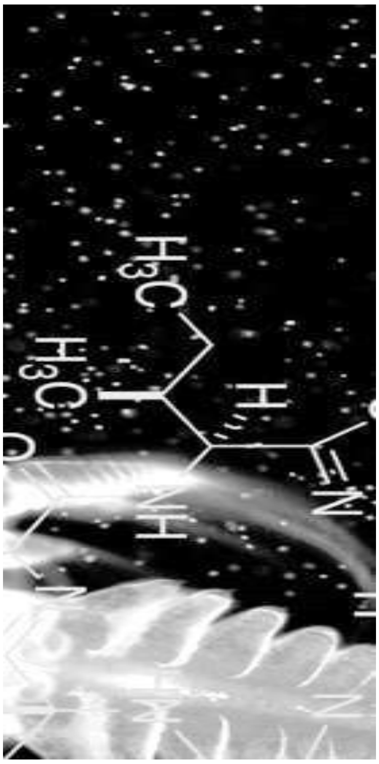
Micropollutants in Berlin’s urban rainwater runoff

A study on occurrence, and management measures for the reduction of micropollutants in Berlin, Germany



Bachelor thesis by Simon Douwe Holsteijn

For completion of the study programme Land- and Water management at Van Hall Larenstein

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Simon Douwe Holsteijn,

Berlin, 21 August 2014

Summary

According to the European Water Framework Directive, 'good ecological and chemical status' must be achieved for all surface waters by 2015 (European Parliament, 2000). Therefore, it is important to extend knowledge on pollutants that run off with urban rainwater. This study has the objective to determine which micropollutants occur in Berlin's urban rain water run-off and how the most detrimental pollutants can be managed in a sustainable manner to reduce their impact on receiving waters.

To reach these objectives, five catchments with different land use characteristics that together represent Berlin were selected for the collection of rainwater samples. These catchments consisted of New buildings (New), Old buildings (Old), One family homes (Ofh), Commercial buildings (Com) and Streets (Str). Actual sampling was done by installing an automated water sampler at each location, together with a flow measuring device to start the sampler during rain events.

The following number of rain events were sampled and analysed; New (n=8), Old (n=7), Ofh (n=6), Com (n=11) and Str (n=4). Samples collected during rain events were processed to one volume proportional composite sample that represents the entire event. This sample was then analysed on the presence and concentration of micropollutants. With that information, measures where determined that can be applied for the reduction of pollutant loads.

Micropollutants from the following groups were found during this study; pesticides / biocides, industrial chemicals, PAH's, heavy metals, tracers, flame retardants and phthalates.

From these groups, the most detrimental are; Nickel, Diuron, Isoproturon, Cadmium, Lead, PFOA, PFOS , polycyclic aromatic hydrocarbons (PAH), Nonylphenol, DEHP, Zinc, Copper, TCPP, Mecoprop, Glyphosphat, OHBT and Di-iso-decylphthalat.

To assess measures for micropollutant reduction, the concept of source-path-threatened object was used to identify where pollutants come from and what pathway they follow to which vulnerable objects. Possible measures to reduce the load of these substances are banning or substituting the pollutant by legislation. Furthermore, vegetation infrastructure, decentralized pre-treatment, infiltration and sedimentation can be applied for reduction of pollutant loads. These measures should be applied in an integrated manner to enhance one another.

Pollutant characteristics -and thus behaviour in the environment- is one of the most relevant criteria for the selection of measures to reduce these substances. The most effective approaches for particle and non-particle bound pollutants are end-of-pipe solutions. These consist of sedimentation systems for particle bound, and infiltration structures for non-particle bound micropollutants. Emitting sources (e.g. traffic) and paths (e.g. air) that contribute to pollutants in urban rainwater run-off are further relevant criteria. These can only be directly reduced by legislation, vegetation infrastructure can however be applied to reduce the mobility of these pollutants.

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WDF	Water Framework Directive
BWB	Berliner Wasser Betriebe
New	Location ‘New buildings’
Old	Location ‘Old buildings’
Ofh	Location ‘One family home’s
Str	Location ‘Streets’
Com	Location ‘Commercial buildings’
MP	Micropollutant
Sd	Standard deviation
EQS	Environmental Quality Standards

1. Introduction

From all paths that lead water out of urban areas, rainwater runoff is expected to be the largest untreated source of potentially high loads of micropollutants (MP) to (urban) surface waters, contributing to the deterioration of these waters. Other paths, such as effluents from wastewater treatment plants and combined sewer overflows are studied to a greater extend, whereas urban storm water has gotten little attention so far.

Following the Water Framework Directive (WFD), decisions need to be taken on how to reduce pollution to improve surface water quality to achieve a 'good ecological and chemical status' for all surface waters by 2015 (European Parliament, 2000).

This study was conducted from March to August 2014. The objectives of this study are to determine; 1) which micropollutants run off with Berlin's urban rainwater, 2) what measures are optimal for the reduction of these MP's.

To structure the objectives written above, the following research questions were developed;

Main research question:

- What are the most detrimental micropollutants in Berlin's urban rainwater runoff and what is the best approach to reduce their impact on receiving waters?

Sub research questions:

- How can rainwater samples be collected for analysis on micropollutants?
- What micropollutants occur in Berlin's urban rainwater runoff?
- What are the most Detrimental micropollutants in Berlin's urban rainwater runoff?
- Which criteria are relevant to reduce the impact of the most detrimental micropollutants?
- How can the impact of the most detrimental micropollutants be reduced?

From all target pollutants that were investigated during this study, measures for counteraction of MP loads will be determined only for the most detrimental substances. The 'most detrimental pollutants' are those, that are listed as 'priority or priority hazardous substance' by the EU-commission ànd pollutants that were found in exceptionality high concentrations during this study. The target pollutants mainly consist of organic micropollutants, other pollutants are also analysed but to a less extend.

To answer the research questions stated above, the following methodology was adopted. Automated rainwater samples were installed at selected measuring locations (n=5) throughout Berlin. Sampled rain events were analysed on the presence and concentration of micropollutants. A literature study was then conducted to investigate micropollution reduction concepts, and to determine how micropollutant loads can be reduced in the most sustainable manner. A case study was conducted for the location 'new buildings' to serve as an example on pollutant reduction.

Readers of this report are expected to have basic knowledge on urban water management.

This report can be roughly divided into two parts; 1) Rainwater sampling and analysis, 2) Measures for micro pollutant reduction in a case study.

In more detailed this report is structured as followed; In Chapter 2 the Research background is described, followed by Materials and Methods in Chapter 3, where information on sewer systems, sampling sights and sampling strategy is given. Outcomes of sampled and analysed events are given in Chapter 4, Results. Chapter 5 consists of a case study where measures for micropollutant reduction are discussed. A critical review of obtained results and recommendations is then given in Chapter 6. Main and sub-research questions are finally answered in Chapter 7, Conclusions. Appendices are provided for more background information.

2. Research background

Since the 1980s, studies have shown that urban storm water runoff contributes to the deterioration of receiving waters such as lakes, and open streams (Brombach, et al., 2005) (US-EPA, 1989). Initial studies mostly focused on conventional pollutants such as heavy metals and PAH's. National and international databases were developed for these pollutants. Furthermore, strategies were developed to reduce their emission and improve management (Saget, 1994).

The focus of recent studies have shifted to a wide array of organic pollutants and pesticides (Barbosa, et al., 2012), which lead to the development of the list of priority substances in the context of the WFD. The main goal of the WFD is to achieve a good chemical state of surface waters. As stated under Article 1(c), "specific measures for the progressive reduction of discharges, emissions and losses of priority substances (PS)" are to be implemented (European Parliament, 2000). In France, studies on pollutants in urban rainwater have been conducted (Barbosa, et al., 2012) with special attention on pollutants from the WFD list and certain metals such as Lead, Copper and Cadmium (Gasperi, et al., 2013).

The first list with priority substances has already been updated once, adding 12 pollutants. This indicates that the development of the list has not been completed yet. Recently, a study was conducted in Berlin that showed the relation between dieback of aquatic plants with rainwater from roof surfaces containing pollutants (Hübner, et al., 2010).

Numerous studies have been focusing on the reduction of micropollutants (Hillenbrand, et al., 2009) and the influence of storm water management concepts (Keßler, 2014). Outcomes of these studies will be applied in during this study.

This study is aimed at improving knowledge on occurrence of micropollutants in Berlin, and procedures for assessing urban rainwater pollution. Main focus is on organic pollutants, pollutants that emerge in high concentrations and the reduction of these pollutants.

3. Materials and Methods

This chapter starts by describing the setup of sewer systems in Berlin (3.1) providing information on type, location and functioning of the sewer system. In 3.2, sampling sights where rainwater samples were collected are described together with selection criteria (3.2.1 – 3.2.5). The general functioning of sample collection is then described (3.3). The last paragraph (3.4) informs about the chosen sampling strategy by providing information on timely distribution of samples during rain events, type of composite sample that was made for analysis and finally the pollutants that were investigated during this study.

3.1 Sewer system setup

The sewers system of Berlin can be roughly divided into 2 parts, the old and the new part (Figure 1). The old part originates from approximately 1873 and was constructed after the design of James Hobrecht (Cambrige University Press, 2005). The improved and separated system was constructed around and after 1920. Sanitary water is transported to wastewater treatment plants, where rain water often directly drains into surface waters without any intervention (Hillenbrand, et al., 2007). At present about 45% of all sewer systems are separated with a rising percentage (Sieker, et al., 2006). The new construction of combined sewer systems is currently prohibited by law. Improved systems, where only the first flush is divided to WWTP are not common (Keßler, 2014).

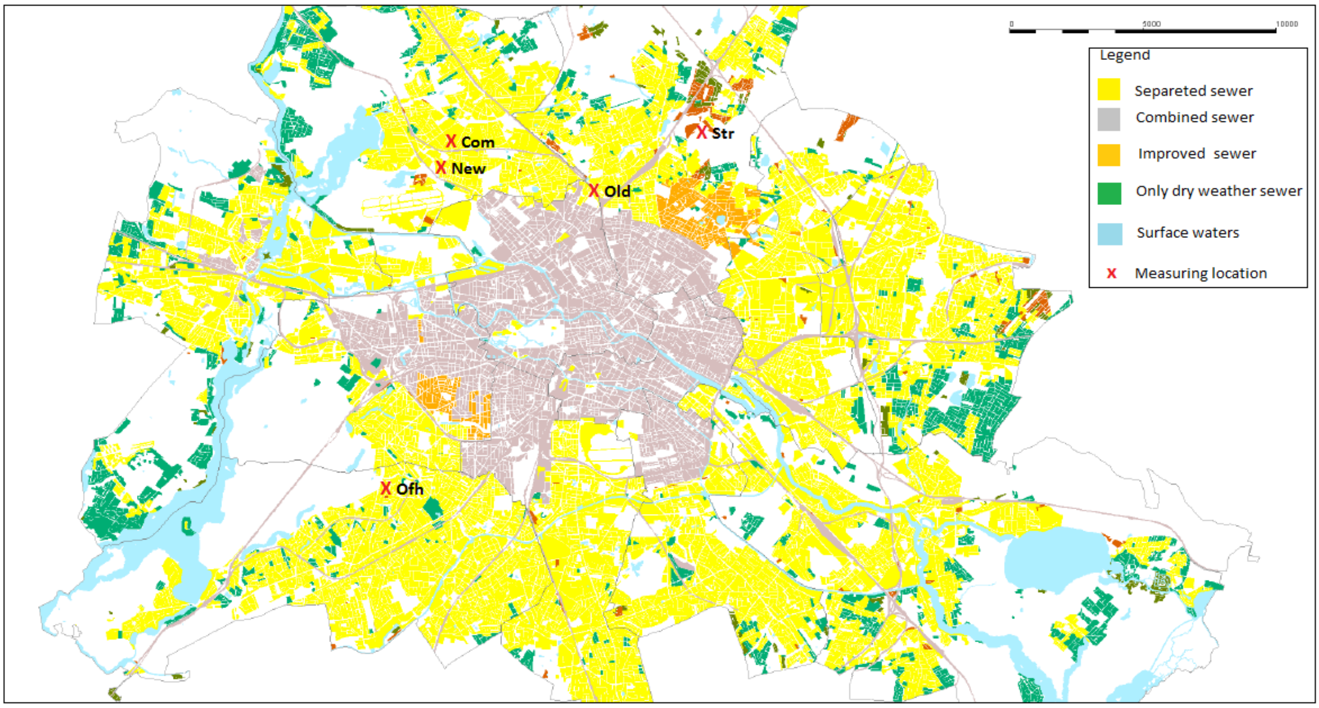

Figure 1: Location of different sewer systems and sampling locations.

Yearly, 74% of Berlin's urban rainwater (44 million m^3) is directly discharged into rivers and urban surface waters. 26% is discharged to wastewater treatment plants via combined sewer systems.

3.2 Sampling sights

Five different areas were chosen to be representative for Berlin (3.2.1). Areas with the following characteristics were chosen; New buildings, Old buildings, Commercial area, One family homes (houses with gardens) and finally Streets. The location of these areas in Berlin can be seen in Figure 1. In 3.2.2, selected sampling sights are introduced. Started is with New buildings (3.2.2.1), Old buildings (3.2.2.2), Commercial area (3.2.2.3), one family homes (3.2.2.4) and finally streets (3.2.2.5).

3.2.1 Selection of sampling sights

To define measuring locations that represent Berlin, an analysis was done using available maps and GIS-Data. A comparison was made between building density, percentage of sealed surface, age of buildings and use of the buildings. This analysis resulted in the definition of 5 urban areas typical for Berlin (Table 1).

Table 1: Overview of areas selected to represent Berlin.

Area type	**Surface of type in Berlin [ha]**	**Part of Berlin with type of area [%]**	**Land use**
Old	3517	14	- Build in 20’s and 30’s - Block buildings
New	2552	11	- Mainly build in 60’s and 80’s - High buildings after war times - Recently developed housing
One family homes	3070	13	- Low buildings with gardens - Villa’s - Buildings with private green
Commercial	3481	14	- Buildings aimed at trade / service - High % of sealing
Streets	8618	36	- Roads in general

In total, 88% of Berlin is represented by the areas listed in Table 1 above.

Following this analysis, sampling sights were selected that represent the summarized land uses best. The following criteria were used for this selection:

- Separated sewer
- Area represents the selected areas from (Table 1) and is homogeneous for that land use
- Accessibility; manhole on side-walk
- No variable backwater from other channels
- Various locations close to one another

3.2.2 *Selected sampling sights*

Following the analysis on catchments that represent Berlin, the areas that were used for rainwater sampling are listed in the chapters below.

3.2.2.1 New buildings (New)

Buildings in this area consist of modern flats with 4 to 12 floors, see Figure 2. This area is interesting for possible influence of new building materials (e.g. Mecoprop from vegetation roofing and the possible washing off of substances from facades) on micro pollutant type and load. Total surface of this area is 16.2 ha, from which an area of 6.3 ha is sealed and connected to the rainwater sewer. The sealed area consists of roof surface (2.4 ha), parking surfaces behind buildings (2.4 ha) and roads (1.5 ha). Rainwater from this catchment drains through a 1000 mm sewer into a retention basin.

Figure 2: Overview of sampling location New buildings, showing catchment characteristics, size and sampling location.

3.2.2.2 Old buildings (Old)

Most buildings in this catchment were built around 1930, the area is typical for the older part of Berlin. Expected is that this area has specific MP types running off due to the application of older building materials and possible false sewer connections. Surface of this catchment is approximately 31.2 ha, of which 11.8 ha is impervious. This sealed area is drained via an egg-shape sewer which measures 800 x 1200 mm. Rainwater runoff is discharged directly into the river Panke. To test changes in legislation over the years (e.g. to compare with 'New buildings') and thus application of various materials, this area is very interesting. Figure 3 provides an overview of catchments and typical sights from within the catchment.

Figure 3: Overview of catchment and general catchment sights.

3.2.2.3 Commercial area (Com)

This area consists of commercial buildings (light industry) and has a total surface area of 37 ha. Approximately 60 % of the area is impervious, which could have significant effects on pollutant load and type found in rainwater. Roofing mostly consists of large flat surfaces. The area drains through a 2000 mm sewer, which finally discharges into open surface water downstream. An overview of this catchment is given in Figure 4.

Figure 4: Catchment containing commercial buildings, overview of area specific characteristics and size (Google earth, 2014).

3.2.2.4 One family homes (Ofh)

This area consists mostly of houses with gardens, see Figure 5. Data collection is thought to be valuable in this area because of expected higher use of pesticides in gardens. Characteristic for this catchment type is the low percentage of impervious surface of only 25%. Runoff characteristics are therefore expected to have less intensity, which may also influence pollutant concentrations. The catchment has a total area of 16.7 ha, from which 3.9 ha is sealed and connected to a rainwater sewer channel with a diameter of 600 mm.

Figure 5: Overview and characteristics of catchment 'One family homes'.

3.2.2.5 Streets (Str)
This catchment consists of 1.3 km of regional roads (2 lanes), together with a traffic light controlled intersection (Figure 6) and parking lots that have a total area of approximately 1.3 ha. These roads are heavily travelled with data on traffic loads ranging from 15.000 - 30.000 cars/24h.

Water from this catchment is transported through a 1000mm sewer into a sedimentation basin and finally infiltration basin. Expected are higher levels of traffic related pollutants such as PAH's and heavy metals (Soclo, et al., 2000).

Figure 6: Overview and catchment characteristics (intersection) of sampling location 'streets' (Google earth, 2014).

3.3 Site installation

Collecting rainwater samples might seem straightforward at first, but sampling locations are often difficult to access and rainfall events difficult to predict. That is why equipment was installed that samples automatically during events. New automated samplers from the brand Hach-Lange, and type Sigma SD 900 were installed in the rainwater channels at all measuring locations. Water level and discharge were measured using flow measure devices from the brand Nivus, type PCM 4. A texting device was installed to signal (by text on mobile phone) when samples were collected. Figure 7 below provides a general overview of installed equipment. A full overview of used equipment can be found in appendix 1, 'Used equipment'. Specific installation information and experiences are listed in appendix 2, 'Installation experiences for rainwater sampling'.

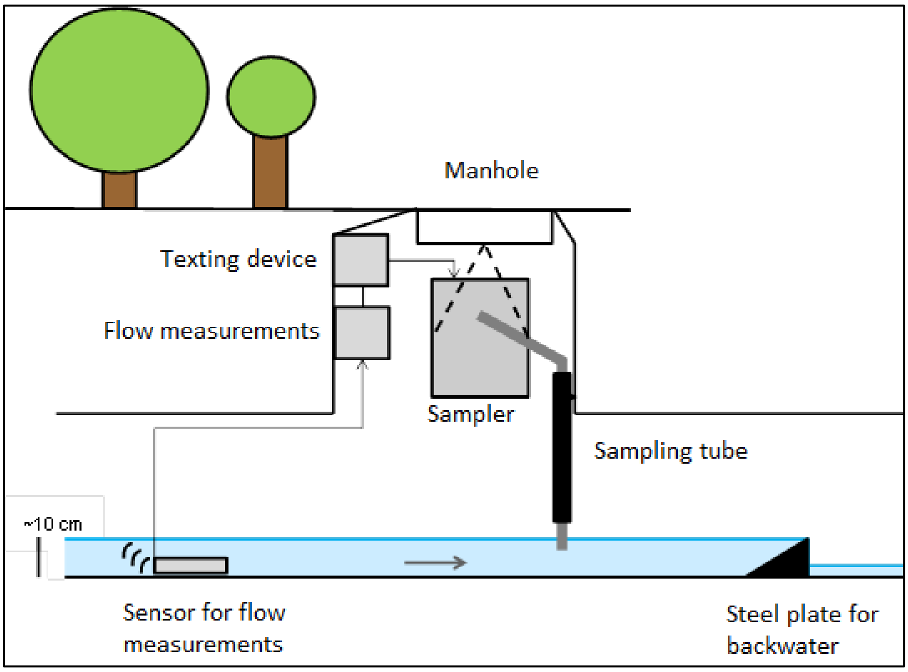

Figure 7: Schematic overview of site installation.

The installed steel plate causes backwater to allow the sampling of the beginning of rain events. It was installed 12 cm high, and with a clearance of 4-5 cm below, to allow the passage of debris (more detailed information is provided in Appendix 2). When water level rises during rain events, the flow measuring device sends a signal via the texting device to the sampler which starts its sampling programme. The texting device sends a text to indicate that sampling is in progress. The samples are retrieved by opening the manhole and lifting out the sampler.

3.4 Sampling strategy

This chapter starts by describing the applied approach for rainwater sampling and type of composite sample made (3.4.1). The pollutants that were analysed during this study, (target pollutants) are then discussed together with the selection of the most detrimental pollutants (3.4.2).

3.4.1 Approach

Concentrations of substances are not distributed evenly throughout the sewer cross-section (Berlamont & Hilde, 1996). To maximize representation of all substances, the actual sampling location (position and height) is of great importance. Following work from Kowalska, et al., 2013, samples ware taken in the middle of the sewer at 8 cm above the sewer bottom.

Because concentrations of (micro) pollutants are also not constant over the duration of an entire storm event (Davis & McCuen, 2005), the objective was to obtain samples from events with various characteristics (e.g. long, short, intensity etc.). Following a discharge analysis (shown in appendix 3, 'Rainfall analysis for choice of sampling strategy'), a total sampling programme length of 4 hours was chosen. Concerning sample collection, focus was on the first 2 hours of events (first flush). Presented below in Figure 8 is a graphical overview of sample distribution throughout the programme. Bottles 1 – 6 (samples 1 – 24) were each filled in a period of 20 minutes (one sample every 5 minutes), in bottles 7 – 8 ,one sample was collected every 15 minutes, summing up to 4 hour of total programme length.

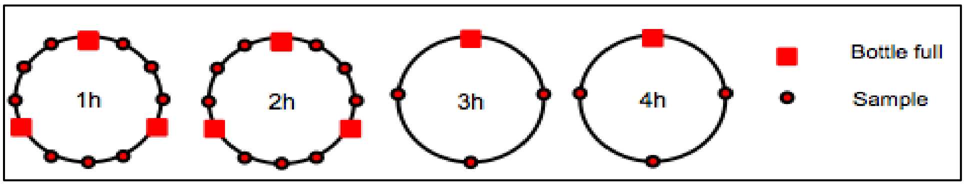

Figure 8: Timely distribution of samples in bottles throughout the sampling programme.

Rainwater samples were retrieved within 24 hours after rain events and cooled to 6 °C for conservation. After opening of the sampler the glass bottles were shut using a plastic lid, the inside of this lid was covered with a Teflon sheet to prevent contamination of the sample.

From all sampling strategies (e.g. grab samples, continues sampling and time paced sampling) volume proportional composite samples were selected because it creates the most representative sample relative to a period of interest. To calculate the composite sample volumes and analyse events, the statistical software Rstudio was used in combination with a specially developed script (an example can be found in Appendix 6). Figure 9, below shows the basic functioning principle of volume proportional composite samples. The discharge during time of sampling is taken into acount. In the example below, volume of bottle V3 (during time V3 in graph on the left) would be taken completey, all other volumes are taken relative to this sample.

All further analysis was outsourced to the laboratory of the Berliner Wasser Betriebe (BWB), Motardstraße 35, 13629, Berlin.

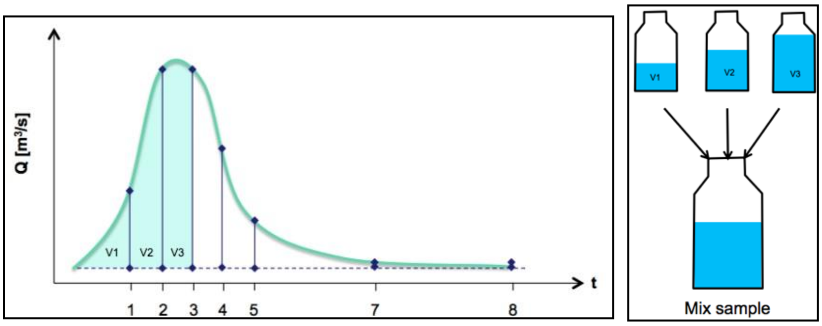

Figure 9: Graphical overview of basic composite sampling technique.

3.4.2 Target and most detrimental pollutants

The groups of target pollutants (mainly organic) that were investigated during this study are listed in this chapter. Next to organic pollutants, heavy metals and parameters such as suspended solids were also analysed.

3.4.2.1 Target pollutants

Table 2 below shows the pollutants that are subject of this study. All pollutants are common in everyday use, many of the substances are components of various products, plasticizers to soften plastics and vulcanization to improve product characteristics. Furthermore, building materials are a significant source of micropollution, with coming substances are thus target pollutants for this study. A complete overview containing all substances can be found in Appendix 4, 'Complete overview of target pollutants'.

Table 2: Target pollutants, together with a typical substance from each group and general use or application.

Substance group (n=x in group)	**Typical substance from this group**	**General use**
Phthalate (8)	DEHP	Plasticizers
Organophosphate (6)	TCEP	Flame retardant, Plasticizers
Organozinc compounds (3)	Tributylzinn	Wood protection
Pesticides / biocides (19)	Mecoprop, Diuron	Gardens, House front paint, Wall protection
Perfluorinated tensides (6)	PFDA	Coatings
PAH (16)	Benzo[a]pyrene	Result of combustion processes
Alkylphenole (3)	Nonylphenol	Plastics, Wear of wheels
Polybromierte Diphenylether (PBDE) (9)	c-pentaBDE	Flame retardant
Benzothiazole (4)	Benzothiazol	Vulcanizing accelerators (car wheels)
Benzotriazole (3)	Benzotriazol	Corrosion prevention, Lubricants (car engines)
Heavy Metals (3-10)	Copper, Zinc	Breaking disk wear, Building materials, industrial activities
Others	MTBE, Bisphenol A, HBCDD	Fuel additive, plastic production, flame retardant

3.4.2.2 Most detrimental pollutants

From all selected target pollutants during this study (n=81), the most detrimental were selected for further analysis (Table 3). The WFD list of ‘priority and hazardous priority substances’ was used as selection criteria to select detrimental substances during this study.

It should be noted that the ‘Most detrimental’ pollutants are not necessarily the most toxic, but rather a critical prioritization following the pollutants frequency, toxicity, and potential for human exposure.

Table 3: Selected most detrimental pollutants from all target substances.

Pollutant	Priority substance	Priority hazardous substance
Nickel	X	-
Diuron	X	-
Isoproturon	X	-
Cadmium	X	X
Lead	X	X
PFOA	X	X
PFOS	X	X
PAH	X	X
Nonylphenol	X	X
DEHP	X	X

The complete list of priority pollutants from within the water framework directive can be found in appendix 5, ‘Priority substances within the WFD’.

4. Results: outcomes and analysis

In this chapter, concentrations of micropollutants are given that are the result from rainwater sampling at the introduced sampling locations. Because some pollutants were found in high concentrations, the previous list (Table 3) containing the most detrimental pollutants is extended (4.1), in Table 4. The results of rainwater sampling are then listed in Table 5 (4.2). In the last part of this chapter, the results are compared between the different measuring locations (4.3).

The following number of events were analysed during this study, New (n= 8), Old (n=7), Com (n=11), Ofh (n=6) and Str (n=4). The number of analysed events differs due to different catchment characteristics and technical problems. Rainfall events with various characteristics were sampled, all events and important characteristics are shown in table format in Appendix 6, 'Characteristics of sampled and analysed events'.

4.1 New list: final detrimental selected substances

Following a first analysis of results, some pollutants were found in exceptional high concentrations. This leads to a broadening of the list of most detrimental pollutants. Table 4 shown below contains the pollutants that were previously selected as detrimental substances, together with the added substances. After the EU-Commission publicized its first list of priority substances, Glyphosate was on the 'Candidate list'. The new list of PS did however not contain this pollutant. Because it cannot be verified if large industrial companies have influence on the listing of pollutants, Glyphosate is also listed as detrimental substance during this study.

The following parts of this report focus on the pollutants listed in Table 4 below.

Table 4: Extended table of most detrimental substances after first analysis of results.

Pollutant	Priority substance	Priority hazardous substance	Found in high concentration / otherwise interesting
Nickel	x	-	-
Diuron	x	-	-
Isoproturon	x	-	-
Cadmium	x	x	-
Lead	x	x	-
PFOA	x	x	-
PFOS	x	x	-
PAH	x	x	-
Nonylphenol	x	x	-
DEHP	x	x	-
Zinc	-	-	x
Copper	-	-	x
TCPP	-	-	x
Mecoprop	-	-	x
Glyphosphat	-	-	x
OHBT	-	-	x
Di-iso-decylphthalat	-	-	x

4.2 Laboratory outcomes

Presented in Table 5 below are the laboratory outcomes that are the result from rainwater sampling and analysis. The mean concentrations of all events are listed, together with standard deviation (sd). All concentrations that were measured during individual events are listed in appendix 7, 'Full results: outcomes all sampled events'. A comparison between found substances at the different measuring locations is made in paragraph 4.3.

Where the concentration of a substance during all sampled events was below the detection limit (DL), this value could not be calculated precisely and is listed as >DL. Where concentrations of individual events resulted in a DL value, the half (e.g. DL / 2) of this value is taken to calculate the mean concentration of all events. The DL is the minimal concentration that used laboratory methods can measure (e.g. When the DL is <5 µg/l, it is possible that the actual concentration ranges from 0 µg/l to 5 µg/l but will never be higher than 5 µg/l while that is within measuring range). These values are listed as DL in the coming tables (Tables 5 and 6) because of this uncertainty.

Table 5: Mean concentrations and standard deviation of substances measured during all events.

Substance (µg/l)	DL	New (n=8)		Old (n=7)		Ofh (n=6)		Com (n=11)		Str (n=4)	
		Mean	sd	Mean	sd	Mean	sd	Mean	sd	Mean	sd
Cadmium	<3,0	<DL	-	<DL	-	<DL	-	1,7	-	<DL	-
Nickel	<10	<DL	-	<DL	-	<DL	-	7,2	5,20	<DL	-
Zinc	<3	123	42,8	849	421	223	77,1	2084	2855	465	194
Copper	<2	54,9	17,5	41,4	16,4	98,0	62,1	799	1610	145	48,0
Lead	<15	8,63	5,99	29,6	21,1	13,4	11,5	47	59	29	15,4
TCPP	<0,10	0,44	0,32	0,43	0,54	0,24	0,17	0,36	0,19	0,13	0,09
Mecoprop	<0,02	1,07	1,05	1,01	0,76	0,46	0,46	0,57	0,58	<DL	-
Diuron	<0,03	<DL	-	0,26	0,21	0,12	0,07	<DL	-	<DL	-
Glyphosphat	<0,02	0,03	0,01	0,10	0,06	0,22	0,16	0,04	0,02	x	x
Isoproturon	<0,03	<DL	-	<DL	-	0,09	0,05	<DL	-	<DL	-
OHBT	<0,02	0,32	0,18	0,38	0,21	0,30	0,17	0,35	0,23	0,81	0
PFOA	<0,03	<DL	-	<DL	-	<DL	-	0,04	0,02	<DL	-
PFOS	<0,05	<DL	-	<DL	-	<DL	-	<DL	-	<DL	-
PAH (All)	<0,050	0,60	0,64	0,66	0,71	0,08	0,06	0,56	0,59	2,80	0
Di-iso-decylphthalat	<0,30	1,48	0,79	4,60	4,98	2,33	1,55	14,5	15,7	8,60	0
DEHP	<0,30	<DL	-	2,26	3,87	0,63	0,65	1,86	1,50	2,27	0
Nonylphenol	<0,10	4,68	4,71	2,63	1,74	4,48	3,51	7,86	5,43	<DL	-
Suspended solids (mg/l)	-	47,5	39,0	82,8	48,8	57,4	57,4	67,3	77,5	280	158

x = Substance not found, DL= Detection limit, <DL=all values are under the detection limit

Discussion

The high standard deviations indicate large variability in this data, this is a good indicator of the importance of influencing parameters (e.g. rain duration, intensity, dry period before rain) on micropollutant concentrations that run off with this rainwater.

This is especially the case with the results for heavy metal concentrations, where high outliers (concentration of 10.000 µg/l at location Com, event of 09.07.2014) were measured. These concentrations can be the effect of a longer dry weather period or prolonged rainfall that aids in the leaching of metals.

The listed concentrations for Str are only based on 4 events, more events should be sampled to gain more reliable results. From the pesticides groups, Glyphosphat is found at every sampling location accept Str. Isoproturon is only found at Ofh with a detectable concentration. This was expected because the relative large percentage of gardens and accompanying use of pesticides.

At all locations accept Com, sampling conditions where modified (See Appendix 2, Installation experiences for rainwater sampling) to improve sampling conditions. These alternations might influence obtained results. Still, because the modifications only had a small influence on pivotal sampling conditions (e.g. sampling height, direction of sampling tube ending) it is expected that this possible influence is not significant.

Seasonal variability cannot be compared by these results as the outcomes listed in Table 5 are only valid for the spring and summer season.

4.3 Occurrence of pollutants: Comparison

The occurrence of pollutants at different catchments is analysed in Table 6 below. Listed are the mean concentrations from high (left) to low (right). To identify the catchment, the same colour is used as in Table 5, these colours are also listed on the right side of the table. The received values that were under the detection range, are listed as <DL.

Table 6: Occurrence of pollutant concentrations at all measuring locations, listed from high to low concentration.

Substances	Mean (µg/l) From high to low				
Cadmium	1,7	<DL	<DL	<DL	<DL
Nickel	7,2	<DL	<DL	<DL	<DL
Zinc	2084	849	465	223	123
Copper	799	145	98,0	54,9	41,4
Lead	46,5	29,6	29	13,4	8,63
TCPP	0,44	0,43	0,36	0,24	0,13
Mecoprop	1,07	1,01	0,57	0,46	<DL
Diuron	0,26	0,12	<DL	<DL	<DL
Glyphosphat	0,22	0,10	0,04	0,03	x
Isoproturon	0,09	<DL	<DL	<DL	<DL
OHBT	0,81	0,38	0,35	0,32	0,30
PFOA	0,04	<DL	<DL	<DL	<DL
PFOS	<DL	<DL	<DL	<DL	<DL
PAH (All)	2,80	0,66	0,60	0,56	0,66
Di-iso-decylphthalat	14,5	8,60	4,60	2,33	1,48
DEHP	2,27	2,26	1,86	0,63	<DL
Nonylphenol	7,86	4,68	4,48	2,63	<DL
Suspended solids (mg/l)	280	82,8	67,3	57,4	47,5
x= Substance not found, <DL= Value under detection limit					

Location ID
New
Old
Ofh
Com
Str

Analysis and Discussion

As can be seen in the table above, the highest concentrations of most of the heavy metals are found in the catchment with commercial land use (Zinc 2084 µg/l, Copper 799 µg/l and Lead 46,5 µg/l). Cadmium however is found in highest concentrations in the catchment with Old buildings. From the pesticides group, Mecoprop is the most significantly detected in New, this indicates the presence of green roofs in this catchment. Mecoprop is used to prevent roots from penetrating the roofing material. Glyphosate is also detected at relatively high levels in 'One family homes' and not at all in at sampling sight Streets. The found concentration at Ofh is expected to originate from pesticide use in gardens. Isoproturon is only detected in concentrations near detection limits, accept for the location 'Ofh'. Nonylphenol is detected with > 4 µg/l at New, Ofh, Com and with a low concentration -under the detection limit- of 0,10 µg/l at Str. As expected, PAH's have the highest concentration in rainwater runoff from streets, these substances originate mainly form incomplete combustion in car engines. DEHP is found at all locations with peak concentrations at Str and Old.

The fact that the results listed in the table above are the outcome of various events is a limitation on the ability to compare between sampling sights. Only one rain event was sampled parallel at all locations. This means that most of the other events had different characteristics (e.g. duration of dry weather before event, volume, duration). Despite this fact, measured concentrations are representative for individual locations.

5. Case study: micropollutant reduction

Now that the type and concentration of ‘the most detrimental pollutants’ that run off with Berlins urban rainwater are known, the focus of this study shifts to the sustainable reduction of these substances. This is done by conducting a case study for the sampling location ‘New buildings’. The concept of source-path-threatened object is used to structure this chapter. This location was chosen because of the direct hydraulic connection to threatened objects (e.g. public swimming water and nature) and spatial possibilities for the implementation of measures for the reduction of MP’S.

In the first part of this chapter an analysis (5.1) on local pollutant sources (5.1.1), pathways (5.1.2), and threatened objects (5.1.3) is done. The second part of this chapter, (5.2) consists of measures that are optimal for reduction of these substances, followed by an exemplary calculation of pollutant load reduction after application of measures.

5.1 Local analysis

This chapter identifies where pollutants come from and which paths lead them to which objects. Main focus is on the area itself, external pollutant inputs are also analysed as the area is not isolated.

5.1.1 Sources

Traffic is an obvious source of pollution. Expected is that most PAH’s, Nonylphenolen, and heavy metals originate from vehicles. *Gardens* are expected to be the main source of pest- and herbicides in the area, since these substances are still widely available in Germany to be used for weed control and management of pests. A significant amount of houses in the area have *balconies.* The use of pesticides and herbicides on balcony’s can contribute to runoff of pollutants but are expected to have less significance. Paint used for the treatment and/or isolation of *facades* (house fronts) is a known source for flame retardants. These surfaces were observed contributors to runoff during precipitation. Almost all *roofs* in the area consist of flat surfaces which have a positive effect on rainwater runoff characteristics, but can lead to higher runoff of applied buildings materials like (e.g. heavy metals). Next to these ‘fixed’ sources, it is possible that faulty use or application of any chemical substance can lead to direct point pollution. Waste containers were observed to be thrown directly into the retention basin.

5.1.2 Pathways

Substances emitted by traffic on roads enter the catchment via air and direct runoff from road surfaces within the catchment. From gardens and public green, direct runoff is expected mainly during high amounts of precipitation. Part of this rainfall will infiltrate directly causing groundwater flow to be a pathway. Pollutants originating from balcony’s can enter the hydraulic cycle by false applications leading to spillage. Rainwater running of from facades and roofs is lead mainly into the rainwater sewer combined with road runoff.

5.1.3 Threatened objects

Main objects in the hydraulic path downstream consist of a retention basin within the catchment and the urban lake ‘Flughafensee’ that is popular for bathing and contains a vulnerable nature reserve.

The nature reserve has exceptional high biodiversity rates studies indicated 200 bird species, approximately 300 beetle species, more than 400 plant species, 40 dragonfly species and various species that are rare worldwide (NABU, 2013).

Before water from the catchment enters the Flughafensee, a sedimentation basin with overflow prevents most particulate bound particles from entering the lake. Algae growth is promoted by a deep-water aeration system, installed in 1986 (Berlin.de, 2005) to protect the lake against nitrification. The city council of Berlin identifies the lake as vulnerable and names external water input a relevant potential pollution source. Furthermore, the city council state that the sedimentation basin does not provide adequate protection against pollutants entering the lake (Berlin.de, 2005).

The retention basin -in the catchment self- is open for access and widely used for recreation. Direct contact with the water is most likely via domestic animals that swim in the basin and children that play around the basin.

Discussion

Danger on the current situation is the possibility of mobilisation of sediments from the retention basins during (extreme) rain events, mainly during the summer period when people swim in the lake. This can lead to a large amount of point source-pollution. Even when small concentrations of particulate bound pollutants (e.g. heavy metals) that do not or hardly break down accumulate in the basin over a longer period of time, concentrations rise to significant levels.

5.2 Measures

Now that source, path and threatened objects are known, measures that are optimal to reduce the amount of pollutants can be determined. Information on state of the art concerning micro pollutant reduction is listed in appendix 8, 'Management of micropollutants'. The most important criteria for MP load reduction are deducted from MP characteristics, these can be found in appendix 9, 'Characteristics of selected micropollutants'.

As can be seen in Figure 10 below, banning substances by legislation is the most effective measure, preventing the need for further elimination of pollutants. However, when pollutants cannot be banned or substituted by legislation due to social-economic factors, source measures come to place. While these types of measures often don't reduce pollutants fully, they can be integrated with decentralized pre-treatment and end-of-pipe solutions.

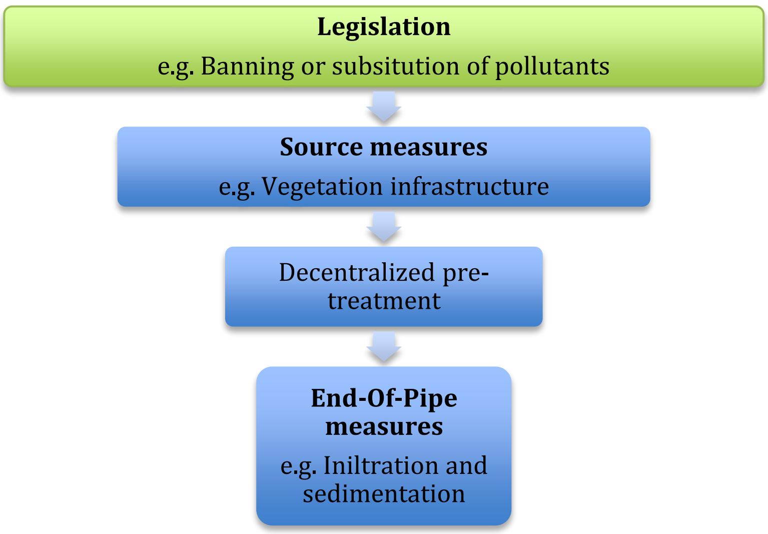

Figure 10: Order of effect and integration of measures.

5.2.1 Source solutions

Emissions caused by traffic from the nearby highway can be reduced near the source using vegetation infrastructure. This will reduce pollutants that enter the catchment via air, improve air quality and reduce concentrated loads in rainwater runoff. The application of green infrastructure on buildings in the catchment self will also aid in sustainable decreasing of pollutants.

5.2.2 Decentralized pre-treatment

Implementation of decentralized pre-treatment is spatially possible in the area. In the current situation some surfaces already discharge into green areas, but without aiming at pollutant reduction. This leads non-particle bound pollutants to flow downstream out of the catchment. Measures aimed at the reduction of all pollutants (particle and non-particle bound), would reduce pollutant mobility and cause less sewer discharge.

5.2.3 End-of-pipe

An analysis on MP characteristics was made (Appendix 9). Here, the % of pollutant attached to the particulate phase, K_{ow} (Octane – water partition coefficient), K_{oc} Values (a measure for the pollutants tendency to be adsorbed to particles) and the DT50 (time in which 50% of the pollutant is biodegraded in the environment) are listed.

Pollutants from the groups heavy metals, PAHs, Phthalate and Nonylphenol are primarily particle bound and will be thus be collected best by the application of a sedimentation basin. Maintenance of this basin is important to grand pollutant removal efficiencies. The substances from the groups Pesticides, Industrial chemicals and are mostly non-particle bound and must therefore by primarily removed by filtration and reduced by biodegrading. Improving the sewer system by diverting the 'first flush' to a waste water treatment plant cannot be applied in this area.

5.2.4 Area after application of measures

This paragraph describes the effects of measures on usage and quality of life in the area.

As said before, the retention basin has recreational value, which needs to be sustained. The implementation of the sedimentation basin comes with risks, which make preventing people from entering necessary. The infiltration structure poses fewer risks, and is more threatened by entrance of people itself. Based on these grounds, the parts of the basin containing the retention and sedimentation structure will need to be closed off to the public. The possible spatial implementation of measures is shown in Figure 11 below. Due to the relative small surface that these structures generally require, recreational values are not significantly decreased.

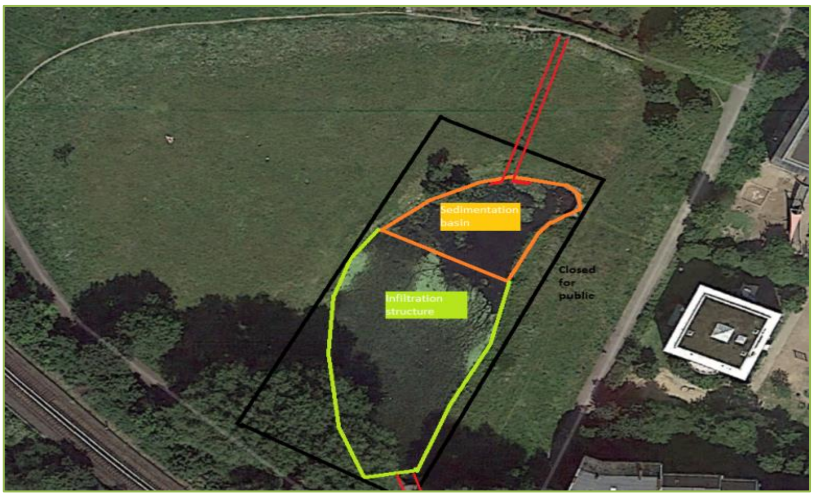

Figure 11: The retention basin with possible application of sedimentation and infiltration structure (Google maps, 2014).

Vegetation infrastructure will improve the living quality in the area by the increased amount of green in the area (Thomas, et al., 2012). Pollutant loads and thus air quality will improve, even sound pollution will be decreased by this vegetation, enhancing quality of life. Decentralized pre-treatment will not have a great impact on the area as this measure can be implemented at locations that are already present (e.g. public green space). Figure 12 provides an overview of the catchment with implementation of measures for micropollutant reduction.

Figure 12: Catchment with implemented measures. Green= vegetation infrastructure, Blue= Decentralized pre-treatment, orange= sedimentation basin, light green= infiltration structure (Google maps, 2014).

5.3 Influence of management measures, an example

In this chapter, the theoretical reduction of the heavy metal Lead by the application of a sedimentation basin is calculated. First, the total load of Lead during measured events is calculated, followed by the calculated reduction after applying the discussed measure. This substance is selected because it is listed as priority hazardous substance and was detected during various events. Followed is with comparison of this load with environmental quality standards set by the WFD.

In Table 7 below, characteristics of sampled rain events where Lead was detected are listed together with found the concentrations of this substance. Calculated is the load for individual events, and the sum of loads from all events.

Table 7: Sum and mean concentrations of Lead during 8 events.

Event Nr.	Date	Event Volume [m³]	Concentrations [µg/l]	Load [g] / event
1	11.05.2014	154	2	0,308
2	12.05.2014	37	2	0,074
3	19.05.2014	125	7,5	0,9375
4	28.05.2014	83	7,5	0,6225
5	05.06.2014	139	7,5	1,0425
6	25.06.2014	108	17	1,836
7	09.07.2014	474	18	8,532
8	10.07.2014	324	7,5	2,43
Sum		1444	-	15,78
Mean		180,5	8,6	1,973

The WFD has set environmental quality standards (EQS) for all priority substances. These standards apply for ‘inside surface waters’ and ‘other surface waters’ and divided into annual average and maximal permissible concentrations (WFD European Union, 2013). The following EQS are set or Lead: 1,2 µg/l annual concentration for inside surface waters and 1,3 µg/l for other surface waters. 14 µg/l is set as the maximal permissible concentration for both types of waters.

As can be seen in Table 7 above, the annual concentration is already exceeded during the event time listed above. The maximal permissible concentration is not exceeded. Rainwater entering the retention basin is diluted, causing the concentration of Lead per litre water to decrease. However, collection in sediments is a current threat. Following the literature study (Appendices 8 and 9) Lead is difficultly soluble in water and highly particle bound (94%). Therefore, sedimentation is a possible measure for reduction of this pollutant.

The begin concentration of 8,6 µg/l is taken, 94% of this concentration is particle bound. This means 6% of the total concentration could pass the sedimentation basin leaving 94% to be collected in the basin. Leading to the reduction of 8,084 µg/l (8,6 * 0,94), thus decreasing the concentration that is not removed to 0,552 µg/l, which is in range with the environmental quality standards of the WDF (WFD European Union, 2013). By integrating this measure with other measures, higher removal percentages could be achieved.

6. Discussion and recommendations

This chapter serves as a link between the results from the rapport and conclusions. It is written in addition to the smaller discussions in the sections 4.2 and 4.3.

The followed methodology proved to be successful for obtaining results. Still, improvements can be made. The programme length of 4 hours proved to be sufficient for sampling various events. Still, the influence of long rain periods on micropollutant concentrations in urban rainwater was not measured as a result. The recommendation is made that the programme length is extended.

Based on literature and practical experience of other studies, the assumption was made that sampling rainwater at 8 cm height in the sewer resulted in the most representative samples. This assumption might still decrease the representativeness of actual concentrations. An improvement can be to develop a technology that samples evenly throughout the sewer cross-section containing water. This however, also increases the complexity of sampling and might thus decrease number of sampled events. The pump of the samplers that were used for rainwater collection consisted of a tube that could not be replaced by Teflon, this might cause an elevated detection of plasticisers. This problem is not easily dealt with, as all available samplers use this pumping principle. However, test samples were made where water was analysed before and after passing the pump. The results from these test showed that there was no significant influence.

Results that were obtained are only valid for the summer season. Rainwater samples also need to be collected in other seasons to gain knowledge about yearly pollutant loads. The selection of the 'most detrimental' micropollutants was based on pollutants that were detected, and the WFD list of priority and priority hazardous substances. These two factors can change over time, substances can be added by the European commission, and occurrence of pollutants may vary. Leading to the need for more continues monitoring of both aspects.

Valuable experiences were obtained during the installation phase of this study. Most important recommendations are to lead the sampling tube with the direction of flow to prevent blockage by litter. Furthermore it is important to select sampling sights that have a good correlation between surface and sewer size to allow good sampling conditions (e.g. water level) during rain event.

Results on measures that can be applied best for the reduction of pollutants in the catchment new buildings are mostly selected on a theoretical basis and are partly only valid for the selected area. The paths, sources and threatened objects are estimated from field trips in the catchments. The determination of measures that reduce micropollutant concentrations is based on concepts. For actual implementation of these measures, detailed calculations and a technical literature review need to be made. All calculations are made for concentrations of micropollutants in the rainwater sewer, this water and thus these concentrations can be diluted which reduces the netto concentration. On the other side, during an rain event which causes more water input than the retention basin contains, these concentrations are valid and will

Applying all measures that are available would have the biggest impact on MP load reduction. For reduction of micropollutants in an area, a cost-benefit analysis should be made. Objectives for benefits (e.g. micropollutant reduction) can be that implemented measures should reduce micropollutant load to European environmental quality standard accepted levels. The costs to reach this objective should be lower than having an objective that aims at the complete removal of all micropollutants.

7. Conclusions

In this chapter, the main and sub-research questions are answered. The main research question is answered first, followed by the sub-research questions.

Main research question:

What are the most detrimental micropollutants in Berlin's urban rainwater runoff and what is the best approach to reduce their impact on receiving waters?

> The most detrimental micropollutants in Berlin's urban rainwater runoff are; Nickel, Diuron, Isoproturon, Cadmium, Lead, PFOA, PFOS, PAH, Nonylphenol, DEHP, Zinc, Copper, TCPP, Mecoprop, Glyphosphat, OHBT and Di-iso-decylphthalat. The best approach to reduce their impact on receiving water is by identifying individual pollutant characteristics, followed by the application of legislation, vegetation infrastructure, decentralized pre-treatment, infiltration and sedimentation based on these characteristics.

Sub research questions:

How can rainwater samples be collected for analysis on micropollutants?

> Rainwater samples can be collected by installing sampling equipment in urban areas where a separated sewer system is in place. An automated sampler in combination with a device that measures water level -and is able to start the sampler during rain events- is installed in the rainwater sewer. The sampling tube should consist of Teflon to prevent contamination of the sample. The actual location of sampling (suction point) is pivotal and can be located in the middle of the sewer, 8 cm above sewer bottom. This seems to be a good approach based on experiences so far.

What micropollutants occur in Berlin's urban rainwater runoff?

> From the results within this study, the following groups of pollutants occur in Berlin's urban rainwater runoff; Pesticides / Biocides, Industrial chemicals, Fuel additives, PAH, heavy metals, Tracers, Flame retardants and Phthalate.

What are the most Detrimental micropollutants in Berlin's urban rainwater runoff?

> According to this study, the following substances are the most detrimental pollutants in Berlin's urban rainwater runoff; Nickel, Diuron, Isoproturon, Cadmium, Lead, PFOA, PFOS ,PAH, Nonylphenol, DEHP, Zinc, Copper, TCPP, Mecoprop, Glyphosphat, OHBT and Di-iso-decylphthalat.

Which criteria are relevant to reduce the impact of the most detrimental micropollutants?

Pollutant characteristics are relevant criteria to reduce the impact of the most detrimental micropollutants. The substance being particle or non-particle bound is the most relevant criteria, it determines the behaviour of substances end thus how their impact can be reduced. A further relevant criterion is a substantial cost-benefit analysis.

How can the impact of the most detrimental micropollutants be reduced?

The impact of the most detrimental micopollutants can be reduced by legislation where detrimental substances are removed at the very source by banning or substitution. Decentralized pre-treatment can be applied to reduce the concentrated load of micropollutants accumulating in rainwater sewers and thus receiving waters. End-of-pipe solutions consist of infiltration and sedimentation. Infiltration targets pollutants that are dissolved in the rainwater, pollutants are collected by the filtration and degraded by increased biological activity. Sedimentation mainly targets particle bound pollutants, particles are allowed to settle in a basin. Maintenance is necessary to remove collected sediments. All measures should be integrated to enhance each other’s pollutant removal capabilities.

Appendices

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Appendix 1, Used equipment

Collecting rainwater samples may seem straightforward at first, but sampling locations are often difficult to access and rainfall difficult to predict. That is why equipment was installed that samples automatically during rain events.

New automated samplers of the type Sigma SD 900 Portable standard (Figure 13) were used for rainwater collection. The top of the sampler consists of a pump and software for programming. The underside of this part consists of a movable arm to distribute the samples to various bottles. The lower part of the sampler contains these bottles (Figure 13, right). An 8 x 1.9 litre bottle configuration was chosen to enable various sampling strategies and to collect sufficient water for analysis on pollutants. By programming the sampler, samples can be collected with different time intervals, allowing collection of e.g. first flush, longer and/or shorter rain events.

To activate the automated sampler at the beginning of rain events, each sampler was combined with a new Nivus PCM4 (Figure 14) that measures and collects data on water level and discharge. The PCM4 uses pressure to measure water level and ultrasound to precisely calculate discharge. Particles that pass the sensor are measured twice through their reflection (Figure 15), thus providing information on water velocity. This is done at different levels to create a curve of velocity at the different water levels that is used to calculate discharge.

To improve sampling conditions, a steal plate was installed in the rainwater channel, downstream from the sampling site to cause approximately 12 cm of backwater during events, allowing for better sampling of smaller events. This barrier was mounted with +/- 4 cm of clearance between the bottom of the channel and barrier to allow the passage of obstacles and to prevent the sampler of sampling previous rain events.

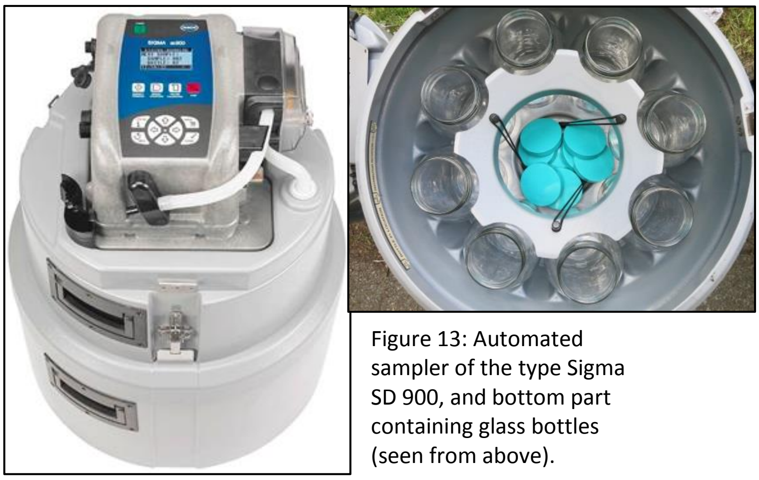

Figure 13: Automated sampler of the type Sigma SD 900, and bottom part containing glass bottles (seen from above).

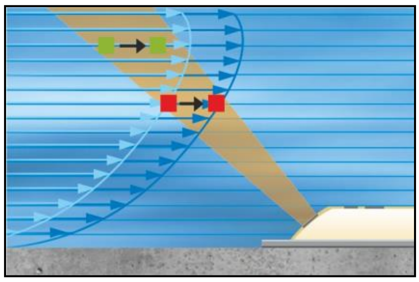

Figure 15: Functioning of sonar to measure water speed from particle reflection.

Figure 14: Flow and discharge measurements, Nivus PCM 4.

Appendix 2, Installation experiences for rainwater sampling

Structure

A description of the sewer characteristics and initial installation of all locations is given. At most locations modifications were made to improve sampling. Motivations for these modifications are also provided, together with effects.

Finally, conclusions and recommendations are given of efforts which improved sampling during this study significantly.

Catchment: New Buildings
Characteristics

This catchment has a total surface of 16.2 ha. Rainwater is transported through a circular concrete sewer with a diameter of 1000 mm. The sewer ends in an open channel, which leads the water into a retention basin. Before the first installation, the channel was cleaned because lots of rocks, sand and leaves were present in the sewer, together with a permanent water level of approximately 8 cm.

Initial installation

The sampling tube installation consisted of a steel pipe fixed in the middle-top of the sewer. The sampling tube was lead through this pipe and extended for a further 3 cm at the end of the pipe (Figure 16). The steel plate (measuring 1000 x 400 mm) was installed downstream at an angle. The lower part fixed to channel bottom and the higher part 11 cm above bottom.

Figure 16: Installation of the steel pipe that leads the sampling tube downwards.

Figure 17: Steel plate fixed to channel bottom, open channel not cleaned.

Problems

Bad maintenance (Figure 17) of the open channel caused permanent backwater in the channel, this level only slowly dropped after extended dry periods. The steel plate kept backwater in the channel but had less to no functionality at this time.

Modifications

Despite the presence of leaves on the steel pipe after events, this sampler tube installation –with a steel pipe going straight down- did not cause significant sampling problems and was not changed. The open channel was cleaned (Figure 18) to reduce permanent backwater conditions. The steel plate was lifted 5,5 cm on the lower part to allow passage of obstacles and still cause backwater during events.

Figure 18: Open part of the channel during maintenance.

Catchment: Old Buildings
Characteristics

This catchment has a total surface of 31.2 ha. Rainwater is transported through an egg-shape concrete sewer which measures 800 x 1200 mm. Due to the egg-shape, water level rose relatively quick in comparison to a round sewer pipe, which caused lots of rain events to be sampled. Toilet paper and other materials were present in the sewer, expected because of wrong connections upstream.

Initial installation

The initial installation (Figure 19) consisted of a steel pipe that was fixed in the top-middle of the sewer going straight down. The sampling tube was lead through this pipe with 5 cm clearance at the end. The sampling tube was cut straight at the end and had 8 cm clearance from the sewer bottom.

The steel plate measured 600 x 500 mm and was installed onto the sewer bottom, the upper part of the plate had a height of 9,5 cm.

Figure 19: Initial installation of steel pipe and sampling tube.

Problems

Litter like leaves, plastic bags and toilet paper were trapped on the steel pipe and sampling tube numerous times (Figure 20).

Expected was that by mounting the steel plate at an angle, waste materials would pass due to increased velocity. This was only partly the case, blockage due to sedimentation occurred. Furthermore this barrier was functioning too good, causing permanent backwater (Figure 22), which presented danger of sampling ‘old’ rain events.

Figure 20: Litter trapped on steel pipe and sampling tube, causing rinse errors and missed samples.

Figure 21: Steel plate causing permanent backwater.

Modifications

To prevent the steel plate from blocking and the sampling of previous events, the bottom part was lifted to 6 cm, upper part at 12,4 cm (Figure 22), allowing litter to pass and water to flow freely. Backwater was now only caused by events that caused significant water level.

To prevent the steel pipe and sampling tube from catching obstacles, a radical change was made. Chosen was to remove the steel pipe completely, and construct the sampling tube to point with the direction of water flow, partly flexible (Figure 23).

This improved sampling tube installation was very successful.

The steel plate was still blocked various times but no further modification was undertaken, blockage was removed after events.

Figure 22: Lower part of steel plate lifted from bottom and effects, blockage still occurred.

Figure 23: Improved installation, preventing the trapping of litter.

Catchment: Commercial area
Characteristics

This catchment has a total surface of 37 ha. Rainwater is transported through a 2000 mm concrete sewer. Due to the high percentage of impervious surfaces and area size, a high amount of events could be sampled.

Installation

The sampler tube was lead into the left-top part of the sewer before bending back downstream, attached to the wall at several points. The last part of the sampling tube was guided through a steel pipe (Figure 24) attached to the lower bottom of the sewer pipe, using a 45 degree angle the sampling tube was flowingly lead to the middle of the sewer. Causing it to point downstream and to be visible from above. The end of the sampling tube extended 3 cm out of the steel pipe.

The steel plate (1900 x 500 mm) was installed with a clearance of 4cm from the sewer bottom and an elevation of 13 cm at the upper part.

Figure 24: Sampler tube and steel pipe after installation.

Figure 25: Litter trapped on steel pipe, end is still clean.

Problems

No problems occurred after installation (Figure 24). Only some leaves and plastic are trapped on the steel pipe (Figure 25), which is removed from above as part of routine maintenance. No leaves stuck on the end of the sampling tube were observed.

An improvement could be to decrease the angle between the steel pipe and water flow to prevent catching litter.

Catchment: One family homes
Characteristics

This catchment has a total surface of 16,7 ha. Rainwater is transported through a circular concrete sewer with a diameter of 600 mm. Only approximately 25% of the area is sealed.

Initial installation

A steel pipe was used and fixed top-middle of the sewer (Figure , left), protecting and guiding the sampler tube. At the end of this pipe, the sampler tube extended 12 cm. The steel plate measuring 600 x 300 mm was installed fixed to the bottom with the upper part elevated 8 cm, directly downstream after the point of sampling (Figure 26, right).

Figure 26: Steel pipe, sampler tube and steel plate after initial installation (left) and after modification (right).

Problems

In general, there were no significant problems. Only a relatively small amount of events were sampled at this location, several possible causes are listed below;

- Small catchment / Sewer
- Big percentage of infiltrating surfaces in area
- Small number of rain events

Modifications

The steel pipe stayed in place. Only the steel plate was lifted 4,5 cm from the bottom against backwater and to allow dirt to pass, upper part after modification was 11 cm (Figure 26).

Catchment: Streets
Characteristics

This catchment has a total surface of 1.3 ha. Rainwater is transported through a 1000mm diameter circular sewer made out of cast iron, covert with a layer (approx. 1,5 cm thick) cement. This part of the sewer discharged in a backwater chamber, approximately 2 meters deeper on the downstream side. No holes could be drilled directly into the cast iron.

Initial installation

The steel plate (measuring 1000 x 400 mm) was installed (Figure 27) -with the lower part fixt to the channel bottom upper part elevated 15 cm- directly where drilling was possible, at the end of the cast iron sewer. This caused the need for the sampler tube to divert inward the sewer (upstream of the steel plate). This was achieved by installing a steel pipe with a 45 degree bend (Figure 28).

Figure 27: Installed steel plate, seen from downstream.

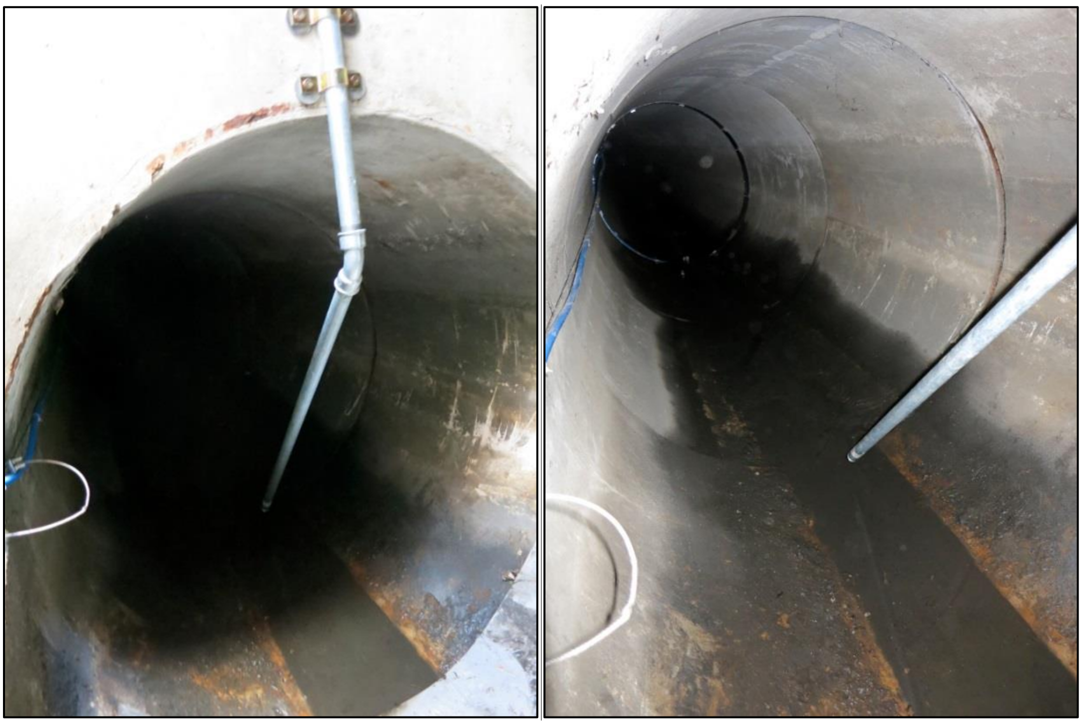

Figure 28: Steel pipe that leads sampler tube into the sewer into the direction of flow.

Problems

Areal characteristics (size of catchment and/or sewer diameter) caused little events to be sampled. The sampling tube was clogged for a period of time right after installation for unknown reasons.

The main problem was the upstream pointing direction of the steel pipe and sampling tube. During many events, this caused rapid blockage of the sampling tube due to litter that got stuck (Figure 29) .

Furthermore the end of the sampling tube was not visible from above.

Figure 29: Blockage of the sampling tube.

Modifications

The steel pipe bending inwards in flow direction was changed with a construction that leads the sampling tube inward at first followed by a curve to lead it back (Figure 30). This had the big advantaged that the sampling tube was now pointing downstream which prevented blockage and decreased the pressure on the construction during (extreme) events. Furthermore the end of the sampler tube was now visible from above.

The steel plate was lifted 5,5 cm at the bottom and installed slightly more downstream. The upper part changed to 18 cm (measuring from upper part of steel plate to bottom of dropping part).

Figure 30: Situation after modifications, steel plate is lifted and sampling tube pointing in downstream direction.

Conclusions and recommendations
All that is written above in this appendix, is concluded here. Note that these conclusions might be only valid for conditions during this study.

- When installing a steel plate for backwater conditions, leave clearance at lower part for passage of sediments and litter.
- Concerning sampling tube installation, go with the flow to prevent blockage and reduce forces working on installation.
- When possible, install the sampling tube and steel plate so, that access for periodic cleaning and visual check-ups are granted.
- An egg-shape sewer provides good sampling conditions due to relative rapid rising of water level at beginning of events.
- Bigger (catchment) is better – a good correlation between catchment and sewer size provide good rising of water levels during events, allowing for good sampling conditions, the same goes for the percentage of impervious surface.

Appendix 3, Rainfall analysis for choice of sampling strategy

By analysing rain event runoff data for Berlin (Table 8), the length of the sampling programme and sample distribution was determined. Discharge data from 2013, measured in a rainwater sewer the area called 'Pücklerteich', Berlin was used for this analysis. 100 rain identical rain events were identified. Chosen was a sampler programme of 4 hours which based on the analysis, allowed sampling of shorter events, longer events, and events with various intensities. To collect first flush samples, bottles 1 – 6 (samples 1 – 24) were each filled in a period of 20 minutes (one sample every 5 minutes), in bottles 7 – 8 ,one sample was collected every 15 minutes, summing up to 4 hour of total programme length.

Table 8: Rainfall analysis Pücklerteich, to determine sampling programme length.

Possible program length (hours)	Events totally sampled	Events not totally sampled		
	100%	**>75%**	**>50%**	**<50%**
1	3	7	16	74
2	15	24	18	43
3	27	19	16	38
4	38	21	15	26
5	51	13	16	20

By choosing a total programme length of 4 hours, all rain events that have a duration of 4 hours or less are sampled completely. Events longer than 4 hours were not sampled completely. As can be seen in the table above, 38 rain events can be sampled completely in 4 hours. 21 events will be sampled for 75%, summing up to 59 events that can be sampled >75%. Choosing a shorter programme length means collecting more samples in a shorter period which decreases the discharge that one sample has to represent in the volume proportional composite sample. This increases accuracy. The downside of this programme length is that only a very small number of events will be sampled completely (e.g. event duration is > 1 hour). On the other side, with a longer programme length of 5 hours, sampling will be more distributed. The individual samples that make up the volume proportional composite sample will thus have to represent a larger time period.

Appendix 4, Complete overview of target pollutants

The target pollutants on which samples were analysed, are listed in Table 9 below.

Table 9: Complete overview of target pollutants.

Non-Pollutants	**Pesticides / Biocides**
BSB5	Carbendazim
CSB	Cybutryn
ortho-Phosphat	Diazinon
Phosphor gesamt	Diuron
Suspended substances	Tebuconazol
Metals (heavy)	2,4-D (2,4-Dichlorophenoxyacetic acid)
Arsenic	2,6-Dichlorbenzamid
Lead	AMPA (Metabolit from Glyphosat)
Cadmium	Isoproturon
Chrom	Mecoprop
Copper	Terbutryn
Nickel	**Industrial chemicals**
Titan	Benzothiazol
Vanadium	Benzotriazol
Zinc	OHBT (2-Hydroxybenzothiazol)
Nonylphenol	Tolyltriazole (Summe 4-/5-Tolytriazol)
2-Phenylphenol	PFOA
4-tert-Octylphenol	PFOS
4-tert-Butylphenol	Phenylsulfonylsarcosin
Bisphenol F	**Fuel addatives**
Bisphenol A	MTBE (2-Methoxy-2-methylpropan)
Tracers	**PAH**
Caffeine	Naphthalin
Acesulfam	Acenaphthylen
Carbamazepin	Acenaphthen
Flame retardant	Fluoren
TnBP (Tri-n-butylphosphat	Phenanthren
TiBP (Tri-iso-butylphosphat)	Anthracen
TCEP Tris(2-chloroethyl) phosphat	Fluoranthen
TCEP Tris(2-chloro-1-methylethyl) phosphat	Pyren
TDCP Tris(1,3-dichloro-2-propyl) phosphat	Benzo[a]anthracen
TBEP Tris(2-butoxyethyl)phosphat	Chrysen
Phthalat	Benzo[b]fluoranthen
Benzylbutylphthalat	Benzo[k]fluoranthen
Dibutylphthalat	Benzo[a]pyren
Diethylphthalat	Dibenz[a,h]anthracen
Dimethylphthalat	Benzo[g,h,i]perylen
Dioctylphthalat	Indeno[1,2,3-c,d]pyren
Diethylhexylphthalat	
Di-iso-decylphthalat	

Appendix 5, Priority substances within the WFD

The full list of priority substacnes within the water framework directive, is presented in Table 10, below.

Table 10: List of priority substances within the water framework directive.

Number	CAS number [1]	EU number [2]	Name of priority substance [3]	Identified as priority hazardous substance
(1)	15972-60-8	240-110-8	Alachlor	
(2)	120-12-7	204-371-1	Anthracene	X
(3)	1912-24-9	217-617-8	Atrazine	
(4)	71-43-2	200-753-7	Benzene	
(5)	not applicable	not applicable	Brominated diphenylethers	X[4]
(6)	7440-43-9	231-152-8	Cadmium and its compounds	X
(7)	85535-84-8	287-476-5	Chloroalkanes, C 10-13	X
(8)	470-90-6	207-432-0	Chlorfenvinphos	
(9)	2921-88-2	220-864-4	Chlorpyrifos (Chlorpyrifos-ethyl)	
(10)	107-06-2	203-458-1	1,2-dichloroethane	
(11)	75-09-2	200-838-9	Dichloromethane	
(12)	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)	X
(13)	330-54-1	206-354-4	Diuron	
(14)	115-29-7	204-079-4	Endosulfan	X
(15)	206-44-0	205-912-4	Fluoranthene	
(16)	118-74-1	204-273-9	Hexachlorobenzene	X
(17)	87-68-3	201-765-5	Hexachlorobutadiene	X
(18)	608-73-1	210-168-9	Hexachlorocyclohexane	X
(19)	34123-59-6	251-835-4	251-835-4	
(20)	7439-92-1	231-100-4	Lead and its compounds	
(21)	7439-97-6	231-106-7	Mercury and its compounds	X
(22)	91-20-3	202-049-5	Naphthalene	
(23)	7440-02-0	231-111-4	Nickel and its compounds	
(24)	not applicable	not applicable	Nonylphenols	X[5]
(25)	not applicable	not applicable	Octylphenols[6]	
(26)	608-93-5	210-172-0	Pentachlorobenzene	X

(27)	87-86-5	201-778-6	Pentachlorophenol	
(28)	not applicable	not applicable	Polyaromatic hydrocarbons (PAH)[7]	X
(29)	122-34-9	204-535-2	Simazine	
(30)	not applicable	not applicable	Tributyltin compounds	X[8]
(31)	12002-48-1	234-413-4	Trichlorobenzenes	
(32)	67-66-3	200-663-8	Trichloromethane (chloroform)	
(33)	1582-09-8	216-428-8	Trifluralin	X
(34)	115-32-2	204-082-0	Dicofol	X
(35)	1763-23-1	217-179-8	Perfluorooctane sulfonic acid and its	X
(36)	124495-18-7	not applicable	Quinoxyfen	X
(37)	not applicable	not applicable	Dioxins and dioxin-like compounds	X[9]
(38)	74070-46-5	277-704-1	Aclonifen	
(39)	42576-02-3	255-894-7	Bifenox	
(40)	28159-98-0	248-872-3	Cybutryne	
(41)	52315-07-8	257-842-9	Cypermethrin[10]	
(42)	62-73-7	200-547-7	Dichlorvos	
(43)	not applicable	not applicable	Hexabromocyclododecanes (HBCDD)	X[11]
(44)	76-44-8/	200-962-3/	Heptachlor and heptachlor epoxide	X
(45)	886-50-0	212-950-5	Terbutryn	

(1) CAS: Chemical Abstracts Service.
(2) EU-number: European Inventory of Existing Commercial Substances (EINECS) or European List of Notified Chemical Substances (ELINCS)
(3) Where groups of substances have been selected, unless explicitly noted, typical individual representatives are defined in the context of the setting of environmental quality standards.
(4) Only Tetra, Penta, Hexa and Heptabromodiphenylether (CAS -numbers 40088-47-9, 32534-81-9, 36483-60-0, 68928-80-3, respectively).
(5) Nonylphenol (CAS 25154-52-3, EU 246-672-0) including isomers 4-nonylphenol (CAS 104-40-5, EU 203-199-4) and 4- nonylphenol (branched) (CAS 84852-15-3, EU 284-325-5).
(6) Octylphenol (CAS 1806-26-4, EU 217-302-5) including isomer 4-(1,1',3,3'-tetramethylbutyl)-phenol (CAS 140-66-9, EU 205-426-2).
(7) Including benzo(a)pyrene (CAS 50-32-8, EU 200-028-5), benzo(b)fluoranthene (CAS 205-99-2, EU 205-911-9), benzo(g,h,i)perylene (CAS 191-24-2, EU 205-883-8), benzo(k)fluoranthene (CAS 207-08-9, EU 205-916-6), indeno(1,2,3-cd)pyrene (CAS 193-39-5, EU 205-893-2) and excluding anthracene, fluoranthene and naphthalene, which are listed separately.
(8) Including tributyltin-cation (CAS 36643-28-4).
(9) This refers to the following compounds: 7 polychlorinated dibenzo-p-dioxins (PCDDs): 2,3,7,8-T4CDD (CAS 1746-01-6), 1,2,3,7,8-P5CDD (CAS 40321-76-4), 1,2,3,4,7,8- H6CDD (CAS 39227-28-6), 1,2,3,6,7,8-H6CDD (CAS 57653-85-7), 1,2,3,7,8,9-H6CDD (CAS 19408-74-3), 1,2,3,4,6,7,8-H7CDD (CAS 35822-46-9), 1,2,3,4,6,7,8,9-O8CDD (CAS 3268-87-9)
10 polychlorinated dibenzofurans (PCDFs): 2,3,7,8-T4CDF (CAS 51207-31-9), 1,2,3,7,8-P5CDF (CAS 57117-41-6), 2,3,4,7,8-P5CDF (CAS 57117-31-4), 1,2,3,4,7,8-H6CDF (CAS 70648-26-9), 1,2,3,6,7,8-H6CDF (CAS 57117-44-9), 1,2,3,7,8,9-H6CDF (CAS 72918-
21-9), 2,3,4,6,7,8-H6CDF (CAS 60851-34-5), 1,2,3,4,6,7,8-H7CDF (CAS 67562-39-4), 1,2,3,4,7,8,9-H7CDF (CAS 55673-89-7),
1,2,3,4,6,7,8,9-O8CDF (CAS 39001-02-0) 12 dioxin-like polychlorinated biphenyls (PCB-DL): 3,3',4,4'-T4CB (PCB 77, CAS 32598-13-3), 3,3',4',5-T4CB (PCB 81, CAS 70362-50-4), 2,3,3',4,4'-P5CB (PCB 105, CAS 32598-14-4), 2,3,4,4',5-P5CB (PCB 114, CAS 74472-37-0), 2,3',4,4',5-P5CB (PCB 118, CAS 31508-00-6), 2,3',4,4',5'-P5CB (PCB 123, CAS 65510-44-3), 3,3',4,4',5-P5CB (PCB 126, CAS 57465-28-8), 2,3,3',4,4',5-H6CB (PCB 156, CAS 38380-08-4), 2,3,3',4,4',5'-H6CB (PCB 157, CAS 69782-90-7), 2,3',4,4',5,5'-H6CB (PCB 167, CAS 52663-72-6), 3,3',4,4',5,5'-H6CB (PCB 169, CAS 32774-16-6), 2,3,3',4,4',5,5'-H7CB (PCB 189, CAS 39635-31-9).
(10) CAS 52315-07-8 refers to an isomer mixture of cypermethrin, alpha-cypermethrin (CAS 67375-30-8), beta-cypermethrin (CAS 65731-84-2), theta-cypermethrin (CAS 71697-59-1) and zeta-cypermethrin (52315-07-8).
(11) This refers to 1,3,5,7,9,11-Hexabromocyclododecane (CAS 25637-99-4), 1,2,5,6,9,10-Hexabromocyclododecane (CAS 3194-55-6), α-Hexabromocyclododecane (CAS 134237-50-6), β-Hexabromocyclododecane (CAS 134237-51-7) and γ Hexabromocyclododecane (CAS 134237-52-8).'.

Appendix 6, Characteristics of sampled and analysed events

This section describes the characteristics (Table 11, next page) of the events that were sampled and analysed during this study.

Below in Figure 31, an example is given of how events were characterized; characteristics of a typical rain event are shown. All events are shown in table format on the next page.

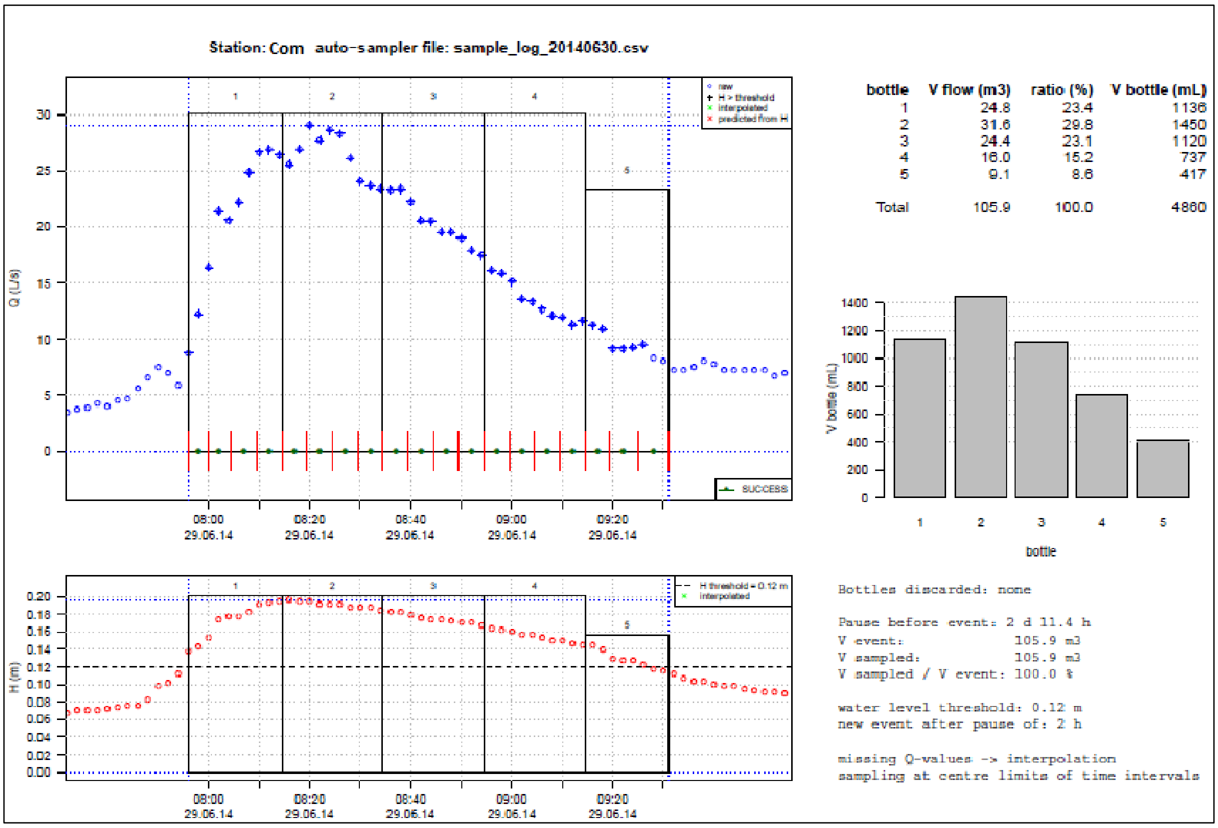

Figure 31: Example of even characterization.

In Table 11, shown below the characteristics of all rain events that were analysed during this study are listed.

Data on rain depth and max intensity are recordings of rainwater measuring stations closest to the measuring locations named this data was obtained from Berliner Wasser Betriebe. V Sampled stands for the amount of discharge during the sampling period (max. 4h). An event is defined as the time between > 10 and <10 cm of water level in the sewer.

Table 11: Characteristics of sampled events.

Location	Event number	Date of event(s)	Event duration [hh:mm]	Rain depth[mm]	Max. Intensity[mm/h]	V Sampled[m³]	% Sampled of total event
New	1	11.05.2014	04:25	5,1	0,6	154	ca 80
	2	12.05.2014	02:45	2,2	0,3	37	ca 80
	3	18.05.2014	07:25	11,2	0,6	125	46
	4	27.05.2014	08:30	7	0,7	83	8
	5	05.06.2014	00:45	3,1	1	139	96
	6	24.06.2014	00:55	1,9	0,6	108	69
	7	08.07.2014	07:50	1,4	1,4	474	100
	8	09.07.2014	06:00	11	1,2	324	91
Old	1	09.05.2014	11:50	3,5	0,2	169	97
	2	12.05.2014	04:05	1,7	0,1	106	100
	3	28.05.2014	2d 20:10	26,6	5,8	145	9
	4	25.06.2014	17:45	25,9	0,8	947	45
	5	07.07.2014	01:30	1,8	0,5	167	100
	6	08.07.2014	07:50	13,7	2,3	914	100
	7	09.07.2014	06:00	11	2,5	861	100
Ofh	1	11.05.2014	04:20	5,4	0,7	6	100
	2	18.05.2013	07:15	13,6	1	22	100
	3	27.05.2014	1d 13:10	41,3	1,1	70	100
	4	08.07.2014	02:15	1,3	3,23	48	100
	5	11.07.2014	02:00	2,4	1,20	106	100
	6	13.07.2014	03:00	4,6	1,67	38	100
Com	1	17.05.2014	04:25	0,8	0,2	56	100
	2	18.05.2014	07:25	11,2	0,6	1072	ca. 40
	3	27.05.2014	08:30	7	0,7	641	9
	4	05.06.2014	00:45	3,1	1	637	0,92
	5	11.06.2014	04:40	1,9	0,2	272	100
	6	29.06.2014	01:25	0,7	0,3	106	100
	7	30.06.2014	00:45	2,4	0,9	291	ca. 90
	8	07.07.2014	00:55	1,5	0,2	194	100
	9	08.07.2014	07:50	1,4	1,4	1612	70
	10	09.07.2014	06:00	11	2,6	2118	95
Str	1	25.06.2014	16:40	19,6	1,8	240	100
	2	08.07.2014	03:00	3	1,4	8	100
	3	08.07.2014	03:00	12,3	4,0	62	100
	4	09.07.2014	22:04	7	5,8	233	99

Appendix 7, Full results: outcomes all sampled events

In this appendix the full outcomes for all sampled events are listed in the tables below. All concentrations are given in µg/l. Started is with Table 12 (new), Table 13 (Old),

Table 14 (Ofh), Table 15 (Str) and finally

Table 16 (Str).

Table 12: All laboratory outcomes measuring location 'New buildings'.

NEW	Unit	11.05.2014	12.05.2014	18.05.2014	27.05.2014	05.06.2014	24.06.2014	08.07.2014	09.07.2014
Cadmium	µg/l	<2,5	<2,5	<1,5	<1,5	<1,5	<1,5	<1,5	<1,5
Nickel	µg/l	<1,5	<1,5	<5	<5	<5	12	<5	<5
Zinc	µg/l	100	81	62	130	160	190	150	110
Copper	µg/l	46	46	25	60	53	78	78	53
Lead	µg/l	2	2	<7,5	<7,5	<7,5	17	18	<7,5
TCPP	µg/l	0,25	0,84	0,64	0,29	x	0,59	x	<0,05
Mecoprop	µg/l	0,36	0,48	0,68	3,4	x	0,53	1,1	0,93
Diuron	µg/l	<0,03	<0,03	<0,03	<0,03	x	<0,03	<0,03	x
Glyphosphat	µg/l	0,02	0,02	0,03	0,03	x	x	x	x
Isoproturon	µg/l	<0,03	<0,03	<0,03	<0,03	x	<0,03	<0,03	x
OHBT	µg/l	0,26	0,3	0,27	0,49	x	0,3	x	x
PFOA	µg/l	<0,01	<0,01	<0,01	<0,03	x	<0,03	x	<0,03
PFOS	µg/l	<0,05	<0,05	<0,05	<0,03	x	<0,05	x	<0,05
PAH (All)	µg/l	<0,050	<0,050	0,25	1,8	x	0,85	x	x
Di-iso-decylphthalat	µg/l	1,1	1,3	1,2	1,2	x	1,8	x	2,3
Diethylhexylphthalat (DEHP)	µg/l	<0,30	<0,30	<0,30	<0,30	x	<0,30	x	<0,30
Nonylphenol	µg/l	1,6	4,3	1,1	14	x	2,4	x	x

Table 13: All laboratory outcomes measuring location 'Old buildings'.

OLD	Unit	09.05.2014	12.05.2014	25.05.2014	25.06.2014	07.07.2014	08.07.2014	09.07.2014
Cadmium	µg/l	<2,5	<2,5	<1,5	<1,5	<1,5	<1,5	<1,5
Nickel	µg/l	<1,5	<1,5	<5	<5	<5	<5	<5
Zinc	µg/l	1.100	730	680	500	1.700	660	570
Copper	µg/l	40	24	28	27	65	46	60
Lead	µg/l	25	17	28	19	72	39	<7,5
TCPP	µg/l	0,31	0,26	<0,05	1,5	x	x	<0,05
Mecoprop	µg/l	0,73	0,28	0,36	0,33	1,8	2	1,6
Diuron	µg/l	0,11	0,17	0,24	0,41	<0,03	0,59	x
Glyphosphat	µg/l	0,14	0,1	0,05	x	x	x	x
Isoproturon	µg/l	<0,03	<0,03	<0,03	<0,03	<0,03	<0,03	x
OHBT	µg/l	0,27	0,36	0,44	0,44	x	x	x
PFOA	µg/l	0,01	<0,01	<0,03	<0,03	x	x	<0,03
PFOS	µg/l	<0,05	<0,05	<0,03	<0,05	x	x	<0,05
PAH (All)	µg/l	x	0,078	0,61	<0,050	1,9	x	x
Di-iso-decylphthalat	µg/l	1,7	> 2,0 (14.9) <5,0 3.4)	1,5	<10 (3.2)	x	2,9	3,4
Diethylhexylphthalat (DEHP)	µg/l	1,1	11	<0,20	0,7	1,2	0,94	0,68
Nonylphenol	µg/l	3,7	3,6	0,6	x	x	x	x

Table 14: All laboratory outcomes measuring location 'One family homes'.

OFH	Unit	11.05.2014	18.05.2014	27.05.2014	08.07.2014	11.07.2014	13.07.2014
Cadmium	µg/l	<2,5	<1,5	<1,5	<1,5	<1,5	<1,5
Nickel	µg/l	<1,5	<5	<5	<5	<5	<5
Zinc	µg/l	220	130	360	180	210	240
Copper	µg/l	81	81	220	84	82	40
Lead	µg/l	2	<7,5	28	<7,5	28	<7,5
TCPP	µg/l	0,31	0,36	<0,05	x	x	x
Mecoprop	µg/l	0,13	0,35	0,16	1,2	x	x
Diuron	µg/l	0,05	0,15	0,12	0,16	x	x
Glyphosphat	µg/l	0,42	0,09	0,16	x	x	x
Isoproturon	µg/l	0,12	0,12	0,06	0,06	x	x
OHBT	µg/l	0,38	0,24	0,28	x	x	x
PFOA	µg/l	<0,01	<0,01	<0,03	x	x	x
PFOS	µg/l	<0,05	<0,05	<0,03	x	x	x
PAH (All)	µg/l	<0,050	0,16	<0,050	x	x	x
Di-iso-decylphthalat	µg/l	1,4	<5,0 (3.9)	0,93	1,7	x	3,7
Diethylhexyl phthalat (DEHP)	µg/l	0,39	1,8	<0,20	0,26	x	0,52
Nonylphenol	µg/l	5,7	7,7	0,05	x	x	x

Table 15: All laboratory outcomes measuring location 'Streets'.

STR	Unit	25.06.2014	08.07.2014	08.07.2014	09.07.2014
Cadmium	µg/l	<1,5	<1,5	<1,5	<1,5
Nickel	µg/l	<1,5	<1,5	<1,5	<1,5
Zinc	µg/l	320	380	410	750
Copper	µg/l	100	150	120	210
Lead	µg/l	31	36	43	<7,5
TCPP	µg/l	0,2	x	x	<0,05
Mecoprop	µg/l	<0,01	x	<0,01	<0,01
Diuron	µg/l	<0,03	x	<0,03	x
Glyphosphat	µg/l	x	x	x	x
Isoproturon	µg/l	<0,03	x	<0,03	x
OHBT	µg/l	0,81	x	x	x
PFOA	µg/l	<0,03	x	x	<0,03
PFOS	µg/l	<0,05	x	x	<0,05
PAH (All)	µg/l	2,8	x	x	x
Di-iso-decylphthalat	µg/l	8,6	x	x	x
Diethylhexylphthalat (DEHP)	µg/l	2	x	1,9	2,9
Nonylphenol	µg/l	0,1	x	x	x

Table 16: All laboratory outcomes measuring location ‘Commercial buildings’.

COM	Unit	17.05.2014	18.05.2014	27.05.2014	05.06.2014	11.06.2014	29.06.2014	30.06.2014	07.07.2014	08.07.2014	09.07.2014
Cadmium	µg/l	<1,5	<1,5	<1,5	<1,5	<1,5	<1,5	<1,5	<1,5	<1,5	3,1
Nickel	µg/l	<5	<5	<5	11	<5	<5	<5	<5	<5	21
Zinc	µg/l	670	140	1.100	2.100	1.000	730	1.200	1.700	2.200	10.000
Copper	µg/l	140	14	190	720	130	80	260	200	960	5.300
Lead	µg/l	45	<7,5	24	150	<7,5	<7,5	39	17	160	<7,5
TCPP	µg/l	0,48	0,37	0,35	0,34	0,21		0,47	x	x	0,29
Mecoprop	µg/l	0,18	<0,01	0,63	0,21	1	x	0,28	1,9	0,58	0,31
Diuron	µg/l	<0,03	<0,03	<0,03	<0,03	<0,03	x	<0,03	<0,03	0,08	x
Glyphosphat	µg/l	0,04	<0,02	0,06	0,04	0,04	x	x	x	x	x
Isoproturon	µg/l	<0,03	<0,03	<0,03	<0,03	<0,03	x	<0,03	<0,03	<0,03	x
OHBT	µg/l	0,39	0,04	0,58	0,28	0,48	x	x	x	x	x
PFOA	µg/l	0,02	<0,01	0,07	<0,03	0,05	x	0,04	x	x	<0,03
PFOS	µg/l	<0,05	<0,05	<0,03	<0,03	<0,03	x	<0,05	x	x	<0,05
PAH (All)	µg/l	0,58	<0,050	<0,050	1,9	0,31	x	0,46	x	x	x
Di-iso-decylphthalat	µg/l	> 20 (51)	>2 (6.7) <5,0 (3.7)	>2,0 (6.7)	<0,50	<10 (9.3)	x	x	x	x	x
Diethylhexyl phthalat (DEHP)	µg/l	> 2,0 (3.7)	2,2	0,31	0,92	0,54	x	1,6	1,4	1,4	4,7
Nonylphenol	µg/l	4,7	2,6	6,2	16	x	x	9,8	x	x	x

Appendix 8, Management of micropollutants

In this section various approaches to manage micropollutants are discussed, where possible, with their working effectiveness.

In the past, rainwater management infrastructure in urban areas was primarily designed for the collection and transport of rainwater runoff. Via sewers and surface water channels, the water is rapidly transported out of the area without harming the urban environment and its buildings (Sieker, 2003).

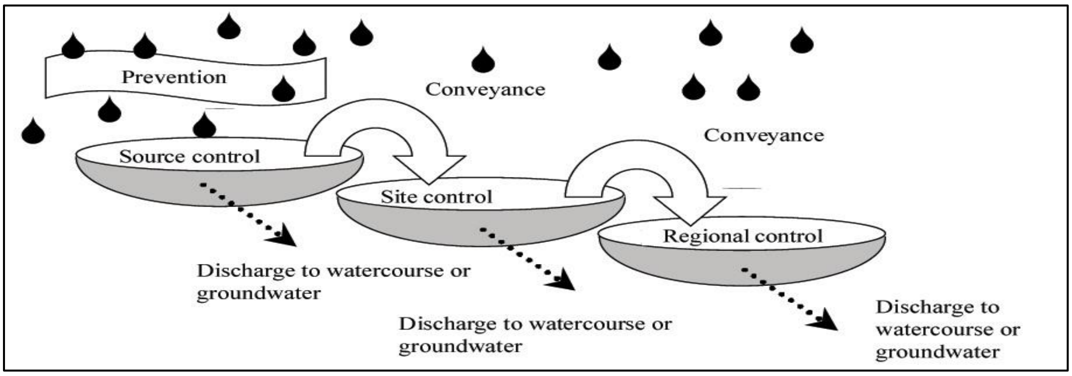

Figure 32: Different levels on which micropollutants can be decreased (Source: Cloudburst.ie).

The implementation of a sustainable storm water management concept can improve urban storm water management in many ways. In this concept, all measures should be integrated to enhance each other (Figure 32). This also means attending the source of the pollution and the path to receiving waters. Further objectives are to reduce surface runoff to a volume that is expected to be correspondent to that of a natural state of the catchment likewise the increase of groundwater recharge and evaporation (Keßler, 2014).

The fates of micropollutants that enter a sewer system mainly depend on the pollutants being dissolved or particle-bound. Displacement into the ground with infiltrating water can take place, or deposition with sediment and suspended matter (Zgheib, et al., 2011), therefore, characteristics of individual substances are studied and listed in appendix 9.

The various approaches for MP reduction include; 1) Avoidance by Legislation (e.g. banning of lead from gasoline), 2) (local) infiltration and de-sealing and 3) improvement of storm water treatment.

Existing technologies and concepts are described in more detail below, together with their reduction potential;

1) Avoidance

Legislation is an important source measure to avoid micropollutants entering rainwater runoff. Good examples are the phasing out of lead from gasoline in many developed countries by substituting, and the increased restriction of Roundup (containing Glyphosate and Mecroprop) use in the Netherlands.

Studies show positive effects of green infrastructure on the reduction of micropollutants in runoff. Reduction effects of 40% are reported for NO_2 and up to 60% for PM (particular matter) by applying green canyons along highways (Thomas, et al., 2012). The trapping of particles on tree leaves was also investigated by (Ottelé, et al., 2010). A difference amount of particles was found between a road sight (n=7000) and woodland location (n=3000).

2) Decentralized processes

Various decentralized processes can treat rainwater run-off. Concepts are available for rainwater running of from roofs, which can be used in buildings with large metal roofing surfaces (made of copper or zinc). These concepts mainly consist of multi stage filter systems, which can be installed in the sewer where rainwater from roofs is collected. Negative about these systems is mainly maintenance and operational costs.

Some specialized infiltration systems are used for road surface run-off since this contains a much higher share of particle-bonded pollutants in comparison to run-off from other surfaces (Hillenbrand, et al., 2007).

Vegetation roofs can prevent high discharge peaks by spreading out the amount of runoff over a longer period of time. This effect reduces the amount of mobilized sediments and thus pollutant load. However research showed the dieback of aquatic organisms due to herbicides applied in roofing materials to serve as root-penetration-protection (Sieker, et al., 2006). Green roofs also act as passive filter of airborne particulate matter. This type of roofs can maybe also decrease pollutant concentrations by biological activity.

Studies have estimated that green roofs can remove up to 0.2 kg of dust particles per year per square meter (Peck & Kuhn, 2008) (Doernach, 1979)found that climbing plants can filter out dust and pollutants.

Surfaces can be decoupled from the sewer system by de-sealing to allow direct rainwater infiltration, thus retaining the water in the local hydrological cycle. This reduces the concentrated load on sewers and receiving waters. For this, local soil conditions should allow infiltration of rainwater.

3) Improved treatment of rainwater run-off

Specialized infiltration systems are used for run-off from road surfaces since this contains a much higher share of particle-bonded pollutants in comparison to run-off from roofs. (Hillenbrand, et al., 2007)

Soil retention filters are used or sedimentation systems are proven to be very effective in decreasing MP concentrations (Kasting, 2004). The use of sack filters is being tested for purification as a multi-stage process with a filter basin which achieves extensive retention of particles and heavy metals through a combined sand/adsorbent layer (Hermann, 2005) and (Gretzschel, 2003).

Infiltration systems can be constructed in various ways, for maximum purification of rainwater runoff, retention and a secondary filter basin can be constructed to enhance both spatial and timely purification thru; separation of solids, adsorption, filter effect, biological breakdown processes (Janel, et al., 2013). Infiltration systems are effective filters, with typical efficiencies for suspended solids > 90% (CWP, 2007); (Hatt, et al., 2008) (Li & Davis, 2008). The removal of metals in infiltration system varies (50-99%) among different studies ((USEPA, 1999) (CWP, 2007).

Improving the sewer system so that the 'first-flush' does not discharge directly into open surface waters, but leads to a WWTP. Saget et al. have defined an first flush when 80% of the pollutant mass is transported in 30% of the total runoff volume (Saget, et al., 1995). Restrictions are that a connection between sewers must be possible, and WWTP capacity.

Conclusion

The following can be concluded from the section above; all pollutants can be reduce by legislation (a banned substance cannot pollute) however, legislation is limited by different social- economic factors.

Decentralized pre-treatment can be applied for all pollutants that runoff with rainwater, air deposited pollutants need to be targeted by vegetation infrastructure. The most important criteria for MP load reduction are deducted from MP characteristics (e.g. is the pollutant particle or non-particle bound). This results in the most effective way of treatment being infiltration and sedimentation.

Appendix 9, Characteristics of selected micropollutants

Table 17 shown below describes the characteristics of selected target substances. The Particulate phase (%) is the measured amount of a pollutants concentration adsorbed to particles. The K_{ow} (Octane – water partition coefficient), is an dimensionless number generally used as an indicator of the tendency of an pollutant to adsorb to soil. It is defined as the ratio of a pollutants concentration in a known volume of octane - water after equilibrium has been reached. A higher K_{ow} value indicates a higher non-polarity of the compound. K_{oc} Values are a measure for the pollutants tendency to be adsorbed to particles rather that remain dissolved in water. In general, strongly adsorbed molecules will not leach or move unless soil erodes.

Degradation of substances can be expressed using DT50 values. DT50 is a measure of the amount of time in the environment required for 50% of the pollutant to degrade. Water solubility and Mobility in the table partly correlate. They are derived from the specific characteristics described above.

Literature where listed values were obtained can be identified by the (number) behind values and the list of sources of the following page.

Table 17: Characteristics of selected most detrimental substances.

Group and substance	Particulate phase (%)	Log K_{OW}	Koc	DT50 (days)	Water solubility	Mobility
Heavy metals						
Cadmium	50 - 80 (7), 94 - 96 (8)	~	~	~	None (9)	Low
Nickel	50 - 80 (7)	-0,57 (21)	~	~	None (9)	Low
Zinc	50 -80 (7)	~	~	~	None	Low
Copper	73 (7)	0,44 (23)	~	7 - 10	Medium	Low
Lead	94 (7)	~	~	~	~	Low
Flame retardants						
TCPP	1,4 (14)	1,44 (3)	67 (13)	167 (14)	~	High
Pesticides						
Mecoprop	21	1,26 (1,4)	~	49	Easy (11)	High
Diuron	19	2,6 (16)	~	6 (16)	Easy (16)	High (16)
Glyphosphat	88,5 (18)	- 2,8 (17)	24 (19)	96,4 (17)	Difficult (17)	High
Isoproturon	~	2,5(22)	122 (21)	1650 (21)	~	High
Industrial Chemicals						
OHBT	~	1,81 (23)	~	13,7(23)	~	Medium
PFOA	~	~	3,7 (24)	130 (25)	Moderate	Medium
PFOS	~	2,57 (25)	4,2 (24)	7300 (25)	~	Low
PAH (gesamt)	>80 (7)	~	~	~	Difficult (9)	Low
Phthalate						
Di-iso-decylphtalat	71 (12)	1,6 (6)	~	-11 (11)	Difficult (12)	Low
Diethylhexylphthalat (DEHP)	~	4,89 (26)	4-5 (26)	~	Low	Low
Alkyphenol						
Nonylphenol	~	5,76 (2)	~	2,5 (9)	Easy (10)	Medium

1) (Tomlin, 1997)
2) (ECHA (European Chemicals Angency), 2012)
3) (Federal Institute for Occupational Safety and Health 2008)
4) (Minnesota Department of Health 2013)
5) (National Library of Medicine, 2014)
6) (Staples, et al., 1997)
7) (Gasperi, et al., 2013)
8) (Mouwerik, et al. 1997)
9) (Hillenbrand, et al., 2009)
10) (National Institute of Technology and Evaluation (NITE), 2010)
11) (University of California, 2008)
12) (NCBI, 2012)
13) (NCBI, 2012)
14) (Organization for Applied Scientific Research (TNO), 2008)
15) (Schult, 2012)
16) (Stasinakis, et al., 2007)
17) (Schuette, 1998)
18) (Aparicio, et al. 2013)
19) (Anon., 2010)
20) (Ecker, 2003)
21) (Zhejiang Rayfull Chemicals, 2009)
22) (Kova lczuk, et al., 2008)
23) (AERU, 2004)
24) (Zareitalabad, et al., 2013)
25) (Russell, 2009)
26) (Department of Ecology, 2011)

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