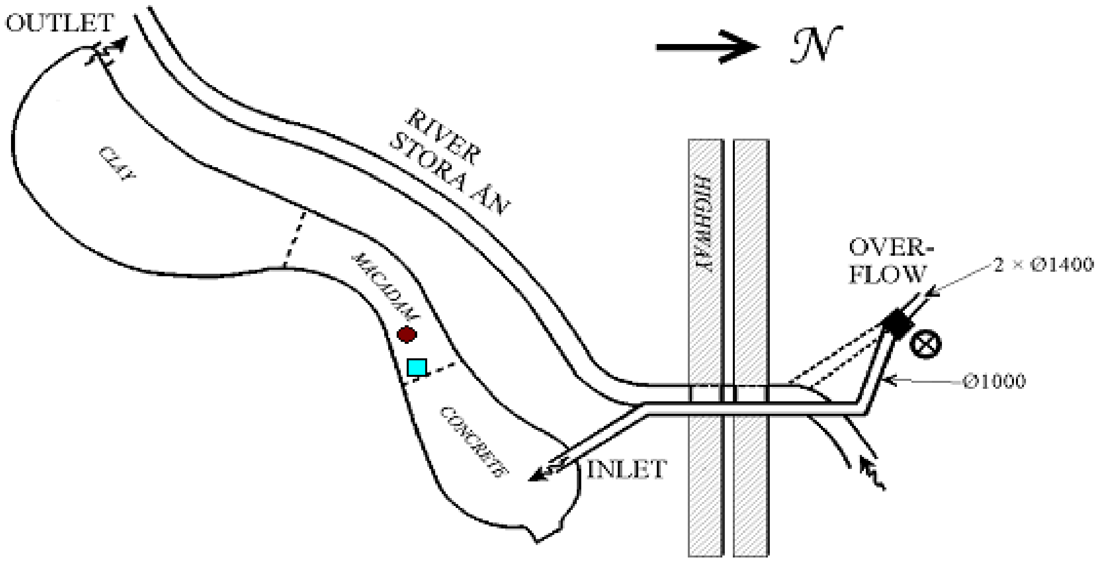
3.1. Release of nutrients, aluminium and iron from the sediments under different conditions

3.1.1. Experimental part

3.1.1.1. Sample location

Sediments were sampled in the Järnbrott pond, in the shallow part (Figure 37) because it is expected to have rather fine particles with higher amount of bound pollutants than at the inlet (German, 2003). On the other hand, the sediment thickness is higher in this location compared to the outlet where the sediments are even finer. This sampling was meant to be representative of the pond. In addition, only the first 5 centimeters of the sediments were sampled in order to have a situation closer to the real situation in the experimental beakers. Indeed, only the first centimeters are interacting with the overlying water column. Water sample for the sediment experiment was taken closer to the inlet compared to sediment sample because at that time the pond was emptied for maintenance and no water was present in the shallow part.

Macro organisms identified as *tubifex* worm (Figure 38) were present in the sediment sample and daphnia (Figure 39) present in the water sample. Their identification was important because the nutrients cycle might be highly affected by the presence of living organisms. The sediments' worms identified as *tubifex* (class *oligochaeta*) are know to be inefficient in reducing pollution in sediments (Wetzel, 2001). However, due to micro water movements associated with *tubifex*'s respiratory behaviour the diffusion rate of NH_4^+ from the sediment to the overlying water layer can be increased several fold (Wetzel, 2001). The *Daphnia* population (order *Cladocerans*) sampled with pond water increased during the experiment, suggesting the presence, in the water sample, of microalgae on which they feed (Clare, 2002). As algae use nitrogen and phosphorus during their life cycle, the presence of these organisms in the experiment beakers will influence the nutrients concentration.



● Sediment sampling site 🟦 Water sampling site

Figure 37: Location of sediments and water sampling

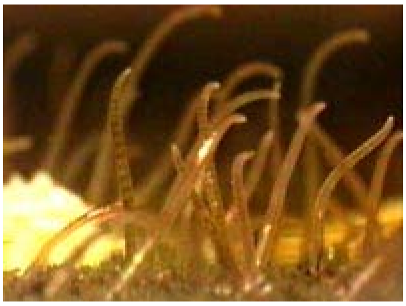


Figure 38: Organisms present in the sediment sample (*Tubifex*)

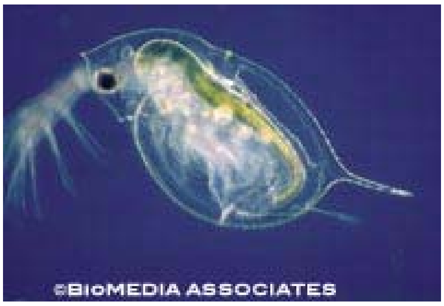
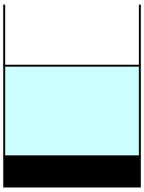
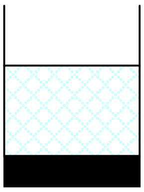
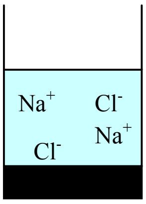
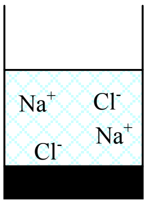
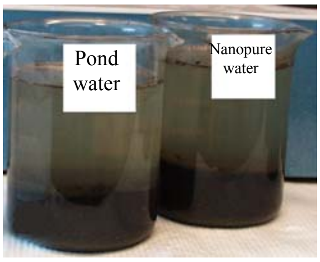
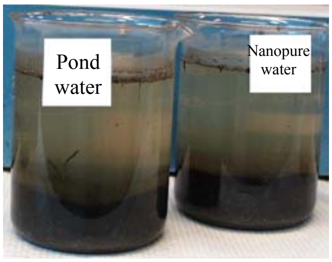
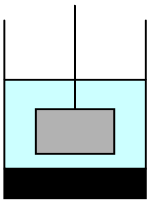
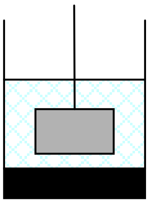
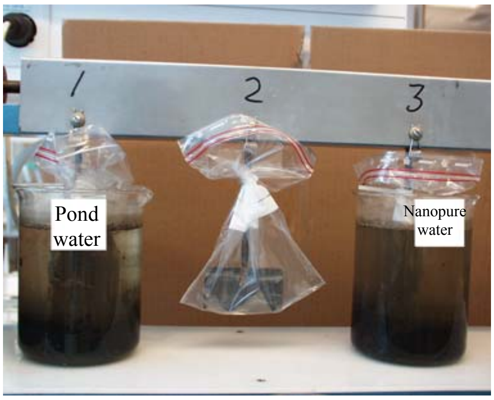


Figure 39: Organisms present in the water sample (Daphnia)

3.1.1.2. Experimental Setup

Table 29: Experimental beakers

Reference beakers		**Beakers with higher conductivity**	
Pond water	Nanopure water	Pond water	Nanopure water
			
			
Beakers under turbulences			
Pond water	Nanopure water		
			
			

Six beakers have been prepared for this experimental work (Table 29). An equal amount of sediments and water has been introduced in each beaker in order to be able to compare the results from beaker to beaker.

The reference beakers contain only sediments and water (pond water for the first reference and nanopure water for the second reference). A conductivity of 11mS/cm has been achieved by adding NaCl to the water (pond water and nanopure water) before pouring this water on the sediments. This value has been chosen in accordance with the conductivity value measured in the Järnbrott pond after a snowmelt event, on the 5th February 1998 (Pettersson, 1999) which washed off salt from the road surface into the pond water. The turbulent conditions in the two last beakers have been achieved using metal agitators wrapped in plastic bags, in order to avoid release of metals from the agitators.

3.1.1.3. Analyses

Aluminium and iron have been analyzed by ICP-MS (see section 2.1.3.2.) and samples prepared according the method described in section 2.1.3.2. As these two metals are present in quite high quantities they have not been affected by air particles contamination that may be the case for the other metals in lower concentrations. The dissolved as well as the total metal concentration have been measured.
The nutrients analyses were performed by spectrometry using Hach equipment DR 2010 model. In order to have more accurate results, double analyses have been made and the mean values have been used.

The Hach method used to measure NO_3^- concentration is based on the reduction of NO_3^- to NO_2^- ion, meaning that both NO_3^- and NO_2^- ions are measured in the same time. However, the amount of NO_2^- is usually very low compared to NO_3^- concentration in water unless stable anoxic conditions occur which was not the case because the water in the beakers were constantly in contact with air. In the following sections, the concentration of NO_3^-+NO_2^- measured by the Hach method 8171 will be referred as NO_3^- concentration In the total-N method, a strong alkaline persulfate digestion converts all forms of nitrogen to NO_3^-. Thus, organic as well as inorganic nitrogen compounds are analyzed in the same time.

As seen in section 1.3.2.2., Figure 4, only one form of phosphorus compound is soluble in water and reactive: PO_4^{3-}. It is the only compound measured by the Hach method 8048. In the case of total-P the same method is used, but an additional digestion procedure is used to convert all form of phosphorus into PO_4^{3-}.
Despite the relative precision of the Hach method, indicated in Table 30, the standard deviation values obtained for replicate analyses were often far above ranging from 0 to 2,7mg/l for total-N concentration for instance.

These parameters were analyzed for pond water prior to the beaker experiment. Water samples have been taken in each beaker three days and seven days after the beginning of the experiment and analyzed to show the evolution of the concentrations over time. Each of these days, water has been sampled with a glass pipette and introduced in a clean glass beaker. After that, the volume required for each analysis (NO_3^-, total-N, PO_4^{3-}, total-P, Fe and Al) has been sampled from this beaker with a micropipette.

Table 30: Methods for analysis of nutrients

Compound analysed	Analytical method	Detection limit	Precision
Aluminium and iron	ICP-MS		
NO_2^-+NO_3^-	Hach 8171		+/- 0,1mg/l
Total-N	Hach 10071		+/- 0,5mg/l
PO_4^{3-}	Hach 8048	0,01 mg/L	+/- 0,02mg/l
Total-P	Hach 8190		+/- 0,09mg/l

3.1.2. Results and discussion

Both nitrogen and phosphorus concentrations show very clear trends, confirming the release of these compounds from the sediments to the overlying water. At the same time, the results show the uptake of nutrients by organisms and adsorption to particles followed by sedimentation process.

3.1.2.1. Nitrogen compounds

Three days after the beginning of the experiment, NO_3^- analyses gave unreliable results. Therefore, in order to draw reliable conclusions, this compound will not be considered in the first part of the discussion.

The nanopure water introduced in the experimental beakers is of course free of nutrients and microorganisms and after only three days, the amount of Total-N is no longer zero. This result shows that nitrogen compounds can be released from the sediments under any conditions, because this rise in concentration has been observed for turbulent conditions, high conductivity conditions as well as for the reference beaker. In addition, in these "nanopure" beakers, the total-N concentration was rising from day three to day seven (Figure 40) whereas NO_3^- concentration was under the detection limit of the method in day seven. It means that nitrogen compounds are released from the sediments in forms other than the easily bioavailable form (NO_3^-). If anoxic conditions occurred close to the sediments, NH_4^+, NO_2^-, organic containing nitrogen compounds can be released (section 1.3.2.2. Figure 3) after a few days of experiment. In addition, the effect of the sediments' worms mentioned above enhances the release of NH_4^+ by their respiration (Wetzel, 2001).

The same phenomenon is observed in the beakers containing pond water: a decrease of NO_3^- concentration (compared to the collected pond water concentration) has been measured correlated with high Total-N concentration (Figure 41). However, in these cases, the effects of microorganisms have to be considered. Indeed, the decrease in NO_3^- can be enhanced by uptake by microorganisms. At the same time, the digestion of microalgal present in water during the analysis procedure accounts for total-N concentration.

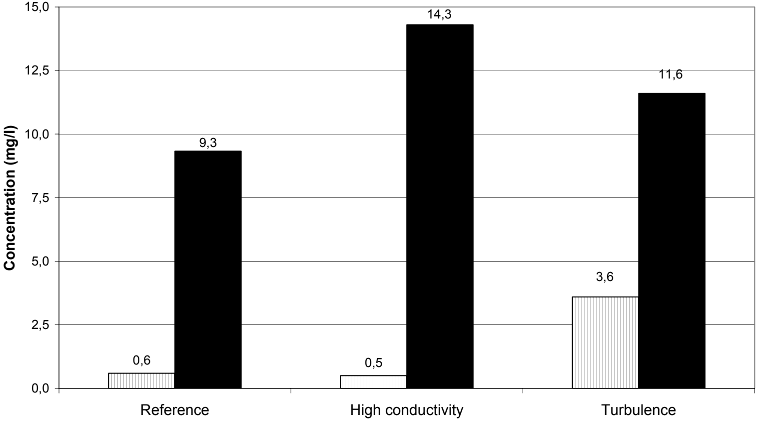


Figure 40: Variation of total-N concentration in beakers containing nanopure water

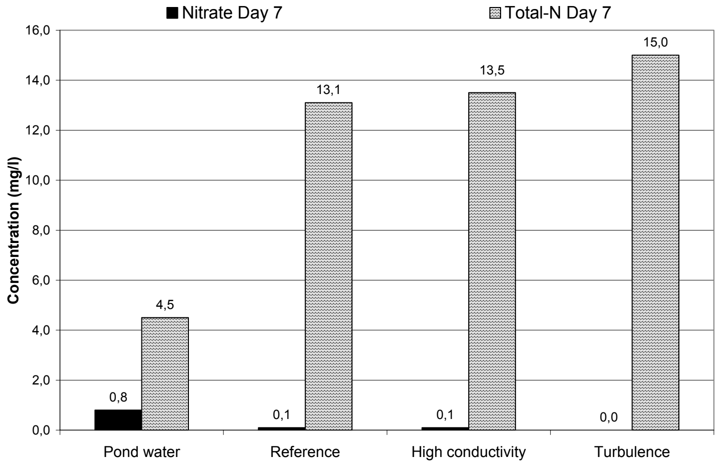


Figure 41: NO_3^- and total-N concentrations, day 7 in beakers containing pond water [14]

Finally, on a long term, the nitrogen compounds do not seem to be affected by the different conditions (high conductivity and turbulences). Indeed, the difference between concentrations in the beakers is not significant enough to draw conclusions on the effect of conductivity or turbulences on the release of nitrogen compounds from the sediments. But important to notice is the release of nitrogen compounds from sediments under all conditions simulated during the experiment.

3.1.2.2. Phosphorus compounds

The detection of both PO_4^{3-} and total phosphorus three days after the beginning of the experiment, in beakers containing nanopure water, shows the release of phosphorus compounds from the sediments under high conductivity, turbulences, as well as for the reference beaker (Figure 42).

The lower concentration of PO_4^{3-} in beakers containing pond water compared to beakers with nanopure water (reference and high conductivity) suggests the uptake of phosphorus by microalgae (Figure 42). The behavior of PO_4^{3-} under turbulent conditions will be explained later on.

The uptake by microorganisms is followed by sedimentation of algae under quiet conditions, leading to a lower total-P concentration as well, except for the beakers under turbulent conditions. This hypothesis of uptake/sedimentation is confirmed by the results that show a lower total-P concentration for beakers containing pond water (and thus organisms) compared to beakers with nanopure water. However, the beakers under turbulent conditions show the reverse trend (Figure 42).

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[14] Since Total-N measurement includes NO_3^- and Total-P includes PO_4^{3-}, conclusions were drawn only when the difference in total concentration exceeds the variation in NO_3^-, respectively PO_4^{3-}.

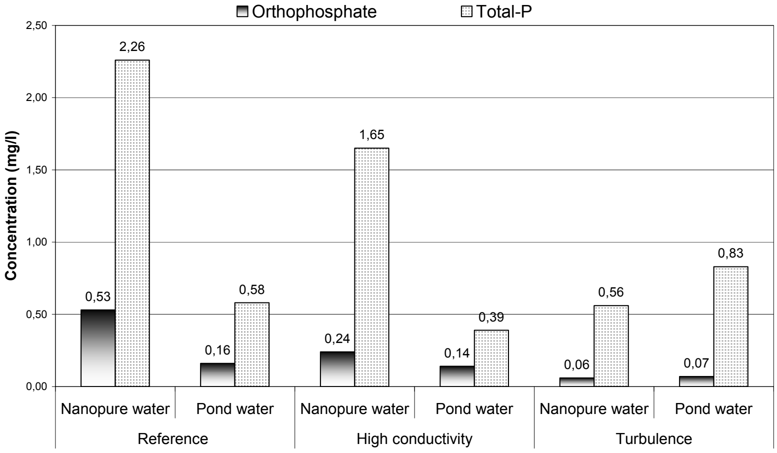


Figure 42: PO_4^{3-} and total-P concentrations, day 3

The study of the evolution of PO_4^{3-} and total-P concentrations for the beakers with nanopure water that are not subjected to high biological activity shows an interesting phenomenon. The decrease in PO_4^{3-} from day three to day seven correlated to the decrease in total-P during the same period of time shows the possibility of adsorption of phosphorus on clay particles (see section 1.3.2.2; Equations 4, 5 and 6) followed by sedimentation. This is confirmed by the results from the nanopure beaker under turbulent condition that show the reverse trend suggesting a release of particles from the sediments followed by desorption of PO_4^{3-} (Figure 43).

The study of iron and aluminium present in clay particles gives another proof: the iron concentration is decreased from day three to day seven for the reference beaker as well as for the beaker under high conductivity whereas iron and aluminium concentrations in the beaker under turbulences show a net increase in concentration (Figure 44).

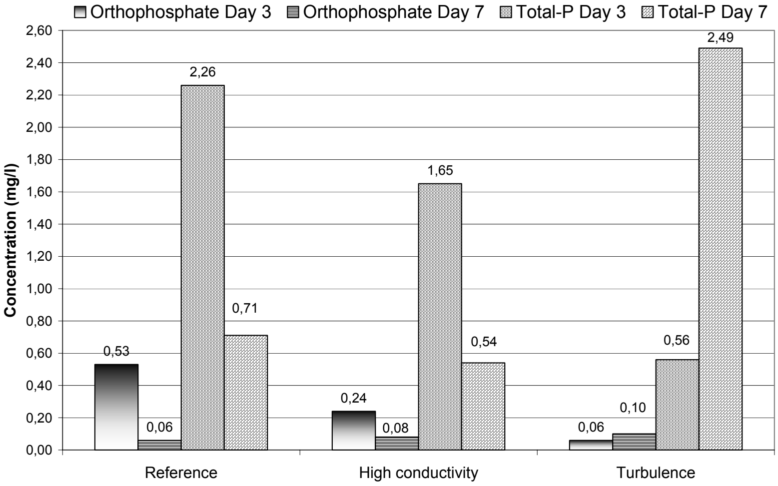


Figure 43: Release of PO_4^{3-} and total-P concentrations in beakers containing nanopure water

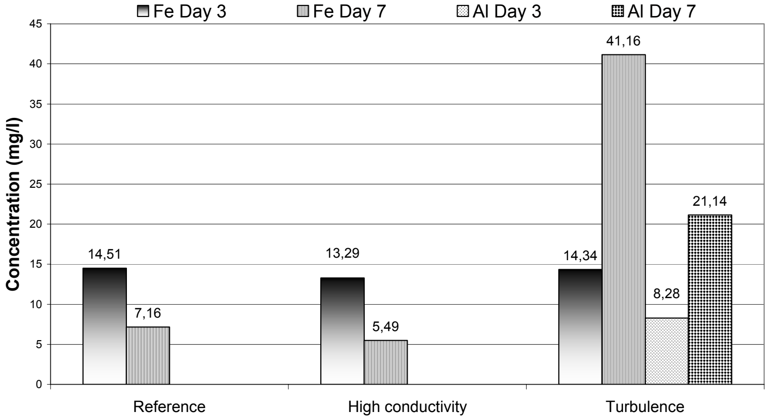


Figure 44: Release of Fe and Al concentrations in the beakers containing nanopure water

3.1.2.3. Conclusions

This short experiment showed interesting results concerning the release mechanisms of nutrients from the sediments to the water column. Indeed, it has been shown that PO_4^{3-} and other forms of phosphorus accounting in the total-P concentration can be released from the sediments. Nitrogen forms, other than NO_3^-, can also migrate from the sediments to the overlying water. On the contrary, uptake of NO_3^- and PO_4^{3-} by organisms can lead to a decrease of dissolved nutrients in the water phase. Finally, it has been proved in this work that phosphorus compounds are highly adsorbed to particles, and have a high affinity with clay.

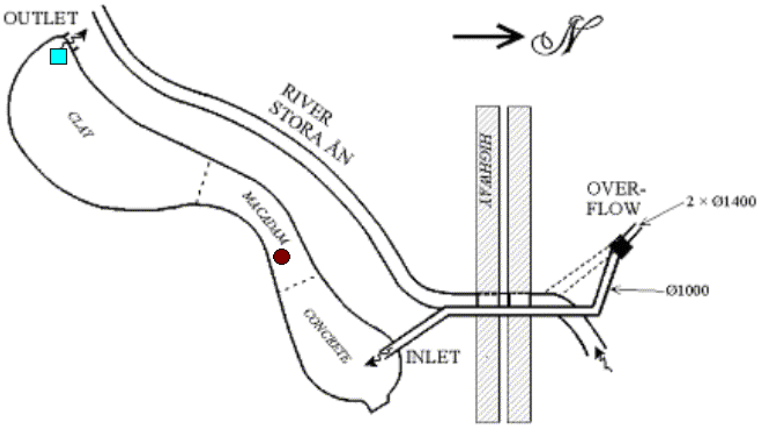
Despite the interesting conclusions drawn from this experiment, some improvements could be done in order to deepen the knowledge and give more reliable results. First, the analysis method has to be changed to reduce the incertitude on the results. Secondly, analyses of NO_2^- and NH_4^+ would give information on nitrogen partitioning. In this case, nitrogen forms released from the sediments could be identified more accurately. Then, this sediment experiment could as well be prolonged for at least one month to have a clearer trend of the concentrations' evolution. Finally, the study of this release under anoxic conditions would be of great interest.

3.2. Release of chromium, cadmium, lead, zinc, nickel and copper from the sediments under different conditions

3.2.1. Experimental part

3.2.1.1. Sample location

Sediments have been sampled in the Järnbrott pond, at the same location as for the first sediment sampling (Figure 45). However, less macro-organisms were this time present in the sediments probably due to a longer maintenance period. The pond has been emptied, letting the sediment layer exposed to the air without overlying water layer. Macro-organisms could have then migrated or died because of unfavorable living conditions. As for the first sediment experiment, only the first centimeters of the sediments have been sampled.



● Sediment sampling site ■ Water sampling site

Figure 45: Location of sediment and water sampling

In order to avoid a too high organisms' population in the pond water, the sample has been taken once the pond was filled up again with rainwater runoff. Then, for practical reasons, water sample for the sediment experiment has been taken at the outlet (Figure 45).

3.2.1.2. Experimental Set-up

Three different beakers were prepared for this experimental work (Table 31). An equal amount of sediments and water has been introduced in each beaker in order to be able to compare the results from beaker to beaker.

Table 31: Set-up of the sediment experiment

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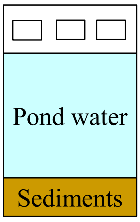
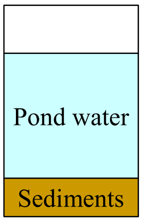
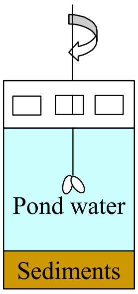
<tr><th colspan="2">Reference beaker</th><th colspan="2">Beaker under anoxic conditions</th></tr>
<tr><td> </td><td></td><td> </td><td></td></tr>
<tr><th colspan="2">Beaker under turbulent conditions</th><th></th><th></th></tr>
<tr><td> </td><td></td><td></td><td></td></tr>
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The reference beaker contains only sediments and pond water. Anoxic conditions were achieved by nitrogen bubbling in the beaker during 10 minutes in order to obtain a dissolved oxygen concentration lower than 1mg/l in the closed beaker during the experiment. The turbulent conditions in the last beaker have been achieved using a plastic agitator rotating at a speed of 1 round/s.

3.2.1.3. Analyses

Both total and dissolved fractions of the metals have been analyzed by an ICP-MS instrument (see section 2.1.3.2.) whose detection limit has been determined for each metal and presented in Table 32.

Sampling in the beakers and preparation procedure for the ICP-MS analysis
In order to minimize biased results resulting from the decreasing volume of the water phase in the bucket over time, the minimum volume (~45ml) required for total and dissolved metal analysis has been sampled on each sampling day with a plastic syringe. From the syringe, the sample was transferred in a plastic container and the required volume taken with a micropipette and introduced into an ICP-MS tube.
The procedure for both dissolved and total metal analysis is the same used for rainwater samples (see section 2.1.3.2.).

Due to its very low concentration, Cd was difficult to measure. The results obtained, especially for the total part, whose procedure uses a high dilution factor was sometimes below the detection limit. It was impossible to draw reliable conclusion on the behavior of cadmium in the different beakers.

Digestion and sample preparation procedure
At the beginning of the experiment, the metal content in the sediments phase has been measured. Compared to the procedure used for the analysis of metals present in the water phase, an additional digestion step is needed for the sediment analysis.
First the sediment samples had to be homogenized, dried at 105°C during one hour and then burned at 550°C during one hour more. Thereafter, 0,5g of sediment has been introduced in a digestion vessel (Figure 46) and 10ml of HNO_3 for trace analysis was added. The sediments were digested in a Microwave Accelerated Reaction System (MARS 5) (Figure 47): the temperature was increased until 175°C and the pressure rise until 300 psi. These conditions were maintained during 3 minutes. After that, the digestion vessels were cooled down during 30 minutes. The overlying acid phase was sampled, introduced into an ICP-MS tube and diluted by a factor 100. Before analysis, Rh internal standard was added in order to have a concentration of 1 ppb in the sample.

A standard sediment material was analyzed in parallel in order to ensure the digestion procedure has been properly run.

Table 32: Detection limits for the ICP-MS method

Metal analysed	Detection limit (ppb)
Cd	0,002
Cr	0,003
Cu	0,002
Ni	0,001
Pb	0,006
Zn	0,004

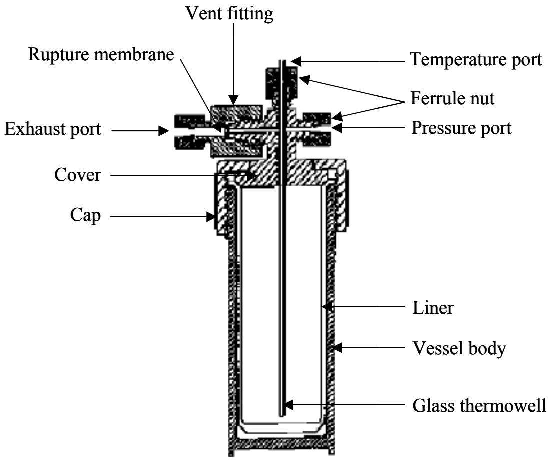

Figure 46: Digestion vessel

Figure 47: Microwave Accelerated Reaction System 5

3.2.2. Results and discussion

3.2.2.1. Initial conditions

The six major metals present in urban runoff (Cd, Cr, Cu, Ni, Pb, Zn) have been analysed in pond water prior to the experiment set-up whereas only four of them (Cd, Cu, Pb, Zn) could be analysed to determine the sediments' content because of contamination of the HNO_3 used for the digestion procedure.

Sediments' analysis

The sediment sample has been carefully mixed and six subsamples have been taken for analysis in order to get a representative value of the metal content of sediments. The incertitude given on each value (Table 33) is the standard deviation calculated from the six subsamples concentration. For the values determined in 1999, several samples have been taken in different locations in the Järnbrott pond, during 5 sampling periods. A total of 73 subsamples were analysed to obtain the values given in Table 33 (German, 2003).

The concentration determined in 2004 are comparable to the results obtained in 1999. A decrease in Cu and Pb content and an increase in Zn content are observed.

Table 33: Metal content in the Järnbrott stormwater sediments in 1997 and 2004

	Cd (µg/g of sed.)	**Cu** (µg/g of sed.)	**Pb** (µg/g of sed.)	**Zn** (µg/g of sed.)
Metal concentration measured in 2004	1,70 +/- 0,14	326 +/- 10	114 +/- 3	1028 +/- 23
Metal concentration measured in 1999[15]	1,5 +/- 0,4	424 +/- 29	152 +/- 9	672 +/- 45

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[15] Source: German, 2003.

Table 34: Metal content in the pond water prior to the sediment experiment

	Cd (µg/l)	**Cr** (µg/l)	**Cu** (µg/l)	**Ni** (µg/l)	**Pb** (µg/l)	**Zn** (µg/l)
Concentration in pond water	0,17 +/- 0,05	1,39 +/- 0,57	16,83 +/- 0,28	8,20 +/-0,56	0,74 +/- 0,07	41,47 +/- 3,0

Pond water analysis

The metal concentrations presented in Table 34 are mean values on three sample's replicates. The incertitude interval given is the standard deviation calculated for the three concentrations measured.

3.2.2.2. Study of the release of heavy metals from sediments

The experiment lasted for one month and water samples have been taken 1, 3, 6, 14 and 29 days after the beginning of the experiment in order to study the evolution of the concentrations over time.

- Evolution of total metal concentrations

Total metal concentrations measured in reference beakers, as well as concentrations from turbulent and anoxic conditions show the similar decreasing trend over time. The Figures 48 and 49 are illustrations of this trend; it shows the results obtained for the total metal concentrations in the reference beaker and the beaker under turbulent conditions respectively.

This decrease in total metal concentration, obtained for the reference beaker, the beakers under anoxic and turbulent conditions might be explained by settling conditions occurring in all the beakers. This settling leads to a decrease in suspended particles and attached pollutants in the water phase and thus a decrease in metal concentration.

It can be noticed that raw pond water concentration, measured before pouring the water on the sediments is lower than the water concentration measured after one day in contact with the

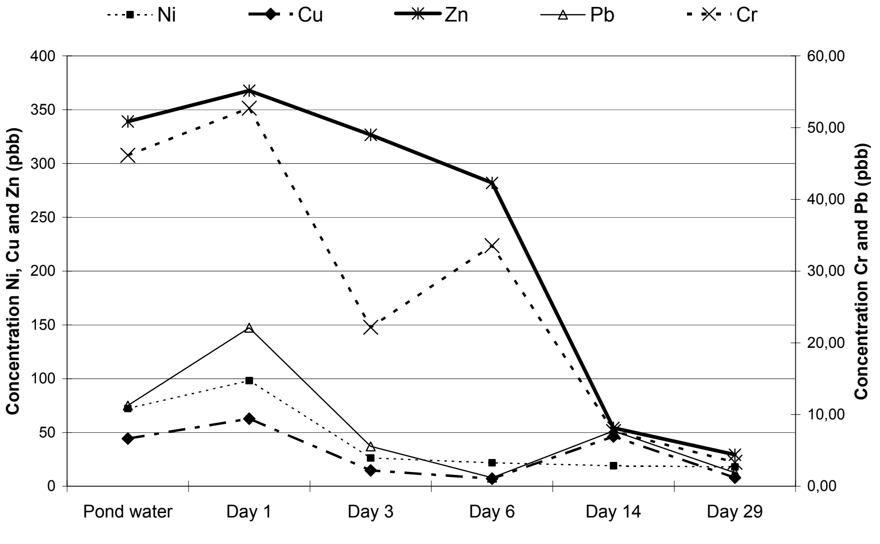

Figure 48: Release of different metals from sediments in the reference beaker

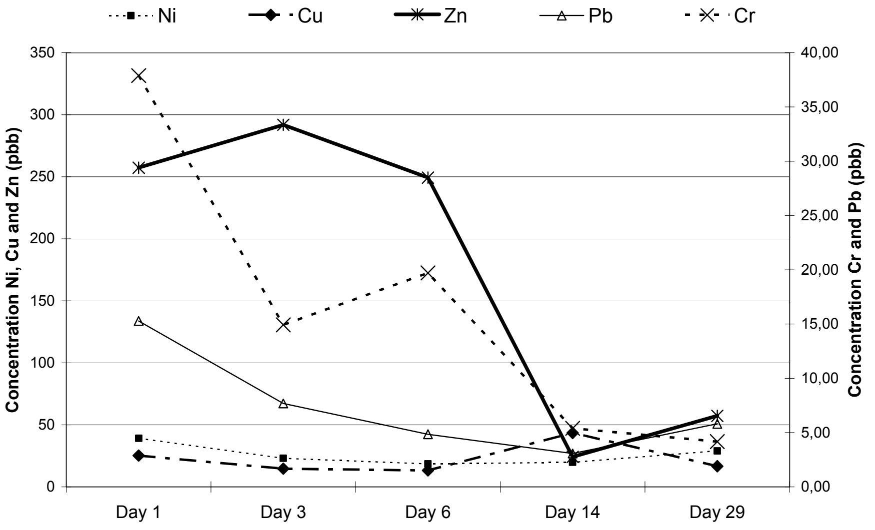

Figure 49: Release of heavy metals from sediments under turbulent conditions

sediments for all metals. This may be explained by resuspension of fine particles and attached metals during the set-up of the experiment. Indeed, when pond water has been poured on the sediments it created turbulences promoting resuspension of sediments and their bound metals.
Concerning the beaker under turbulent conditions, the release of different metals does not match with the expected behaviour; a resuspension of particulate matter and bounded metals and an important increase in total metal concentrations was expected under turbulent conditions. However, the results show a decrease in total metal concentration for all metals between day 1 and day 29, even if slight increases are shown by the graph between day 6 and day 14 for example (Figure 49).

Observation from the experiment clearly showed a clearing of the water phase over time in the beaker under turbulent conditions. This might be due to the low rotation velocity creating conditions that promote flocculation and thus help the sedimentation process.
From this, we can conclude that anoxic or turbulent conditions do not lead to great release of total metals from the sediments to the overlying water, at least not under the conditions of this experimental study.

- Evolution of dissolved metal concentrations

Concerning the dissolved part, the results are more mitigated: a decrease is observed for Pb, Zn, and Cu under all conditions. The Figure 50 shows the trend obtained for the reference beaker; the other beakers are not presented here but have the same concentration trends for Pb, Zn and Cu.

The decrease can be explained by the migration of free metals from the water phase to the particulate phase, followed by adsorption and sedimentation.
It has to be noted the increasing concentration for Pb, from the raw pond water to the first day of the experiment. As for the total metal, it can be explained as well by a resuspension of fine particles inferior to 0,45µm during the set-up of the experiment. In fact the particles or colloids inferior to 0,45µm are counted in the dissolved fraction, which is the result of the filtration on cellulose acetate filter of 0,45µm of porosity. It is also possible to explain this by a resuspension of bigger particles on which Pb can be adsorbed followed by migration process driving Pb from the particles to the water phase.

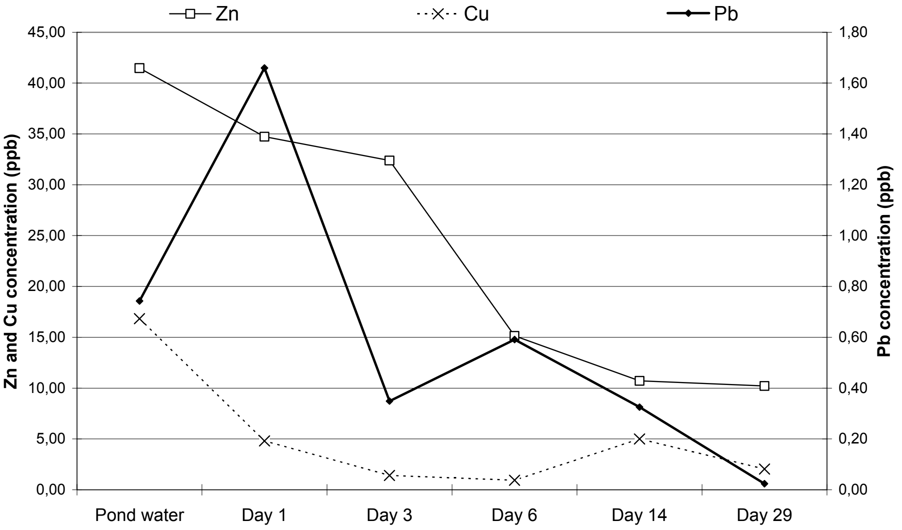

Figure 50: Variations of dissolved Zn, Cu and Pb concentrations in the reference beaker

On the contrary, an increase in dissolved Cr and Ni concentrations over time is observed for reference, anoxic and turbulent beakers (Figure 51).

This phenomenon will be explained further on by analyzing the partitioning of these metals between particulate and water phases.

- Effects of anoxic and turbulent conditions on metals' concentration

The evolution of metal concentration for the different conditions leads to interesting conclusions. For total metal concentrations (except cadmium), the highest concentrations shift from the reference beaker, in day 1 to anoxic conditions in day 6 and 14 and then to the turbulent conditions day 29 (Figures 52 to 55).

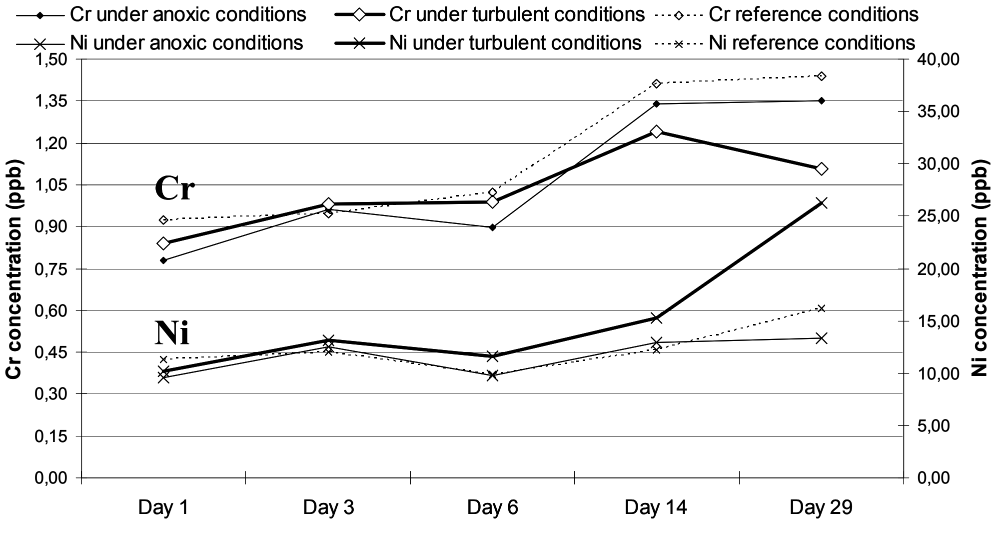

Figure 51: Variations of dissolved Cr and Ni concentrations for reference, anoxic and turbulent beakers

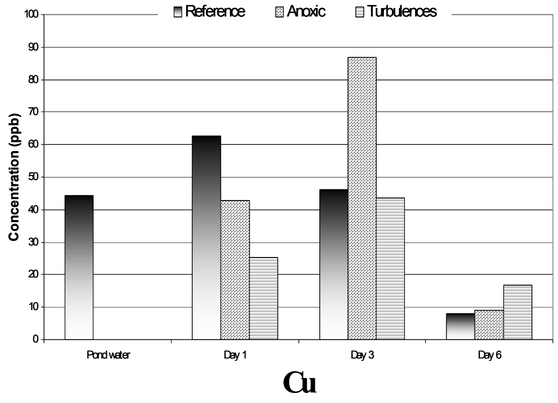

Figure 52: Total Cu concentration

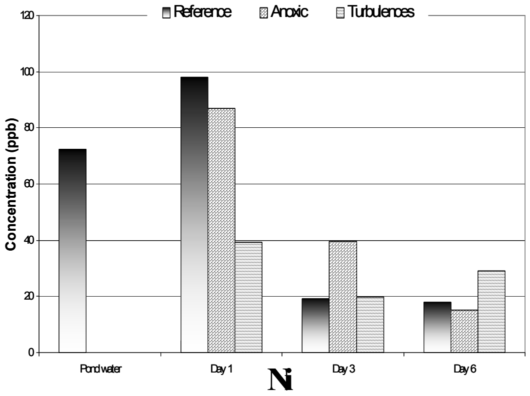

Figure 53: Total Ni concentration

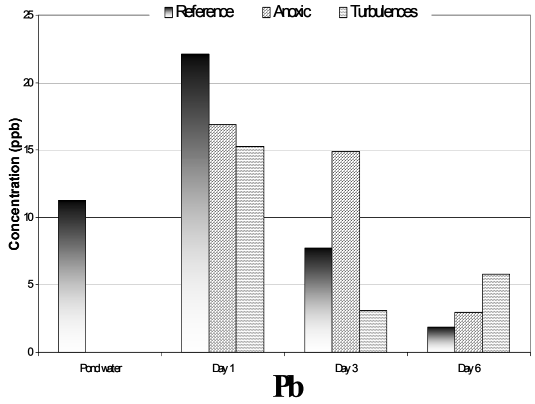

Figure 54: Total Pb concentration

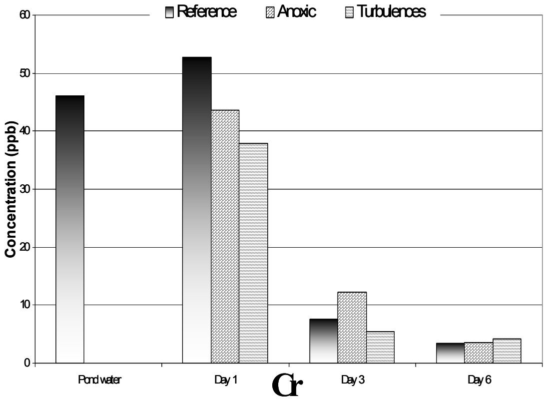

Figure 55: Total Cr concentration

This evolution showing the highest total concentration for different conditions depending on the experiment time, leads to the conclusion that, in addition to settling mechanisms, other processes occur under anoxic and turbulent conditions leading to a lower settling velocity and thus a lower decrease in total metal concentrations, compared to the reference beaker.

Concerning the beaker under turbulent conditions, it has been shown above that the first mechanism occurring is the flocculation of particles followed by sedimentation, accounting for the net decrease in total metal concentrations. However, once the concentration is significantly decreased by this process (from day 1 to day 14 for instance), the efficiency of the flocculation seems to be decreased, leading to a higher concentration under turbulent conditions than others (Figures 51, 52, 53 and 54). This decrease in efficiency can be due to resuspension of very fine particles competing with settling. This is especially noticeable for lead and nickel, metals for which the total concentration increases from day 14 to day 29. These two metals are then probably highly adsorbed on very fine particles and thus easily resuspended when the fine fraction of sediments reaches the water column.

- Study of metal partitionning

The partitioning of heavy metals between dissolved phase (including free metals and colloids inferior to 0,45µm) and particulate phase (including colloids superior to 0,45 µm and metals adsorbed on bigger particles) gives interesting results.

The percentage of metal in dissolved form shows a net increase over time under every condition (Figures 56 and 57 are given as an example) (except for Pb). Two processes can explain this phenomenon:

- The sedimentation mechanism that decreases the amount of suspended solids and their attached metals and thus increases the dissolved proportion of metals which are not or less subjected to sedimentation,
- The diffusion of metals from the particulate to the dissolved phase driven by the gradient of concentration between the high metal concentration on the particles and the lower concentration in the water phase.

To draw conclusions on which of these processes prevail, the partitioning results have to be correlated with the evolution of dissolved metal concentration. Indeed, if the first mechanism prevails, the dissolved metal concentration won't be increased over time, only the proportion is changing. If the second mechanisms prevail, an increase in the dissolved metal concentration over time is expected.

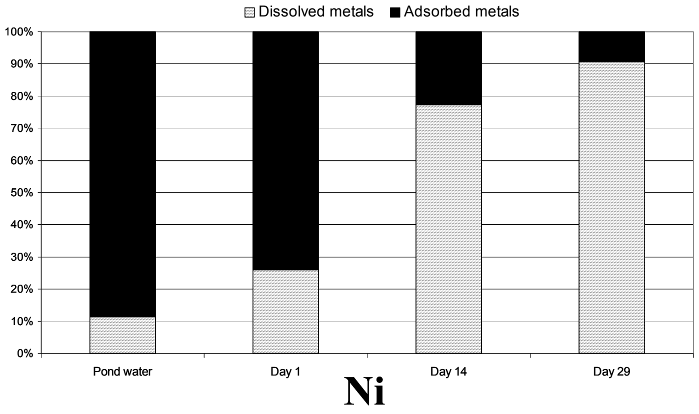

Figure 56: Partition for Ni under turbulent conditions

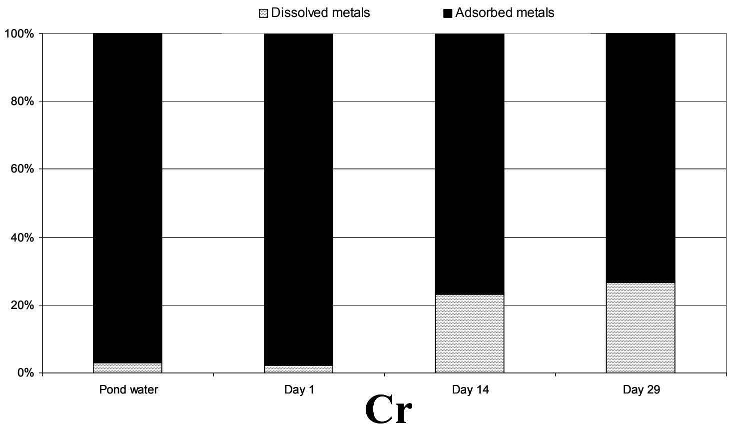

Figure 57: Partition for Cr under anoxic conditions

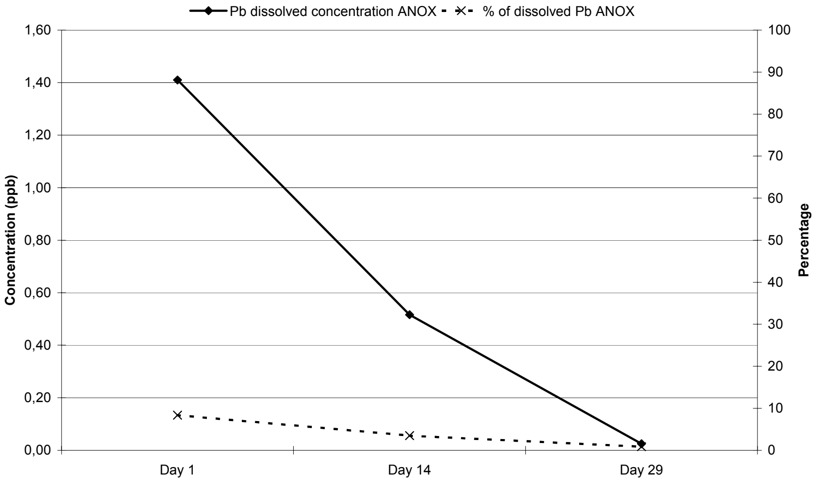

Figure 58: Release of Pb dissolved concentration and partition under anoxic conditions

As seen above, dissolved Cr and Ni concentrations increase over time (Figure 51). In addition, for these two metals, the part of dissolved metal is highly increasing from day 1 to day 29. Indeed Figures 56 and 57 show as an example the evolution Ni under turbulent conditions and the evolution of Cr under anoxic conditions. We can then conclude that the diffusion from the particulate to the water phase is an important phenomenon leading to release under anoxic and turbulent conditions compared to the reference beaker.

A smaller increase in the dissolved percentage of Cu (from 7,5% to 30,4%) and Zn (from 11% to 37%) has been recorded. In addition, the decrease of dissolved concentration over time, as shown in Figure 48. The increase of the dissolved fraction may be due to the decrease of the particles' concentration and attached metals by sedimentation. This mechanism is faster that the decrease of the dissolved fraction by adsorption on particles, leading to this small increase in percentage of dissolved metal.

The very small fraction of Pb in dissolved and colloids inferior to 0,45µm (inferior to 2% for reference and anoxic and inferior to 5% for turbulent conditions on day 29) correlated with the drastic decrease in dissolved concentration over time show that Pb has a very high affinity with particles and is highly insoluble and unlikely to be released in the water column even under anoxic or turbulent conditions. The Figure 58 highlights this mechanism for anoxic conditions which occurs in similarly in the other beakers.

3.2.2.3. Conclusions

This experiment confirms the high correlation between metals and particles and their efficient removal by sedimentation under any conditions. An interesting conclusion from the experiment is the possibility of metal removal by flocculation under low turbulences. However, it can also lead to the resuspension of the finest particles fraction and attached metals, especially Pb and Ni. Pb seems to be very insoluble under every type of conditions.
The dissolved fraction, which is of concern when it comes to health issues, shows different behaviour according the metal. From this study it seems that Ni and Cr are more soluble than Cu, Zn and Pb and thus easily released from the sediments under bio available form, especially when anoxic and turbulent conditions are achieved.

Finally, repeating this experiment with nanopure water could give additional indications. A study on the heavy metal partition should be done in order to prove that the metal release is linked to particle size.

Concerning sample preparation, a lower dilution for total metal determination would allow the study of Cd, which is a very toxic compound.

4. Conclusions

From the results obtained in this thesis, despite the small specific pond area ($40m^2$/ha impervious area), the Järnbrott pond removes most of the pollutants. Suspended solids, phosphorus, oxygen demanding substances, PAH and most of the heavy metals (except Cu and Ni) are removed to a large extent. Most of these pollutants have been studied before (in 1997) in this pond and show similar removal efficiencies, except for Cu, Zn and Total-N which have been negatively affected by the changes in the pond morphology.

In 2004, a part dealing with the study of Co, Cr, Ni, PO_4^{3-}, the different forms of nitrogen and PAH has been added, and then extended the study compared to 1997.
From this additional study, it is possible to conclude that PAHs, which are persistent organic pollutants and considered as priority pollutants all over the world, are decreased to a large extent by the removal mechanisms in the Järnbrott pond. On the contrary, nitrogen compounds have been produced in the pond during the measurement period, leading to negative removal efficiencies. When compared to the removal efficiency calculated in 1997, which shows much better removal efficiency even for the autumn time, it can be concluded that the growing vegetation in and around the pond strongly affects the removal efficiency for these compounds. Concerning Co and Cr, the long-term removal efficiency calculated is good whereas the values for Ni show a probable production of Ni in the pond or a contamination during the sampling or analysis procedures. Nevertheless, the outlet concentrations of these three metals are not too alarming for the environment.
Comparison between pollutants' inlet concentrations measured in 1997/1998 and 2004 would have been interesting. Indeed, it is then possible to check if emissions in the catchment's area are still the same or changed sensibly since 1997 and if pollutants are in larger or lower amounts.
A comparison of rain characteristics between storm events monitored in 2004 and in Autumn 1997, may have helped explaining the differences in removal efficiencies between these two measurement periods.
Moreover, additional studies on PAHs removal need to be carried out in order to be able to highlight possible seasonal trend. For example, the winter concentrations are expected to be higher than during the other season due to the use of winter tires.

In addition to this study of pollutant removal efficiencies in the Järnbrott pond, it has been shown by the laboratory study that nutrients can be released from sediments, whether turbulences or high conductivity conditions are occuring or not. According to the results given by the sediment experiment carried out for heavy metals; finest particles and their attached metals (mainly Pb and Ni) can be released under turbulent conditions. In addition, Cr and Ni seems to be much more soluble than the other metals and thus able to be released from the sediments in their dissolved form when turbulent, anoxic or quiescent conditions are achieved.
Finally, it seems sensible to consider the sediments as a potential source for pollutants (mainly nitrogen compounds and some particular heavy metals) to the pond water and thus the receiving waters. Then, removing bottom sediments on a regular basis might help in achieving better removal efficiency for these pollutants. In addition, harvesting the pond vegetation at the beginning of the autumn period might help in removing nutrients from the water phase. However, studies have to be carried out during the spring and summer time in order to be sure that the removal efficiencies will not be negatively affected by harvesting.

Indeed, in spring and summer, the uptake of nutrients by plants might be a significant removal mechanism for nutrients.

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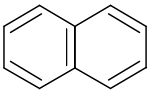
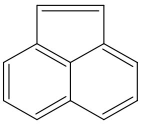
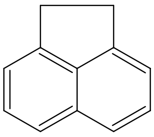
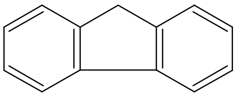
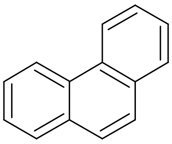
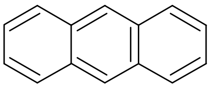
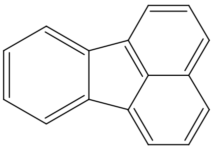
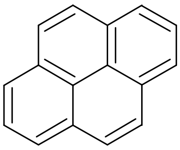
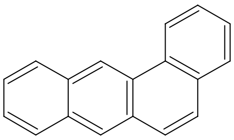
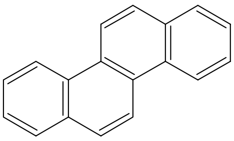
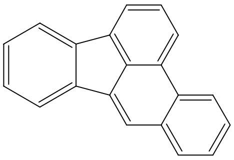
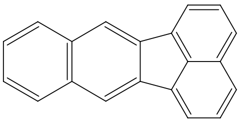
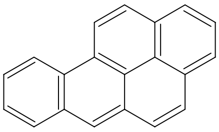
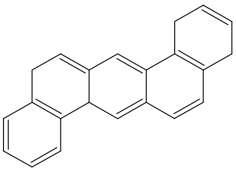
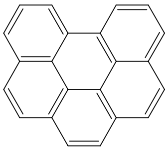
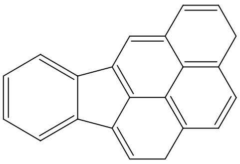
APPENDICES

APPENDIX 1: Polycyclic aromatic hydrocarbons

☠: carcinogenic PAHs

Compound analysed	K_{ow}	Compound analysed	K_{ow}
 Naphtalene	3,30	 Acenaphthylene	3,94
 Acenaphthene	3,92	 Fluorene	4,2
 Phenanthrene	4,52	 Anthracene	4,56
 Fluoranthene	5,07	 Pyrene	5,08
 ☠Benz[a]anthracene	5,91	 ☠Chrysene	5,73
 ☠Benzo[b]fluoranthene	5,78	 ☠Benzo[k]fluoranthene	6,11
 ☠Benzo[a]pyrene	6,20	 ☠Dibenzo[ah]anthracene	6,75
 Benzo[ghi]perylene	6,9	 ☠Indeno[1,2,3-cd]pyrene	6,7

APPENDIX 2: EPA guidelines

Heavy metals in water

Concentration in µg/l	**Class 1**	**Class 2**	**Class 3**	**Class 4**	**Class5**
	Very low	**Low**	**Moderately high**	**High**	**Very high**
As	<0,4	0,4 – 5	5 – 15	15 – 75	>75
Cd	<0,01	0,01 – 0,1	0,1 – 0,3	0,3 – 1,5	>1,5
Cr	<0,3	0,3 – 5	5 – 15	15 – 75	>75
Cu	<0,5	0,5 – 3	3 – 9	9 – 45	>45
Ni	<0,7	0,7 – 15	15 – 45	45 – 225	>225
Pb	<0,2	0,2 – 1	1 – 3	3 – 15	>15
Zn	<5	5 – 20	20 – 60	60 – 300	>300
	Risk of biological effects				
	None or very little	Little	Primarily in acidic water and in soft water with low concentrations of humus and nutrients	Increased risk	High risk even with brief exposure

Nutrients in lakes

Phosphorus

Class	**Level**	**Total phosphorus concentrations (µg/l)**		**Description**
		May-Oct	**August**	
1	Low	<12,5	<12,5	Oligotrophic
2	Moderately high	12,5 - 25	12,5 – 23	Mesotrophic
3	High	25 - 50	23 - 45	Eutrophic
4	Very high	50 - 100	45 - 96	
5	Extremely high	>100	Unspecified	Hypertrophic

Nitrogen

Class	**Level**	**Total nitrogen concentrations (µg/l)**
		May-Oct
1	Low	<300
2	Moderately high	300 - 625
3	High	625 - 1250
4	Very high	1250 - 5000
5	Extremely high	>5000

PAHs

Swedish guideline values in polluted groundwater to assess the current conditions:

Level	**Sum of the 7 carcinogenic PAHs (µg/l)**	**Sum of the 9 non-carcinogenic PAHs (µg/l)**
Not very serious	<0,2	<10
Moderately serious	0,2 – 0,6	10 – 30
Serious	0,6 – 2	30 – 100
Very serious	>2	>100

COD

Class	**Level**	**Level of COD_{Mn} (mg/l)**
1	Very low	<4
2	Low	4 - 8
3	Moderately high	8 - 12
4	High	12 - 16
5	Very high	>16

APPENDIX 3: Measurement results

INLET RESULTS

	Measurements		Storm event 1 (16/10/2004)		Storm event 2 (18/10/2004)		Storm event 3 (22/10/2004)		Storm event 4 (29/10/2004)		Storm event 5 (12/11/2004)		Storm event 6 (18/11/2004)		Storm event 7 (24/11/2004)				
			C_1 (mg/l)	M_1 (g)	C_2 (mg/l)	M_2 (g)	C_3 (mg/l)	M_3 (g)	C_4 (mg/l)	M_4 (g)	C_5 (mg/l)	M_5 (g)	C_6(mg/l)	M_6 (g)	C_7(mg/l)	M_7 (g)	**Σm_i (g)**	**ΣV_i (m^3)**	**SMC_{in} (mg/l)**
Oxygen demand	BOD_5				3,100	70732,7	7,470	116599,2			0,487	6040,1	1,430	18528,5	7,097	122646,9	**334547**	**81067**	**4,13**
	COD		9,000	55890,0	5,000	114085,0	10,000	156090,0			10,076	124968,0	11,392	147603,1	6,668	115224,0	**713860**	**87277**	**8,18**
Suspended matter	TSS		26,670	165620,7	15,930	363474,8	46,940	732686,5	39,417	244580,4	50,518	626579,1	57,660	747100,6	39,616	684595,7	**3564638**	**93482**	**38,13**
	VSS		24,000	149040,0	6,630	151276,7	20,070	313272,6	13,330	82712,7	6,787	84176,4	25,380	328848,7	13,617	235315,9	**1344643**	**93482**	**14,38**
Nutrients (mg/l)	NO_3-N (+NO_2-N)		0,620	3850,2	0,410	9355,0	0,090	1404,8			1,008	12496,8	1,815	23514,0	1,008	17426,2	**68047**	**87277**	**0,78**
	NO_2-N		0,020	124,2	0,007	159,7	0,014	218,5			0,016	197,9	0,022	289,6	0,017	285,2	**1275**	**87277**	**0,01**
	NO_3-N		0,600	3726,0	0,403	9195,3	0,076	1186,3			0,992	12298,9	1,792	23224,4	0,992	17141,0	**66772**	**87277**	**0,77**
	NH_3-N		0,037	229,8	0,019	433,5	0,110	1717,0			0,202	2499,4	0,234	3036,3	0,193	3326,8	**11243**	**87277**	**0,13**
	Tot-N		1,500	9315,0	1,000	22817,0	1,700	26535,3			2,099	26035,0	2,745	35565,0	1,833	31684,0	**151951**	**87277**	**1,74**
	PO_4-P		0,120	745,2	0,050	1140,9	0,050	780,5			0,063	781,1	0,068	884,8	0,062	1077,3	**5410**	**87277**	**0,06**
	Tot-P		0,210	1304,1	0,104	2373,0	0,180	2809,6			0,160	1978,7	0,145	1880,9	0,110	1901,0	**12247**	**87277**	**0,14**
			C_1 (CFU/100ml)		C_2 (CFU/100ml)		C_3 (CFU/100ml)		C_4 (CFU/100ml)		C_5 (CFU/100ml)		C_6 (CFU/100ml)		C_7 (CFU/100ml)				
Bacteria	E.Coli						9000						9300		4100				
	Coliforms						120000						37000		23000				
	Cl. perfringens						140						450		320				
			C_1 (PFU/100ml)		C_2 (PFU/100ml)		C_3 (PFU/100ml)		C_4 (PFU/100ml)		C_5 (PFU/100ml)		C_6 (PFU/100ml)		C_7 (PFU/100ml)				
	Somatic coliphages												176		268				
	F-specific RNA bacteriophages												300		132				
	Intestinal enterococci												730		764				
			C_1 (µg/l)	M_1 (g)	C_2 (µg/l)	M_2 (g)	C_3 (µg/l)	M_3 (g)	C_4 (µg/l)	M_4 (g)	C_5 (µg/l)	M_5 (g)	C_6(µg/l)	M_6 (g)	C_7(µg/l)	M_7 (g)	**Σm_i (g)**	**ΣV_i (m^3)**	**SMC_{in} (µg/l)**
Heavy metals	Cd	Total	0,36	2,26	0,39	8,80	0,24	3,79	0,94	5,84	0,15	1,91	0,30	3,87	0,35	6,04	**32,52**	**93482**	**0,35**
		Dissolved	0,10	0,60	0,07	1,56	0,04	0,68	0,14	0,86	0,32	3,96	0,08	1,08	0,22	3,76	**12,50**	**93482**	**0,13**
	Co	Total	1,26	7,84	0,84	19,20	1,99	31,05	1,67	10,35	1,38	17,15	1,70	22,03	2,09	36,08	**143,70**	**93482**	**1,54**
		Dissolved	0,22	1,39	0,18	4,06	0,23	3,58	0,50	3,13	0,31	3,90	0,50	6,48	1,08	18,65	**41,20**	**93482**	**0,44**
	Cr	Total	7,37	45,80	6,52	148,75	7,58	118,29	18,70	116,04	4,65	57,68	9,29	120,33	16,41	283,63	**890,52**	**93482**	**9,53**
		Dissolved	1,27	7,90	1,31	29,89	1,72	26,79	4,51	28,00	1,27	15,77	3,62	46,89	13,96	241,25	**396,49**	**93482**	**4,24**
	Cu	Total	503,11	3124,29	518,27	11825,38	42,17	658,30	46,45	288,22	39,12	485,24	31,73	411,14	47,95	828,71	**17621,29**	**93482**	**188,50**
		Dissolved	21,97	136,44	13,50	308,03	12,10	188,85	15,98	99,15	16,53	205,01	16,11	208,68	22,85	394,82	**1540,96**	**93482**	**16,48**
	Pb	Total	6,41	39,81	5,45	124,39	11,97	186,79	12,77	79,22	9,01	111,78	7,60	98,50	7,80	134,77	**775,25**	**93482**	**8,29**
		Dissolved	0,98	6,07	0,83	18,94	0,72	11,21	1,23	7,66	0,68	8,49	0,74	9,57	0,89	15,45	**77,40**	**93482**	**0,83**
	Zn	Total	344,91	2141,91	321,87	7344,16	138,63	2163,80	140,55	872,10	133,06	1650,33	123,81	1604,20	161,11	2784,10	**18560,61**	**93482**	**198,55**
		Dissolved	40,96	254,37	38,89	887,35	26,51	413,72	70,34	436,47	50,70	628,88	43,60	564,96	190,86	3298,18	**6483,94**	**93482**	**69,36**
	Ni	Total	16,56	102,81	17,66	402,95	10,11	157,79	23,21	144,02	7,27	90,15	10,23	132,58	7,46	128,91	**1159,21**	**93482**	**12,40**
		Dissolved	3,04	18,86	3,07	70,05	3,39	52,99	7,78	48,25	3,59	44,56	7,10	91,94	6,35	109,76	**436,41**	**93482**	**4,67**

▒ For these compounds, the analysis couldn’t be carried out

INLET RESULTS (PAH)

	Measurements	Storm event 1 (16/10/2004)		Storm event 2 (18/10/2004)		Storm event 3 (22/10/2004)		Storm event 4 (29/10/2004)		Storm event 5 (12/11/2004)		Storm event 6 (18/11/2004)		Storm event 7 (24/11/2004)				
		C_1 (µg/l)	M_1 (g)	C_2 (µg/l)	M_2 (g)	C_3 (µg/l)	M_3 (g)	C_4 (µg/l)	M_4 (mg)	C_5 (µg/l)	M_5 (mg)	C_6(µg/l)	M_6(g)	C_7(µg/l)	M_7(g)	**Σm_i (g)**	**ΣV_i (m^3)**	**SMC_{in} (µg/l)**
PAHs	Naphtalene	0,06	*0,37*	0,05	*1,14*	0,05	*0,78*	0,06	*0,37*	0,05	*0,62*	0,06	*0,78*	0,20	*3,49*	**7,55**	**93482**	**0,08**
	Acenaphthylene	0,09	*0,56*	0,08	*1,83*	0,08	*1,25*	0,09	*0,56*	0,06	*0,74*	0,08	*1,04*	1,28	*22,18*	**28,15**	**93482**	**0,30**
	Acenaphthene	0,05	*0,31*	0,05	*1,14*	0,05	*0,78*	0,05	*0,31*	0,05	*0,62*	0,05	*0,65*	0,06	*0,95*	**4,76**	**93482**	**0,05**
	Fluorene	0,05	*0,31*	0,05	*1,14*	0,05	*0,78*	0,05	*0,31*	0,05	*0,62*	0,05	*0,65*	0,05	*0,79*	**4,60**	**93482**	**0,05**
	Phenanthrene	0,13	*0,81*	0,02	*0,46*	0,16	*2,50*	0,05	*0,31*	0,10	*1,24*	0,05	*0,65*	0,07	*1,27*	**7,23**	**93482**	**0,08**
	Anthracene	0,01	*0,06*	0,01	*0,23*	0,02	*0,31*	0,01	*0,06*	0,01	*0,12*	0,01	*0,13*	0,01	*0,16*	**1,08**	**93482**	**0,01**
	Fluoranthene	0,14	*0,87*	0,06	*1,37*	0,22	*3,43*	0,10	*0,62*	0,19	*2,36*	0,09	*1,17*	0,12	*2,06*	**11,88**	**93482**	**0,13**
	Pyrene	0,14	*0,87*	0,06	*1,37*	0,23	*3,59*	0,12	*0,74*	0,20	*2,48*	0,09	*1,17*	0,17	*3,01*	**13,23**	**93482**	**0,14**
	*Benz[a]anthracene	0,05	*0,31*	0,01	*0,23*	0,07	*1,09*	0,01	*0,06*	0,06	*0,74*	0,02	*0,26*	0,05	*0,79*	**3,49**	**93482**	**0,04**
	*Chrysene	0,07	*0,43*	0,03	*0,68*	0,09	*1,40*	0,05	*0,31*	0,09	*1,12*	0,04	*0,52*	0,09	*1,58*	**6,05**	**93482**	**0,06**
	*Benzo[b]fluoranthene	0,06	*0,37*	0,03	*0,68*	0,10	*1,56*	0,05	*0,31*	0,09	*1,12*	0,03	*0,39*	0,06	*1,11*	**5,54**	**93482**	**0,06**
	*Benzo[k]fluoranthene	0,02	*0,12*	0,01	*0,23*	0,05	*0,78*	0,02	*0,12*	0,04	*0,50*	0,02	*0,26*	0,03	*0,48*	**2,49**	**93482**	**0,03**
	*Benzo[a]pyrene	0,03	*0,19*	0,02	*0,46*	0,08	*1,25*	0,04	*0,25*	0,08	*0,99*	0,03	*0,39*	0,06	*0,95*	**4,47**	**93482**	**0,05**
	*Dibenzo[ah]anthracene	0,01	*0,06*	0,01	*0,23*	0,01	*0,16*	0,01	*0,06*	0,02	*0,25*	0,01	*0,13*	0,04	*0,63*	**1,52**	**93482**	**0,02**
	Benzo[ghi]perylene	0,06	*0,37*	0,02	*0,46*	0,07	*1,09*	0,03	*0,19*	0,08	*0,99*	0,03	*0,39*	0,16	*2,69*	**6,18**	**93482**	**0,07**
	*Indeno[123cd]pyrene	0,04	*0,25*	0,02	*0,46*	0,05	*0,78*	0,02	*0,12*	0,06	*0,74*	0,02	*0,26*	0,13	*2,22*	**4,83**	**93482**	**0,05**
	Σ 16 EPA-PAH	0,74	*4,60*	0,24	*5,48*	1,20	*18,73*	0,47	*2,92*	1,00	*12,40*	0,42	*5,44*	1,10	*19,01*	**68,57**	**93482**	**0,73**
	*Σ 7 carcinogenic PAHs	0,27	*1,68*	0,10	*2,28*	0,45	*7,02*	0,17	*1,05*	0,44	*5,46*	0,16	*2,07*	0,41	*7,13*	**26,70**	**93482**	**0,29**
	Σ 9 non carcinogenic PAHs	0,47	*2,92*	0,14	*3,19*	0,70	*10,93*	0,30	*1,86*	0,58	*7,19*	0,26	*3,37*	0,73	*12,67*	**42,14**	**93482**	**0,45**
	Volume (m^3)	6210		22817		15609		6205		12403		12957		17281				

🟦 The real value is inferior to the one displayed.

OUTLET RESULTS

	Measurements		Storm event 1 (16/10/2004)		Storm event 2 (18/10/2004)		Storm event 3 (22/10/2004)		Storm event 4 (29/10/2004)		Storm event 5 (12/11/2004)		Storm event 6 (18/11/2004)		Storm event 7 (24/11/2004)				
			C_1 (mg/l)	M_1 (g)	C_2 (mg/l)	M_2 (g)	C_3 (mg/l)	M_3 (g)	C_4 (mg/l)	M_4 (g)	C_5 (mg/l)	M_5 (g)	C_6(mg/l)	M_6 (g)	C_7(mg/l)	M_7 (g)	**Σm_i (g)**	**ΣV_i (m^3)**	**SMC_{out} (mg/l)**
Oxygen demand	BOD_5		4,300	*23443,6*	3,110	*85515,7*	2,540	*36675,1*	▨	▨	0,680	*7286,2*	2,440	*27091,3*	7,363	*104121,8*	**284134**	**83348**	**3,41**
	COD		7,000	*38164,0*	4,000	*109988,0*	7,000	*101073,0*	▨	▨	6,000	*64290,0*	6,705	*74448,0*	9,000	*127278,0*	**515241**	**83348**	**6,18**
Suspended matter	TSS		8,000	*43616,0*	5,020	*138034,9*	10,040	*144967,6*	22,170	*99986,7*	25,833	*276803,8*	22,500	*249817,5*	22,218	*314212,3*	**1267439**	**87858**	**14,43**
	VSS		12,000	*65424,0*	3,360	*92389,9*	5,030	*72628,2*	7,580	*34185,8*	6,750	*72326,3*	8,950	*99371,9*	13,875	*196214,5*	**632540**	**87858**	**7,20**
Nutrients (µg/l)	NO_3-N (+NO_2-N)		1,700	*9268,4*	0,670	*18423,0*	2,400	*34653,6*	▨	▨	2,000	*21430,0*	2,339	*25968,2*	2,500	*35355,0*	**145098**	**83348**	**1,74**
	NO_2-N		0,050	*272,6*	0,009	*247,5*	0,025	*361,0*	▨	▨	0,027	*289,3*	0,029	*320,8*	0,032	*452,5*	**1944**	**83348**	**0,02**
	NO_3-N		1,650	*8995,8*	0,661	*18175,5*	2,375	*34292,6*			1,973	*21140,7*	2,310	*25647,4*	2,468	*34902,5*	**143155**	**83348**	**1,72**
	NH_3-N		0,240	*1308,5*	0,024	*659,9*	0,021	*303,2*	▨	▨	0,150	*1607,3*	0,197	*2186,4*	0,260	*3676,9*	**9742**	**83348**	**0,12**
	Tot-N		2,700	*14720,4*	1,100	*30246,7*	3,200	*46204,8*	▨	▨	3,800	*40717,0*	3,249	*36076,1*	3,700	*52325,4*	**220290**	**83348**	**2,64**
	PO_4-P		0,061	*332,6*	0,037	*1017,4*	0,050	*722,0*	▨	▨	0,039	*417,9*	0,039	*431,4*	0,110	*1555,6*	**4477**	**83348**	**0,05**
	Tot-P		0,110	*599,7*	0,079	*2172,3*	0,091	*1313,9*	▨	▨	0,100	*1071,5*	0,092	*1024,1*	0,120	*1697,0*	**7879**	**83348**	**0,09**
			C_1 (CFU/100ml)		C_2 (CFU/100ml)		C_3 (CFU/100ml)		C_4 (CFU/100ml)		C_5 (CFU/100ml)		C_6 (CFU/100ml)		C_7 (CFU/100ml)				
Bacteria	E.Coli (ant/100ml)		▨		▨		9000		▨		▨		4100		7500				
	Coliforms (ant/100ml)		▨		▨		57000		▨		▨		73000		37000				
	Cl.perfringens (CFU/100ml)		▨		▨		210		▨		▨		280		270				
	▥		C_1 (PFU/100ml)		C_2 (PFU/100ml)		C_3 (PFU/100ml)		C_4 (PFU/100ml)		C_5 (PFU/100ml)		C_6 (PFU/100ml)		C_7 (PFU/100ml)				
	Somatic coliphages		▨		▨		▨		▨		▨		428		688				
	F-specific RNA bacteriophages		▨		▨		▨		▨		▨		212		724				
	Intestinal enterococci		▨		▨		▨		▨		▨		390		927				
			C_1 (µg/l)	M_1 (g)	C_2 (µg/l)	M_2 (g)	C_3 (µg/l)	M_3 (g)	C_4 (µg/l)	M_4 (g)	C_5 (µg/l)	M_5 (g)	C_6(µg/l)	M_6 (g)	C_7(µg/l)	M_7 (g)	**Σm_i (g)**	**ΣV_i (m^3)**	**SMC_{out} (µg/l)**
Heavy metals	Cd	Total	0,31	*1,70*	0,53	*14,50*	0,13	*1,86*	0,28	*1,24*	0,10	*1,04*	0,32	*3,55*	0,25	*3,56*	**27,46**	**87858**	**0,31**
		Dissolved	0,10	*0,55*	0,06	*1,62*	0,04	*0,53*	0,10	*0,45*	0,23	*2,44*	0,14	*1,59*	0,13	*1,87*	**9,06**	**87858**	**0,10**
	Co	Total	0,03	*0,15*	0,74	*20,47*	0,78	*11,33*	1,62	*7,32*	0,52	*5,58*	0,94	*10,48*	1,22	*17,28*	**72,62**	**87858**	**0,83**
		Dissolved	0,27	*1,47*	0,15	*4,06*	0,25	*3,59*	0,52	*2,34*	0,33	*3,52*	0,49	*5,45*	0,65	*9,14*	**29,57**	**87858**	**0,34**
	Cr	Total	6,70	*36,53*	7,31	*200,87*	4,62	*66,70*	17,45	*78,68*	2,59	*27,78*	6,59	*73,12*	11,96	*169,17*	**652,85**	**87858**	**7,43**
		Dissolved	1,81	*9,88*	1,31	*35,93*	1,58	*22,79*	4,84	*21,84*	1,43	*15,32*	3,78	*41,92*	11,88	*167,99*	**315,66**	**87858**	**3,59**
	Cu	Total	495,31	*2700,41*	526,65	*14481,17*	20,38	*294,31*	38,09	*171,81*	18,80	*201,41*	18,96	*210,52*	32,35	*457,46*	**18517,08**	**87858**	**210,76**
		Dissolved	11,00	*59,97*	11,93	*327,98*	10,86	*156,87*	9,24	*41,69*	13,46	*144,21*	10,70	*118,78*	19,00	*268,75*	**1118,24**	**87858**	**12,73**
	Pb	Total	2,47	*13,45*	4,66	*128,14*	4,85	*69,97*	8,14	*36,71*	2,91	*31,21*	3,72	*41,31*	5,23	*73,94*	**394,73**	**87858**	**4,49**
		Dissolved	0,42	*2,29*	0,74	*20,27*	0,82	*11,82*	1,21	*5,47*	0,83	*8,87*	0,55	*6,14*	0,74	*10,43*	**65,29**	**87858**	**0,74**
	Zn	Total	283,89	*1547,75*	308,65	*8486,95*	74,01	*1068,60*	109,55	*494,05*	69,19	*741,32*	82,28	*913,59*	116,03	*1640,89*	**14893,15**	**87858**	**169,51**
		Dissolved	33,06	*180,26*	32,87	*903,75*	26,98	*389,55*	49,71	*224,19*	46,56	*498,89*	37,81	*419,76*	81,60	*1154,03*	**3770,44**	**87858**	**42,92**
	Ni	Total	22,26	*121,37*	20,80	*571,94*	11,47	*165,68*	28,47	*128,41*	8,56	*91,69*	9,82	*109,01*	4,42	*62,49*	**1250,58**	**87858**	**14,23**
		Dissolved	8,66	*47,23*	4,25	*116,89*	7,35	*106,12*	14,14	*63,77*	7,11	*76,19*	8,87	*98,50*	7,53	*106,50*	**615,19**	**87858**	**7,00**

▨ For these compounds, the analysis couldn't be carried out

OUTLET RESULTS (PAH)

	Measurements	Storm event 1 (16/10/2004)		Storm event 2 (18/10/2004)		Storm event 3 (22/10/2004)		Storm event 4 (29/10/2004)		Storm event 5 (12/11/2004)		Storm event 6 (18/11/2004)		Storm event 7 (24/11/2004)				
		C_1 (µg/l)	*M_1 (g)*	C_2 (µg/l)	*M_2 (g)*	C_3 (µg/l)	*M_3 (g)*	C_4 (µg/l)	*M_4 (mg)*	C_5(µg/l)	*M_5(mg)*	C_6 (µg/l)	*M6 (g)*	C_7(µg/l)	*M_7(g)*	**Σm_i (g)**	**ΣV_i (m^3)**	**SMC_{out} (µg/l)**
PAHs	Naphtalene	0,06	*0,33*	0,06	*1,65*	0,06	*0,87*	0,05	*0,23*	0,05	*0,54*	0,05	*0,56*	0,04	*0,62*	**4,77**	**87858**	**0,00**
	Acenaphthylene	0,08	*0,44*	0,08	*2,20*	0,08	*1,16*	0,06	*0,27*	0,06	*0,64*	0,06	*0,67*	1,22	*17,23*	**22,60**	**87858**	**0,00**
	Acenaphthene	0,05	*0,27*	0,05	*1,37*	0,05	*0,72*	0,05	*0,23*	0,05	*0,54*	0,05	*0,56*	0,05	*0,74*	**4,42**	**87858**	**0,00**
	Fluorene	0,05	*0,27*	0,05	*1,37*	0,05	*0,72*	0,05	*0,23*	0,05	*0,54*	0,05	*0,56*	0,04	*0,62*	**4,30**	**87858**	**0,00**
	Phenanthrene	0,04	*0,22*	0,04	*1,10*	0,09	*1,30*	0,03	*0,14*	0,05	*0,54*	0,04	*0,44*	0,05	*0,74*	**4,47**	**87858**	**0,00**
	Anthracene	0,01	*0,05*	0,01	*0,27*	0,01	*0,14*	0,01	*0,05*	0,01	*0,11*	0,02	*0,22*	0,01	*0,12*	**0,97**	**87858**	**0,00**
	Fluoranthene	0,03	*0,16*	0,04	*1,10*	0,09	*1,30*	0,06	*0,27*	0,03	*0,32*	0,04	*0,44*	0,08	*1,11*	**4,71**	**87858**	**0,00**
	Pyrene	0,03	*0,16*	0,03	*0,82*	0,09	*1,30*	0,07	*0,32*	0,04	*0,43*	0,05	*0,56*	0,10	*1,35*	**4,94**	**87858**	**0,00**
	*Benz[a]anthracene	0,01	*0,05*	0,01	*0,27*	0,02	*0,29*	0,03	*0,14*	0,01	*0,11*	0,01	*0,11*	0,03	*0,37*	**1,34**	**87858**	**0,00**
	*Chrysene	0,01	*0,05*	0,01	*0,27*	0,04	*0,58*	0,02	*0,09*	0,01	*0,11*	0,02	*0,22*	0,04	*0,62*	**1,94**	**87858**	**0,00**
	*Benzo[b]fluoranthene	0,02	*0,11*	0,02	*0,55*	0,03	*0,43*	0,04	*0,18*	0,02	*0,21*	0,02	*0,22*	0,03	*0,49*	**2,20**	**87858**	**0,00**
	*Benzo[k]fluoranthene	0,01	*0,05*	0,01	*0,27*	0,02	*0,29*	0,02	*0,09*	0,01	*0,11*	0,01	*0,11*	0,01	*0,12*	**1,05**	**87858**	**0,00**
	*Benzo[a]pyrene	0,01	*0,05*	0,01	*0,27*	0,03	*0,43*	0,03	*0,14*	0,01	*0,11*	0,01	*0,11*	0,02	*0,25*	**1,36**	**87858**	**0,00**
	*Dibenzo[ah]anthracene	0,01	*0,05*	0,01	*0,27*	0,01	*0,14*	0,01	*0,05*	0,01	*0,11*	0,01	*0,11*	0,07	*0,98*	**1,72**	**87858**	**0,00**
	Benzo[ghi]perylene	0,02	*0,11*	0,02	*0,55*	0,03	*0,43*	0,02	*0,09*	0,02	*0,21*	0,02	*0,22*	0,02	*0,25*	**1,86**	**87858**	**0,00**
	*Indeno[123cd]pyrene	0,02	*0,11*	0,02	*0,55*	0,03	*0,43*	0,02	*0,09*	0,02	*0,21*	0,02	*0,22*	0,02	*0,25*	**1,86**	**87858**	**0,00**
	Σ 16 EPA-PAH	0,10	*0,55*	0,11	*3,02*	0,47	*6,79*	0,34	*1,53*	0,07	*0,75*	0,12	*1,33*	0,30	*4,31*	**18,28**	**87858**	**0,00**
	*Σ 7 carcinogenic PAHs	0,05	*0,27*	0,05	*1,37*	0,17	*2,45*	0,16	*0,72*	0,05	*0,54*	0,03	*0,33*	0,12	*1,72*	**7,42**	**87858**	**0,00**
	Σ 9 non carcinogenic PAHs	0,10	*0,55*	0,11	*3,02*	0,30	*4,33*	0,18	*0,81*	0,07	*0,75*	0,09	*999,27*	0,18	*2,58*	**1011,32**	**87858**	**0,01**
	Volume (m^3)	5452		27497		14439		4510		10715		11103		14142				

🟦 The real value is inferior to the one displayed.

APPENDIX 4: Removal efficiencies

	Measurements		Removal efficiencies for single storm events (%)							Long-term removal efficiency (%)
			Storm 1	Storm 2	Storm 3	Storm 4	Storm 5	Storm 6	Storm 7	
Oxygen demand	BOD_5			0	66	▒	-40	-71	-4	17
	COD		22	20	30	▒	40	41	-35	24
Suspended matter	TSS		70	68	79	44	49	61	44	62
	VSS		50	49	75	43	1	65	-2	50
Nutrients (mg/l)	NO_2-N		-150	-29	-79	▒	-69	-29	-94	-60
	NO_3-N		-175	-64	-3025	▒	-99	-29	-149	-124
	NH_3-N		-549	-26	81	▒	26	16	-35	9
	Tot-N		-80	-10	-88	▒	-81	-18	-102	-52
	PO_4-P		49	26	0	▒	38	43	-76	13
	Tot-P		48	24	49	▒	37	36	-9	33
Heavy metals	Cd	Total	14	-37	47	71	37	-7	28	10
		Dissolved	-4	14	15	27	28	-72	39	23
	Co	Total	98	12	61	3	62	44	41	46
		Dissolved	-21	17	-8	-3	-4	2	40	24
	Cr	Total	9	-12	39	7	44	29	27	22
		Dissolved	-43	0	8	-7	-12	-4	15	15
	Cu	Total	2	-2	52	18	52	40	33	-12
		Dissolved	50	12	10	42	19	34	17	23
	Pb	Total	62	15	60	36	68	51	33	46
		Dissolved	57	11	-14	2	-21	25	18	10
	Zn	Total	18	4	47	22	48	34	28	15
		Dissolved	19	15	-2	29	8	13	57	38
	Ni	Total	-34	-18	-14	-23	-18	4	41	-15
		Dissolved	-185	-38	-116	-82	-98	-25	-19	-50
PAHs	Naphtalene		■	■	■	■	■	■	78	🟪
	Acenaphthylene		■	■	■	■	■	■	■	🟪
	Acenaphthene		■	■	■	■	■	■	■	🟪
	Fluorene		■	■	■	■	■	■	■	🟪
	Phenanthrene		69	-100	44	40	50	20	29	34
	Anthracene		■	■	■	■	0	■	5	🟪
	Fluoranthene		79	33	59	40	84	56	34	58
	Pyrene		79	50	61	42	80	44	45	60
	*Benz[a]anthracene		80	0	71	-200	83	50	43	59
	*Chrysene		86	67	56	60	89	50	53	66
	*Benzo[b]fluoranthene		67	33	70	20	78	33	46	58
	*Benzo[k]fluoranthene		50	0	60	0	75	50	68	55
	*Benzo[a]pyrene		67	50	63	25	88	67	68	68
	*Dibenzo[ah]anthracene		■	■	0	■	50	■	■	🟪
	Benzo[ghi]perylene		67	■	57	33	75	33	89	🟪
	*Indeno[123cd]pyrene		50	■	40	0	67	0	86	🟪
	Σ 16 EPA-PAH		86	54	61	28	93	71	72	72
	*Σ 7 carcinogenic PAHs		81	50	62	6	89	81	70	70
	Σ 9 non carcinogenic PAHs		79	21	57	40	88	65	75	67
Bacteria	Coliforms		▒	▒	55	▒	▒	-100	-60	🟪
	E.coli		▒	▒	0	▒	▒	55	-85	🟪
	Cl.perfringens		▒	▒	-50	▒	▒	40	15	🟪
	Somatic coliphages		▒	▒	▒	▒	▒	-145	-160	🟪
	F-specific RNA bacteriophages		▒	▒	▒	▒	▒	30	-450	🟪
	Intestinal enterococci		▒	▒	▒	▒	▒	45	-20	🟪

▒ For these compounds, the analysis couldn't be carried out

🟨 The real value is superior to the one displayed because the outlet concentration was lower than the detection limit.

■ Both inlet and outlet concentrations were lower than the detection limit, thus the removal efficiency couldn't be calculated.

🟪 Long-term removal efficiency couldn't be calculated.

APPENDIX 5: Evolution of outlet concentration for the storm event on the 17th of November 2004

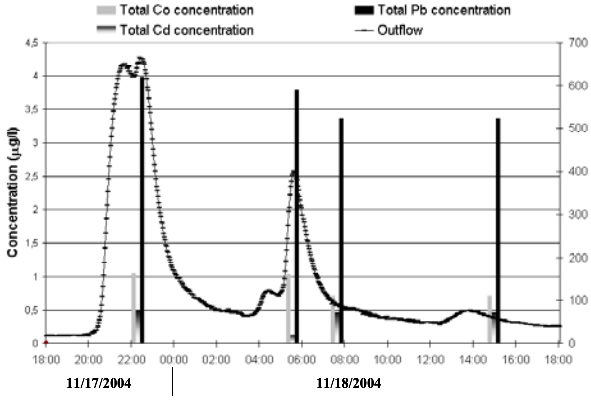


Figure 1: Co, Cd and Pb concentrations at the outlet

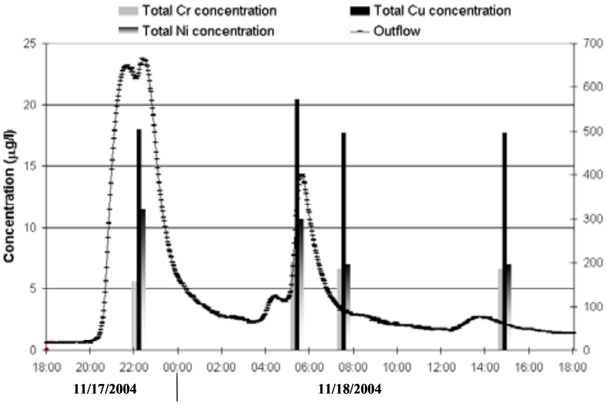


Figure. 2: Cr, Cu and Ni concentrations at the outlet

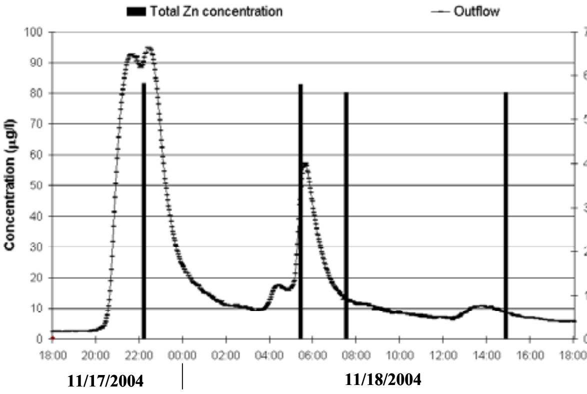


Figure. 3: Zn concentrations at the outlet

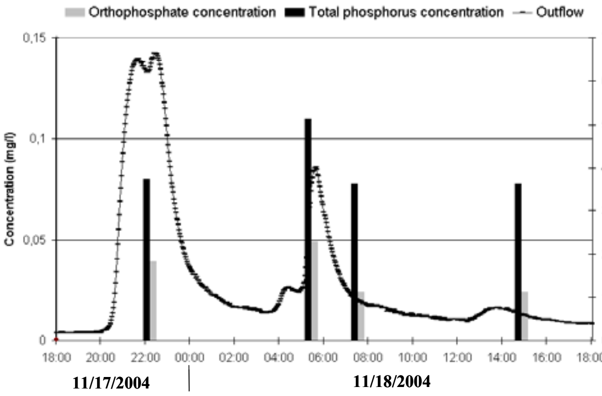


Figure. 4: PO_4^{3-} and Total-P concentrations at the outlet

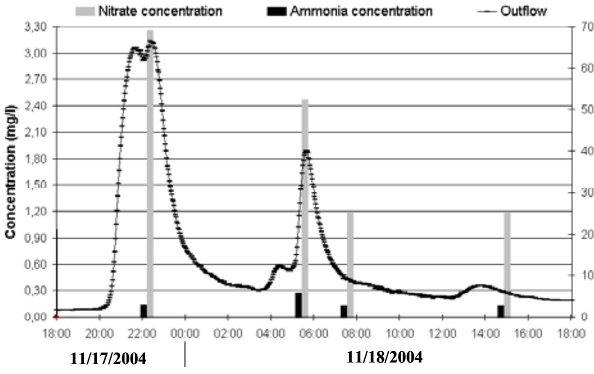


Figure. 5: NO_3^- and NH_4^+ concentrations at the outlet

APPENDIX 6: Documentation of bacteria’s removal efficiency

Table 35: Effect of pond depth and residence time on coliforms removal efficiency (Kurz, 1999)

Experimental conditions: depth = 1,0 m and residence time = 5 days	
Parameters	**Removal efficiency**
Total suspended solids (mg/l)	**99,8%**
Total coliforms (CFU/100 ml)	**64,0%**
Fecal coliforms (CFU/100 ml)	**98,2%**
Experimental conditions: depth = 2,7 m and residence time = 5 days	
Parameters	**Removal efficiency**
Total suspended solids (mg/l)	-81,4%
Total coliforms (CFU/100 ml)	-284,5%
Fecal coliforms (CFU/100 ml)	88,5%
Experimental conditions: depth = 1,0 m and residence time = 14 days	
Parameters	**Removal efficiency**
Total suspended solids (mg/l)	72,2%
Total coliforms (CFU/100 ml)	4,2%
Fecal coliforms (CFU/100 ml)	76,4%
Experimental conditions: depth = 2,7 ft and residence time = 14 days	
Parameters	**Removal efficiency**
Total suspended solids (mg/l)	73,3%
Total coliforms (CFU/100 ml)	37,9%
Fecal coliforms (CFU/100 ml)	69,2%