REPORT

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Ammonia toxicity:
Impact assessment of combined sewer overflows on the River Spree in Berlin

Project acronym: MIA-CSO

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Title

Ammonia toxicity: Impact assessment of combined sewer overflows on the River Spree in Berlin

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Abstract

Combined sewer overflows can lead to acute, critical conditions for aquatic organisms in receiving surface waters (Borchardt et al. 2007; FWR 1998; Harremoes et al. 1996; Krejci et al. 2004; Lammersen 1997). Based on the river type of the River Spree, CSO impacts of possible concern were identified to be high ammonia (NH_3) and low dissolved oxygen concentrations (DO) (Senatsverwaltung für Stadtentwicklung 2001; Leszinski et al. 2007). For DO, existing continuous measurements from the River Spree from 2000 to 2007 were assessed in detail in the KWB report by Riechel (2009). However, Riechel (2009) neglected NH_3 toxicity assessment, since no continuous NH_3 measurements were available. The present report aims at filling this gap by estimating the potential for toxic NH_3 concentrations in the River Spree with recent data.

Based on stormwater impact guidelines for ammonia, critical total ammonium concentrations ($[NH_{4,tot}] = [NH4^+] + [NH_3]$) were calculated and compared to continuous $NH_{4,tot}$ measurements in the Berlin River Spree. $NH_{4,tot}$ was measured i) at a heavily CSO impacted river stretch (year 2011) and ii) at a monitoring station several kilometres downstream of the combined sewer area (years 2010 and 2011).

The analysis led to the following results:

- Two years of continuous $NH_{4,tot}$ measurements showed clear increases in $NH_{4,tot}$ due to CSO but no occurrence of critical toxicity levels for cyprinid fish, according to Lammersen (1997).
- Maximal observed concentration of ~1.3 mg-N-$NH_{4,tot}$ l^{-1} was ~5 times smaller than the lowest existing threshold, which would need to be exceeded for 24 h to be considered as critical. The observed maximal concentration peak had a duration of only 3 h. The threshold, corresponding to the 3 h-duration would be even ~8 times higher than the observed ~1.3 mg-N-$NH_{4,tot}$ l^{-1}.
- Ammonia toxicity would only be possible if maximal $NH_{4,tot}$ occurred during highest sensitivity of the river due to very high pH > 9. However, it was observed that pH drops significantly during CSO impacts due to low pH in rain water, which makes pH > 9 during CSO very unlikely.

Given the results, the risk for ammonia toxicity due to CSO is judged as very low, particularly in comparison with regular problematic DO conditions after CSO events in summer.

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1 Introduction

Combined sewer overflows can lead to acute, critical conditions for aquatic organisms in receiving surface waters (Borchardt et al. 2007; FWR 1998; Harremoes et al. 1996; Krejci et al. 2004; Lammersen 1997). Based on the river type of the River Spree, CSO impacts of possible concern were identified to be high ammonia (NH_3) and low dissolved oxygen concentrations (DO) (Senatsverwaltung für Stadtentwicklung 2001; Leszinski et al. 2007). For DO, existing continuous measurements from the River Spree from 2000 to 2007 were assessed in detail in the KWB report by Riechel (2009). The assessment showed that DO drops regularly below critical thresholds after CSO, violating existing immission-based guidelines. Riechel (2009) neglected NH_3 toxicity assessment, since no continuous NH_3 measurements were available. The present report aims at filling this gap by estimating the potential for toxic NH_3 concentrations in the River Spree with recent data.

Since available probes measure concentrations of total ammonium ($[NH_{4,tot}] = [NH4^+] + [NH_3]$) and not fish toxic NH_3, the NH_3 thresholds defined by stormwater impact guidelines have to be transcribed to critical $NH_{4,tot}$-concentrations to be comparable to measurements. NH_3 impact assessment is carried out in two steps: First critical NH_3-concentrations are calculated by taking into account the currently measured T and DO. In a second step the calculated NH_3-thresholds are transcribed to critical $NH_{4,tot}$-concentrations regarding the currently measured pH. The resulting critical $NH_{4,tot}$ concentrations are compared to continuous measurements of 2011 within the river stretch most impacted by CSO and with continuous measurements for 2010 and 2011 at a monitoring station several kilometres downstream of the combined sewer area. The applied methods and data bases are briefly explained in section 2, results are shown and discussed in section 3.

2 Materials and Methods

2.1 Calculation of critical NH_3-concentration

According to the EU fish directive (EU 2006), concentrations > 0.025 mgN-NH_3 L^{-1} should be avoided in surface waters. Since the EU fish directive (2006) does not take into account the dependency of ammonia toxicity on temperature (T) and oxygen saturation (oxsat), other immission-based guidelines should be used for a detailed assessment of CSO impacts. The Lammersen approach (1997) includes correction for T and oxsat and was used in the following to calculate critical NH_3 concentrations in the River Spree and the "Landwehrkanal", based on the equation:

$$\begin{aligned} NH_{3,crit} &= NH_{3,crit}(T = 5°C, oxsat = 100\%, \Delta t) \\ &\cdot \max(1;1+(T-5)\cdot 0.12) \\ &\cdot \min(1;\max(0.33;0.33+(oxsat-30)\cdot 0.00957)) \end{aligned} \tag{1}$$

where the second line shows temperature correction, which leads to lower NH_3-toxicity for higher temperatures (Erickson 1985) and the third line shows correction for oxygen saturation oxsat [%], which is linearly increasing between 30 % ≥ oxsat ≤ 100 % (Alabaster 1979). oxsat is the percentage of the measured DO of DO concentration at saturation DO_{sat}, calculated based on the equation by Weiss (1970):

$$\mathrm{DO}_{\mathrm{sat}} = e^{(-173.4292+249.6339*100/\mathrm{T_{kel}}+143.3483*\ln(\mathrm{T_{kel}}/100)-21.8492*\mathrm{T_{kel}}/100)} \cdot 1.4276 \tag{2}$$

where T_{kel} [K] = T [°C] + 273.15. Based on equation (1) critical NH_3 concentrations can be calculated for a given situation in the river. $NH_{3,crit}$ is defined for eight different durations Δt of high NH_3 concentration, where 10 minutes is the shortest and 24 hours the longest Δt considered (Lammersen 1997):

- $NH_{3,crit}$(T = 5°C, oxsat = 100 %, Δt = 10 min) = 0.4697 mg-N-NH_3 L^{-1} and
- $NH_{3,crit}$(T = 5°C, oxsat = 100 %, Δt = 24 h) = 0.0469 mg-N-NH_3 L^{-1}

2.2 Calculation of critical total ammonium concentration

Typically $NH_{4,tot}$ concentration is measured in water samples (usually indicated in mg N-NH_4 L^{-1}). As a result $NH_{3,crit}$ is transformed into [$NH_{4,tot}$] = [NH_3] + [NH_4^+], depending on pH and T (Stumm and Morgan 1996):

$$\mathrm{NH}_{4,\mathrm{tot,crit}} = \mathrm{NH}_{3,\mathrm{crit}} + \mathrm{NH}_{3,\mathrm{crit}} \cdot 10^{(\mathrm{pKa(NH4)-pH})} \tag{3}$$

where pKa(NH4) is assumed to be linearly T-dependent in the expected T-range (0 - 25 °C):

$$pKa(NH4) \approx -0.032 \cdot T + 10.057 \tag{4}$$

2.3 Monitoring data

Within the project MIA-CSO, $NH_{4,tot}$ was measured with an ion-selective probe (s::can Ammolyzer) at the monitoring station "Tegeler Weg" (A in Fig. 1) from March to August 2011. During this time period the probe was cleaned and tested for sensitivity once per week. Electronic potential E [mV] was validated semi-automatically based on the methodology by Mourad and Bertrand-Krajewski (2002) as outlined in Caradot et al. (2011). Finally the validated data points were calibrated to weekly samples of NH_4^+ (calculated from photometric measurements of $NH_{4,tot}$ and pH) using a first order logarithmic relationship $\log[NH_4^+] = a \cdot E + b$, simplified from the Nernst equation (Stumm and Morgan 1996). This simplified approach assumes that variations in potassium (K), temperature and ionic strength are small within a calibration window. Calibration windows were chosen to cover periods between several weeks and less than a day, depending on observed drift and variation. Measurements of K have indicated that variations in the River Spree are indeed very small. Since absolute temperature is used in the Nernst equation, variations of few °C have little impact.

In addition, measurements with an ion-selective probe (WTW) at the monitoring station "Sophienwerder" (B in Fig. 1), measured from 2010 to 2011 by the Berlin Senate Department of Health, Environment and Consumer Protection (SenGUV), were used. The probe was tested on a weekly basis and calibrated with a one-point calibration if necessary.

$NH_{4,tot,crit}$ was calculated from DO, pH and T, which were continuously monitored at both stations by SenGUV (Fig. 1).

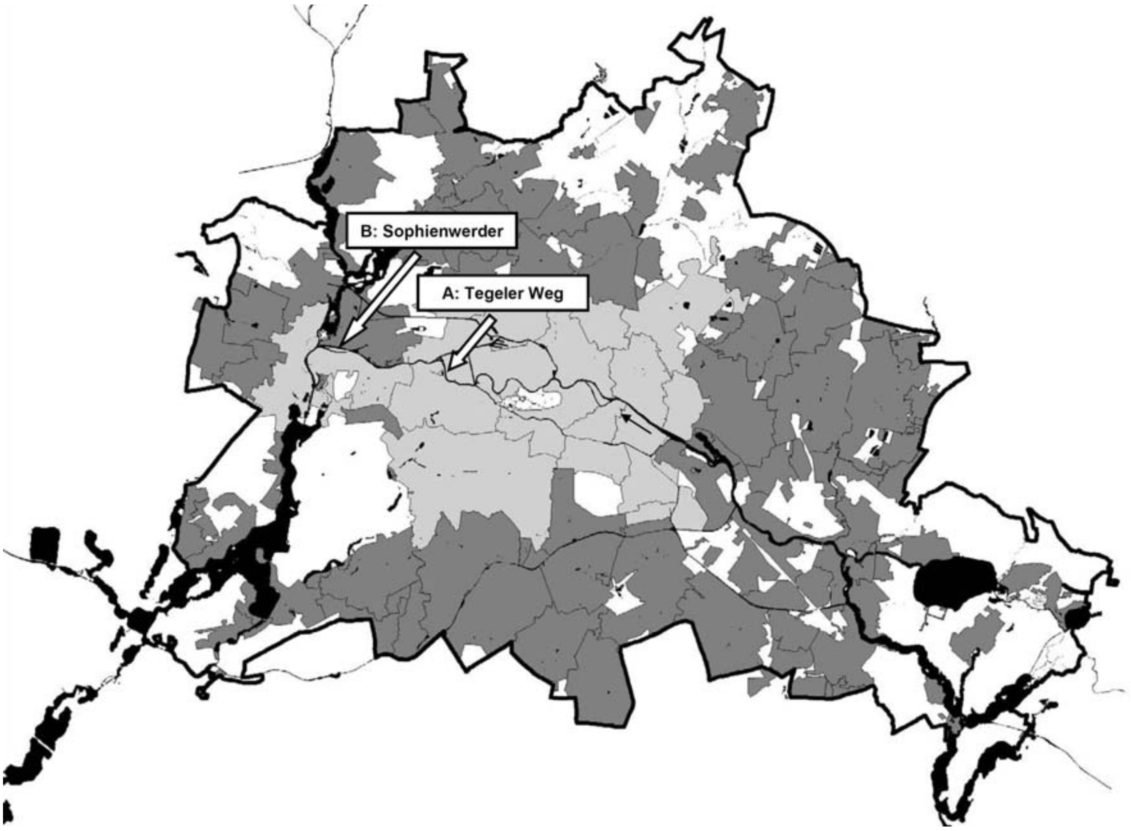

Figure 1: Overview of monitoring stations A (Tegeler Weg) and B (Sophienwerder) along the River Spree. The River Spree flows from East to West through the combined sewer area (indicated light grey) in the centre of Berlin.

3 Results and Discussion

3.1 Validation of NH_4 measurements

Fig. 2 compares continuous $NH_{4,tot}$ measurements with grab samples analysed in the laboratory. At station A (Tegeler Weg) grab samples were taken weekly or, if possible, during stormwater influence. Comparison shows good agreement between continuous data and grab samples, both for dry and wet weather conditions (Fig. 2a). Similarly, weekly grab samples at Station B (Sophienwerder) indicate good agreement with continuous measurements (Fig. 2b). Gaps in both data series are the result of various issues with continuous measurements. The range of observed concentrations is in line with 24h-mixed samples taken in the “Landwehrkanal” (a tributary channel of the River Spree) during the year 1997 (Senatsverwaltung für Stadtentwicklung 2001).

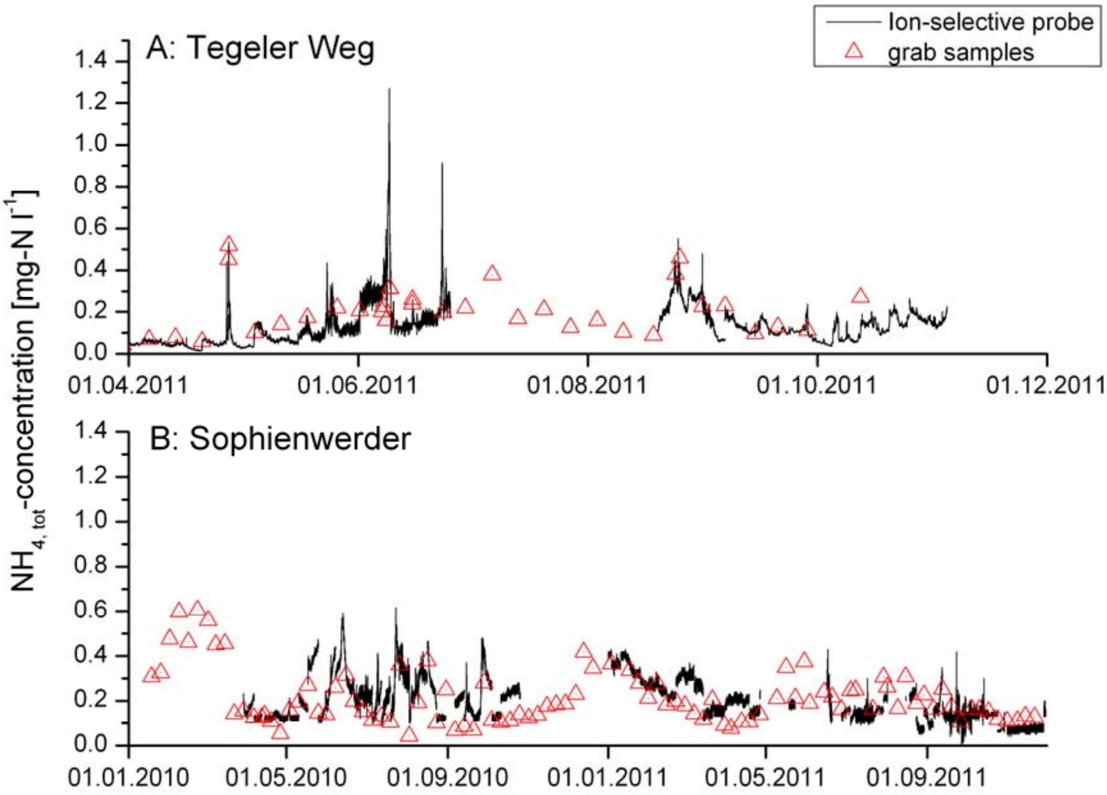

Figure 2: Comparison of continuous measurements at monitoring stations A (Tegeler Weg) and B (Sophienwerder) with grab samples analysed in the laboratory (A: own analysis and BWB lab, B: weekly grab samples by SenGUV).

3.2 Seasonal patterns of critical ammonium concentrations

Equation (3) allows calculation of the threshold for the critical concentration of total ammonium $NH_{4,tot,crit}$ depending on T, pH and DO. If this is done for a longer time series of the River Spree, a clear seasonal pattern can be seen (Fig. 3). Minimal (and therefore most sensitive) $NH_{4,tot,crit}$ in the range of 1 mg-N-$NH_{4,tot}$ l^{-1} typically occur over a short period in spring (March to April). For the remainder of the year $NH_{4,tot}$ only gets critical at values in the range of 10 mg-N-$NH_{4,tot}$ l^{-1}.

Fig. 3 also shows that the pattern in $NH_{4,tot,crit}$ is inverse to the seasonal development of pH, whereas T and DO are of minor influence. Low $NH_{4,tot,crit}$ occur if pH is above ~8.5, which is only observed during algal bloom in spring. In other words, critical conditions are expected if elevated $NH_{4,tot}$ concentrations coincide with high pH > 8.5.

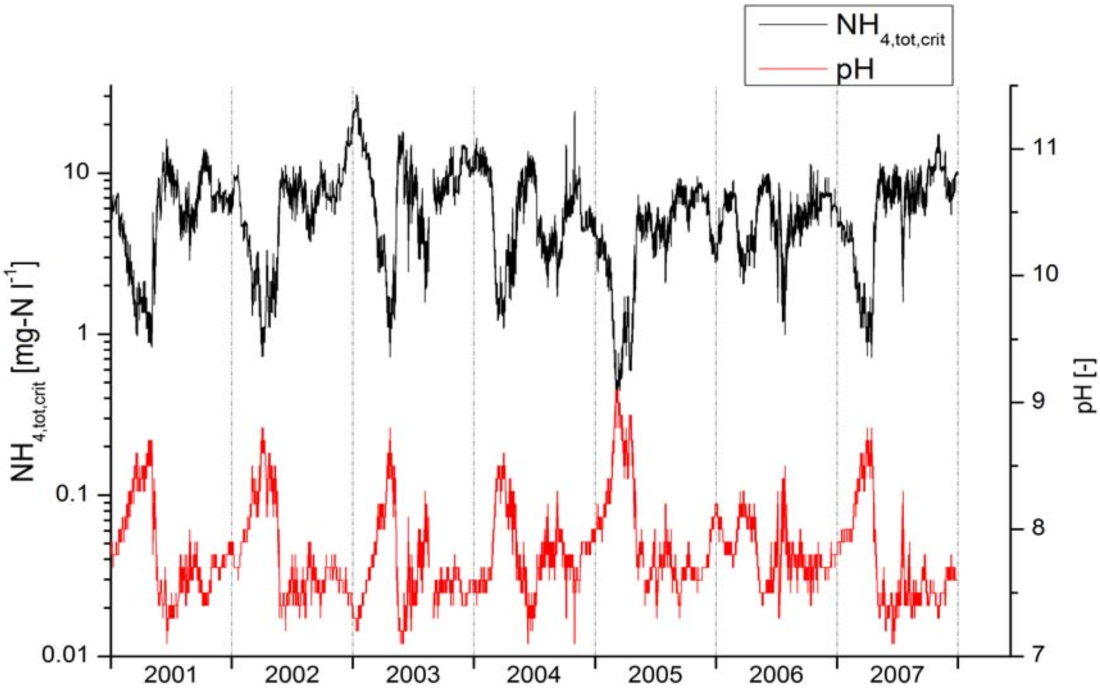

Figure 3: Seasonal patterns of critical ammonium threshold $NH_{4,tot,crit}$ for 24 h exposure and pH at the measuring station B (Sophienwerder).

3.3 Comparison of measurements with critical ammonium concentrations

Fig. 4 compares $NH_{4,tot}$ concentrations observed at monitoring stations A (Tegeler Weg) and B (Sophienwerder) with critical thresholds $NH_{4,tot,crit}$ at 10 min and 24 h exposure. For both monitoring stations observed concentrations remain clearly below 24 h-thresholds for the entire monitoring period. Minimal gaps between measured $NH_{4,tot}$ and critical threshold $NH_{4,tot,crit}$ at elevated concentrations are between 3 and 5 mg-N-$NH_{4,tot}$ l^{-1} at both monitoring stations (> 4 times higher than observed concentrations).

Peak values in the range of 1 mg-N-$NH_{4,tot}$ l^{-1} during CSO had a duration between 2 and 6 h at station A (Tegeler Weg). As a result critical 24 h exposures are not very likely. According to Lammersen (1997) the observed events would fit into the class with exposure 2 h ≤ Δt < 6 h. For this class thresholds $NH_{4,tot,crit}$ are about 50 % higher, compared to 24 h exposure (Lammersen 1997). As a result, $NH_{4,tot}$ concentrations would have to be > 8 times higher than observed to be considered as critical.

To put results into perspective, it is useful to compare how DO developed in 2011 after CSO with respect to the Lammersen guidelines (see Riechel (2009) for calculation of DO_{crit}). In Fig. 5 impacts of seven CSO events at monitoring station A (Tegeler Weg) are shown for $NH_{4,tot}$ (Fig. 5a) and DO (Fig. 5b), marked with letters A-G. While $NH_{4,tot}$ peaks are clearly visible for all the events, $NH_{4,tot}$ is far from reaching critical (24 h) level as discussed above. In contrast four of the seven events led to DO concentrations below critical 10 min levels. The 24 h threshold for DO is violated almost continuously from mid-May to the beginning of July and for several weeks in July and August (despite an exceptionally cool summer).

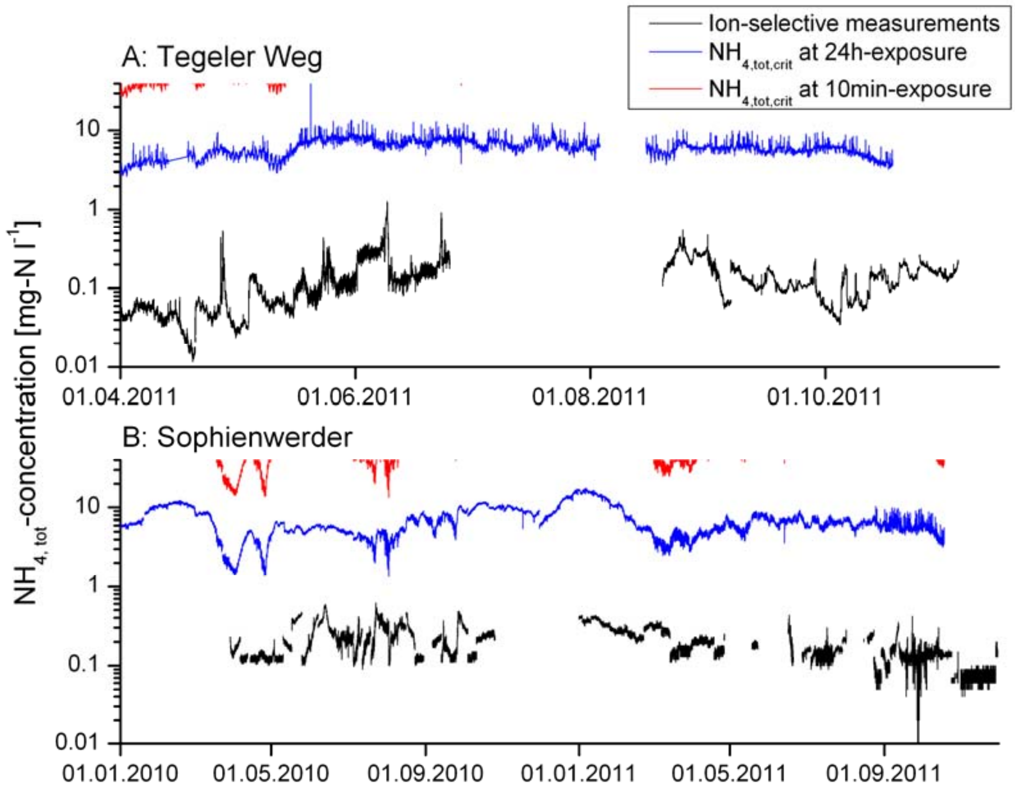

Figure 4: Continuous ammonium ($NH_{4,tot}$) measurements versus critical concentrations ($NH_{4,tot,crit}$) (eq 3) at stations A (Tegeler Weg) and B (Sophienwerder)

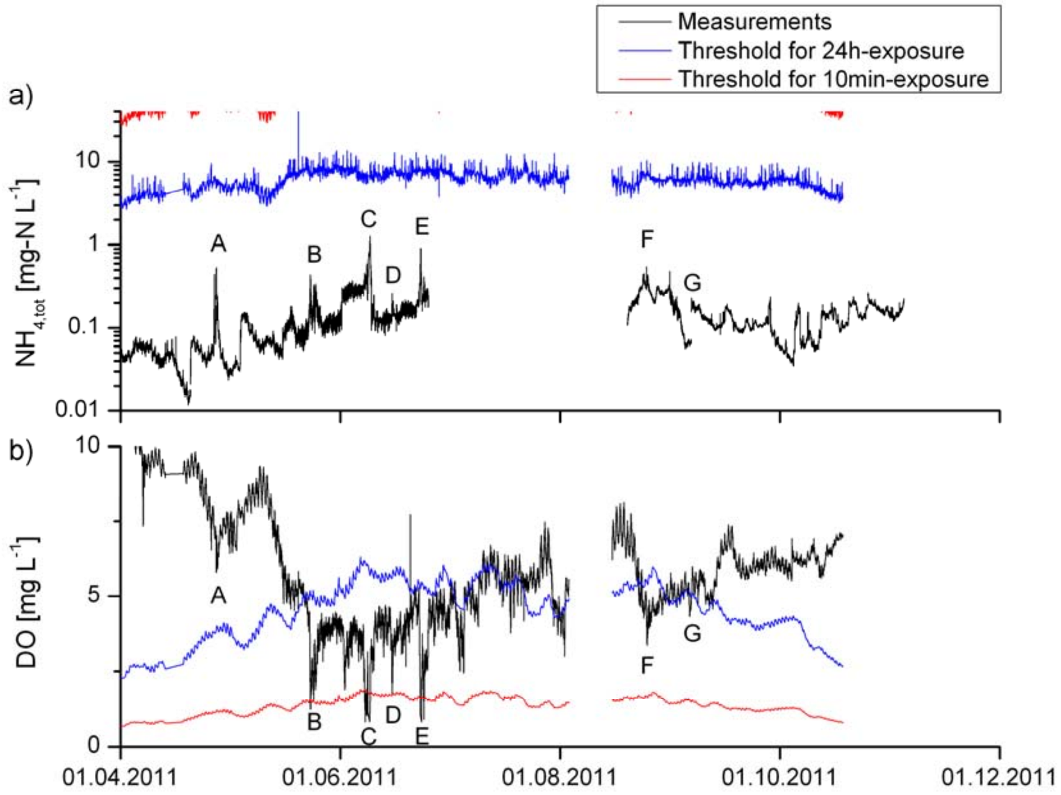

Figure 5: Station A (Tegeler Weg): Continuous $NH_{4,tot}$ (a) and DO measurements (b) with respective thresholds for critical concentrations of $NH_{4,tot}$ and DO (Lammersen 1997). Letters A-G indicate CSO impacts, which follow major recorded rain events.

Since continuous measurements of $NH_{4,tot}$ were not available for previous years, detailed impact assessment could only be done for the years 2010 and 2011. Nonetheless, it is important to assure that the conditions influencing the critical threshold $NH_{4,tot,crit}$ (T, DO and particularly pH) have not been significantly different in the years before. For example, a higher pH would have lead to a higher portion of toxic ammonia NH_3 and to a lower corresponding threshold $NH_{4,tot,crit}$ indicating an increased sensitivity to NH_4-loadings from CSO. Table 1 compares average monthly values from 2010 and 2011 derived from continuous measurements with monthly averages and standard deviations for the entire time series at station B (Sophienwerder). Apart from DO in January 2011 all the measured values from the time period 2010 to 2011 are well within the 95 % quantile of the entire time period 2000 to 2011. As a result, observations in Figures 4 and 5 cannot be explained by special boundary conditions in the monitoring years 2010 and 2011.

Table 1: Comparison of monthly averages for water temperature, pH and dissolved oxygen from the years 2010 and 2011 with monthly averages and standard deviations for the entire time series for monitoring station B (Sophienwerder). "!" indicates that values are outside the 95%-quantile of the entire data series. Assuming a normal distribution of all measured values, the 95%-quantile is represented by the range around the average limited by +/- two times the standard deviation.

Month	Temperature [°C]			pH [-]			Dissolved oxygen [mg/l]		
	2000-2011 (avg ± stdev)	2010 (avg)	2011 (avg)	2000-2011 (avg ± stdev)	2010 (avg)	2011 (avg)	2000-2011 (avg ± stdev)	2010 (avg)	2011 (avg)
Jan	2.5 ± 1.7	0.6	1.3	7.8 ± 0.2	7.8	7.4	12.8 ± 0.9	12.8	10.7 **!**
Feb	3.1 ± 1.7	1.3	1.7	7.9 ± 0.3	7.6	7.8	13.3 ± 0.9	12.2	12.5
Mar	5.6 ± 2.2	4.7	5.6	8.3 ± 0.3	7.9	8.0	13.6 ± 1.1	13.2	13.5
Apr	12.1 ± 2.8	11.6	13.8	8.3 ± 0.3	8.1	7.9	11.5 ± 1.3	11.2	9.6
May	18.2 ± 2.7	14.5	18.5	7.7 ± 0.3	7.8	7.6	7.6 ± 1.9	8.7	7.4
Jun	21.6 ± 2.4	20.4	22.2	7.5 ± 0.2	7.7	7.5	6.4 ± 1.3	6.9	5.6
Jul	22.9 ± 2.1	24.9	20.9	7.7 ± 0.2	7.8	7.6	6.7 ± 1.3	6.7	6.7
Aug	22.6 ± 1.7	22.0	20.9	7.7 ± 0.2	7.7	7.6	6.7 ± 1.2	6.9	6.8
Sep	18.8 ± 2.4	16.6	18.6	7.6 ± 0.2	7.7	7.5	7.3 ± 1.1	8.9	6.9
Oct	13.3 ± 2.9	10.6	13.0	7.6 ± 0.1	7.5	7.6	8.6 ± 1.0	9.0	8.2
Nov	8.2 ± 2.2	7.3		7.6 ± 0.1	7.5		10.2 ± 1.0	9.5	
Dec	4.0 ± 2.5	0.3		7.7 ± 0.2	7.6		12.0 ± 0.9	11.6	

3.4 Likelihood of critical ammonium concentrations

In the study by Senatsverwaltung für Stadtentwicklung (2001) for the "Landwehrkanal" it is suggested that observed $NH_{4,tot}$-concentrations "in combination with high trophic status", could lead to critical NH_3 levels. For "high trophic status" pH > 8.5 was assumed. For our study, we tested the hypothesis for the River Spree by combining the highest observed $NH_{4,tot}$-peak (maximal observed concentration of 1.27 mg-N-$NH_{4,tot}$ l^{-1} with a concentration > 0.9 mg-N-$NH_{4,tot}$ l^{-1} for ~3 h) with the maximal observed pH (2000-2011) of 9.1. Indeed, this would have led to a critical condition with a violation of the 2 h threshold of ~0.5 mg-N-$NH_{4,tot}$ l^{-1} as well as the 1 h threshold of ~0.83 mg-N-$NH_{4,tot}$ l^{-1} by Lammersen (1997) (equations 1 to 4 at T = 15 °C, oxsat = 80 % and pH = 9.1). So, although no critical $NH_{4,tot}$ levels were observed in 2010 and 2011, the possibility of critical ammonia toxicity at high $NH_{4,tot}$ concentrations during maximum seasonal pH > 9 cannot be completely ruled out.

However, there is an additional aspect that makes critical ammonia toxicity less likely. Fig. 6 shows the effect of two CSO events (shaded area) with intermediate dry periods on DO and pH at station B (Sophienwerder). While pH increases during dry periods, probably from increasing algal growth, pH decreases rapidly by up to 0.5 units after rain events, in parallel to DO. The same behaviour can be observed at station A (Tegeler Weg) in 2011, even if less expressed due to generally lower pH (Fig. 7). For each of the CSO events in Fig. 7 pH drops while $NH_{4,tot}$ increases. The phenomenon can be explained by low buffer capacity of pure rain water, which typically shows pH-values between 5 and 6. As a result, pH > 9 (with low $NH_{4,tot,crit}$) is very unlikely during times when $NH_{4,tot}$ is high as a result of a major CSO event.

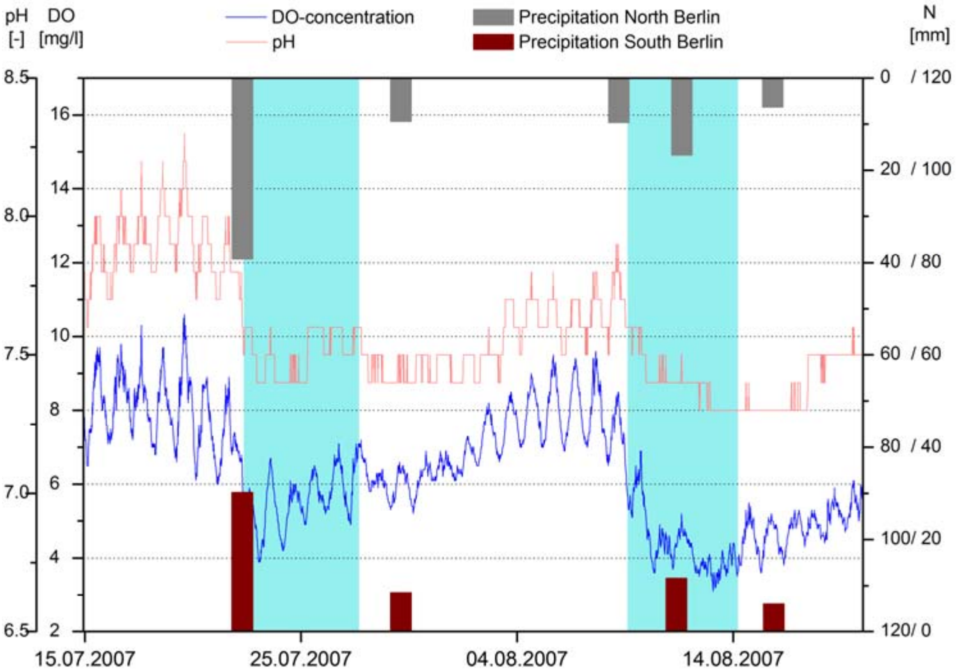

Figure 6: Station B (Sophienwerder): Development of DO and pH after storm events (shaded area) and during dry weather periods.

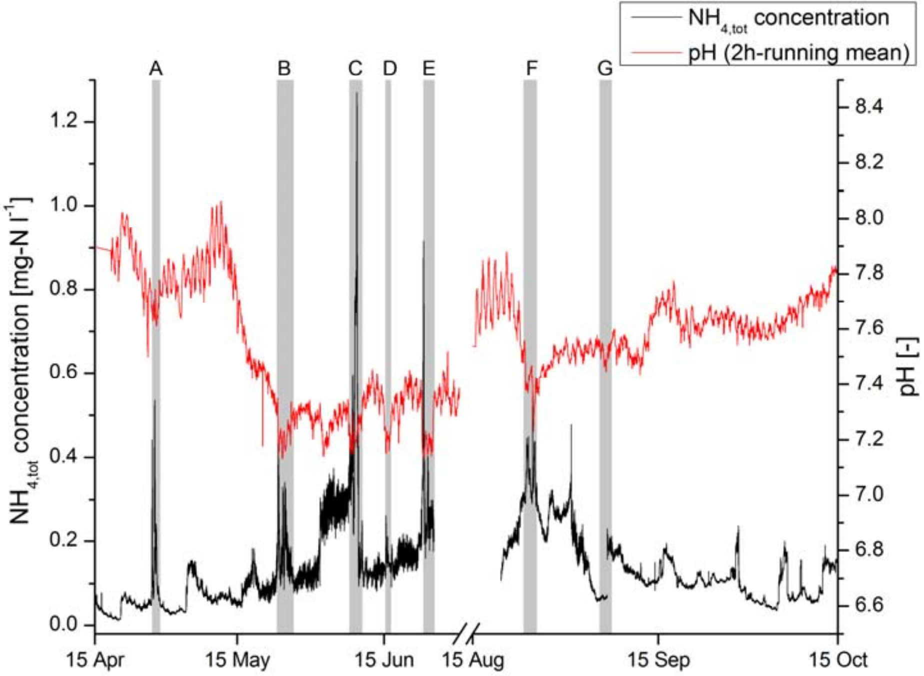

Figure 7: Station A (Tegeler Weg): Comparison of continuous $NH_{4,tot}$ with pH in 2011. Letters A-G indicate same CSO events as in Fig. 5. Note break in x axis over period between July 1st and August 15th without $NH_{4,tot}$ measurements.

4 Conclusions

The likelihood for critical ammonia toxicity due to CSO in the Berlin River Spree is judged as very low due to the following findings:

- Two years of continuous $NH_{4,tot}$ measurements at two points in the CSO-impacted stretch of the River Spree showed clear increases in $NH_{4,tot}$ due to CSO but no occurrence of critical toxicity levels for cyprinid fish, according to Lammersen (1997).
- Maximal observed concentration of ~1.3 mg-N-$NH_{4,tot}$ l^{-1} was ~5 times smaller than the lowest existing threshold, which would need to be exceeded for 24 h to be considered as critical. The observed maximal concentration peak had a duration of only 3 h. The threshold, corresponding to the 3 h-duration would be even ~8 times higher than the observed ~1.3 mg-N-$NH_{4,tot}$ l^{-1}.
- Ammonia toxicity would only be possible if maximal $NH_{4,tot}$ occurred during highest ammonia sensitivity of the river due to very high pH > 9. However, it was observed that pH drops significantly during CSO impacts due to low pH in rain water, which makes pH > 9 during CSO very unlikely.

The minimal remaining risk for critical ammonia conditions during CSO is in sharp contrast with regular problematic DO conditions after CSO events in summer. As a result, CSO mitigation should focus on DO while ammonia toxicity seems negligible. Nevertheless, given the observed correlation of DO decrease and $NH_{4,tot}$ increase after CSO, an improvement of the DO problematic will also improve ammonia situation.

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