

Reduction of stormwater runoff toxicity by wet detention ponds

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Abstract

The toxicity of stormwater runoff was investigated by a battery of tests using *Vibrio fischeri* (bacteria), *Selenastrum capricornutum* (algae) and *Daphnia magna* (crustaceans) as test organisms. The stormwater was highly toxic to the algae, lesser toxic to the crustaceans and non-toxic to the bacteria, i.e. the bacterial test was the least sensitive of the protocols applied. Treatment of the stormwater by aluminum salts was tested by adding aluminum in concentrations ranging from 2 to 40 mg Al L⁻¹. Aluminum concentrations up to 10 mg Al L⁻¹ reduced the toxic effect of the runoff whereas aluminum in concentration above 20 mg Al L⁻¹ was toxic.

Introduction

Stormwater runoff contains a wide range of contaminants [1]. Pollutants like PAH's, biocides, heavy metals and nutrients are often found in varying but significant concentrations. Due to the content of various contaminants, stormwater runoff has been found to be toxic to the aquatic environment [2, 3, 4], with potential negative ecological impacts on receiving waters.

Toxic effects are estimated by exposing test organisms to the potential toxic sample or compound followed by a calculation of the inhibition of the test organism. The inhibition can be growth inhibition, mobility inhibition, inhibition of the reproduction and etceteras. Inhibition is expressed as a given effect concentration (EC) after a given exposure time. That is, EC₅₀ is the concentration giving an inhibition equal to 50% after a certain exposure time and EC₁₀ is the concentration giving an inhibition

equal to 10% after a certain exposure time. Toxicity is not an absolute estimation but a relative measurement characteristic for the test organism applied, resulting in different EC₅₀ values for the same compound. Therefore, it is important to consider which organisms that are relevant to use as test organisms for environmental samples such as stormwater runoff. The optimal solution is to use a battery of toxicity tests to reveal the ecological impacts of a sample [5].

To reduce the content of nutrients, organic matter and the different organic and inorganic micro pollutants, the stormwater runoff can be led through a wet detention pond where sedimentation and uptake by plants reduce the concentration of the contaminants. To improve sedimentation, a flocculent such as aluminum can be added to the water phase. It is well known that aluminum can reduce the content of phosphorous in the water phase in lakes [6], but whether aluminum addition also reduces the toxic effect of the water phase has not been identified.

The objective of this study is to investigate how addition of aluminum affects the toxicity of stormwater runoff. The toxic effect is estimated applying three different toxicity tests. The results of the study can be applied to determine whether addition of aluminum to wet detention ponds can reduce the toxic effect of stormwater by adding similar quantities of aluminum as typically used to remove phosphorous from the water phase.

Method

Collection and storage of samples

Stormwater runoff samples were collected from a wet detention pond located in the southern part of Odense, Denmark. The wet detention pond is constructed as a part of the EC LIFE-treasure project [7] and is placed in a green area next to a catchment with light industry and associated roads (Figure 1). The catchment has an area of 27.4 ha of which 11.4 ha are impervious, resulting in an estimated runoff of 55,500 m³ year⁻¹. The stormwater runoff is pretreated in a grit chamber before entering the pond.

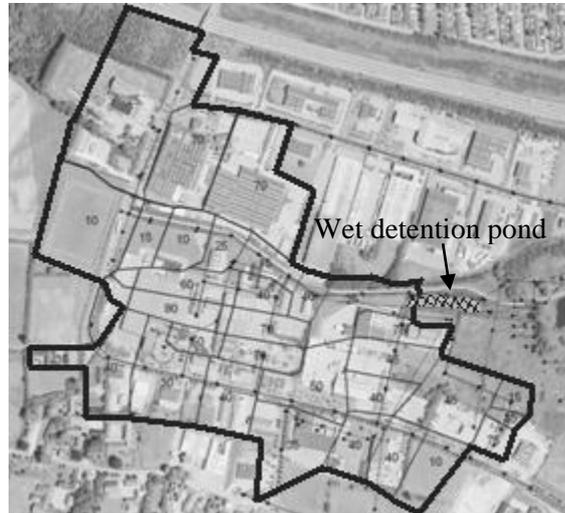


Fig. 1: Wet detention pond from where the samples were collected. The appurtenant catchment is outlined.

Stormwater runoff for analysis was collected from the center of the pond. The samples were collected in glass bottles over a two month period and stored at 5°C until analysis.

Preparation of samples prior to analysis

Four samples were collected over a two month period, two samples in February 2008 (sample I and II) and two at the beginning of April 2008 (sample III and IV). Due to a natural content of microalgae in the samples, the samples were filtered through a 0.45 µm filter, prior to toxicity tests. All four samples were analyzed for toxic effects using different toxicity tests. The last two samples were treated by aluminum addition to investigate its potential influence on the toxic effect.

The samples collected in April were divided into aliquots of 320 mL in 500 mL glass bottles. Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$) was added to a final aluminum concentration of 0, 2, 5, 7 and 10 mg Al L⁻¹ (sample III) and a concentration of 0, 10, 20, 30 and 40 mg Al L⁻¹ (sample IV). The aliquots were placed on a shaker for 1 h to ensure thoroughly mixing and afterwards left to settle for 3 days at 5°C. Three days was chosen as this is the minimum hydraulic retention time for a typical Danish wet detention

pond for stormwater treatment [8]. After the 3 days, the supernatant was extracted without disturbing the settled precipitate. The supernatant was tested for toxic effects by three different toxicity tests. The natural pH-value for sample III and IV prior to aluminum addition was 8.76 and 8.78, respectively. The products of the dissociation and hydration of the aluminum salt at these pH-values is mainly Aluminum hydroxide ($\text{Al}(\text{OH})_3$) and to a lesser extent Aluminate ion ($\text{Al}(\text{OH})_4^-$). Aluminum hydroxide could be observed as visible flocks in the aliquots with an aluminum concentration equal to 5 mg Al L^{-1} and above.

Toxicity tests

Toxicity tests were chosen on the basis the following criteria: The tests should be validated and comply with a standard; an existing protocol should be available; the tests should use organisms on different trophic levels; and the tests should be cost-time efficient. These criteria led to three different tests, using bacteria (*Vibrio fischeri*), algae (*Selenastrum capricornutum*) and crustaceans (*Daphnia magna*) as test organisms. *Vibrio fischeri* is a marine bacterium and will therefore not be found naturally in wet detention ponds. However, the test is commonly used and relative fast, giving the result after only 30 min and was on this basis included in the test battery. The last two tests use organisms which are indigenous to freshwater. All three tests are designed to measure acute toxic effects.

The test using *Vibrio fischeri* is based on the bacteria capacity to emit luminescence, meaning that the less luminescence the bacteria produce, the more stressed are the bacteria due to exposure to toxic substances. Specific volumes of the samples and different dilutions hereof were mixed with bacteria suspension (duplicate for each dilution). The luminescence was measured after 0, 5, 15 and 30 min of exposure to the sample on a M500 analyzer from SDI in the Microtox® Acute mode. Decrease in luminescence relative to a control gives an expression for the toxic effect and EC-values can be estimated. As *Vibrio fischeri* is a marine bacterium, the runoff samples were adjusted to a salinity of 2% prior to analysis. An advantage of this test is that for each dilution, a very large number of test individuals are applied, minimizing statistical fluctuations. The whole test

was carried out according to the international standard DS/EN ISO 11348-1.

The algal test is based on growth inhibition of the algae due to toxic substances. A specific volume of an algae suspension is added to a dilution series of a sample. Triplicates were made for each dilution. The growth rate was hereafter estimated by measuring the optical density (OD) at 670 nm after an exposure time of 0, 24, 48 and 72 hours. The growth rate of the algae is inhibited by toxic substances and a relative inhibition to a control can be calculated. In this study the toxicity test kit Algaltokit FTM, MicroBioTests Inc., was applied and the tests were carried out using 10 cm cuvettes as incubation chambers. An UVmini-1240 spectrophotometer from Shimadzu was used to measure the OD₆₇₀. Approx 10,000 algae cells ml⁻¹ were added to each cuvette at the beginning of each test, which due to the high number of individuals minimized the statistical fluctuations. The test is based on the international standard DS/EN ISO 8692.

The last test in this study applied the Crustacea Cladocere *Daphnia magna* as test organism. The ability of the daphnia to swim is affected by toxic compounds and is therefore used as an expression of the toxic effect. The daphnia were exposed to dilutions of a sample and immobile daphnia were counted after 24 and 48 hours. 20 daphnia were exposed to each dilution of the sample, which was a much lower number of individuals than for the two other tests, resulting in larger statistical fluctuations. For each test, a control was made to ensure that the immobilization was caused by the toxic effect and not by any physical stresses. In this study the toxicity test kit Daphtokit FTM, MicroBioTests Inc., was applied, based on the international standard DS/EN ISO 6341.

Results and discussion

Data obtained from the four samples and the three toxicity tests were analyzed according to the respective standards. Dose-response curves were obtained and EC₅₀ and EC₁₀ values were estimated when possible.

It was a general conclusion for the samples tested that the bacteria test was less sensitive than both the Daphtokit FTM and Algaltokit FTM. This is consistent with previous reported observations [2, 9]. The stormwater

runoff had no observable effect on the luminescence readings (data not shown), indicating that the samples were non-toxic. The daphnia were only inhibited by undiluted aliquots i.e. 100% stormwater runoff. Estimations of EC_{50} values were therefore not possible. The inhibition by 100% stormwater runoff samples was in the magnitude of 20-50% after 48 h of exposure, indicating a low toxic effect. The algal test was on the other hand much more sensitive to the toxic compounds in the runoff. Hence, calculation of EC_{50} values was possible, giving EC_{50} values in two groups: sample I and II had a low EC_{50} about 10% dilution (after 72 h of exposure) and sample III and IV had a relative high EC_{50} about 85% dilution (after 72 h of exposure). The significant difference in toxic effect may be due to a strong natural algal blossom in the wet detention pond, beginning in the end of marts. This algal blossom may cause removal of toxic compounds from the water phase due to uptake by the algae and sorption at their surfaces. When the samples were filtrated prior to analysis, all contaminants absorbed or adsorbed by the algae were removed from the sample. Even though there were large differences between the toxic effects of the samples, the samples were in general toxic to the test organisms and treatment by adding aluminum was relevant.

The EC_{50} values obtained by the algal test (72 h exposure) and standard deviation for the different aliquots from the sample III and IV, are shown in Figure 2.

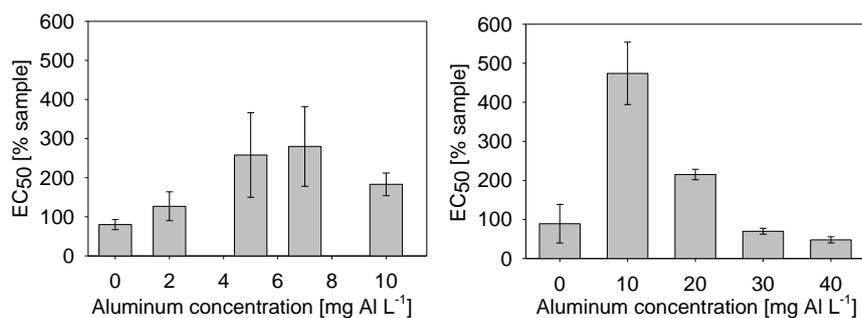


Fig. 2: EC_{50} values and standard deviations for the aliquots from sample III (left graph) and sample IV (right graph) measured with the algal test. A high EC_{50} -value is equivalent to a low toxic effect.

EC₅₀ values above 100% dilution were calculated by extrapolation of the dose-response curve and not by concentration of the samples, e.g. by evaporation. As shown in Figure 2 the toxic effect of the stormwater runoff decreased with increasing aluminum concentration up to 7 mg Al L⁻¹. Above 7 mg Al L⁻¹ the toxic effect increased with increasing aluminum concentration. In the aliquots added 30 and 40 mg Al L⁻¹, the toxic effect was greater than for the pure sample. That is, aluminum reduced the toxic effect of the stormwater runoff up to a certain level. Above this level the aluminum itself became the source of the toxic effect. In Figure 3, EC₁₀ values and standard deviations of the aliquots from sample III and IV are shown (72 h exposure).

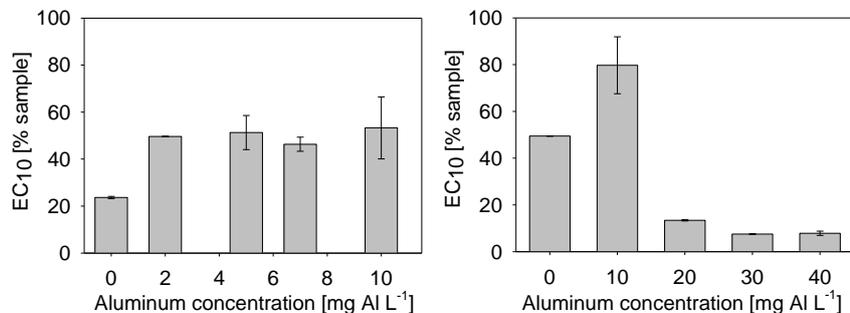


Fig. 3: EC₁₀ values and standard deviations for the aliquots from sample III (left graph) and sample IV (right graph) according to the algal test. The higher the EC₁₀-values, the lower the toxic effect.

The EC₁₀ values were all below 100% and therefore estimated by interpolation. Figure 3 shows the same tendencies as Figure 2, i.e. lower toxic effect for aluminum concentrations between 2 and 10 mg Al L⁻¹ compared with stormwater runoff without aluminum. As shown, highest EC₅₀ occurs at 10 mg Al L⁻¹. At 20 mg Al L⁻¹, the EC₁₀ is lower than the EC₁₀ for the aliquot without aluminum addition. This is not consistent with the EC₅₀ for the same aliquot, where the EC₅₀ is indicating that this aliquot has a lower toxic effect than the aliquot without aluminum addition. In principle, the EC₁₀ and EC₅₀ should show the same tendency. However, due to uncertainties in the tests and their interpretation, deviations from this might happen. Due to this uncertainty, it cannot be concluded whether the addition of 20 mg Al L⁻¹ to stormwater runoff has a positive or

negative effect on the toxicity. It is therefore, in order to avoid toxic effects, recommended to add not more than 10 mg Al L⁻¹ when treating stormwater runoff.

The tendency for the daphnia test was the same as for the algae test, i.e. untreated stormwater runoff had a significant toxic effect as well as runoff added 30 and 40 mg Al L⁻¹; showing an inhibition at 25% and 95% in the undiluted aliquots with 30 and 40 mg Al L⁻¹, respectively. The other aliquots did not show any significant toxic effects. With the bacterial test, the observation of an increasing toxicity in the aliquots with 30 and 40 mg Al L⁻¹ was not observed - most likely due to the relative poor sensitivity of the test.

The limit between beneficial and toxic effects caused by the addition of aluminum will be different at other pH-values due to the equilibrium between the speciation of the aluminum hydroxides. The equilibrium influences the solubility and floc formation and thereby the removal of toxic substances and the toxic effect of the aluminum hydroxides itself due to different speciation hereof.

At pH 8.2, EC₅₀ for the microalgae *Selenastrum capricornutum* equal to 460 µg Al L⁻¹ is reported [10]. The EC₅₀ reported is low compared with the results in this study where aluminum began to show toxic effect at a concentration level of 20,000 - 40,000 µg Al L⁻¹. The large difference is probably due to the nature of the samples tested in this study, resulting in removal of toxic substances and phosphorus by reactions with aluminum as well as side reactions with organic matter. Because of these reactions the aluminum may become unavailable to the test organisms.

Addition of aluminum to lakes to obtain optimal phosphorus removal efficiency is reported in the range from 2 to 30 mg Al L⁻¹ with the most cost-effective dosing between 2 and 5 mg Al L⁻¹ [6, 11]. The most effective decrease in toxic effect was in this study obtained in the range from 7 to 10 mg Al L⁻¹, slightly higher than the cost-effective dose for phosphorus removal. The higher EC₅₀ achieved with addition of 7 to 10 mg Al L⁻¹ compared to the EC₅₀ at 5 mg Al L⁻¹ should be considered insignificant, taking the higher cost in consideration. The cost-effective concentration of aluminum for reduction of toxic effects is therefore

around 5 mg L^{-1} . This correspond to a consumption of approximately $300 \text{ kg Al year}^{-1}$ for the stormwater pond from where the samples originated.

Conclusion

The stormwater runoff analyzed in this study was found to show toxic effects according to two of three applied toxicity tests. The stormwater was highly toxic to the algae, lesser toxic to the crustaceans and non-toxic to the bacteria – revealing that the bacteria *Vibrio fisheri* was the least sensitive organism and that the algae *Selenastrum capricornutum* was the most sensitive organism. Two stormwater runoff samples showed a high toxic effect to the algae with EC_{50} -values at 10% dilution and two samples showed a lower toxic effect with EC_{50} -values at 85% dilution.

To assess the impact of aluminum on the toxic effect of stormwater runoff, aluminum was added to two samples in concentrations ranging from 2 to 40 mg Al L^{-1} . The toxicity test using the algae *Selenastrum capricornutum* showed reduced toxic effect for aliquots with aluminum concentration from 2 to 10 mg Al L^{-1} compared with the toxic effect for pure stormwater runoff. That is, the aluminum may reduce the toxic effect in stormwater runoff. At concentration levels above 20 mg Al L^{-1} , aluminum itself becomes toxic and the toxic effect is higher than for the pure runoff. This limit between beneficial and toxic effects will depend on a number of water quality parameters, as concentration of organic matter, phosphorous, toxic compound, pH etceteras.

The most effective aluminum concentration to reduce toxic effects was in this study found to be 7 mg Al L^{-1} . However, the most cost effective aluminum concentration is 5 mg Al L^{-1} which corresponds with the interval typically applied for cost-effective phosphorous removal.

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