Stormwater treatment – Sorption of organic biocides from paints and renders

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Water and Environmental Engineering
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by

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Preface

This master thesis has been performed at Water and Environmental Engineering at the Department of Chemical Engineering in collaboration with the Department of Environmental Science at Aarhus University in Roskilde and Nordvästra Skånes Vatten och Avlopp.

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Abstract

In recent years, the fact that stormwater is not as clean as previously assumed have been addressed. A variety of chemicals have been pointed out as more problematic than others. This report will focus on organic biocides found in paints, renders and flat roofs in an urban milieu. It will aim to assess sorption as a local treatment method and to develop and test a model for source identification. As a way of reducing analysis costs Disperse Black 2, an azo-dye, with similar physiochemical properties as the biocides which can be detected using a spectrophotometer, was used as a substitute. Adsorption batch tests were carried out using powdered activated carbon (PAC) and vermiculite. Adsorption isotherms were analyzed to establish adsorption mechanisms and the general adsorption efficiency was assessed both for the substitute and for the biocides. PAC was found to efficiently remove Disperse Black 2 (94% at 0.24 g PAC L^{-1}) as well as the biocides (>99% at 0.24 g PAC L^{-1}). The vermiculite had a lower efficiency for both Disperse Black 2 (19% at 0.24 g vermiculite L^{-1}) and the biocides (83-91% at 0.3 g vermiculite L^{-1}) but is a cheaper material to use.

Keywords: organic biocides, stormwater, sorption, PAC, vermiculite
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1 Introduction

1.1 Background
Clean water is an essential part of life on earth. Without it, the large biodiversity we know and cherish would not exist, or would at least look entirely different (Hammer and Hammer, 2012). Not only would the ecosystems suffer but the success story that is humanity would most likely not have unraveled the way it has without the access to clean water.

In prehistoric time rivers and lakes were the main source of fresh water and dwellings would be placed in connection with these surface waters. With time, people developed ways to transport water in aqueducts, channels and pipes and to access new sources by digging and drilling wells. These methods meant that new areas of land could be inhabited and the villages grew to cities (Weismann, 2007). There was just one problem with these expansions – how to handle the increase of waste produced?

The first solution was to flush the waste and wastewater out into the freshwater source or let it infiltrate down to the groundwater table. This is a relatively good solution when the amounts of waste and wastewater are small. But with increasing populations in combination with increasing industrialization and waterborne sewages (they were introduced together with indoor plumbing and flush toilets during the late 1800’s and early 1900’s) the amount and the properties of the waste changed. Before, the household waste was thrown onto the streets and fecal matter was disposed in dry toilets and cesspools. The sewage systems removed the imminent risk of diseases spreading in the cities, but brought a new problem. The surface waters were now subject to direct discharge of untreated wastewater, the same waters that were used as freshwater sources. In order to remove large particulate matter sedimentation tanks were introduced. However these only remove about 50% of the organic matter present in the water. Secondary treatment steps, consisting of trickling filters where the water infiltrates through gravel beds removing the dissolved organic matter, were not introduced until 1910 (Hammer and Hammer, 2012). In 1914 treatment with activated sludge was presented by Edward Ardern and William T. Lockett in the paper "Experiments on the Oxidation of Sewage Without the Aid of Filters" and is to date the most commonly used biological treatment method (Bengtson, 2013). Later, the treatment methods were developed and more steps introduced in order to remove nutrients (i.e. nitrogen and phosphorus), heavy metals, and pathogens (Hammer and Hammer, 2012).

Today, the municipal wastewater treatment facilities are taking care of large amounts of sewage water (originating from households, industries, etc.) and rainwater runoff (stormwater) in combined and separate systems. The first systems were combined so that both sewage water and stormwater were carried in the same pipes. This is still the case in many older cities and city centers. The modern practice is to separate the two streams in order to minimize fluctuations in the treatment plants and to minimize the need for combined sewage overflows (CSOs) where untreated water would bypass the treatment plant and be released directly to receiving waters (the recipients) (Hammer and Hammer, 2012).
Stormwater has, until very recently, been seen as more or less clean and the handling of it has been based on this assumption. The practice has been, and in most countries still is, to infiltrate or release the water directly to a recipient (Bester et al., 2011) with only the occasional stormwater retention pond or other structures built to prevent stormwater peaks to erode river banks and flood water courses. With the changing view on clean water as an endless resource, the idea of treating stormwater from agriculture, road networks and other urban areas started to form. As a first measure new retention ponds and wetlands were introduced which were facilitated to reduce nutrient and heavy metal loads through sedimentation and biological treatment before releasing the water to the recipients (Hammer and Hammer, 2012). This was done in order to reduce the eutrophication, a major issue in most recipients of agricultural runoff (Brönmark and Hansson, 2005).

In an urban environment precipitation will come in contact with various surfaces, such as roads, buildings and parking lots, which all are contaminated to different degrees. These contaminants will be dissolved or suspended in the water (Hammer and Hammer, 2012). Compounds found in stormwater include trace metals, nutrients, pathogens, polyaromatic hydrocarbons (PAHs), pesticides and biocides (Grebel et al., 2013).

Most water treatment research, and thus development, has been focusing on compounds with high abundance, such as nutrients, but in recent years it has become evident that compounds found at lower concentrations can cause severe problems. There has, for example, been an intensified research on how to remove medical residues in the wastewater treatment plants (Horsing et al., 2011) since they may cause hormonal disturbances in most aquatic organisms, among other unwanted effects, and will spread to both surface and groundwaters (Ternes et al., 2002).

One group of compounds that pose a significant risk to the aquatic biodiversity, but have been neglected in water treatment until very recently, is the biocides. Many of these have the same or similar effects as the herbicides used in agriculture but are mostly found in urban structures and building materials. Examples of sources are façades, roofs and gardens (Bollmann et al., 2014a). The fact that some biocides are used in gardens, e.g. on lawns and fruit trees, might prove a problem.

Only a few studies have been conducted on release, environmental fate and how to remove these biocides once they enter the watercourses. This thesis will focus on the organic biocides used in façades and roofs being released to stormwater and how to remove them before causing any harm.
1.2 Aim
The aim of this study was to assess sorption as a local treatment method of biocide contaminated stormwater originating from façades and flat roofs in the urban environment. In addition, a wish to develop and evaluate a method for the identification of housing areas acting as sources of biocides was expressed.

This gave rise to the following research questions:

- Is sorption a good method for removal of biocides originating from façades and roofs?
- What sorption materials are of interest?
- How does one test the efficiency of the sorption materials?
- Can a first suitability test of the sorption materials be made using an easily detected compound as substitute for the organic biocides?
- How is a potential urban source identified?
- On what level, within the stormwater system, would it be optimal to place a treatment facility?
2 Background to compounds, methods and mechanisms

This chapter aims to give the reader a short introduction of the compounds, methods and mechanisms discussed. The scope covers the present approach to stormwater treatment, the fields of application, release mechanisms and methods of removal in addition to the toxicity and ecological risks and effects of biocides. In addition, the organic biocides most commonly found in building materials are introduced to give a deeper understanding of the compounds and their area of use.

2.1 Stormwater treatment approaches

There are three main approaches when trying to reduce the amount of pollutants from urban areas reaching the recipients. The first is downstream removal, also known as end-of-pipe treatment. This is the classical approach where the water is transported to and treated at a wastewater treatment plant (U.S. Epa, 2013). This approach has a few flaws; not all polluted water will reach a treatment plant due to separate sewage systems, where stormwater is not at all or insufficiently treated, or due to release of water at CSOs during storm events (Hammer and Hammer, 2012).

The second is upstream removal, where the water is treated at or close to the source, minimizing the risks of losses directly to the environment. This approach makes it possible to design the treatment specifically to the compounds released and is known as best management practices (BMPs) (Eriksson et al., 2011). However, the solutions used here, such as swales, infiltration surfaces and retention ponds have a limited treatment range and lifespan why new, more specific methods are being developed.

The third, and perhaps the most important approach is source control where the use and releasing of the pollutant is restricted, through substitution, legislations or voluntary initiatives, preventing it from reaching harmful concentrations in the environment (Eriksson et al., 2011).

2.2 Present use of biocides

Pesticides and herbicides have been widely used over the years, as plant protection and to control the presence of pests and weeds in agriculture, horticulture and in urban areas (Eu-98/8/Ec, 1998). A group of compounds with similar properties but a different area of application is the biocides. According to the European definition (Eu-98/8/Ec, 1998) these compounds are used for non-plant protection, targeting fungi, algae and other microorganisms. However, since the desired effects of biocides are often found in herbicides and pesticides many of these compounds have double labeling and fields of application. Due to this vague distinction between groups it can be hard to establish the actual source when analyzing stormwater (Wittmer et al., 2010).

Biocides are found in a large variety of products but this study will focus on those found in building materials used in façades and roof coverings. In this category the biocides are most commonly found in materials such as paints, renders, woodworks, and bitumen sheets used on
flat roofs. In paints they prevent degradation both in the wet paint (in-can protection) and after application (dry-film protection). The reason for this addition is that the paint is susceptible to biological growth. When stored in cans there is a risk of bacterial contamination and both aerobic and anaerobic growth leading to changes in the physical properties of the product. When on the wall the coating will be subject to bacterial, fungal and algal growth causing discoloration and chipping of the paint (Contant et al., 2010).

Through studying the different species of algae and other phototrophs (organisms harvesting energy from sunlight) on painted surfaces in Latin America Gaylarde and Gaylarde (2000) could extrapolate the number of species in the world. They concluded that there is an estimate of \(4 \times 10^6\) species of phototrophs growing on painted surfaces throughout the world. This large biodiversity of algae, fungi and cyanobacteria calls for use of more than one chemical compound in order to control them. In paints and renders a mixture of 3 to 5 different biocides is usually used (Burkhardt et al., 2011).

### 2.3 General ecological risks and effects of biocides

When released into the environment there are a number of processes deciding the fate of the biocide. Either it is washed out with rain or enters the soil directly depending on where it is distributed; it can then reach surface or ground water if not degraded through different processes along its path (Figure 2.1) (Bollmann et al., 2014b).

![Diagram of urban stormwater biocides](image_url)

**Figure 2.1** The general sources, fates and sinks of biocides in urban stormwater (Bollmann et al. (2014b) with kind permission)

There are large environmental risks with biocides entering soils and surface waters without any treatment. The biocides will reach and act on the naturally occurring organisms in the
matrices. These effects can either be lethal or sublethal and if severe enough they will not
only affect the individual but be noticeable on population level and possibly on an ecosystem
level as well. Lethal effects will result in death, the cause can vary but the end result is the
same. Sublethal effects can take many forms and can be both acute and chronic. Acute effects
are a result of a single exposure over a short period of time (usually within 24 h). Chronic
effects are sublethal effects such as infertility, behavioral changes, and unsuccessful breeding
as a result of long-term exposure to a toxin (Walker et al., 2012).

Not only is dose and time of exposure important in assessing toxicity and effects. The
bioavailability, route of uptake and susceptibility is of major importance as well. It has been
established that aquatic ecosystems are generally more sensitive than their terrestrial
counterparts. The reason for this difference is thought to be the fact that aquatic organisms are
constantly exposed to the compounds via the media (water) and uptake occurs over gills and
through diffusion over membranes in addition to active uptake though the gastro-intestinal
tract. For terrestrial organisms, on the other hand, the main route of uptake is active uptake of
the compound via drinking and eating. Secondary routs include diffusion through skin or
lungs (Walker et al., 2012).

Chemicals acting as photosynthesis inhibitors (most algaecides) will mainly have direct
effects on the organisms dependent on photosynthesis as energy source (all phototrophs). But
when primary producers are affected negatively this will echo through the entire food chain.
Some compounds have stronger effects on the higher plants and some on the single cell algae.
This difference in susceptibility may cause paradigm shifts within water bodies turning clear
water lakes, dominated by higher plants, into an algae dominated water, or vice versa,
resulting in major habitat changes. If the number of planktonic algae decreases drastically
there will be a lack of food for the zooplankton and invertebrates causing these numbers to
decline. This decrease would affect the growth of fish and other species depending on these
organisms as a food source. An increase of algae would, on the other hand reduce visibility
and light penetration reducing the number of higher plants and visual hunters such as pike
(Walker et al., 2012).

2.4 Toxicity testing and predicted no effect concentrations (PNEC)
It is difficult to compare the toxicities of different compounds due to their different routes of
uptake, sites of action and effects, among other things. It can also be problematic to compare
the toxicity of a single compound but on different organisms. In order to enable this, a
standard method for ecotoxicity testing has been developed. These tests will give an
approximate dose with a toxic response of 50%. One of the most widely used concepts is the
Lethal Concentration 50% or LC50. This is the concentration of a toxin that will cause a lethal
outcome for 50% of the individuals of a population exposed to the chemical. Sometimes other
effects are assessed, such as reproduction or growth rather than lethality, and the term used is
then Effect Concentration or EC. Comparing EC50 or LC50-values for different compounds
tested on the same organism (Daphnia magna is commonly used) is a way to compare
toxicity. However, this does not give any information on toxicity in other organisms, trophic
interactions, or how ecosystems will be affected since the test is based on single species in-
laboratory experiments (Walker et al., 2012).
When looking at ecosystems, concentrations that would kill half a population is not something one would want. Instead, another term is used for these scenarios, the Predicted No Effect Concentration or PNEC. This is a concentration based on the fact that only concentrations low enough not to have any effect on the organisms in an ecosystem should be allowed. The PNEC is estimated using the LC$_{50}$ or EC$_{50}$ for the most sensitive organism tested in the lab and dividing this with a safety factor (usually 1000). This safety factor is used in order to compensate the uncertainties caused by extrapolating one-species laboratory test toxicity data to describe field toxicity for other species in a natural environment (Walker et al., 2012). In the case of the organic biocides assessed in this report the PNEC values are in the size of ng/L (Burkhardt et al., 2009).

2.5 Biocides in building materials

In the literature, four groups of organic biocides that are more commonly used in façade materials can be identified: isothiazolinones, triazines, carbamates, and phenylureas (Wittmer et al., 2010, Wittmer et al., 2011, Bester et al., 2011, Bester and Schaefer, 2009, Burkhardt et al., 2011, Styszko et al., 2014, Burkhardt et al., 2007, Coutu et al., 2012, Bollmann et al., 2014a). In roof coverings, such as bitumen sheets, one of the most common biocides is a Triazole, Mecoprop (Burkhardt et al., 2011, Bollmann et al., 2014b). These compounds will be described and discussed below.

Isothiazolinones

The isothiazolinones are a group of broad spectra biocides with antifungal and antibacterial properties. They are used by the industry in cooling water, pulp and paper water treatment, in storage tanks, as wood preserver and as antifouling agents. They are also used in household products as preservers in cosmetics, shampoos and paints (Wealth Ocean Inc., 2014).

Some of the more commonly used compounds in this group are Benzo-isothiazolinone (BIT), n-Octyl-isothiazolinone (OIT) and 4,5-dichloro-2-octyl-isothiazolinone (DCOIT) (Table 2.1) (Bester et al., 2011). DCOIT is found in antifouling paints used on ship hulls and other marine structures and is sold as sea-nine 211® (Price and Readman, 2013). OIT is found in wood preservatives, industrial setups and in household products. In USA it is found in a wide range of products such as carpets, vinyl floors, mattresses (foam and covers), pillows (foam, feather and down), textiles, leather preservers, polymer and rubber products (Cecbp, 2009). BIT is used in the industry where long-term preservation for bacterial control is required. Examples of these conditions are mineral processing and closed loop cooling systems (Williams, 2007).

Other substances in this group include 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT), 2-methyl-4-isothiazolin-3-one (MIT) (Williams, 2007) and methylisothiazolinone (MI)(Bollmann et al., 2014a).

The isothiazolinones are electrophiles and inhibit growth and metabolism through reacting with critical enzymes causing cell death. One group of enzymes that are affected is the dehydrogenases of which some are part of the tricarboxyl acid cycle and energy production. Most of these key enzymes are found in both aerobic and anaerobic microorganisms why the isothiazolinones are considered broad spectrum biocides. The inhibition of enzymes will lead
to inhibition of essential cell functions such as respiration and ATP production (production of energy). There are multiple routes of uptake into the cell. Some are fast and some are slower. DCOIT and CMIT are taken up rapidly causing inhibition within minutes while MIT will enter the cell through diffusion, a much slower process. Mere inhibition of important functions will, however not kill the cell but reduce growth and reproduction. Cell death will only occur if the microorganism is exposed to the compound for several hours (Williams, 2007). In addition these compounds are readily biodegraded (half-lives between 1 and 17 hours) and the toxicity of their metabolites is only approximately 4-5 orders of magnitude lower than the toxicity of the parent compound (Williams and Jacobson, 1999).

**Triazines**

The triazines are a group of chemicals that act on the photosystem of plants why it is only affecting photosynthesizing organisms. Members of this group are used in agriculture as herbicides controlling unwanted growth (e.g. atrazine). Two compounds that are more relevant in this case are terbutryn, and cybutryn (Table 2.1) (Price and Readman, 2013). Terbutryn have been used to control weeds in agriculture (as Igran 500 FW and Topogard 500 FW) (Brandhorst Dahao, 2006) as well as submerged and free-floating weeds and algae. Since 2003 the agricultural use is prohibited, but terbutryn is still allowed as biocide additive why it can be found in paints and renders. Due to this fact it is perfect to use as tracer element when looking at leachates from coatings (Burkhardt et al., 2011). Terbutryn will not affect soil communities but is relatively toxic to algae, fish and aquatic invertebrates and show tendencies to bio-concentrate. However, the mobility through most soils is relatively low and most of the compound will be adsorbed in the top 5-10 cm of the soil column (Brandhorst Dahao, 2006).

Cybutryn, commercially named Irgarol 1051, have been widely used as antifouling agent in paints used on hulls and other marine structures to prevent algal growth. This field of application opened up in 1989 when the use of tributyltin (TBT) was restricted by the European Community (Price and Readman, 2013). However, in later years many countries have been banning the use of Irgarol 1051 in marine environments due to its persistence in water (aquatic half-life of Irgarol 1051 is 100 days) (Thomas and Brooks, 2009). There is hardly any biodegradation occurring (see half-life) but the compound will be photodegraded when exposed to sunlight and the metabolite M1 is created. This metabolite is approximately 12 times less toxic but due to its higher persistence it is found in higher concentrations in nature. Although it has a lower toxicity than the mother compound it has been found to be more toxic than for example atrazine (Okamura et al., 2000). One effect of Irgarol 1051 exposure in marine environments is coral bleaching. This results in mass death of corals and coral reefs (Price and Readman, 2013).

**Carbamates**

The main use of carbamates is as insecticides in agriculture and horticulture but some of them are used as fungicides preventing molds to grow in and on different substrates. The general mode of action is inhibition of the enzyme acetylcholinesterase (Thomas and Brooks, 2009). The most commonly used fungicidal carbamate is iodocarb (IPBC) which is found in paints, textiles, paper coatings, plastics, adhesives and wood preservatives. It is a broad spectrum
fungicide but its exact mode of action is unknown. The general thought is that the toxic effect is caused by the iodine since elemental iodine will corrode membranes and denature proteins. Due to the physiochemical properties of the compound (Table 2.1) it is assumed to have relatively high mobility in soils why there could be a potential risk of groundwater contamination. However, IPCB is readily degraded both in terrestrial and aquatic environments. In water the compound is mainly hydrolyzed forming the metabolite PBC. In soils, the antimicrobial properties disables biodegradation and the main degradation process is thought to be biotransformation (Juergensen et al., 2000).

Another broad range fungicidal carbamate is carbendazim (Table 2.1). Carbendazim is used in agriculture to protect crops from fungal diseases, and as seed dressing. In forestry it is used as a wood preservative (Usaid, 2012) and is further used in building materials and façades (Bester et al., 2011, Burkhardt et al., 2011, Burkhardt et al., 2007, Wittmer et al., 2010). It is also the main metabolite of other biocides, e.g. biomyl. The compound interacts with the cell microtubules influencing cell division and is mainly toxic to fungi but has also been found toxic to e.g. earth worms. It is potentially harmful to aquatic organisms but due to its physiochemical properties it is strongly bound to the soil particles and will most likely be found in sediments if it reaches surface waters (Inchem, 1993).

**Phenylureas**
These compounds are represented by diuron and isoproturon (Table 2.1). Diuron is one of the main booster biocides used for antifouling in the world (Price and Readman, 2013) but was originally introduced as an herbicide and has been heavily used in agriculture. The chemical name for the compound is N-(3, 4-dichlorophenyl)-N. Diuron is a photosystem II inhibitor and will bind to certain proteins in the chloroplast membranes which will block electron transport between different binding sites. Due to this blockage the cell can’t fixate CO₂ resulting in reduced photosynthesis and production of ATP. This will lead to a lack of energy in plants and algae and prevent growth. The blockage of electron transport will also set of a chain reaction where free radicals are produced. These radicals will affect the abundance of chlorophyll and carotenoids, and cause the cell to loose water (Moncada, 2004). It has also been suggested that diuron is carcinogenic (Bester et al., 2011). The real issue with this compound (together with cybutryn) is that it is highly persistent in water. When originating from antifouling paints it can be transported long distances and effect the aquatic plant and algae community in large areas (Price and Readman, 2013). The low K_{oc} value of diuron indicates low sorption to soils and sediments and suggests that the compound is easily transported long distances causing problems in aquatic environments even when distributed on land. It will however bind to organic matter (Moncada, 2004).

Isoproturon is used to control annual grasses and broad-leaved plants in the cultivation of cereals (Who, 1996). It is also used as algaecide to preserve façades and building materials (Bollmann et al., 2014a). Due to its mobility in soils the compound is readily transported into surface and ground waters. The main degradations routes are hydrolysis and photochemical degradation. However both processes are slow and the compound have a half-life of about a month in temperate climates (Who, 1996).
Triazoles
Mecoprop or MCPP is a chlorophenoxy herbicide and was first introduced as weed control in agriculture in the 1960’s. Today it is mainly used in lawns (>97% of total yearly consumption in USA), golf courses (2%) and sports fields since it acts on broad-leafed plants and does not affect grass (U.S. Epa, 2007). It is also found in bitumen membranes used on flat roofs (Burkhardt et al., 2011). The compound interacts with the plant growth through increased cell-wall plasticity, biosynthesis of proteins and production of ethylene causing the cells to divide and grow at increased speed damaging the vascular tissues (U.S. Epa, 2007). In short the plant grows too fast and can’t support its own body, hence collapsing (Walker et al., 2012). The active substance MCPP-p is regarded as non-persistent in the environment due to its physiochemical properties (Table 2.1) and will easily move through soil and water due to low sorption rates to soil. Degradation of the compound depends on the environment. In aqueous solution it is photodegraded and in soils it can be biodegraded. Depending on the form of degradation the end product differs, main metabolites are 4-chloro-2-methylphenol, o-cresol, and carbon dioxide. These are thought to have less or the same toxicity as the mother compound (U.S. Epa, 2007).

Nanoparticles
In addition to the use of organic biocides there has been an increase in usage of inorganic biocides (Scown et al., 2010). Nanoparticles are generally defined as particles with a size ranging from 1 to 100 nm (Guo et al., 2013) and among the most common ones are nanosilver (NS), titanoxide (TiO₂) and carbon nanotubes. These are all used for their antimicrobial properties and can be found in a multitude of products. For example, the major sources for TiO₂ are cosmetics, paints, sprays, coatings, metals and plastics (Scown et al., 2010). For NS some sources are fabrics, swimming pools (Algedyn), plastics, coatings etc. (Nowack et al., 2011) but it is also used in medical care as wound dressing, antibacterial gels and as coatings on medical instruments (Guo et al., 2013).

Nanosilver has shown a great potential as an antibacterial compound acting on all types of bacteria, even those that are antibiotic-resistant. However, it is hard to provide a good environmental safety when using high concentrations of these nanoparticles in surface coatings. This is due to the reduced efficiency caused by aggregation and uncontrollable release of ions. The mechanism behind the bactericidal effects are not known and together with the general targets there are large risks of unwanted effects on non-target organisms (Guo et al., 2013). It would therefore be of interest to remove the nanosilver from wastewater and surface water; however this is not within the scope of this thesis.
Table 2.1 Physiochemical properties, mode of action and other information on the biocides most commonly found in building materials and façades

<table>
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<th>Group Name</th>
<th>Product Type &amp; Use</th>
<th>Non-target org. &amp; effects</th>
<th>Mode of action</th>
<th>Metabolism &amp; Metabolites</th>
<th>Chemical properties ¹</th>
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</tbody>
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| Benzisothiazolinone (BIT) 2634-33-5 | Herbicide/Algaecide² | Moderate to high toxicity in aquatic fauna² | Inhibition of vital enzymes³ | - | WS: 22.2 g L⁻¹  
Log K<sub>ow</sub>: 0.64  
Log K<sub>D</sub>: 1.538  
p<sub>vap</sub>: 2.6×10⁻⁵ mm Hg  
PNEC: - | Water: -  
Soil: - |
| Octylisothiazolinone (OIT) 26530-20-1 | Herbicide/Algaecide⁴ | Contact dermatitis and asthma⁴ | Inhibition of vital enzymes³ | - | WS: 309 mg L⁻¹  
Log K<sub>ow</sub>: 2.61  
Log K<sub>D</sub>: 2.926  
p<sub>vap</sub>: 2.0×10⁻⁴ mm Hg  
PNEC: 13 ng L⁻¹⁵ | Water: >30 days⁴  
Soil: immobile but microbial degradation after 120 days⁴ |
| Dichlorooctylisothiazolinon, SeaNine 211 (DCOIT) 64359-81-5 | Algaecide⁴ | Contact dermatitis and asthma⁴ | Inhibition of vital enzymes³ | N-octyl oxamic acid, 4,5 dichloro-thiazole and N-octyl carbamic acid⁶ | WS: 27 mg L⁻¹  
Log K<sub>ow</sub>: 3.59  
Log K<sub>D</sub>: 3.355  
p<sub>vap</sub>: 2.3×10⁻⁶ mmHg  
PNEC: 8 ng L⁻¹⁵ | Water: < 24 h⁶  
Soil: - |
| Triazines |
|-----------------|-------------|-----------------|-----------------|-----------------|
| **Terbutryn**  | **Herbicide/Algecide** | **Inhibition of Photosystem II** | **GS 28620** | **WS**: 42 mg L⁻¹  
| (TB) 886-50-0 | **Algae, fish and invertebrate** | | | **Log Kᵦ**: 3.77  
| | **Biocide additives** | | | **Log Kₒ**: 2.783 |
| | | | | **pᵥap**: 2.4×10⁻⁶ mm Hg |
| | | | | **PNEC**: 34 ng L⁻¹ |
| | | | | **Water**: 180-240 days  
| | | | | **Soil**: 380 days (sediment) |

| Cybutryn, Irgarol 1051 | **Algaecide** | **Coral bleaching** | **Inhibition of Photosystem II** | **M1(2-methylthio-4-tertbutylamino-6-s-triazine)** | **WS**: 20 mg L⁻¹  
| (IRG) 28159-98-0 | | | | | **Log Kᵦ**: 4.07  
| | | | | | **Log Kₒ**: 2.404  
| | | | | | **pᵥap**: 3.7×10⁻⁶ mm Hg  
| | | | | | **PNEC**: 1 ng L⁻¹  
| | | | | | **Water**: 100-250 days (sea water)  
<p>| | | | | | <strong>Soil</strong>: persistent in anaerobic sediments |</p>
<table>
<thead>
<tr>
<th>Group Name</th>
<th>Product Type &amp; Use</th>
<th>Non-target org. &amp; effects</th>
<th>Mode of action</th>
<th>Metabolism &amp; Metabolites</th>
<th>Chemical properties</th>
<th>Half-lives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbamates</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Carbendazim (CD) 10605-21-7</td>
<td>Fungicide¹¹</td>
<td>Toxic to earth worms¹¹</td>
<td>Inhibition of acetylcholinesterase¹²</td>
<td>Hydrolysis and biodegradation gives 2-aminobenzimidazole¹¹</td>
<td>WS: 3.1 g L⁻¹ Log Kᵦ: 1.55 Log Kᵦ: 2.584 pᵥap: 5.4×10⁻⁹ mm Hg PNEC: 34 ng L⁻¹⁵</td>
<td>Water: 2 months (aerobic) 25 months (anaerobic)¹¹ Soil: 3-12 months¹¹</td>
</tr>
<tr>
<td>Iodocarb (IPBC) 55406-53-6</td>
<td>Fungicide¹²</td>
<td>Wood preservative¹²</td>
<td>Inhibition of acetyl cholinesterase/iodine toxicity¹²</td>
<td>Metabolite: PBC¹³</td>
<td>WS: 436 mg L⁻¹ Log Kᵦ: 2.45 Log Kᵦ: 2.455 pᵥap: 4.6×10⁴ mm Hg PNEC: 26 ng L⁻¹⁵</td>
<td>Water: 139 days¹⁴ Soil: 2 h-8 days (aerobic)¹³</td>
</tr>
</tbody>
</table>
### Phenylureas

<table>
<thead>
<tr>
<th>Compound</th>
<th>Usage</th>
<th>Environmental Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diuron (DR)</strong> 330-54-1</td>
<td>Algaecide and herbicide</td>
<td>Inhibition of Photosystem II</td>
</tr>
<tr>
<td></td>
<td>Antifouling paints</td>
<td></td>
</tr>
<tr>
<td><strong>Isoproturon (IP)</strong> 34123-59-6</td>
<td>Algaecide and herbicide</td>
<td>Inhibition of Photosystem II</td>
</tr>
<tr>
<td></td>
<td>Control of annual grass and broad leaved plants</td>
<td></td>
</tr>
<tr>
<td>Group Name</td>
<td>Product Type &amp; Use</td>
<td>Non-target org. &amp; effects</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Triazoles</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Mecoprop (MCPP) 93-65-2 | Herbicide | Control of broad-leaved plants ¹⁶ | Non-target plants, Aquatic environments ¹⁶ | Increased cellular division and growth leading to collapse ¹⁶ | Aqueous photolysis ¹⁵ | WS: 471 mg L⁻¹  
Log K<sub>ow</sub>: 2.94  
Log K<sub>D</sub>: 1.686  
p<sub>vap</sub>: 4.6×10⁻⁴ mm Hg  
PNEC: - | Water: 4.9-7.2 days ¹⁶  
Soil: - |

WS = Water Solubility; K<sub>ow</sub> = octanol-water partitioning coefficient; K<sub>D</sub> = soil adsorption coefficient; p<sub>vap</sub> = vapor pressure; PNEC = Predicted No Effect Concentration

2.6 Release of biocides

When studying release of biocides from building materials it is actually desorption that is assessed. To describe these desorption rates and patterns of the organic biocides two main methods have been used, field studies and laboratory studies. Burkhardt et al. (2007) conducted a field study in an urban catchment area including residential and commercial buildings with render façades and flat roofs (none older than 8 years). Water was collected at certain nodes in the stormwater system. At each point an amount of water in proportion to the flow was collected and analyzed. The analysis showed that there were significant concentrations of most biocides in the stormwater system.

A few years later the same research team introduced gutters at the bottom of the façades of two buildings, one newly built and one 4 years old. This was done in order to be able to look at in-field desorption of the two biocides terbutryn and diuron. The results showed that the amount of terbutryn leaching from the new façade was between 100 and 800 μg L⁻¹, which are at least three orders of magnitude above the PNEC for aquatic environments. The levels of other compounds measured were approximately 1000 times higher in runoff from the new façade compared to the runoff from the older building (Burkhardt et al., 2011).

In addition to the field studies they also executed laboratory experiments where panels were covered with render to simulate a standard façade. Four biocides (diuron, terbutryn, Irgarol1051 and carbendazim) were added to the render (1.5 g/m²) and the panels were subjected to water spraying over the surface. This simulated rain corresponded to 6 years of rainfall (6,800 mm) and was distributed over 80 days. Sampling of the runoff was done on both entire “rain” events and time dependent over single events. When analyzing the results they found that the concentrations of biocides in the runoff decreased with between one and two orders of magnitude from day one and day 80. Not only did the concentration vary over the 80 days but within each individual runoff event suggesting that even short rain events would contribute to pollution of the surface waters (Burkhardt et al., 2011).

Another laboratory test was conducted by Styszko et al. (2014) in order to determine the partitioning of biocides between renders and rainwater at equilibrium and if the amount of polymer in the render affect the partitioning constant. The test were conducted as batch tests where the biocides were mixed with render and dried, then pulverized and put in contact with water until equilibrium was reached. In general they found that desorption equilibria differ between biocides and that increasing the polymer content would be a possible measure to reduce desorption of some compounds (e.g. iodicarb and carbendazim).
2.7 Methods of removal
When looking at possible ways of removing the biocides from the water courses there are a number of possible and potent methods that could be used. Some, like ozone and UV treatment, are advanced, energy craving and high maintenance (Hammer and Hammer, 2012). These methods are therefore not appropriate for treatment of relatively small amounts of stormwater and will not be discussed here. Other methods that would be more plausible to use are biological degradation and sorption. These methods need no energy input and would be possible to implement in existing stormwater systems.

2.7.1 Biological degradation
In general, removal is microorganisms degrading compounds and extracting energy. This mechanism is commonly utilized in traditional wastewater treatment both in activated sludge treatment, where the organisms are kept in suspension, and biological filtration, where the organisms grow on a substrate such as stones (Hammer and Hammer, 2012). However, looking at the nature of the biocides (long half-lives, toxicity and non-target effects, Table 2.1) it can be assumed that no or very limited effect is achieved through biodegradation and any degradation will be in the form of co-metabolism.

2.7.2 Sorption
Sorption is a general term describing two phenomena, absorption and adsorption. Absorption is defined as “when a substance permeates another”, e.g. water is absorbed by tissue paper. Here the entire bulk or volume of the absorbent material is part of the process. Adsorption on the other hand is adhesion of a substance to a surface (Atkins and De Paula, 2006), such as the binding of metal ions to clay particles.

The interactions between adsorbent, the molecules, and adsorbate, the solid surface, can be divided into two categories: the relatively weak, and reversible physical adsorption, and the stronger, and sometimes irreversible, chemical adsorption. The dominant mechanism depends on the nature of the adsorbent and adsorbate. Physical adsorption or physisorption occurs when van der Waals forces bind the adsorbing molecules to the solid substrate. On the other hand, chemical adsorption or chemisorption results from the formation of chemical bonds, such as covalent bond or ionic bonds, between the solid substrate and the adsorbing molecules. Due to the nature of these bonds, the molecules adsorbed through chemisorption are bound much harder to the surface than the molecules attached through physisorption (Atkins and De Paula, 2006). Chemisorption is widely used in water treatment, e.g. by adsorbing unwanted contaminants and in the form of ion exchange. The latter is the most common method used for water softening (Hammer and Hammer, 2012).

2.7.3 Solution adsorption isotherms
Adsorption isotherms are used as a first experimental tool when assessing the capacity of a material, such as activated carbon, vermiculite or clay particles, for adsorption of a specific molecule. By looking at the shape of the isotherm a first idea of the specific adsorption phenomenon or suitability of the adsorbent is obtained (Moreno-Castilla, 2004).
The amount of adsorption or adsorption capacity of the adsorbent \((q_e)\) can be described as a function of the concentration of adsorbate in the solution at equilibrium \((C_e)\) and if all other parameters are constant (such as temperature) (Limousin et al., 2007). This function is known as the adsorption isotherm and can be visualized by plotting \(C_e\) against \(q_e\) (Eq. 1) (Horsing et al., 2011).

\[ q_e = K_D \times C_e \quad \text{(Eq. 1)} \]

In general the isotherm will take one of four main shapes (Limousin et al., 2007). In some cases the Langmuir type is described as three different cases rather than two, resulting in five shapes (Moreno-Castilla, 2004):

- The “C” or Long-linear isotherm is a straight line passing through the origin (Figure 2.2 A). This isotherm is not common for adsorption from solutions but will describe the initial adsorption on homogenous surfaces. The shape indicates that the ratio between \(q_e\) and \(C_e\) is constant at any concentration. This ratio is denoted \(K_D\) or partitioning coefficient (Moreno-Castilla, 2004).

- The “L” or Langmuir type isotherm is frequently found, even when the Langmuir theory is not satisfied (Moreno-Castilla, 2004). Two cases can be seen, When the curve shows a strict asymptotic plateau (Figure 2.2 B) and when it doesn’t (Figure 2.2 C) (Limousin et al., 2007). The latter is also referred to as the “F” type or Freundlich isotherm. This is most common for heterogeneous adsorbents (Moreno-Castilla, 2004). The shape of the isotherm indicates that the ratio between \(q_e\) and \(C_e\) is decreasing with increasing concentrations of solute resulting in a concave curve (Limousin et al., 2007).

- The “H” or the high affinity isotherm is a version of the “L” isotherm (Figure 2.2 D), is characterized by a steep initial slope before leveling out as a strict asymptotic plateau (Limousin et al., 2007).

- The “S” or Sigmoidal isotherm indicates that at least two opposing mechanisms cause the ratio between \(q_e\) and \(C_e\) to become sigmoidal (Figure 2.2 E). This occurs when e.g. non-polar organic compounds binds to clay particles. First the affinity is very low but once the clay particle is covered the affinity increases (Limousin et al., 2007).

By assessing how well the different isotherm equations, used to model the adsorption, fit the data a better understanding of what forces are dominant in the sorption process can be achieved (Limousin et al., 2007). Other than the linear model there are two commonly used isotherm equations for modeling adsorption are the Langmuir (Eq. 2) and Freundlich models (Eq. 4).
The five main types of isotherms as commonly described in the literature

The Langmuir isotherm is based on the assumption that the adsorbate will form an idealized monolayer on a uniform surface. In addition it is assumed that there is a strong specific interaction between the surface and the adsorbate, meaning that once a molecule occupies a site no further sorption can take place at that site (Limousin et al., 2007).

If these assumptions are fulfilled the following equation can be used to describe the isotherm:

\[ \frac{x}{m} = q_e = \frac{a q_{max} C_e}{1 + a C_e} \]  
(Eq. 2)

Where

- \( x = \) mass of adsorbate adsorbed (mg)
- \( m = \) mass of adsorbent (g)
- \( C_e = \) equilibrium concentration (mg L\(^{-1}\))
- \( a = \) Langmuir constant (L mg\(^{-1}\))
- \( q_{max} = \) maximum adsorption if only one layer adsorption is considered (mg g\(^{-1}\))
The non-linear form (Eq. 2) can be evaluated through linearization:

\[
\frac{c_e}{q_e} = \frac{c_e}{q_{max}} + \frac{1}{aq_{max}} \quad \text{(Eq. 3)}
\]

If the plot of \( \frac{c_e}{q_e} \) against \( C_e \) follows a straight line, it will generate a slope of \( \frac{1}{q_{max}} \) and an intercept value of \( \frac{1}{aq_{max}} \). The adsorption can be described by the Langmuir isotherm equation. However, any deviation from linearity would suggest that the assumptions made are incorrect. This could be explained by irregularity of the surface or there are interactions between the adsorbed molecules in addition to the interactions between sorbate and sorbent. One of the essential characteristics of the Langmuir model can be expressed as a dimensionless constant \( R_L \), the separation factor or equilibrium factor (Weber and Chakravorti, 1974).

\[
R_L = \frac{1}{1+aC_0} \quad \text{(Eq. 4)}
\]

Where \( C_0 \) is the initial concentration (mg L\(^{-1}\)).

The value of \( R_L \) indicates whether the adsorption system is irreversible \((R_L = 0)\), favorable \((0 < R_L < 1)\), linear \((R_L = 2)\), or unfavorable \((R_L > 0)\) (Deniz and Saygideger, 2010).

If the Langmuir model seems unfit to describe the isotherm the Freundlich model can be used (Limousin et al., 2007). This model assumes that there is no combination or dissociation of molecules during adsorption and that the only type of adsorption taking place is physical adsorption.

The Freundlich equation can then be written as follows:

\[
q_e = K_f \times C_e^n \quad \text{(Eq. 5)}
\]

Where \( K_f \) (L kg \(^{-1}\)) and \( n \) (dimensionless) are empirical constants.

This function is easily linearized using logarithms.

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{(Eq. 6)}
\]

This gives a linear plot with \( \log q_e \) on the y-axis, \( \log C_e \) on the x-axis, \( \frac{1}{n} \) as the slope and \( \log K_f \) as the point of intersection (Freundlich, 1906).
2.8 Using a substitute substance

When analyzing the abundance of organic biocides in water, high performance liquid chromatography is used (Bester and Lamani, 2010). The equipment for this analysis is not readily available at most laboratories and the cost for analyzing one water sample is high. In an attempt to cut the number of analysis made elsewhere by doing a first assessment on suitability of the materials using a substitute substance was developed and tested.

One analytical instrument commonly available in laboratories is a spectrophotometer why a compound with a known light absorbance maxima could be used. In addition the compound needed to have similar physiochemical properties as the organic biocides discussed in section 2.5.

A group of possible candidates were the azo-dyes. This is a very diverse group of compounds making it possible to find a substitute for most organic pollutant and hopefully other compounds as well. This would simplify the initial steps when assessing sorption materials. The azo-dyes are mainly used in the food and textile industries. A number of different dyes were assessed based on their partitioning between soils and water (K_D). Optimally a number of dyes with K_D-values within the range of the organic biocides (from 1.5 to 3.4, Table 2.1) should be tested but in this case one was singled out and used. A non-toxic dye, 4-(4-aminophenyl) azo-2-methoxy-5-methyl-Benzenamine or commonly known as Disperse Black 2 (Figure 2.3), used in the textile industry was found suitable. This compound has a log K_D of 2.97 and a water solubility of 26.65 mg/L at 25°C (U.S. Epa, 2012).

Figure 2.3. The chemical structure of Disperse Black 2
3 Materials and methods

Based on the information gathered during the literature study a method for identifying potential sources of organic biocides was formulated. A method for the sorption of the biocides was developed using trial and error, and four possible sorption materials were evaluated.

3.1 Identification method

In order to identify potential urban areas that could be considered as diffuse sources of organic biocides there are three main aspects to look at. These are:

- the materials used in façades and roofs,
- the age of the buildings and/or the time elapsed since last renovation,
- and the possibility to take samples and introduce treatment facilities.

The type of building materials used is of interest since this will indicate whether or not there is any risk of biocides leaching at all since not all materials contain these compounds. Looking at the age of the material or building will provide information on how high the leaching rate is. Test results show that during the first 5-8 years after construction or renovation the compounds will leach in considerable amounts and after this period the rates are very low (Burkhardt et al., 2007, Contant et al., 2010, Coutu et al., 2012).

A number of residential areas in the municipality of Helsingborg, in the south of Sweden, were assessed in order to find a possible location for sampling. Two of these were Mariastaden and Gustavslund.

Mariastaden was built around Maria Park, an old hospital rebuilt into residential complexes in the 1990’s. There is a mixture of old brick buildings and newer single-family houses and housing estates of which most have render façades. The first houses were constructed in 1995 and the area has been growing since (Helsingborgs Stad, 2014). The stormwater handling system is an open system where the runoff is lead to gravel swales and left to infiltrate or lead to ditches and retention ponds found in the area.

The oldest parts of Gustavslund were established between 1960’s and the 1980’s but a few years ago the area started to expand again. This new neighborhood consists of mainly single-family houses, town houses and a few housing estates (Friberg, 2011). The most common façade materials are rendering and bricks but wood and metal sheets are used on some (Figure 3.1). There are two main types of roofing, the most common is tiles and the other is bitumen sheets. Some smaller buildings, used as recycling centers and storage, have been equipped with green roofs covered with sedum.
All buildings have drainpipes leading the roof runoff directly into an underground piping system. Runoff from façades will either infiltrate next to the building ending up in drainage pipes and groundwater reservoirs, or become surface runoff entering the stormwater pipes via manholes in the streets. The underground piping leads the water into a newly constructed retention pond.

Today the pond receives stormwater from buildings, roads, parking lots within the new area south of the pond. In a near future another area, a field south east of the pond, will be urbanized and the runoff will be lead to the pond as well.
In order to establish whether any biocides reach the pond through runoff an analysis of the water was carried out. To ensure the presence of stormwater runoff four samples were taken in four consecutive rainy days (8-11th of April). A more detailed overview of the rain events can be seen in Figure 3.2. These samples were stored in 4°C before sent to analysis by high performance liquid chromatography (HPLC) using a neutral methanol/water gradient and tandem mass spectrometry (MS/MS). The instrument was an API 4000 (Applied Biosystems Sciex, Framingham, MA, USA), coupled to a Dionex Ultimate 3000 HPLC (Dionex Germeringen, Germany).

Figure 3.2 Top left: The retention pond Gustavslund with the outlet in the foreground (Photo: Maja Ekblad). Top right: The inlet where water samples were taken (Photo: Maja Ekblad). Bottom: A schematic over the retention pond Gustavslund. The inlet, seen in picture top right, is marked with a black circle (Friberg, 2011)
3.2 Sorption materials

The following sorption materials were assessed and evaluated:

**Vermiculite** – a naturally occurring mineral consisting of hydrated magnesium aluminum silicate. It can be found in Australia, Brazil, Bulgaria, Kenya, South Africa, Uganda, USA and Zimbabwe among other places. The mineral is heated and forms accordion shaped particles that are compressible, non-reactive, incombustible, lightweight and most important highly absorbent (The Vermiculite Association, 2014). The specifications for the vermiculite were as follows: Langmuir surface area 13.7 m² g⁻¹ and the total pore volume was 0.044 cm³ g⁻¹ of which 1.95×10⁻⁴ cm³ g⁻¹ is micropores.

**Activated carbon** – this material can be produced using any material with high organic carbon content, often used materials are hardwood charcoal, lignite and nut shells. The process include controlled combustion and the end result is a microporous carbon material that can absorb large amounts of various compounds (Hammer and Hammer, 2012). In this experiment a granular carbon, Eheim Karbon filter carbon, and a powdered activated carbon (PAC) (Merck, 102186 Charcoal activated) was used. The specifications for the PAC were as follows: Langmuir surface area was 1036 m² g⁻¹ and the total pore volume was 0.61 cm³ g⁻¹.

**Leca** – or Light Expanded Clay Aggregate is a material consisting of plastic clay that is heated and expanded in a rotary kiln resulting in a hardened, porous aggregate that will withstand most external stress. The material is found in building blocks, in roads, agriculture, flower pots etc. (Guo et al., 2013).

**Sand** – 0.5 mm prewashed quartz aquaria sand (ZOLUX® Quartz Aquarium no 05) was used as a negative reference. It was assumed that the quartz would not adsorb the compounds due to its surface.

3.3 Sorption tests

As sorption was found to be the main method for removal of organic biocides four different materials were tested and the possibility to use substitute substances evaluated.

3.3.1 Disperse Black 2

Through a number of tests (which are all described in Appendix 2) the limitations of using the azo-dye Disperse Black 2 were established. Firstly, a concentration similar to the concentrations of different biocides found in stormwater was considered. However this caused problems when running absorbance analysis in the spectrophotometer and when weighing the adsorbents. Using a higher concentration brought the issue of solubility at room temperature.

During these experiments a first suitability assessment of the adsorbents was made and only two materials were found somewhat efficient, namely the vermiculite and the PAC. As predicted, the quartz sand showed no or very low sorption. The leca showed some ability to sorb the dye but this was very limited compared to the PAC and vermiculite. The granular carbon brought on another issue. It seems that this compound is readily
adsorbing the dye but is also releasing a substantial amount of small particles which disturbs the spectrophotometry analysis. Although the granules were thoroughly rinsed and the samples were filtered these particles still caused problems.

**Method**

A 12.5 mg L\(^{-1}\) (0.5 mol L\(^{-1}\)) Disperse Black 2 solution was prepared using tap water (20°C) and homogenized using a magnetic stirrer. The adsorbents were weighed and put in 16 plastic tubes (40 ml) according to Table 3.1. Disperse Black 2 solution, 25 ml, was added to each tube. In addition, three controls: one with only 25 ml Disperse Black 2 solution, one with 0.01 g activated carbon and 25 ml deionized water, and one with 1.0 g vermiculite and 25 ml deionized water were prepared. All tubes were put on a shaking table for 2 hours (100 cycles min\(^{-1}\)).

*Table 3.1 The concentrations of sorbents used with Disperse Black 2 (g L\(^{-1}\))*

<table>
<thead>
<tr>
<th>PAC [g L(^{-1})]</th>
<th>Vermiculite [g L(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.024</td>
<td>0.24</td>
</tr>
<tr>
<td>0.032</td>
<td>0.40</td>
</tr>
<tr>
<td>0.040</td>
<td>1.2</td>
</tr>
<tr>
<td>0.080</td>
<td>2.0</td>
</tr>
<tr>
<td>0.160</td>
<td>4.0</td>
</tr>
<tr>
<td>0.240</td>
<td>12.0</td>
</tr>
<tr>
<td>0.320</td>
<td>20.0</td>
</tr>
<tr>
<td>0.400</td>
<td>40.0</td>
</tr>
</tbody>
</table>

All samples were then filtered using vacuum filtration to remove the adsorbent. The vacuum filtration set-up consisted of one Büchner flask, a cylindrical funnel, a funnel base with sand core plate, a metal clamp and a rubber hose connected to an aspirator. The samples were filtered over glass microfiber filters (GC/F; VWR Denmark) and the resulting filtrate was pipetted into empty Dr Lange LKT-cuvettes (LCW 906, 13 mm).

The light absorbance (Abs) in the filtrate was measured at 452 nm for all samples using a spectrophotometer, (VIS-spectrophotometer DR 2800).

The range of PAC was found to include too high concentrations and was modified according to Table 3.2. A new test was conducted using the improved range of PAC, 250 ml conical flasks and 150 ml Disperse Black 2 solution (12.5 mg L\(^{-1}\)). The samples were put in a desktop incubation shaker (Adolf Kuhner AG, Schweiz) for 2 hours (150 cycles min\(^{-1}\), at 20°). All samples were then filtered using vacuum filtration and glass microfiber filters (GC/F; VWR Denmark) and the filtrate was transferred into LKT-cuvettes. The light absorbance was measured as described above.
3.3.2 Organic biocides

Based on the results of the sorption tests with Disperse Black 2 the following test using a mixture of commonly occurring biocides was conducted. The wider range of PAC was used and a slight change of the vermiculite range was made. It would have been optimal to use concentrations of biocides close to naturally occurring concentrations and compare the sorption of these with the one of the azo-dye. However these low concentrations would cause problems due to the limitation of the spectrophotometer.

Method

A stock solution with 12 different organic biocides (Appendix 6) and a concentration of 100 μg mL⁻¹ (or 100 mg L⁻¹) for each biocide (kindly gifted by Kai Bester, Department of Environmental Science - Environmental chemistry & toxicology, Aarhus University, Roskilde) was diluted 10 000 times to 10 ng L⁻¹ using MiliQ water. The adsorbents were weighed according to Table 3.2 and put into 250 ml Erlenmeyer flasks. Using volumetric flasks 150 ml of the diluted solution was added to each Erlenmeyer flask and put in a desktop incubation shaker (Adolf Kuhner AG, Schweiz) for 2 hours (150 cycles min⁻¹, at 20°C). All samples were then filtered using vacuum filtration and glass microfiber filters (GC/F; VWR Denmark).

<table>
<thead>
<tr>
<th>PAC [g L⁻¹]</th>
<th>Vermiculite [g L⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>0.4</td>
</tr>
<tr>
<td>0.008</td>
<td>1.2</td>
</tr>
<tr>
<td>0.016</td>
<td>2.0</td>
</tr>
<tr>
<td>0.024</td>
<td>4.0</td>
</tr>
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<tr>
<td>0.240</td>
<td>70.0</td>
</tr>
<tr>
<td>0.320</td>
<td>80.0</td>
</tr>
</tbody>
</table>

The filtrate was transferred into 200 ml blue cap glass bottles, stored in a dark cool box at 6°C and sent for analysis. In addition two controls were prepared with 150 ml biocide solution together with 0.040 g PAC L⁻¹ and 20 g vermiculite L⁻¹ respectively. These were left in the desktop shaker for 24 hours and thereafter transferred to 200 ml blue cap glass bottles with no further treatment. These were sent for analysis together with the other samples. The analysis was done using high performance liquid chromatography (HPLC).
with a neutral methanol/water gradient and tandem mass spectrometry (MS/MS).(Vorkamp et al., 2014, Bester and Lamani, 2010).

### 3.3.3 Adsorption isotherms

Using a calibration curve (Appendix 2.1.1) the concentration of Disperse Black 2 left in the solution ($C_e$, mg L$^{-1}$) was calculated (Eq. 6).

$$C_e = 66.092 \times Abs - 0.3316 \quad (\text{Eq. 6})$$

With this information together with the known initial concentration ($C_0$), the amount of solute retained by the adsorbent ($q_e$, mg g$^{-1}$) can be calculated (Eq. 7).

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (\text{Eq. 7})$$

$V$ is the volume of solution (L) and $m$ is the mass of adsorbent added (g).

The sorption isotherms were plotted using the models described in section 2.7.3.
Results and discussion

As a way of identifying residential areas as sources of organic biocides a checklist was created and two areas were evaluated according to this. Stormwater was collected from one of these areas and the biocide content analyzed.

Sorption was evaluated as a method of removal. Two main adsorbents were tested using a dye and a stock solution with organic biocides. Adsorption isotherms were created for each biocide and adsorption material in order to establish what adsorption forces are predominant.

A number of methods of implementing adsorption as a way of treating stormwater were discussed.

4.1 Development of identification method

The age of the buildings together with the design of the stormwater handling system in Mariastaden render this area unfit for sampling. The main problem would be to obtain water samples from the façades since most rainwater is infiltrated in gardens or swales along the streets and only small amounts would reach ditches and ponds during an average rain event.

In Gustavslund, the low age of the buildings, the materials used in façades and roofs together with stormwater running in pipes will increase the risk of biocides reaching the retention pond in high concentrations. Therefor this area was selected when sampling and analyzing stormwater in pursuit of biocides.

Stormwater samples were collected in the retention pond of Gustavslund and analyzed at Aarhus University in Roskilde testing for 13 different biocides. Seven out of these compounds were detected in the stormwater, although some were detected at concentrations lower than the calibration standards (Table 4.1). Out of the seven biocides detected in the water samples five are commonly used in building materials and façades. The other two (tebuconazole (TBU) and propiconazole (DMI)) are fungicides in the triazole group, same as mecoprop (MCPP). These two are not used for material protection but rather in agriculture and private gardening (Danish Environmental Protection Agency Depa, 2011). The presence of these two compounds is most likely due to runoff from gardens and farmlands mixing in with runoff from roofs, façades and roads before reaching the retention pond were samples were taken. However, both compounds are found in low concentrations far below the PNEC (Table 4.1).

Since most of the compounds were found at concentrations below the calibration standard for the analysis method it is hard to tell whether they exceed the PNEC and thereby cause harm in the ecosystem or not. In the case of diuron (DR) it is clear that all samples contain concentrations above PNEC, as do the carbendazim (CD) in at least one of the samples. Due to the low PNEC for OIT it is likely that one or more of the samples might exceed this although the concentrations are below the calibration standard.
These results implicate that if nothing is done in order to reduce the amount of organic biocides in the stormwater the biota might be affected by their presence since more than one compound exceed the PNEC.

Table 4.1. The biocides found in the stormwater collected in the retention pond of Gustavslund and the corresponding concentrations in μg L⁻¹. In the case where a compound was detected but the concentration were below calibration standards are denoted <0.04. PNEC (predicted no effect concentration) for each compound is added as reference

<table>
<thead>
<tr>
<th>Sample</th>
<th>Biocide concentrations [μg L⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IP</td>
</tr>
<tr>
<td>Day 1</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>Day 2</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>Day 3</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>Day 4</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>PNEC</td>
<td>0.021*</td>
</tr>
</tbody>
</table>

*Calculated with EPI Suite™ v4.11 of the U.S. EPA **Anses (2014)

4.2 Sorption tests

Sorption tests were carried out in lab-scale in order to evaluate the suitability of the two sorbents (PAC and vermiculite) removing organic biocides in stormwater. In addition, sorption tests using the azo-dye Disperse Black 2 were carried out in hope of developing an easy and cost efficient method to eliminate sorption materials before running advanced mass spectroscopy analyzes with the biocides.

4.2.1 Disperse Black 2

The overall result shows that the PAC is a better adsorbent although vermiculite shows potential for use in adsorption of the Disperse Black 2. Raw data can be found in Appendix 3, 4 and 5.

PAC

The first PAC test, using 40 ml vials and 25 ml solution, showed high adsorption throughout the range (57.7-99.5%, Table 4.2). However, the five highest PAC concentrations show almost total adsorption (94.2-99.5%) which indicates that the range of PAC concentrations used was not optimal.

A lower range of PAC concentrations was used in the second sorption test. The new adsorption was between 33.6% and 98.7%. The results show a consistently lower adsorption than the first test which might be explained by the change in method.

The 24 h sample (0.04 g PAC L⁻¹) showed a 94.7% adsorption, compared with 82.6% after two hours contact time. This suggests that the assumption that a two hour contact
time would suffice was incorrect and a longer contact time would improve the results. In order to determine the actual contact time needed in order to reach equilibrium a test looking at the adsorption depending on contact time rather than biocide concentration should be conducted. These tests would be of use when producing adsorption isotherms and for laboratory work. However, when implementing a real life solution these long contact times would not be possible to achieve why the effect of the shorter contact time is also of interest.

**Vermiculite**

The vermiculite shows a much lower adsorption potential than the PAC. At 400 g L\(^{-1}\) the PAC adsorbed close to 100% but the vermiculite adsorbed less than 20%. For the range of vermiculite concentration tested the adsorption was between 13.8% and 56.6% (Table 4.2) which would suggest that the concentrations used do not cover the entire range needed.

The three lowest concentrations show a decreasing adsorption with increasing amounts of vermiculite. At these low concentrations the number of granules put into each vial is small and the result could perhaps be explained by irregularities in size and surface area of the granules. These irregularities would affect the available contact area and thereby the adsorption.

*Table 4.2 The adsorbed amount of Disperse Black 2 in percentages. Uncertain values are written in italics*

<table>
<thead>
<tr>
<th>PAC [g L(^{-1})]</th>
<th>Adsorbed dye [%] Test 1</th>
<th>Adsorbed dye [%] Test 2</th>
<th>Vermiculite [g L(^{-1})]</th>
<th>Adsorbed dye [%]</th>
</tr>
</thead>
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<td>0.004</td>
<td>-</td>
<td>33.6</td>
<td>0.240</td>
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</tr>
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<td>0.008</td>
<td>-</td>
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</tr>
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<td>-</td>
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<td>2.000</td>
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</tr>
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<td>0.080</td>
<td>96.8</td>
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<td>40.00</td>
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<tr>
<td>0.240</td>
<td>94.2</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.320</td>
<td>99.5</td>
<td>98.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.400</td>
<td>97.9</td>
<td>-</td>
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<td>-</td>
</tr>
</tbody>
</table>
4.2.2 Organic biocides

The overall result of the adsorption tests shows that the PAC is a better sorbent although vermiculite shows high affinity for the organic biocides used. Raw data can be found in Appendix 7 and 8.

**PAC**

The PAC concentration range based on the results from the Disperse Black 2 experiments was found to be too high in regards to adsorption of organic biocides since almost total adsorption was reached for most compounds (Table 4.3) with most concentrations below level of quantification (LOQ) or even level of detection (LOD). This would imply that the organic biocides have a higher affinity towards the PAC than the azo-dye Disperse Black 2. The only compound showing a reliable increase of adsorption with increasing PAC concentrations is the methylisothiazolinone (MI) and at concentrations of 0.024 g PAC L\(^{-1}\) and higher the MI concentration in the solvent is below the LOD, why only seven values can be used. The 24 hour adsorption sample gave non-reliable results why it has been excluded.

If PAC would be used as sorbent of organic biocides, lower concentrations than the ones tested would be sufficient in order to remove almost all pollutants. It is also important to remember that these test were carried out using a stock solution with biocide concentrations much higher than the ones found in the retention pond of Gustavslund.

**Vermiculite**

The vermiculite shows a lower adsorption capacity than the PAC, which is consistent with the tests run with Disperse Black 2. The organic biocides do, however, show higher affinity towards the vermiculite than the aforementioned azo-dye. The relative adsorption of the organic biocides spans between 77.0% and 99.4% (Table 4.4).

For most of the biocides the removal is improved when the vermiculite concentration is increased. MI, BIT, MCPP, and IPCB however are found at relatively low residual concentrations at low vermiculite concentrations and when the concentration is increased slightly when the adsorption is decreased. For example only 77% of the initial MCPP is adsorbed at a vermiculite concentration of 3.0 g L\(^{-1}\) compared to the 96.5% removed at 0.06 g vermiculite L\(^{-1}\). The adsorption of MCPP and IBPC is increased again with even higher vermiculite concentrations. For MI and BIT this increase is not obtained with increasing vermiculite concentrations.

One possible explanation for the decrease in adsorption with increasing adsorbent concentration could be interactions between the different biocides in the standard solution. This could be established by running the experiments testing the adsorption of one compound at the time. Thus the behavior of single biocides could be compared with the compounds in combination with others.

Another possible explanation for the decreased adsorption seen for MI, BIT, MCPP, and IPCB is that the high buoyancy of vermiculite together with the method of stirring would
have prevented contact between the liquid containing the biocides and the vermiculite. The high buoyancy of the vermiculite would keep it afloat even if the container was kept on a desktop incubation shaker which would stir the content. At lower vermiculite concentrations the stirring would be enough to keep the granules in suspension but with higher concentrations the stirring might have been insufficient why not all vermiculite would come in contact with the liquid at the same rate. At the highest concentrations the sheer amount of vermiculite added would mean that a larger amount of granules would be in contact with the liquid even if the stirring was insufficient to ensure total contact. In order to avoid this problem in future research another type of flasks or bottles should be used (not the conical flasks) in combination with a horizontal shaker to ensure contact between sorbents and biocide mixture.

In terms of reaction time, most of the biocides seem to reach equilibrium after the two hours contact time (IP, DR, TB, IRG, OIT and TBU). For the other five biocides (MI, BIT, MCPP, IPCB and CD) it seems that a longer contact time would increase the adsorption, based on the 24 h contact time. Note that four out of these five are the same compounds which showed divergent adsorption patterns. This indicates that the initial decrease in adsorption with increasing vermiculite concentrations could possibly be counteracted by extending the contact time.
Table 4.3 The adsorbed amount of organic biocides in percent. Values proceeded by > indicate that biocide concentrations in the solvent were below level of quantification or level of detection for the certain compound.

<table>
<thead>
<tr>
<th>PAC [g L(^{-1})]</th>
<th>MI [%]</th>
<th>BIT [%]</th>
<th>MCPP [%]</th>
<th>IP [%]</th>
<th>DR [%]</th>
<th>IBPC [%]</th>
<th>CD [%]</th>
<th>TB [%]</th>
<th>IRG [%]</th>
<th>OIT [%]</th>
<th>TBU [%]</th>
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<td>90.6</td>
<td>&gt; 99.2</td>
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<td>&gt; 99.2</td>
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<td>99.1</td>
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<td>&gt; 99.7</td>
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<td>&gt; 99.7</td>
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</table>
Table 4.4 The adsorbed amount of organic biocides in percent. The 24 hours sample was prepared with a vermiculite concentration of 3 g L⁻¹

<table>
<thead>
<tr>
<th>Vermiculite [g L⁻¹]</th>
<th>MI [%]</th>
<th>BIT [%]</th>
<th>MCPP [%]</th>
<th>IP [%]</th>
<th>DR [%]</th>
<th>IBPC [%]</th>
<th>CD [%]</th>
<th>TB [%]</th>
<th>IRG [%]</th>
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<td>90.0</td>
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<td>99.1</td>
<td>91.0</td>
<td>90.7</td>
<td>88.9</td>
<td>85.0</td>
</tr>
</tbody>
</table>
4.3 Adsorption isotherms

When interpreting the results from the adsorption tests using the models described in section 2.7.3 a first linear representation was made in order to classify the adsorption mechanisms. After this first analysis the results were plotted according to the Langmuir and the Freundlich models to closer assess the mechanisms responsible for the adsorption in these tests.

4.3.1 Disperse Black 2

Two materials were used in the adsorption test using Disperse Black 2; powdered activated carbon (PAC) and vermiculite. An additional two tests were run with the PAC using two different ranges of adsorbent concentrations. For the first test a higher range was used (between 24 and 400 mg L⁻¹) and as this did not show much of a gradient the second test was carried out with a lower range (between 4 and 320 mg L⁻¹). An optimal scenario would be to see similar trends when plotting the results. The first test results were fitted to a polynomial curve with quite good result (Figure 4.1) which would suggest that the adsorption can be described by either the Langmuir or the Freundlich model (compare with Figure 2.2 B and D).

![Figure 4.1 The adsorption isotherm for the first test using PAC. The shape of the trend line suggests that the Freundlich or Langmuir models might describe the mechanisms based on the five main isotherm types (Figure 2.2). The light grey data point is not included in the curve fitting due to unreliable value](image)

As a second step the data was plotted using the two models (Figure 4.2) and by comparing the coefficient of determination ($R^2$) it can be determined whether the model is applicable or not. In this case none of the models fit very well but the Freundlich ($R^2 \approx 0.61$) is a better description than the Langmuir model ($R^2 \approx 0.34$). This would imply that there is only physical adsorption occurring when Disperse Black 2 attach to the PAC surfaces.
Figure 4.2 A linear representation of how well the results coincide with the two adsorption models, Langmuir on the left and Freundlich on the right. Although no perfect fit could be found the Freundlich model is a better match than the Langmuir.

The results from the second test were plotted and a trend line was fitted (Figure 4.3). In this case a linear trend line gave the best result. This type of adsorption isotherm is unusual when looking at solutions, except for initial adsorption (Moreno-Castilla, 2004). One explanation to the shape of this isotherm could be that not even the highest concentration of PAC adsorbed all of the dye. Had the range been wider the shape might have been more similar to the first.

Figure 4.3 The adsorption isotherm for the second test using PAC. A linear trend line was the best fit.

Although the initial plot suggested a linear isotherm when plotted according to the Freundlich and Langmuir models the results show a closer fit to the Freundlich model (Figure 4.4).
Figure 4.4 A linearization of the two adsorption models. The Freundlich model, on the right, has a better fit than the Langmuir, on the left, suggesting physical adsorption is more likely to dominate.

To assess the mechanisms involved in the adsorption of Disperse Black 2 onto the mineral vermiculite the resulting values were plotted and an exponential trend line was fitted (Figure 4.5). The shape of this isotherm would suggest that the adsorption might follow a sigmoidal curve (Figure 2.2 E). However, since the range of adsorbent concentrations used in this test would only adsorb up to about 50% (Table 4.2) it is impossible to predict what the entire isotherm would look like. Assumed that the sigmoidal shape is correct, the adsorption can be explained as an initially slow process due to low affinity between the solute and the surface. When the amount of adsorbed solute increases so does the affinity causing the adsorption process to speed up (Limousin et al., 2007).

Figure 4.5 The adsorption isotherm of Disperse Black 2 for the test using vermiculite. An exponential trend line was found most adequate to describe the adsorption isotherm. The light grey data points are not included in the curve fitting due to unreliable values.

However, when looking at the possibility of explaining the adsorption with another model both the Langmuir and the Freundlich model seems appropriate (Figure 4.6). The sigmoidal shape is based on an initial monolayer adsorption changing into multilayer why the Langmuir
model might have a better fit at this initial stage but at higher adsorbent concentrations the Freundlich isotherm could prove a better representation.

Figure 4.6 A linear representation of the compatibility of the results and the two adsorption models. The higher $R^2$ value for the Langmuir model, on the left, suggest that chemical adsorption is dominant in an early stage but the high $R^2$ value for the Freundlich model, on the right, implies that physisorption is taking over at a later stage.

4.3.2 Organic biocides
The PAC concentration in this test ranged between 4 and 320 mg L$^{-1}$ and for the vermiculite the range was 0.4 to 30 g L$^{-1}$. Unfortunately the concentrations of PAC used were too high resulting in almost total adsorption of the organic biocides why only one adsorption isotherm could be produced for this adsorbent. This isotherm was made using the values of the biocide MI. The first linear representation shows an exponential increase in adsorption with increasing PAC concentrations (Figure 4.7). If this isotherm is compared to the five standard isotherms (Figure 2.2) it could be assumed that the adsorption resembles the first section of a sigmoidal isotherm. This could imply that the MI is adsorbed slowly at first but after a while the rate increases and equilibrium is reached quickly.

Figure 4.7 The adsorption isotherm for MI with PAC as adsorbent. An exponential trend line was found most adequate to describe the adsorption isotherm.
When the adsorption was calculated using the two adsorption models, Langmuir and Freundlich it was found to correspond quite well to both. However the Langmuir model is a slightly better match (R² ≈ 0.99) than the Freundlich model (R² ≈ 0.91) (Figure 4.8). This would suggest that the compound is adsorbed through both chemisorption and physical adsorption. The q_max was calculated to 69 mg MI per g PAC. It would have been interesting to be able to compare this amount with the maximum adsorption of the other compounds to be able to say something more general about how well biocide adsorb to PAC.

Looking at the vermiculite the concentration range was better calibrated and results were obtained for all biocides. Four of these (MI, BIT, MCPP and IBPC) did however not show any linearity why they were not analyzed in this step. As for the other seven compounds the first linear representations show a very similar adsorption pattern (Figure 4.9). The shapes suggests that the adsorption might follow a sigmoidal isotherm (Figure 2.2) since they resemble the first half of this standard isotherm. This pattern was also seen in the case of Disperse Black 2 adsorbing to the vermiculite.
Figure 4.9 A first representation of the adsorption of organic biocides onto vermiculite. They all seem to follow a sigmoidal curve suggesting initial chemical sorption transcending into physical sorption with time. The light grey data point is not included in the curve fitting due to an unreliable value.
In order to tell what adsorption mechanism is the prevalent in regards to the different organic biocides the results were plotted according to the linearized Langmuir and Freundlich isotherms.

The adsorption of isoproturon (IP) matches the Langmuir isotherm better \((R^2 \approx 0.91)\) than the Freundlich \((R^2 \approx 0.75)\) (Figure 4.10), which means that chemical adsorption in a monolayer is the most probable adsorption mechanism. The \(q_{max}\) was calculated to 13.4 ng IP g\(^{-1}\) vermiculite, the lowest value in the test.

![Figure 4.10](image1.png)

*Figure 4.10 The adsorption isotherm for the biocide IP with vermiculite as adsorbent, Langmuir on the left and Freundlich on the right. The Langmuir isotherm was found to have the best fit, based on \(R^2\), suggesting chemical adsorption is dominant at this stage.*

The adsorption of diuron (DR) matches the Langmuir isotherm better \((R^2 \approx 0.95)\) than the Freundlich \((R^2 \approx 0.66)\) (Figure 4.11) which means chemical adsorption in a monolayer is the most probable mechanism. The \(q_{max}\) was calculated to 25.5 ng DR g\(^{-1}\) vermiculite.

![Figure 4.11](image2.png)

*Figure 4.11 The adsorption isotherm for the biocide DR with vermiculite as adsorbent, Langmuir on the left and Freundlich on the right. The Langmuir isotherm was found to have the best fit, based on \(R^2\), suggesting chemical adsorption is dominant at this stage.*
The adsorption of carbendazim (CD) matches the Langmuir isotherm better ($R^2 \approx 0.98$) than the Freundlich ($R^2 \approx 0.94$) (Figure 4.12) which means chemical adsorption in a monolayer is the most prevalent mechanism. However, the fact that the Freundlich isotherm have a good fit would suggest that physical sorption takes place as well. This fits with the Sigmoidal curve seen in figure 4.9. The $q_{\text{max}}$ was calculated to 83.9 ng CD g$^{-1}$ vermiculite.

The adsorption of terbutryn (TB) coincides more with the Langmuir isotherm ($R^2 \approx 0.99$) than with the Freundlich ($R^2 \approx 0.82$) (Figure 4.13). This means that monolayered chemical adsorption would be the most dominant mechanism. The relatively high $R^2$ for the Freundlich isotherm suggests that physisorption will also occur. The $q_{\text{max}}$ was calculated to 61.3 ng TB g$^{-1}$ vermiculite.

Figure 4.12 The adsorption isotherm for the biocide CD with vermiculite as adsorbent, Langmuir on the left and Freundlich on the right. The Langmuir isotherm was found to have the best fit, based on $R^2$, suggesting chemical adsorption is dominant at this stage.

Figure 4.13 The adsorption isotherm for the biocide TB with vermiculite as adsorbent, Langmuir on the left and Freundlich on the right. The Langmuir isotherm was found to have the best fit, based on $R^2$, suggesting chemical adsorption is dominant at this stage.
The adsorption of irgarol (IRG) matches the Langmuir isotherm better ($R^2 \approx 0.99$) than the Freundlich ($R^2 \approx 0.84$) (Figure 4.14) which means chemical adsorption in a monolayer is the most probable mechanism. The $q_{\text{max}}$ was calculated to 54.9 ng IRG g$^{-1}$ vermiculite.

The adsorption of octylisothiazolinone (OIT) fits the Langmuir isotherm better ($R^2 \approx 0.98$) than the Freundlich ($R^2 \approx 0.74$) (Figure 4.15) which means chemical adsorption in a monolayer is the most probable mechanism. The $q_{\text{max}}$ was calculated to 58.5 ng OIT g$^{-1}$ vermiculite.

The adsorption of tebuconazole (TBU) fits the Langmuir isotherm better ($R^2 \approx 0.97$) than the Freundlich ($R^2 \approx 0.86$) (Figure 4.16). Yet again, this indicates that a monolayer chemical adsorption is the most dominant mechanism. The $q_{\text{max}}$ was calculated to 297.0 ng TBU g$^{-1}$ vermiculite, which is the highest value for all of the organic biocides in this test.
4.4 Disperse Black 2 as a substitute substance

Looking at the possibility of using Disperse Black 2 as a substitute substance when assessing the efficiency of a sorption material it is obvious that the azo-dye is less prone to be adsorbed by both PAC and vermiculite compared to the organic biocides. However, the dye does show similar patterns when analyzing the isotherms and in both cases are the PAC the better adsorbent but vermiculite is not a bad adsorbent.

It would be of interest to look at other dyes in order to see if more suitable substances could be found.

4.5 Placement and layout of a treatment facility

The possible placements of a treatment facility would be in manholes, as a cassette on a pipe, or as a horizontal flow filter at the end of the pipe alternatively at the outflow of the pond (Figure 4.20). Some important factors to look at when deciding on where to place the treatment would be contact time between sorption material and storm water, the permeability of the material (a dense material will increase contact time but will also increase the risk of flooding upstream), amount of maintenance needed, accessibility and cost.

In a manhole the water could be lead through a column filled with sorption material. In this case the contact time would be in the range of seconds why the pollutants affinity for the material, in this case the organic biocides for the sorbent, must be very high in order to remove any significant amounts. Based on the test results the PAC would be a possible material to use. There are a number of products on the market which are lowered into the manholes, from e.g. FlexiClean (www.flexiclean.eu), Kenrex Envirotech (www.kenrex.se)
and Sweden Water Purification AB (www.swepur.se). Stormwater will flow through the filter media and impurities will be removed. Positive features include easy access and maintenance, and a broad spectrum of sorption materials can be used why a wide range of contaminants can be targeted.

Figure 4.17 The general principals of a manhole system where water enters the manhole, filters through the column and exits at the bottom. Although there are other solutions than the one portrayed the general idea is the same (photo: Maja Ekblad)

As a rule of thumb manholes will be placed at all intersections of pipes, when there are changes in gradient, size, or alignment, and no more than between 90 and 150 m apart, depending on pipe dimensions (Hammer and Hammer, 2012). In any residential area the number of manholes will quickly add up resulting in a large number of filters needed and making an installation costly. The filter media needs renewing approximately once a year (Flexiclean Ab, n.d.) adding to the expenses and amount of maintenance. In addition almost all of the drainpipes leading water away from rooftops in Gustavslund are directly connected to the underground stormwater pipes (Figure 3.1) resulting in polluted water bypassing the filters. If clogged the stormwater will quickly rise in the system causing streets to flood and decreased treatment efficiency.

A cassette or a retention reservoir (Figure 4.18), which can be installed on a length of the pipe (Figure 4.20), could be used instead of the filter columns put into manholes. These systems are mainly used as a way to retain rainwater and increase infiltration (Örebro Stad, 2010) and could be combined with a sorption material to remove pollutants. There are for example products on the market where the storm water fills a cassette in which filters are placed on the floor. At a certain water level the water will start to rise in the filters and pollutants are removed. The water is then released to a recipient (Contech Engineered Solutions, 2014).

By placing this structure on the pipe leading out into the retention pond all stormwater collected in the entire residential area will pass through and a larger volume can allow longer contact time. In addition the maintenance and cost could be kept down since only one cassette
or reservoir would be needed. There are still risks of flooding the upstream pipes if the grain size of the filter media is too small or the dimensions of the cassette or retention reservoir are insufficient. There is no need for extra retention in this system since all stormwater is lead to a retention pond. When planning a new residential area without the possibility to introduce an open surface retention pond the cassette could be a good alternative. This would provide both treatment and retention reducing the amount of dangerous substances and the risk of erosion in the recipient.

The third option would be to introduce a horizontal flow filter-bed at the outlet of the retention pond (Figure 4.19) which would ensure a steady flow and simplify the design. Here the adsorption material can be mixed in the filter-bed. The risk of flooding the upstream system is minimized since water will flow freely to the pond and maintenance is reduced to digging out the bed and replacing the filter media every few years. In addition, if constructed as a free surface wetland there could be an increase in biological and photo-degradation of the pollutants due to increased exposure to sunlight and an increased biological growth. However, not all of the pollutants targeted in this report are susceptible to either photo-degradation or biological degradation. The latter since they inhibit most degraders. If an open surface filter-bed is constructed there is a risk of increased mosquito populations since the standing water might act as breeding ground (Stauffer, 2014). Although there are hardly any vector borne diseases transmitted by mosquitoes in Sweden today (Niklasson and Vene, 1996) they are a nuisances.

Based on the situation in Gustavslund the most suitable and the most implementable treatment method would be the filter-bed. However, the best method might vary from case to case.
Figure 4.20 A schematic map over the stormwater pipe system in the residential area of Gustavslund (within the slashed line). Flow directions are indicated with arrows. The retention pond is here represented by an oval, some manholes have been marked with black dots, possible placements of a cassette (marked with a square shape) and horizontal flow filter (marked with a triangle) can also be seen. Map: Helsingborgs Stad (2014); Stormwater structures: NSVA (2014)
5 Conclusions

The method for biocide source identification, based on age of the buildings, materials used and the type of stormwater system, seems fit seeing that the analysis made on stormwater from Gustavslund showed biocide concentrations up to 0.73 $\mu$g L$^{-1}$, well above PNEC values. If applied on other residential areas the result would hopefully conform to the ones for Gustavslund, enabling identification of possible biocide sources in an urban environment.

The initial evaluation of sorption material, using the substitute substance Disperse Black 2, showed that only two out of three materials were suitable for use in the sorption tests. These two were the silica rich mineral vermiculite and the powdered activated carbon.

Sorption is a good way to remove organic biocides from storm water. Of the two materials tested PAC is the better adsorbent. The fact that PAC is a better adsorbent was expected since the compound has a much higher specific area than the vermiculite. What is more surprising is that the vermiculite was such a good adsorbent despite its low specific area and pore volume.

Disperse Black 2 was found to show similar patterns as most of the organic biocides. This suggests that it could be used to test if a sorbent is efficient or not. However, the amount adsorbed dye was over all lower than for the biocides and the choice of dye may not be optimal since particles from the PAC interfered with the black dye when analyzed using spectrophotometry.

The best suited treatment method for the residential area, Gustavslund in Helsingborg, would be the horizontal flow filter-bed if built at the outlet of the retention pond. Thus it would be relatively easy to implement. It would also be possible to control contact times and the setup is relatively low maintenance. A cassette or a retention reservoir would also be a possible choice but the existing retention pond makes further retention of little use. There are also plans on building a new residential area connected to the same pond through another piping system which means that two cassettes would be needed.
6 Further studies

The results of this study show that new and/or newly renovated buildings with render façades and flat roofs will contribute to organic biocides entering the stormwater systems. The results also suggests that adsorption is one possible way of removing them before causing harm to the biota.

In regards of sorption of organic biocides it would be interesting to look at how the materials would work under different physical conditions such as changing pH or contact times. It would also be of interest to investigate the kinetics between biocides and sorption materials in more detail.

The use of substitute substances seemed to be a possible way to reduce analysis costs and in a first suitability test of sorption materials. It would however be very interesting to test a larger variety of compounds, specifically azo-dyes. These test would hopefully lead to finding substances corresponding more closely to one specific organic biocide or groups of compounds making the analysis even more reliable.

If one thinks bigger, a natural step forward would be to test the materials in the field. It would be of great interest to first of all test the water quality at the outlet to see if any reduction of organic biocides take place in the water phase of the retention pond. A second step would be to test the reduction potential of the two sorption materials through implementing a horizontal flow filter-bed and analyzing the outlet.
7 References

ANSES 2014. AGRITOX- Database on active plant protection substances.


# 8 Appendix

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Weather conditions for sampling days

Day 1 – Tuesday 8/4 2014

Heavy rain, wind ca 5m/s south west. The water in the pond was heavily polluted with particles due to high run-off.

Day 2 – Wednesday 9/4 2014

Light rain, wind ca 11m/s west north west. Less run-off but quite some waves on the pond hitting the south shore and the outlet.

Day 3 – Thursday 10/4 2014

No or very little rain, wind ca 2-3m/s south east. Very little run-off and clear water.

Day 4 – Friday 11/4 2014

Medium rain, wind ca 3-5 m/s south east. Medium high run-off.
# Development of laboratory sorption method

The method of analysis was refined stepwise. For the first step, information found in literature and gained from discussions with co-supervisors Kai Bester and Anna Ledin, together with previously obtained knowledge.

Step one included finding a suitable substitute substance to be used, sketching the outline of the method and testing it.

Step two was based on the results in step one and changes in the method was made accordingly.

## 2.1 Method development

### 2.1.1 Calibration curve

#### Idea

In order to be able to convert absorbance, measured in the spectrophotometer, to concentrations a calibration curve was needed. The idea is to measure the light absorbance in samples with known increasing concentrations, such as a dilution series. If, when plotting the results, they can be described by a linear equation \( r^2 > 0.98 \) this linear expression can be used to translate absorbance to concentrations.

#### Method description

A dilution series was prepared starting with a Disperse Black 2 concentration of 10 mg/L and diluting it to 8, 6, 4 and 2 mg/L. The absorbance was measured at \( \lambda = 452 \text{ nm} \) and the results were plotted in Excel.

#### Results

When plotting the absorbance using linear regression the following equation was obtained:

\[
C_o = 66.092 \times \text{Abs} - 0.3316
\]

An \( r^2 \)-value of 0.998 verified the significance of the linearization (Figure 2.1).
A simple, small scale sorption method was needed and by merging methods described for biocide and dyestuff sorption, together with the available instruments and materials, a first outline was drawn. The resulting methods consisted of a batch test using a shaking table, a centrifuge and a spectrophotometer. In the first trial only two of the sorption materials were used, sand and activated carbon.

The sand was used as a negative reference and it was thought none of the dye would sorb to it. The activated carbon on the other hand was used since it is usually a very good sorbent and will in most cases sorb large amounts of substances.

The concentration of the azo-dye used was based partly on information found in the literature but also on concentrations of biocides found in stormwater.

**Method description**

500 ml stock solution of 0.2 moles L\(^{-1}\) Disperse Black 2 was made with tap water and stored in 8°C. Sand and activated carbon was added in four 40 ml plastic tubes. Two different masses were used, 1 and 2 g. 35 ml of solution was added in each tube and these were placed on a shaking table for 2 hours (220 cycles min\(^{-1}\)). The samples were centrifuged for 10 min at 6000 rph and the supernatant was pipetted into empty DrLange LKT-cuvettes (LCW 906, 13 mm).

The light absorbance before and after sorption was measured using a spectrophotometer, (VIS-spectrophotometer DR 2800). These measurements were conducted at all wavelengths
between 449 and 453 nm due to the fact that no maximum absorbance wavelength but a range was found.

Results

The absorbance before sorbents were added was quite low (Table 2.1) and after the 2 hour contact time the values were higher in all samples. This phenomenon is especially clear when looking at the samples with activated carbon.

The spectrophotometry showed a slightly higher light absorbance at 452 nm than at the other wavelengths for most samples.

Table 2.1. The mean values of light absorption before and after exposure to sorption materials measured at all wavelengths. The last two rows show the amount light absorbed by particles released from the sorbent materials

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>λ</th>
<th>449nm</th>
<th>450nm</th>
<th>451nm</th>
<th>452nm</th>
<th>453nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td></td>
<td>0.032</td>
<td>0.035</td>
<td>0.034</td>
<td>0.037</td>
<td>0.036</td>
</tr>
<tr>
<td>Sand, 1g</td>
<td></td>
<td>0.060</td>
<td>0.058</td>
<td>0.059</td>
<td>0.060</td>
<td>0.058</td>
</tr>
<tr>
<td>Sand, 2g</td>
<td></td>
<td>0.072</td>
<td>0.068</td>
<td>0.068</td>
<td>0.066</td>
<td>0.066</td>
</tr>
<tr>
<td>Activated carbon, 1g</td>
<td></td>
<td>0.077</td>
<td>0.074</td>
<td>0.073</td>
<td>0.074</td>
<td>0.073</td>
</tr>
<tr>
<td>Activated carbon, 2g</td>
<td></td>
<td>0.128</td>
<td>0.117</td>
<td>0.117</td>
<td>0.118</td>
<td>0.115</td>
</tr>
<tr>
<td>Sand &amp; water</td>
<td></td>
<td>0.010</td>
<td>0.016</td>
<td>0.011</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>Activated carbon &amp; water</td>
<td></td>
<td>0.086</td>
<td>0.086</td>
<td>0.083</td>
<td>0.083</td>
<td>0.086</td>
</tr>
<tr>
<td>Sand, corrected</td>
<td></td>
<td>0.050</td>
<td>0.042</td>
<td>0.048</td>
<td>0.048</td>
<td>0.046</td>
</tr>
<tr>
<td>Carbon, corrected</td>
<td></td>
<td>-0.009</td>
<td>-0.012</td>
<td>-0.010</td>
<td>-0.009</td>
<td>-0.013</td>
</tr>
</tbody>
</table>

Problems

There was a higher light absorbance after sorption than before. This was most likely caused by particles originating from the sorbents.

When centrifuging the samples the activated carbon is not prone to form a pellet but stay afloat in the liquid.

Solutions and improvements

In order to be able to get any information from the first analysis, a test using only tap water and 1g of each sorbent was performed. This enabled measuring the release of light absorbing particles from the sand and activated carbon respectively (Table 2.1). When taking this into account, the sand seems not to sorb any dye and the activated carbon have sorbed it all. The reason for the negative values is most likely difference in particle content in the two sets of samples.
The low light absorbance before exposure to sorbents makes the test sensitive to particles released from the sorbents and there is a clear disturbance from both the sand and the activated carbon. This risk is reduced by increasing the disperse Black 2 concentration 5 times.

To solve the problem with particles being released from the sorption material and interfering with the spectrophotometry measurements the speed of the shaking table was lowered, the activated carbon was washed before use to remove the majority of small particles and a filtration step introduced.

2.1.3 Second sorption test

Idea

This step was carried out in order to test whether the changes proposed above improved the method and to make a first test of the suitability of the sorption materials. Seeing that the sand did in fact not sorb any Disperse Black 2 why it was not used in this step.

Method description

In order to wash the activated carbon 200 ml of water was added and it was shaken and rinsed until no more particles were released (for this particular carbon 6 times was enough). The activated carbon was then dried at 105°C over-night and then kept in an air-tight container.

250 ml of 1 mol L\(^{-1}\) Disperse Black 2 solution (25 mg L\(^{-1}\)) was prepared and was kept at 8°C. Due to the solubility of the compound (26.65 mg L\(^{-1}\) at 25°C) the solution was heated slightly while on a magnetic stir to avoid oversaturation.

0.01 g of each sorbent (Leca, vermiculite and activated carbon) was added to plastic tubes in duplicates. 25 ml 1 M Disperse Black 2 solution was added to each tube and was shaken on shaking table for 2 hours. All samples were centrifuged for ten minutes before being filtrated.

The vacuum filtration set-up consisted of one Büchner flask, a cylindrical funnel, a funnel base with sand core plate, a metal clamp and a rubber hose connected to an aspirator. The samples were filtered over glass microfiber filters (GC/F; VWR Denmark) and the filtrate was transferred into LKT-cuvettes. The light absorbance was measured at 452 nm.

Results

The results suggest that the three sorbents all have an effect on the concentration of Disperse Black 2. All absorbance measurements show a decrease in absorbance of between 12 and 18% (Table 2.2). However there is still a problem with particles from the activated carbon.
Table 2.2 The sorption of Disperse Black 2 using three sorption materials

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Mean absorbance</th>
<th>Mean concentration [mg L⁻¹]</th>
<th>Reduction [mg L⁻¹]</th>
<th>Reduction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non</td>
<td>0.080</td>
<td>8.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.069</td>
<td>7.1</td>
<td>1.3</td>
<td>15.5</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>0.071</td>
<td>7.4</td>
<td>1.0</td>
<td>11.9</td>
</tr>
<tr>
<td>Leca</td>
<td>0.067</td>
<td>6.9</td>
<td>1.5</td>
<td>17.9</td>
</tr>
</tbody>
</table>

Problems

The results from the spectrophotometry show that far from all the added Disperse Black 2 was dissolved before conducting the sorption experiment. A probable explanation for this is that the solution was stored at 8°C and not heated to a temperature where the solubility would allow 25 mg L⁻¹.

Solutions and improvements

To be able to test the hypothesis that the temperature of the solution was in fact causing the low absorbance a solubility test was made.

2.1.4 Solubility test

Idea

This step was carried out in order to establish how much Disperse Black 2 is soluble at different temperatures.

Method description

25 ml of the dye solution (1 mol L⁻¹ Disperse Black 2) was transferred into three identical glass bottles. One was stored in a refrigerator (ca 8°C), one was stored in an incubator (ca 37°C) and the last was kept at room temperature (ca 20°C) over night.

The exact temperature was measured before proceeding with the experiment. Using a pipette, 8 ml of each solution was transferred into 3 LKT-cuvettes. The rest of each solution was filtered over glass microfiber filters (GC/F; VWR Denmark) and transferred into LKT-cuvettes. The light absorbance was measured at 452 nm and the formula obtained from the calibration curve was used to calculate corresponding concentrations.
Results

There is a clear difference between the two lower temperatures and the highest (Table 2.3). The reason for the highest concentration not corresponding to the added amount of dye could be explained by the calibration curve only covering up to 10 mg L$^{-1}$ and it may not be linear at higher concentrations. There is also a difference in concentration before and after filtration suggesting that some dye is removed in this process. This might be an issue when looking at the adsorption to sorption materials.

Table 2.3 Solubility of Disperse Black 2 at three different temperatures

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Unfiltered conc. [mg L$^{-1}$]</th>
<th>Filtered conc. [mg L$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6</td>
<td>12.0</td>
<td>8.9</td>
</tr>
<tr>
<td>20.1°C</td>
<td>11.9</td>
<td>9.8</td>
</tr>
<tr>
<td>35.7°C</td>
<td>18.3</td>
<td>14.8</td>
</tr>
</tbody>
</table>
### 3 PAC test 1 with dye

<table>
<thead>
<tr>
<th>PAC [g L(^{-1})]</th>
<th>PAC [g 25ml(^{-1})]</th>
<th>Abs [452 nm]</th>
<th>Ce [mg L(^{-1})]</th>
<th>(x/m=)q(_e) [mg g(^{-1})]</th>
<th>log Ce</th>
<th>log (x/m)</th>
<th>1/Ce</th>
<th>1/q(_e)</th>
<th>Adsorbed [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.024</td>
<td>0.0006</td>
<td>0.085</td>
<td>5.287</td>
<td>300.5</td>
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<td>0.19</td>
<td>0.0033</td>
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<td>0.0008</td>
<td>0.022</td>
<td>1.123</td>
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<td>2.55</td>
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<td>2.511</td>
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<td>2.40</td>
<td>0.40</td>
<td>0.0040</td>
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</tr>
<tr>
<td>0.08</td>
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<td>0.011</td>
<td>0.396</td>
<td>151.3</td>
<td>-0.40</td>
<td>2.18</td>
<td>2.53</td>
<td>0.0066</td>
<td>96.8</td>
</tr>
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<td>0.16</td>
<td>0.004</td>
<td>0.009</td>
<td>0.264</td>
<td>76.5</td>
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<td>3.79</td>
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<tr>
<td>0.4</td>
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<td>0.264</td>
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<td>1.49</td>
<td>3.79</td>
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## 4 PAC test 2 with dye

Concentration before adsorption: 9.84 mg L$^{-1}$ Disperse Black 2

<table>
<thead>
<tr>
<th>PAC</th>
<th>PAC</th>
<th>Abs</th>
<th>$C_e$</th>
<th>$x/m=q_e$</th>
<th>log $C_e$</th>
<th>log $(x/m)$</th>
<th>$1/C_e$</th>
<th>$1/q_e$</th>
<th>Adsorbed [%]</th>
</tr>
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<tbody>
<tr>
<td>0.004</td>
<td>0.0006</td>
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<td>6.542</td>
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<td>7.63</td>
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## 5 Vermiculite test with dye
CONCENTRATION BEFORE ADSORPTION: 9.84 mg L\(^{-1}\) Disperse Black 2

<table>
<thead>
<tr>
<th>Vermiculite [g L(^{-1})]</th>
<th>Vermiculite [g 25ml(^{-1})]</th>
<th>Abs [452 nm]</th>
<th>C(_e) [mg L(^{-1})]</th>
<th>x/m=q(_e) [mg g(^{-1})]</th>
<th>log C(_e)</th>
<th>log (x/m)</th>
<th>1/C(_e)</th>
<th>1/q(_e)</th>
<th>Adsorbed [%]</th>
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<tbody>
<tr>
<td>0.24</td>
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<td>0.159</td>
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<tr>
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<td>0.038</td>
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<tr>
<td>1.2</td>
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<td>0.111</td>
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<td>5.12</td>
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<td>0.71</td>
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<td>0.412</td>
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<tr>
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<td>0.1</td>
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<td>0.31</td>
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## 6 Biocides in stock solution

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Concentration [µg mL⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylisothiazolinone</td>
<td>MI</td>
<td>157.85</td>
</tr>
<tr>
<td>Benzisothiazolinone</td>
<td>BIT</td>
<td>101.35</td>
</tr>
<tr>
<td>Mecoprop</td>
<td>MCPP</td>
<td>104.35</td>
</tr>
<tr>
<td>Carbendazim</td>
<td>CD</td>
<td>109.10</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>IP</td>
<td>109.25</td>
</tr>
<tr>
<td>Diuron</td>
<td>DR</td>
<td>103.10</td>
</tr>
<tr>
<td>Iodocarb</td>
<td>IPBC</td>
<td>104.60</td>
</tr>
<tr>
<td>Terbutryn</td>
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</tr>
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<td>Cybutryn</td>
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<td>Octylisothiazolinone</td>
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<tr>
<td>Tebuconazole</td>
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</tr>
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<td>Dichlorooctylisothiazolinone</td>
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<tr>
<td>Compounds</td>
<td>TBU</td>
<td>OIT</td>
</tr>
<tr>
<td>-----------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>initial concentration [μg/mL]</td>
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<tr>
<td>Limit of detection (LOD)</td>
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</tr>
<tr>
<td>Limit of quantification (LOQ)</td>
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<td>&lt; LOD</td>
</tr>
<tr>
<td>PAC 0.0012</td>
<td>0.50</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>PAC 0.0024</td>
<td>0.90</td>
<td>&lt; LOD</td>
</tr>
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<td>PAC 0.0036</td>
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<td>&lt; LOQ</td>
</tr>
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<td>PAC 0.0048</td>
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<td>&lt; LOD</td>
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<tr>
<td>PAC 0.006</td>
<td>1.20</td>
<td>&lt; LOQ</td>
</tr>
<tr>
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<td>&lt; LOQ</td>
</tr>
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<td>&lt; LOD</td>
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<tr>
<td>PAC 0.048</td>
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<td>&lt; LOD</td>
</tr>
<tr>
<td>Compounds</td>
<td>TBU</td>
<td>OIT</td>
</tr>
<tr>
<td>-----------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Initial concentration [μg/mL]</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>18.90</td>
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<td>Verm. 0.18</td>
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<td>16.60</td>
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<td>6.20</td>
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<td>Verm. 12.0</td>
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<td>5.80</td>
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<tr>
<td>Verm. 24h 3.0</td>
<td>17.30</td>
<td>13.20</td>
</tr>
</tbody>
</table>
Sorption av organiska biocider i dagvatten

Regnvatten har länge ansett vara rent men detta är inte sant. Giftiga ämnen läcker från färgen och putsen på våra hus och påverkar de organiser som lever i våra sjöar och åar. Hur ska man göra för att få bukt med detta problem?

Regnvatten, eller dagvatten som det kallas efter att det hamnat på marken, har länge ansetts vara rent. Detta är inte sant eftersom allt regn som faller i staden, på vägar, väggar, hustak och trädgårdar, förörebas av dessa ytor. På senare år har forskningen tittat på vilka kemikalier som finns i dagvattet och hur dessa påverkar djur och växter.


För att kunna hindra biociderna att nå känsliga vattendrag testades en metod där olika material används för att adsorbera föroreningarna. Material som testades var pulveriserat aktivt kol (PAK), krossade LECA-kulor, samt ett naturligt mineral, vermikulit. I ett första försök att testa materialens adsorptionsförmåga användes ett färgämne som substitut då analyser av biocider är mycket kostsamt. LECA visade sig vara en dålig adsorbent då höga koncentrationer av färgämnet fanns kvar i lösningen medan vermikulit och PAK båda adsorberade mer färg.

I nästa steg blandades en lösning med 13 olika biocider med olika koncentrationer av PAK och vermikulit. Efter två timmar filtrerades materialen bort och den resterande lösningen skickades på analys. Resultatet visade att redan vid små mängder PAK adsorberades nästan alla biocider. För att uppnå samma resultat med vermikulit krävs större mängder (ungefär 100 gånger så mycket). Då vermikulit är betydligt billigare skulle det ändå kunna vara lönsamt att använda mineralet.


Sammanfattningsvis är både PAK och vermikulit möjliga att använda vid rening av dagvatten. Det som avgör vilket material som är bäst lämpat är faktorer som metod, kontakttid, underhållsfrekvens samt ekonomi.