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Sorption and Degradation Potential of Pharmaceuticals in Sediments from a Stormwater Retention Pond

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Abstract: Stormwater retention ponds commonly receive some wastewater through misconnections, sewer leaks, and sewer overloads, all of which leads to unintended loads of organic micropollutants, including pharmaceuticals. This study explores the role of pond sediment in removing pharmaceuticals (naproxen, carbamazepine, sulfamethoxazole, furosemide, and fenofibrate). It quantifies their sorption potential to the sediments and how it depends on pH. Then it addresses the degradability of the pharmaceuticals in microcosms holding sediment beds and pond water. The sediment-water partitioning coefficient of fenofibrate varied little with pH and was the highest (average log Kd: 4.42 L kg\(^{-1}\)). Sulfamethoxazole had the lowest (average log Kd: 0.80 L kg\(^{-1}\)), varying unsystematically with pH. The coefficients of naproxen, furosemide and carbamazepine were in between. The degradation by the sediments was most pronounced for sulfamethoxazole, followed by naproxen, fenofibrate, furosemide, and carbamazepine. The first three were all removed from the water phase with half-life of 2–8 days. Over the 38 days the experiment lasted, they were all degraded to near completion. The latter two were more resistant, with half-lives between 1 and 2 months. Overall, the study indicated that stormwater retention ponds have the potential to remove some but not all pharmaceuticals contained in wastewater contributions.

Keywords: emerging micropollutant; wastewater; constructed pond; sediment bed; microcosm

1. Introduction

The presence of pharmaceuticals in receiving waters can be due to a high daily consumption [1] combined with incomplete removal by wastewater treatment plants [2,3]. They can also originate from combined sewer overflow, when a mixture of stormwater and wastewater is discharged into the receiving environment during storm event [4]. Separate storm sewers can also discharge pharmaceuticals during rainy as well as dry weather, their presence in storm sewer discharges comes from misconnected wastewater pipelines [5], cross-connections between storm and foul sewers, leakage between pipes, and overload of sewer pipelines [6–8]. A typical example is carbamazepine, which concentration in a combined sewer overflow peaks during the first flush of a rain event, ranging from 175 ng L\(^{-1}\) to 923 ng L\(^{-1}\) [9]. The concentration of pharmaceuticals and other pollutants in storm sewer runoff fluctuates over time, depending on the catchment, the condition of the sewer network, and the frequency and intensity of rainfall events. Often it is low compared to concentrations in raw wastewater [10]. Nevertheless, for substances where wastewater treatment plants have efficient removal ability, substances discharged from storm drainage systems can be a significant contribution to pharmaceuticals in the receiving water [11].

An increasing part of the urban stormwater runoff is treated prior to discharge by decentralized and low-tech treatment systems such as artificial ponds, commonly known as retention ponds, wet
ponds or wet detention basins \[6,12,13\]. They can hold the runoff water from days to weeks, allowing various natural processes to proceed in their water phase and sediments. Sorption and degradation are the main processes that determine the fate of organic pollutants in such sediment-water systems \[14\]. The former is especially critical in determining the transport and mobility of pollutants \[15\]. In the case of organic pollutants, sorption may influence degradation as well, as the adsorbed pollutant can become the object of further chemical and/or biological degradation. Hence, the combination of sorption and degradation has important environmental implications on the fate of organic pollutants in stormwater treatment systems.

It is well known that sorption of pollutants is strongly affected by the matrix’ content of organic matter, clay minerals, temperature and the pH \[16\–18\]. Degradation is more associated with the activity of microorganisms present in the sediment-water system \[18,19\], where redox potential and oxygen condition are main factors \[20\–23\]. Studies have already shown that stormwater retention ponds can reduce pollutants including polycyclic aromatic hydrocarbons (PAHs), heavy metals and biocides by processes like adsorption, sedimentation and degradation \[24\–26\]. However, less is known about the fate of pharmaceuticals in such ponds, especially the removal mechanisms and the main factors that govern removal rates.

The objective of this study was to contribute to the understanding of the fate of pharmaceuticals in stormwater retention ponds, with a focus on the role of sorption and degradation in pond sediments. This was achieved by (a) studying the sorption of selected pharmaceuticals to stormwater pond sediments under environmentally realistic pH conditions; (b) quantifying the degradation rate and overall removal efficiency in microcosms under different oxygen regimes.

2. Materials and Methods

2.1. Materials

The compounds selected for observation were naproxen (NAP), carbamazepine (CAR), sulfamethoxazole (SUL), furosemide (FUR), and fenofibrate (FEN). These compounds are representatives of five common therapeutic categories that have been frequently detected in surface water \[27\–30\]. Standards of NAP (>98%), CAR (>98%), SUL (>98%), FUR (>98%), and FEN (>98%) were purchased as powder from Sigma-Aldrich. Isotopically labeled standard carbamazepine-d\(_2\) was purchased from Santa Cruz Biotechnology and fenofibrate-d\(_6\) were from Qmx Laboratories. Physicochemical properties of the five compounds are given in Table 1. Formic acid was purchased from Sigma-Aldrich. Stock solutions were prepared in methanol and acetonitrile (LC-MS grade, Th. Geyer).

<table>
<thead>
<tr>
<th>Name and CAS Number</th>
<th>Structure</th>
<th>Physical and Chemical Characteristics</th>
<th>Therapeutic Category</th>
<th>Species at pH</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>5  6  7  8</td>
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<tr>
<td>Naproxen 22204-53-1</td>
<td><img src="image" alt="Naproxen Structure" /></td>
<td>MW: 230.3  log K(_{OW}): 3.18  pK(_a): 4.15</td>
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</tr>
<tr>
<td>Carbamazepine 298-46-4</td>
<td><img src="image" alt="Carbamazepine Structure" /></td>
<td>MW: 236.3  log K(_{OW}): 2.45  pK(_a): 13.9</td>
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<tr>
<td>Sulfamethoxazole 723-46-6</td>
<td><img src="image" alt="Sulfamethoxazole Structure" /></td>
<td>MW: 253.3  log K(_{OW}): 0.89  pK(_a): 1.6, 5.7</td>
<td>Antibiotic</td>
<td>0/– 0/– – –</td>
</tr>
</tbody>
</table>
Table 1. Cont.

<table>
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<th>Name and CAS Number</th>
<th>Structure</th>
<th>Physical and Chemical Characteristics</th>
<th>Therapeutic Category</th>
<th>Species at pH</th>
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<td>MW: 330.7</td>
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<tr>
<td>Furosemide 54-31-9</td>
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<td>log $K_{OW}$: 2.03</td>
<td>Diuretic +/− (a)</td>
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<td></td>
<td></td>
<td>$pK_a$: 3.9</td>
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<td>Fenofibrate 49562-28-9</td>
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<td>MW: 360.8</td>
<td>Lipid regulator</td>
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<td></td>
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<td>log $K_{OW}$: 5.19</td>
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<td></td>
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<td>$pK_a$: −</td>
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</tbody>
</table>

*a charge of the relevant species at the pH: (+−) zwitter.

2.2. Sampling

All samples were collected at the same time in January 2017, from a stormwater retention pond in Brabrand, Denmark. The pond has a permanent water surface of 6400 m$^2$, with an averaged water depth of 1.14 m. Sediments were collected with a 5 cm diameter corer, at 0.5 m water depth, from three randomly chosen places close to the inlet of the pond. The top 5 cm of the sediments were used in the experiments. After transfer to the laboratory, the sediments from the three locations were gently mixed and homogenized before use. Water samples were collected into 5 L glass bottles. All collected samples were immediately transferred to the laboratory and kept in the dark at 5 °C. Sediment properties are shown in supplementary material Table S1.

2.3. Sorption Experiment

To determine the effect of pH on the sorption behavior of the selected pharmaceuticals, a batch equilibrium method following OECD guideline 106 [31] was applied. Briefly, the pond water was first filtered (0.3 µm glass fiber filter) to remove particles, and 10 g of freeze-dried sediment and 100 mL of the filtered water were placed into 100 mL glass bottles. The suspensions were spiked with pharmaceuticals at six concentrations (50, 100, 200, 500, 1000, and 1500 µg L$^{-1}$), and adjusted to fixed pH values (5, 6, 7 and 8) using 1 M HCl and 0.1 M NaOH. Although pharmaceutical in nature waters typically ranges from ng L$^{-1}$ to µg L$^{-1}$, the high concentration used in sorption studies has been commonly used in lab [32–34]. The bottles were covered with aluminum foil and shaken continuously by a mechanical shaker (110 rpm) at 23 °C for 24 h. Initial trials had shown that equilibrium would be reached within this time period. A subsample from each bottle was then collected and centrifuged in a microcentrifuge tube at 7800 rpm for 15 min. After that, 800 µL of the supernatant was transferred to a 2 mL low adsorption vial and stored at −18 °C in the dark until analysis. All experiments were conducted in triplicate.

The amount of adsorbed pharmaceuticals was calculated as the difference between the mass initially added and the mass remaining in the solution upon equilibrium, as Equation (1):

$$C_s = \frac{(C_0 - C_e) \times V}{M},$$

where $C_0$ and $C_e$ are the initial and equilibrium concentrations in the water phase, respectively (µg L$^{-1}$). $V$ is the water volume (L) and $M$ is the organic matter of the sediments (g) used in the batch tests. $C_s$ is the concentration of pharmaceuticals adsorbed onto the sediments, normalized to the organic matter (OM) of the sediments (µg (g OM$^{-1}$)). The sorption isotherms were then fitted to a Freundlich isotherm model as Equation (2):

$$C_s = K_f \times C_e^{1/n},$$

where $K_f$ is the Freundlich distribution coefficient (g$^{1−1/n}$ L$^{1/n}$ kg$^{-1}$) and $n$ is the linearity parameter.

Partitioning coefficient ($K_d$, L kg$^{-1}$), which describes the concentration ratio of the compound between the sediment organic matter content and the liquid phase at equilibrium was calculated. It is
used to assess the mobility and fate of chemicals in the environment [35,36]. In this study, $K_d$ values were expressed as the slopes of the Freundlich isotherms at zero concentration.

### 2.4. Removal Kinetics in Microcosm

In an intact water-sediment system, a decrease of a compound in the water phase does not necessarily imply that the removed amount has been completely sorbed or completely mineralized. Its fate is governed by a combination of diffusion into the matrix, sorption, and biological and chemical degradation, for example, hydrolysis and oxidation. In stormwater ponds, oxygen conditions vary substantially over the day and over the seasons [37]. Usually the water phase and the sediment surface is aerobic while the deeper sediments are anaerobic. Therefore, to simulate a natural pond system, microcosm experiments were set up to study the effect of available oxygen on the removal of the pharmaceuticals and hereby achieve an improved understanding on the processes governing their fate.

Three types of microcosms (hereafter 'cosms') were established (Figure 1). The first two were kept aerobic (AE) and anaerobic (ANAE) by aerating the water phase with air and $N_2$, respectively. The third was designed to mimic a real-life water-sediment scenario (RE): no gas was sent in and the water was left undisturbed. For all cosms, the ratio of water volume to wet sediment mass was 2.44 mL g$^{-1}$. This ratio, on the high side of what is found in retention ponds, was chosen intentionally to manifest the sediment processes, which are the focus of the study. For the AE and ANAE cosms, 90 g of wet sediments and 220 mL of pond water were filled in glass bottles, resulting in approximately 2 cm deep sediment beds and 8 cm deep water phases. For RE cosms, 180 g of wet sediments and 440 mL of pond water were placed in 2 L crystallizing dishes, yielding sediment bed depths of approximately 1.5 cm and water depths of 2.5 cm (Figure 1). After being filled with sediments and water, all cosms were covered with aluminum foil to minimize photochemical reactions. AE and ANAE cosms were sealed with caps fitted with butyl rubber stoppers. Controls and blanks were conducted for all types of cosms, and each type of cosm was conducted in triplicate, resulting in a total of 27 cosms.

![Figure 1. Schematic diagram of the process of the microcosm experiment (left) and experimental reactors for AE, ANAE and RE microcosms (right).](image-url)
After the sediment beds had settled for approximately 3 days, the cosms were pre-conditioned to have the desired oxygen conditions. A one-week process achieved the conditions by flushing AE cosms with air for 20 min every 3 h, and flushing ANAE cosms with N\textsubscript{2} for 3 h each day. Prior to the introduction of pharmaceuticals, the oxygen was equilibrated for another week. During this week, the cosms were slowly shaken to evenly diffuse the gases without disturbing the settled sediment beds. Before the introduction of pharmaceuticals, the stability of the bed condition was confirmed by vertically profiling the cosms for redox potential and pH. AE cosms were also profiled for dissolved oxygen. Redox and pH microsensors with a tip diameter of 100 µm using Ag/AgCl electrode as reference electrode were purchased from Unisense, Denmark, and oxygen microsensors with a tip diameter of 140 µm were purchased from Loligo Systems, Denmark. All profiling were performed by a motorized micro-manipulator (Thorlabs, Sweden) with a spatial resolution of 100 µm.

A mixture of pharmaceuticals was spiked into the water phase and incubated at 23 °C for 38 days. The procedure of aerating was kept the same as in the equilibrium period for the 38 days. The concentration change in the water phase was monitored by sampling 2 mL of water on days 0, 1, 2, 4, 7, 10, 16, 22, 28, and 38 using a glass syringe. The syringe was cleansed with 2 mL of 50/50 methanol/acetone after each sampling. The 2 mL subsample and the 2 mL of washing solution were combined in a Teflon centrifuge tube and mixed by ultra-sound sonication for 10 min. The mixture was then centrifuged at 7800 rpm for 15 min, 800 µL of the supernatant was then collected and transferred into a 2 mL low adsorption vial. All collected samples were stored at −18 °C in the dark until LC-MS analysis. Prior to termination of the experiments, the sediment beds were again profiled.

A first-order decay model was applied to quantify the sediment elimination rate of the studied compounds using Equation (3). The dissipation half-lives (DT\textsubscript{50}) of the compounds were estimated as the time to halve the amount of the compound in the water phase of the system using Equation (4). All simulations and statistics were performed in SigmaPlot (13.0).

\[ C_t = C_0 \times e^{-kt}, \quad (3) \]
\[ DT_{50} = \frac{\ln 2}{k}, \quad (4) \]

where \( C_0 \) and \( C_t \) (µg g\textsuperscript{-1}) are the concentrations of a pharmaceutical transferred into the sediments (normalized to dry weight) at time zero and time \( t \) (d), and \( k \) (d\textsuperscript{-1}) is a first-order rate constant.

2.5. Extraction

Pharmaceuticals were extracted from the sediments upon the termination of the cosm experiment using microwave-assisted solvent extraction. After decanting the water phase from the cosms, the sediments were freeze-dried and gently ground. For each cosm, four sediment sub-samples of approximately 1.5 g was placed in a 100 mL PTFE extraction vessel, to which a mixture of 20 mL of 35/35/30 of methanol/acetone/miliQ was added as an extraction solution. The microwave program followed the method used by [38] to extract pharmaceuticals from river water and sediments. The steps were: preheating at 700 W for 5 min up to 60 °C, followed by 600 W for 5 min up to 100 °C and extraction at 700 W at 100 °C for 20 min. The extracted solution was transferred to a Teflon centrifuge tube and centrifuged at 7800 rpm for 20 min. 800 µL of the supernatant was then collected and stored at −18 °C in the dark until analysis. To assess the recovery of the extractions, the dry sediments were spiked with 100 µL of 10 mg L\textsuperscript{-1} isotopically labeled fenofibrate-d\textsubscript{6} and went through the whole extraction as well as the analysis procedures. An individual recovery was determined for each extraction vessel by comparing the mass of extracted fenofibrate-d\textsubscript{6} to the mass initially spiked.

Results show that the average recovery was 91.1%, with a standard deviation of 9.5%. The extracts from each extraction vessel were corrected by their corresponding recovery.
2.6. Chemical Analysis

Individual stock solutions of the pharmaceuticals were prepared from powder in 50/50 methanol/acetonitrile (LC-MS grade, Sigma-Aldrich, Steinheim, Germany). A mixture including all five pharmaceuticals was prepared from the individual stock solutions, to a concentration of 100 mg L\(^{-1}\) of each compound. The mixture was used to spike both the sorption and cosm experiments. Isotopically labeled carbamazepine-d\(_3\) was added as an internal standard into each low adsorption vial before analysis by high-performance liquid chromatography equipped with a mass spectrometer (HPLC-MS, Dionex Ultimate 3000/MSQ Plus, Thermo-Scientific, Waltham, MA, USA) with an electrospray interface (ESI). The compounds were separated by a C-18 column (L = 150 mm, ID = 2 mm, particles size = 4 \(\mu\)m, Thermo Scientific). A multi-step gradient of LC-MS grade water (A) and 0.1% formic acid in acetonitrile (B) used was: 0–1 min 10% B, 1–21 min 10 to 90% B, 21–24 min 90 to 10% B. The capillary voltage of the MS was set to 3000 V and the probe temperature was at 340 °C. Positive ionization mode was used for all the selected compounds in single ion monitoring (SIM), and the identification of substances was based on the retention time, together with the matching of the diagnostic ions and the standards (Table S2). The limit of detection (LOD) and quantification (LOQ) were determined as the lowest concentration which gave a signal to noise ratio at 3 and 10, respectively (Table S3).

3. Results and Discussion

3.1. Sorption

Sorption was assessed through simulation using a Freundlich model (Equation (2), Figure 2). To allow comparison between the determined sorption constants \((K_f)\), all combinations of pharmaceuticals and pH were simulated applying the same exponent \((n)\), obtained to 1.43 by minimizing the overall root mean error for all 20 combinations of the five pharmaceuticals and the four pH conditions. The Freundlich simulations yielded an average coefficient of determination \((R^2)\) of 0.9655, ranging from 0.8218 for the weakest correlation (sorption of SUL at pH 7) to 0.9995 for the strongest correlation (sorption of FEN at pH 6) (Table S4).

![Figure 2](image-url)  
*Figure 2.* Sorption isotherms of pharmaceuticals to sediments under four pH conditions, with all isotherms normalized to the organic matter of the sediments. The solid points show the measured data; the solid lines represent the best fit of a theoretical Freundlich isotherm. Note the differences in axis scales.
The sorption of the electroneutral compounds (CAR and FEN) differed at the four pH-values, but without any trend to increase or decrease with pH. However, sorption of the ionic compounds NAP, SUL and FUR, which were primarily present in their anionic form at the applied pH conditions, did exhibit a trend to decrease with increasing pH (except for SUL at pH 7). Schaffer et al. [39] reported similar observations for NAP in column experiments with a natural sandy aquifer material and [34] for SUL in natural agricultural soil. In both studies, the sorption affinity decreased with increases of pH. Since the sediment surfaces probably were predominantly negatively charged due to natural organic matter and clay mineral surfaces [40], it can be assumed that the sorption of NAP, FUR and SUL was mainly driven by the electrostatic interaction with sediment surfaces. This assumption is also in agreement with Martínez-Hernández et al. (2014) [41], who investigated the sorption of selected pharmaceuticals and personal care products to organic and inorganic particles.

Several studies have shown that the sorption of sulfonamide antibiotics tends to decline with the increase of pH [42–47]. However, in some cases, surface complexation may affect the overall behavior of sorption for organic compounds [40,48,49], which could be an explanation for the slight increase of $K_d$ for SUL at pH 7.

There was a positive relationship between log $K_d$ and log $K_{ow}$ (Figure 3, right), which can be described by a log $K_{ow}$-based linear function. This finding is consistent with Maskaoui et al. (2007) [50], who assessed the partitioning of river colloids and selected pharmaceuticals. The deviation in the log $K_d$-log $K_{ow}$ relationship in the present study might have been caused by pH. However, the relation with pH was not proportional to the dissociation of the compounds. During a sorption process, various interaction mechanisms between a compound and the sediments, such as ion exchange, chemical bonding and surface complexation, may influence the overall sorption behavior of the compound to different levels. Nevertheless, the obtained results confirm that both the pH of the sediment system and the hydrophobicity of the compound were important for the sorption capacity.

![Figure 3](image-url)

**Figure 3.** Partitioning coefficients (log $K_d$) versus pH of the sediment-water system and the octanol-water partitioning coefficient (log $K_{ow}$) of the substances.

### 3.2. Sorption and Degradation in Cosms

Upon spiking the cosms with pharmaceuticals, all compounds continuously declined in the water phases (Figure 4). Their removal was generally fastest in the cosms with high oxygen content (AE) compared to the anaerobic (ANAE) and undisturbed (RE) cosms. Pharmaceuticals in the latter two behaved more or less the same in terms of water phase decline. The controls showed that most substances were stable in the absence of a sediment bed. FEN, an exception, did decrease significantly in the AE and ANAE controls, and also to some degree in the RE controls. However, the decrease of
FEN was still much slower in the controls than in the cosms that contained sediment beds. The blanks showed that no cross-contamination occurred during the sub-sampling. Microsensor profiling showed that redox potential stayed high in the water and sediments of the AE cosms, while it decreased through the experiment in the RE cosms and the ANAE cosms (Figure S1). For all cosms, pH in the sediment beds increased throughout the experiment, from slightly below 7 to slightly above 7. Dissolved oxygen was profiled for the RE cosms only, and showed an increase over the course of the experiment.

![Figure 4](image-url)  
**Figure 4.** The measured concentration of pharmaceuticals in the water phase in the aerobic (AE), anaerobic (ANAE) and undisturbed microcosms (RE).

It can be assumed that the elimination of pharmaceuticals in the cosms was a combination of sorption, diffusion and degradation, but the role played by each process is difficult to discern at a glance. For all the cosms and all pharmaceuticals, the removal from the water phase was fastest during the first 2 days, after which the rate tended to slow down (Figure 4). The fast initial removal can be explained by diffusive mass transfer into the sediments, followed by sorption to the sediment matrix. Upon saturation of the sediments’ sorption capacity, removal of pharmaceuticals from the water phase will have been governed by degradation. For the sake of simplification of data interpretation, it was assumed that sorption and diffusion were the sole factors causing the removal from the water phase during the first 2 days of the experiment, upon which equilibrium was assumed to have been reached. Degradation was then assumed to take over and further sorption neglected. Hence, the degradation rates calculated using Equation (2) took day 2 as time zero.

Upon termination of the cosm experiment, the mass balance in the water-sediment system was quantified by extracting the pharmaceuticals from the sediments (Figure 5). The difference between the originally added amounts and the amounts recovered from the sum of the sediment and water compartments was assumed to correspond to the amount eliminated by processes in the sediments (Figure 5).

For all conditions, SUL was degraded the most, followed by NAP, FEN, FUR, and CAR (Figure 5). The conditions under which the degradation took place had some impact on the elimination of substances, albeit this was not conclusive. The undisturbed systems (RE) tended to have the highest removals for most substances.
was achieved in the aerobic cosms (AE) (Table S5). The degradation rates in the anaerobic cosms
under all tested conditions, resulting in an average DT50 of 36.5 ±

Even though CAR only sorbed moderately to the sediments (Figure 2), sorption was the main
cause of its elimination from the water compartment. This indicates that the initial elimination of CAR
from the water phase was more associated with sorption onto and diffusion into the sediments than
to degradation. At the end of the experiment, an average of 35 ± 4.2% of the initially added CAR
remained in the water phase, while 36 ± 2.8% of it was extracted from the sediments (Figure 5). This
left a missing mass of approximately 29 ± 6% which was assumed degraded. The low contribution
from degradation to the overall removal from the water compartment indicates that the high stability
of CAR was caused by a low degradability, which is consistent with [51] finding that this chemical
is highly resistant to degradation during sewage treatment. The missing mass corresponded to a
degradation rate ranging from 0.0186 ± 0.0012 day−1 to 0.0194 ± 0.0014 day−1 for anaerobic and
aerobic cosms, respectively. CAR exhibited high recalcitrance towards degradation in the sediments
under all tested conditions, resulting in an average DT50 of 36.5 ± 0.8 day (Table S5). The DT50 value
obtained in this study is smaller than the 47 day reported by Löffler et al. (2005) [52], who studied
the fate of pharmaceuticals in systems containing sediments and water from a creek. However, the
organic matter of the sediments in that study was only half of that of the present study’s sediments.
On the other hand, they used a somewhat lower water/sediment ratio (1.5 mL g−1), which would tend
to counteract the effect of a lower organic matter content. In this context, it is important to note that
the water/sediment ratios applied in various studies differ, which complicates comparison between
studies. Under idealized conditions and assuming that degradation only takes place in or on the
sediments, a doubling of the water/sediment ratio would cause a halving of observed water phase
degradation rates and a doubling of DT50 values.

FUR was slightly less resistant to degradation than CAR. Its shortest DT50 value, 22.2 ± 2.1 day,
was achieved in the aerobic cosms (AE) (Table S5). The degradation rates in the anaerobic cosms
were less than half of those of the aerobic ones (AE) (0.0144 ± 0.0014 d⁻¹ and 0.0314 ± 0.0029 day⁻¹, respectively). Based on the mass balance, the aerobic cosms had the least FUR remaining in the water compartment (24.1 ± 5.1%) with approximately 66.1 ± 7.9% degraded, while the anaerobic cosms had 37.1 ± 8% in the water phase with approximately 51.8 ± 9.5% been degraded. Although the sorption experiment showed that FUR and CAR had comparable adsorption affinities (Figure 3), the extracted amount was much less for FUR (average of 14 ± 6.2%). This indicates that FUR was more degradable than CAR, and especially under aerobic conditions. So far, hydrolysis and photolysis have been mostly considered as the removal mechanisms of FUR in water [53], while its biodegradation has not been reported so far [54].

The degradation rate for FEN was one order magnitude higher than that of CAR and FUR (ranging from 0.210 ± 0.006 d⁻¹ in anaerobic to 0.517 ± 0.0076 d⁻¹ in aerobic cosms). Undisturbed cosms were found to have the shortest DT₅₀ value (2.4 ± 0.1 d), and aerobic cosms had the longest (3.3 ± 0.04 d). Overall, 96.8 ± 1.5% of FEN was degraded during the experiment, with only 2.9 ± 1.4% adsorbed to the sediments (Figure 5). The adsorbed amount agreed poorly with the high sorption affinity found in the sorption experiment (Figure 3), which can be explained by that the adsorbed FEN was rapidly degraded in the sediments. This suggests that degradation is a fast and dominating process in FEN removal.

The removal of NAP and SUL were comparable, where both compounds had similar half-lives (average DT₅₀ = 7.7 ± 0.5 d and 5.2 ± 1.4 d, respectively) and similar remaining percentages in the water phase (averages of 0.16 ± 0.3% and 0.3 ± 0.5%, respectively). However, the sediments seemed to facilitate a faster removal of SUL under anaerobic conditions (0.16 ± 0.0008 d⁻¹), but showed no clear trend for NAP (Table S5). Nevertheless, the rate constant of NAP somewhat lower yet still comparable to that reported by Koumaki et al. (2017) [14], who studied the environmental fate of pharmaceuticals in a river water-sediment system under various redox conditions (0.1835 ± 0.0148 d⁻¹ at aerobic and 0.1063 ± 0.0103 d⁻¹ at anaerobic conditions), but applying a higher water/sediment ratio (3 mL g⁻¹).

For all tested conditions, almost all the SUL and NAP were eliminated from the water compartment (Figure 5), with the majority being degraded (99.6 ± 0.6% and 98.6 ± 0.5%, respectively). The readily degradability of NAP (more than 75%) was also reported by [55] in silica sand containing different sources of water, but the water/sand ratio was not stated and the data hence are not comparable. The extracted amount of SUL (0.04 ± 0.02%) agrees well with its weak tendency towards adsorption (Figure 3), while less NAP than expected was extracted (1.2 ± 0.3%), indicating that degradation played an important role in removing NAP, compared to adsorption. Wilt et al. [56] also found that NAP was almost completely removed by sediments from a constructed wetland in batch experiments, but at a lower water/sediment ratio (8 mL g⁻¹), with biodegradation contributing more than 70% of the total removal.

The present study suggests that degradation of the selected pharmaceuticals predominantly took place in the sediments of the cosms and that sorption attenuated some pharmaceuticals in this matrix. For many full-scale stormwater ponds the water/sediment ratio is roughly around 5–15 mL g⁻¹, depending on water depth and amount of deposited sediments, i.e., somewhat higher than the ratio of 2.44 mL g⁻¹ applied in the present study. Their water phase removal rates can hence be expected to be slower than in the cosms. Furthermore, the water residence time in stormwater retention ponds is often shorter than the expected half-life of some of the substances. Nevertheless, this study demonstrates that, stormwater ponds are capable of eliminating pharmaceuticals like FEN. Hence, under these circumstances, conventional wastewater treatment plant is not the only way to mitigate its environmental impacts. For substances with a lower degradability, sorption to the sediments might enhance subsequent degradation, as it allows attenuation of the substance and hence providing more time for degradation. However, for substances like CAR and FUR, with low degradability and moderate sorption affinity to sediments, stormwater detention ponds probably will have limited efficiency.
4. Conclusions

This study suggested that the sorption of selected pharmaceuticals to the sediments in stormwater retention ponds was affected both by pH and the hydrophobicity of the compound. Comparing all substances investigated, the impact of their hydrophobicity (log $K_{OW}$ 0.89 to 5.19) was though more important for the overall sorption than was pH. For NAP and FUR, however, pH did play an important role as log $K_d$ values decreased by approximately a value of one when pH increased from 5 to 8, while for FEN, CAR, and SUL, it played a lesser role, or no role at all.

SUL was the most readily degradable substance, followed by NAP, FEN, FUR, and CAR. Nearly all traces of the first three pharmaceuticals were removed from the water phase and degraded by or sorbed to the sediments within the 38 days the experiment ran. The last two substances were only moderately degraded or sorbed. The overall results indicate that stormwater retention ponds have the potential to mitigate SUL, NAP, and FUR, while these systems most likely will have little effect on FUR and CAR. It is hence clear that stormwater retention ponds can play a role in removing part of the less-persistent pharmaceuticals that they sometimes receive from storm drainage systems. The actual removal efficiency and the importance of sorption versus degradation will depend on the design of the system and its operational conditions. Overall it can be concluded that shallow systems with low water to sediment ratios and systems with long retention times will enhance mitigation of pharmaceuticals originating from an undesired discharge of wastewater into storm drainage systems.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/11/3/526/s1, Figure S1: Vertical profile of aerobic (AE), anaerobic (ANAE) and undisturbed (RE) microcosms before and after incubation in terms of redox potential (left), pH (middle) and dissolved oxygen concentration (right), Table S1: Properties of the sediment, Table S2: Identification of the selected pharmaceuticals in SIM mode by LC-MS, Table S3: Limit of detection and quantification of the compounds in water and sediments, Table S4: Freundlich model fitting result and sediment-water distribution coefficient. $K_f$ $(\mu g \cdot 1^{-1} \cdot n L^{-1} \cdot g^{-1})$, $K_d$ $(L \cdot kg^{-1})$, Table S5: The fitting results of first-order decay model.

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