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Ecological risk assessment of zinc from stormwater runoff to an aquatic ecosystem

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ABSTRACT

Zinc (Zn) risks from stormwater runoff to an aquatic ecosystem were studied. Monitoring data on waterborne, porewater, and sediment Zn concentrations collected at 20 stations throughout a stormwater collection/detention facility consisting of forested wetlands, a retention pond and first order stream were used to conduct the assessment. Bioavailability in the water column was estimated using biotic ligand models for invertebrates and fish while bioavailability in the sediment was assessed using acid volatile sulfide-simultaneously extracted metal (AVS-SEM). The screening level assessment indicated no significant risks were posed to benthic organisms from Zn concentrations in sediments and pore water. As would be expected for stormwater, Zn concentrations were temporally quite variable within a storm event, varying by factors of 2 to 4. Overall, probabilistic assessment indicated low (5–10% of species affected) to negligible risks in the system, especially at the discharge to the first order stream. Moderate to high risks (10–50% of species affected) were identified at sampling locations most upgradient in the collection system. The largest uncertainty with the assessment is associated with how best to estimate chronic exposure/risks from time-varying exposure concentrations. Further research on pulse exposure metal toxicity is clearly needed to assess stormwater impacts on the environment.

1. Introduction

Considerable progress has been made in the past 30 years with respect to reducing contaminant loadings to aquatic environments resulting from point source discharges (e.g., municipal and industrial wastewater outfalls). Increasingly, attention is turning toward the regulation of non-point source discharges associated with stormwater runoff. In fact, because of their ubiquitous nature and the volume of water associated with non-point sources, non-point (stormwater) discharges can represent a significantly greater loading to the environment of many common toxicants (e.g., metals and pesticides) when compared to point source discharges.

Initial attempts in the last decade to regulate non-point sources have typically used the regulatory tools designed for point sources. For example, in the United States, stormwater runoff in many areas is now being regulated under National Pollutant Discharge Elimination System (NPDES) permits. In many cases, when brought into the NPDES framework, stormwater runoff may be required to meet the same criteria as point source discharges, e.g., ambient water quality criteria (AWQC). Sampling for compliance in these scenarios is often conducted directly from discharges with no consideration of environmental fate. Similarly, a number of environmental investigations on the impact from stormwater runoff have also used AWQC and/or standard whole effluent toxicity (WET) tests to assess impacts (Bailey et al., 1999; Hall and Anderson, 1988; Heijerick et al., 2002).

While this approach to assessing stormwater impacts may be expedient from a regulatory perspective, it ignores several important principles that distinguish stormwater runoff from point source discharges. First, unlike point source discharges, stormwater runoff tends to be pulsatile in nature with contaminants occurring at relatively high concentrations for relatively short periods of time (e.g., minutes to hours). Second, collection of stormwater samples directly from rooftops or other collection systems results in samples that are in considerable disequilibrium with the environment. When runoff travels even short distances from the sources to receiving water bodies, substantial changes in ion content (e.g. pH, hardness, and alkalinity), partitioning and speciation can occur to alter contaminant bioavailability. In combination, we hypothesize these factors can lead to the overestimation of impacts from stormwater runoff when the default assumptions used to assess point source discharges are applied.

The objective of this study was to characterize the transport of Zn runoff in a stormwater collection system and assess the potential risks of this runoff to the aquatic ecosystem in a first order stream adjacent

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to the Seattle–Tacoma International Airport (STIA). The risk assessment described in this paper was conducted in two tiers. The first tier screened potential Zn risks in water and sediments by location using deterministic estimates of Zn exposure and effects. Those locations where potential risks from Zn were clearly negligible were excluded from further evaluation. Locations retained for further evaluation were assessed probabilistically and included a more rigorous estimation of bioavailable Zn using biotic ligand models (BLMs) for fish and invertebrates.

2. Problem formulation

The study site was located near the Seattle–Tacoma International Airport (STIA). The airport is located in SeaTac, Washington and is operated by the Port of Seattle. Ranking about 18th in size among U.S. airports, STIA occupies over 1000 ha (2500 ac) with stormwater draining to two principal watersheds — Miller and Des Moines Creeks. The Miller Creek watershed contains approximately 2000 ha of predominantly urban area. The STIA occupies about 5% of the entire Miller Creek watershed drainage area, a portion of which is the focus of this study.

The storm drainage system (SDS) for the airport collects stormwater runoff from approximately 400 ha. The SDS drains primarily the runways, taxiways, terminal and cargo facility roofs and roads near the airport. This runoff is collected in enclosed drainage systems and discharged via outfalls from 12 principal drainage areas. The four outfalls that drain to Miller Creek via a stormwater detention pond are the subject of this study.

The four stormwater collection outfalls from the airport (S1, S2, S3, and S4) that drain to the Miller Creek watershed, all drain into the Lake Reba Detention Facility (LRDF), which in turn drains to Miller Creek (Fig. 1). Storm runoff from sources other than STIA combines with the S1–S4 outfalls and drains to the LRDF, notably from State Highway SR518 and commercial and residential areas of the City of SeaTac. Given the complexity of the drainage system, the study needed to develop an appropriate sampling network to allow characterization of sources and sinks. This network contains five subbasins, each with multiple sampling locations. Some of these subbasins lump several runoff sources, while others reflect discrete runoff and associated metal contributions. The sinks for expected metal removal are two wetlands and the LRDF. Multiple sampling locations were used to characterize changes in runoff quality as it passes through these sinks.

2.1. Runoff sources

This sub-basin includes two cargo building Zn–Al alloy (Galvalume®) roofs (Fate and Transport (FT)1), another cargo building Zn alloy roof and roadway area (FT2), which combine to form stormwater outfall S1. Runoff from State Highway 518 (SR518) and an associated off ramp (FT3) joins with the S1 (FT1 + FT2) flows, all of which are reflected in the measurements at sample point FT4 along with additional ungaged runoff from SR518 (ung518). The FT4 sample point is where the entire enclosed drainage system daylights at a conventional outfall.

2.2. Wetland 1

Wetland 1 is a deciduous forested system of approximately 2 ha that conveys runoff in a single or multiple braided channels with substrates varying from highly organic to fine sand. This sub-basin receives upstream input via FT4 (upstream sources) and includes sample points FT5, FT6, and FT7, which are spaced along the drainage channel within the wetland to reflect longitudinal changes in water chemistry. After traveling a total of approximately 450 m from the FT4 point, the flows discharge to the LRDF through a culvert at FT8. Flows travel through approximately 150 m of galvanized corrugated metal pipe immediately before entering the LRDF at FT8. During a storm event, Wetland 1 has the potential to bypass some of the incoming runoff to Wetland 2. Wetland 1 also receives ungaged runoff from SR518 (ung518a).

2.3. Wetland 2

A minor gravel roadbed separates Wetlands 1 and 2. The 1.9 ha Wetland 2 is very similar to Wetland 1 in plant community. This subbasin receives runoff from stormwater outfalls S3, S4, an adjacent public road and Wetland 1 Bypass. Flows travel approximately 335 m through Wetland 2 before discharging to the LRDF through a culvert at

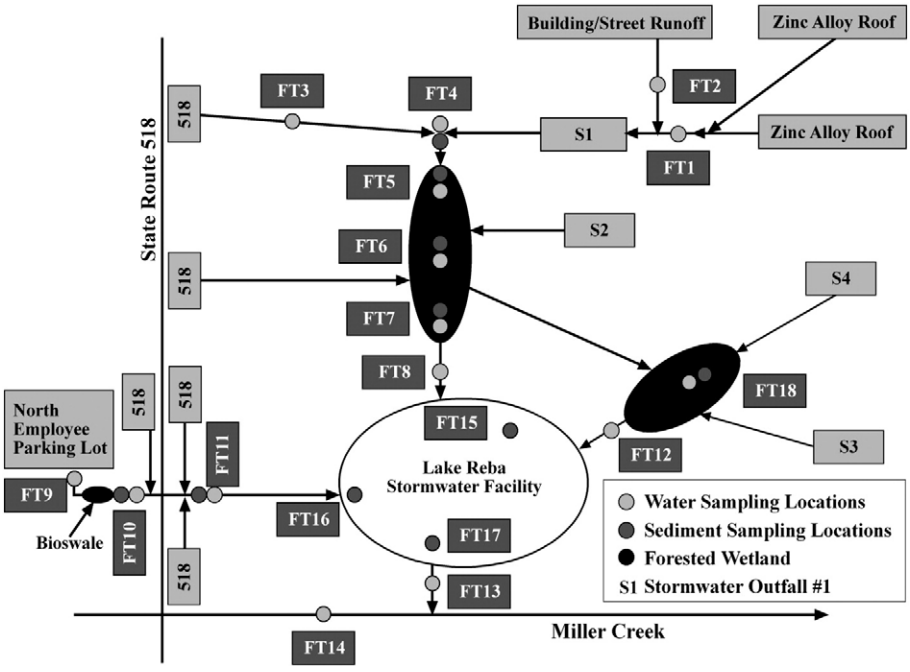

Fig. 1. Schematic overview of sampling stations and stormwater flow.

sample station FT12. Drainage channels and substrates are similar to Wetland 1. Flows travel through approximately 150 m of galvanized corrugated metal pipe cross culverts (for maintenance access roadways) immediately before entering the LRDF at FT12.

2.4. North Employee Parking Lot

The 12 ha North Employee Parking Lot (NEPL) is another important source of runoff water and Zn to the system. An actively used portion of approximately 10 ha of this asphalt paved lot provides parking for 3300 passenger vehicles. Runoff from NEPL is collected in an enclosed drainage system constructed of galvanized slot drains and HDPE pipe trunks. The runoff first passes through a large (4900 m^3) detention vault (inlet is FT9), then through a grassed bioswale designed for stormwater treatment (outlet FT10). The NEPL runoff from this bioswale then combines with ungaged SR518 runoff to pass through an asphalt lined ditch, under SR518, and finally receives additional ungaged runoff (ung518b) before discharging to the LRDF through a culvert at FT11.

2.5. Lake Reba Detention Facility

The 1.7 ha LRDF is a stormwater detention facility constructed in 1972 that receives inputs from Wetland 1 (FT8), Wetland 2 (FT12), NEPL (FT11) and occasional runoff from a minor ungaged open area. The LRDF provides stormwater treatment with an outlet structure that limits the peak discharge rate of stormwater runoff to the receiving water, Miller Creek. The FT14 station is located in Miller Creek upstream of the LRDF outfall to provide upstream reference data for the Creek. The LRDF has highly organic sediments (ostensibly peat) overlain by 30 to 60 cm of water in the dead storage (permanent pool of approximately 4900 m^3). The live storage depth of the LRDF is approximately 1.5 m and provides about 15000 m^3 of detention.

2.6. Aquatic receptors

The study area consists of forested wetland habitat that drains to the LRDF, which in turn drains to Miller Creek. The Miller Creek watershed provides habitat for coho salmon (*Oncorhynchus kisutch*), threespine stickleback (*Gasteroseus aculeatus*), pumpkinseed sunfish (*Lepomis gibbosus*), black crappie (*Pomoxis nigromaculatus*), and cutthroat trout (*Oncorhynchus clarki*). Fish species in the portion of the Miller Creek watershed being evaluated in this assessment are limited to cutthroat trout, pumpkinseed sunfish, and threespine stickleback. The latter two warmwater species are associated with lentic water bodies, such as the LRDF. Several fish passage barriers limit Coho salmon spawning to the lower reaches of the creek, which are more than 2 km downstream from the study area. Macroinvertebrates identified in Miller Creek include insects from the families Ephemeroptera, Plecoptera, Trichoptera, Coleoptera, and Diptera. Non-insect macroinvertebrates include flatworms (Turbellaria), oligochaetes, freshwater clams (Pissidiidae), snails (*Ferrissia* sp.), amphipods (*Crangonyx* sp.), and isopods (*Caecidotea* sp.).

No data are available on invertebrate communities specific to the LRDF and no biological data are available for the forested wetlands upstream of the LRDF. For this risk assessment, we assume that the LRDF contains a relatively diverse mixture of invertebrates, including zooplankton such as cladocerans and benthic macroinvertebrates such as aquatic insect larvae, small crustaceans, and oligochaetes. The forested wetlands consist of a complex system of small channels that overflow during storm events. There is no evidence that fish are found in these forested wetlands and invertebrates are probably limited to benthic species, such as insect larvae and small crustaceans.

2.7. Assessment endpoints and measures of effect

As defined in USEPA (1998), assessment endpoints are explicit expressions of the actual environmental value that is to be protected, operationally defined by an ecological entity and its attributes. The assessment endpoint for this risk assessment was "species richness or diversity of aquatic life communities" in the habitats described previously (e.g., Wetland 1, Wetland 2, and Miller Creek). The assessment endpoint was evaluated using measures of exposure and measures of effect (USEPA, 1998). Measures of exposure were Zn concentrations in surface water, sediment, and pore water, along with additional tools for assessing Zn bioavailability (BLM for surface water data and AVS-SEM for sediments). Measures of effect were Zn water quality standards (WQS), Zn species sensitivity distributions (SSDs), and equilibrium sediment partitioning guidelines (ESG) for metal mixtures.

3. Exposure characterization

Water samples were collected at a total of 15 stations for limited characterization. Of these, five stations were identified as being representative of conditions in different areas of the overall drainage system: FT4, FT5, FT8, FT11, and FT13. Each of these stations was subjected to a more intensive characterization in which 1-h composite water samples were collected every other hour for 96 h during three separate storm events. For each storm event, dissolved Zn, calcium, magnesium, sodium, dissolved organic carbon, and pH were measured in four to five of the collected samples. The samples analyzed were selected based on the storm event hydrograph with emphasis on characterizing concentrations during periods representing first flush, rising, peak and falling limbs and return to near pre-event levels. Consistent with AWQC, acute and chronic sampling durations of 1 h and 96 h, respectively, were used (USEPA, 1991). Thus, each 1-h composite sample represented a possible acute Zn exposure. For chronic Zn exposures, the 96-h time-weighted average of the 1-h composite samples was used.

Bulk sediment, AVS-SEM, and pore water were collected at a total of seven stations: FT4, FT5, FT6, FT7, FT15, FT17, and FT18. The sediment analyses in this assessment focused on the pore water and AVS-SEM data, as these allow for consideration of Zn bioavailability in sediment. Sediment samples were only collected during the first storm event because they are unlikely to respond to short-term changes in waterborne Zn concentrations that might occur between storm events and, as discussed later, the Zn pore water and AVS-SEM concentration data from this first sampling event suggested there are no potential Zn risks to benthic biota via the sediment.

Pore water was sampled using "peepers". Each peeper was constructed using an HDPE vial from LA Plastics (Los Angeles, CA) (2.2 cm outside diameter × 2.7 cm tall). Each "snap" type vial cap was drilled out and the burrs were removed. Vials were rinsed and filled with deionized water and a 0.4 μm polycarbonate osmotic membrane (Osmonics, Inc. #K04CP04700 Minnetonka, MN) was placed over each vial and the cap closed. Vials were then stored submerged in deionized water (zero head-space) until they were deployed in the field.

Each peeper was inserted 4–6 cm below the sediment surface at each station then tied with a length of fishing line to a 1 m length of PVC pipe anchored into the sediment. Because each peeper only yielded 5–6 mL of water, it was necessary to use 12–13 peepers per station to ensure that sufficient sample volume was available for analysis. After two weeks equilibration, the peepers were retrieved and the peeper water extracted using a disposable plastic syringe with a stainless steel needle. Samples from individual peepers were composited into a single sample at each station.

Sediment samples were collected at the time of peeper retrieval using pre-cleaned (acid rinsed) stainless steel spoons. At each station, a 500 mL and a 60 mL wide-mouth glass jar with teflon-lined lid were

completely filled, immediately capped, and placed on ice. The 500 mL jar sample was analyzed for grain size and total organic carbon while the 60 mL jar sample was analyzed for acid volatile sulfide-simultaneously extracted metal (AVS-SEM). Samples for AVS-SEM were analyzed within 1 week of collection.

3.1. Analytical methods

Zinc, calcium, magnesium and sodium were measured by inductively coupled plasma emission spectrometry (Leeman PS1000). Alkalinity was measured using titrimetric methods. Dissolved organic carbon (DOC) was measured using a total organic carbon analyzer (Astro 2001, Hach Co., Loveland, Colorado). Water sample pH was measured directly using a combination electrode (Hach). Total suspended solids (TSS) were measured gravimetrically. Analysis of AVS-SEM in sediment samples was conducted using the method described in Allen et al. (1993), with sulfide determined gravimetrically (Leonard et al., 1993). Total organic carbon (TOC) content was determined using the Walkey–Black method (Nelson and Sommers, 1996). Sediment grain size was determined in accordance with ASTM D422.

4. Effects characterization

4.1. Screening level assessment

Acute and chronic Washington State WQS (Washington State Department of Ecology, 1997) for Zn were used in the screening level effect characterization for both surface water and pore water (chronic only). The WQS are based on dissolved metal and are hardness-dependent:

$$\textit{Acute WQS}\ (\textit{dissolved}, \mu g/L) = (0.978)(e^{(0.8473[\ln(\textit{hardness})] + 0.8604)}) \quad (1)$$

$$\textit{Chronic WQS}\ (\textit{dissolved}, \mu g/L) = (0.986)(e^{(0.8473[\ln(\textit{hardness})] + 0.7614)}) \quad (2)$$

Sediments were also assessed using the ESG approach for metal mixtures (USEPA, 2000). In this approach, metal exposure is characterized as:

$$\Sigma SEM - AVS / foc \quad (3)$$

where, ΣSEM is the sum (on a molar basis) of the simultaneously extracted metals, AVS is the molar concentration of acid volatile sulfide and *f*oc is the fraction of organic carbon in the sediment. The resulting values were then compared against a benchmark threshold of 130 μmol ΣSEM/g organic carbon (oc) for toxicity (USEPA, 2005).

4.2. Probabilistic assessment

Effects were characterized in the probabilistic assessment for surface water using acute and chronic SSDs. Sources of acute and chronic toxicity data were the USEPA's AWQC document for Zn (USEPA, 1987; USEPA, 1996) and data published after this document which met the USEPA's guidelines for criteria development (Stephan et al., 1985).

An acute SSD based on 57 species was developed and assumed to be representative of a generic diverse aquatic community. This SSD was used in the probabilistic risk estimates for all surface water sampling stations. However, as discussed above, aquatic receptors at many of the locations are expected to be limited to benthic macroinvertebrates. Brix et al. (2005) has previously shown that these taxa are distinct with respect to their sensitivity to Zn. Accordingly, separate acute SSDs were developed for the following groups as per this previous study: (1) cladocerans; (2) other crustaceans; (3) other invertebrates; (4) insects; and (5) fish (warmwater and coldwater fish appear to have similar sensitivities to Zn over the relevant range of exposure concentrations at the site, so all fish species were pooled). These additional SSDs identify which taxonomic groups are driving the risk estimates and allow for an estimation of risks to those taxonomic groups assumed most prevalent at the sites being evaluated.

The acute SSDs were developed using a log-logistic regression model, as the sigmoidal form of this model tends to provide a good fit to toxicity data (Aldenberg and Slob, 1993; Parkhurst et al., 1995). Species mean acute values (SMAVs) were normalized to a hardness of 50 mg/L (as $CaCO_3$) before deriving the SSDs (Fig. 2a and b). Overall, the log-logistic model provided a good fit to the toxicity data for each taxonomic group (r^2 ranged from 0.83 to 0.98). However, for the cladoceran data in particular, the log-logistic regression model appeared to overestimate Zn toxicity in the lower tail of the distribution. For essential metals such as Zn, both homeostatic control mechanisms (Borgmann and Norwood, 1995; Muyssen and Janssen, 2001; Rainbow and Dallinger, 1993) and naturally occurring background metal concentrations (Garrett, 2000) dictate the need for a threshold below which no effects on aquatic life will be observed (Brix et al., 2001). Accordingly, alternative models were fitted to the acute Zn data for cladocerans using the software program SPSS (SPSS, 1999). A logarithmic model ($r^2 = 0.97$), which is essentially linear over the range of Zn toxicity values for cladocerans, was chosen to develop the cladoceran SSD (Fig. 2b).

Similar to the acute cladoceran toxicity data, the log-logistic model provided a good fit to the chronic toxicity data ($r^2 = 0.95$), but overestimated toxicity in the lower tail of the distribution. Brix et al. (2001) previously used a Pareto model to characterize the threshold response for copper, another essential metal, and used this model to develop chronic SSDs. The Pareto model does provide a better fit to the raw chronic Zn data (Fig. 3), although it slightly underestimates

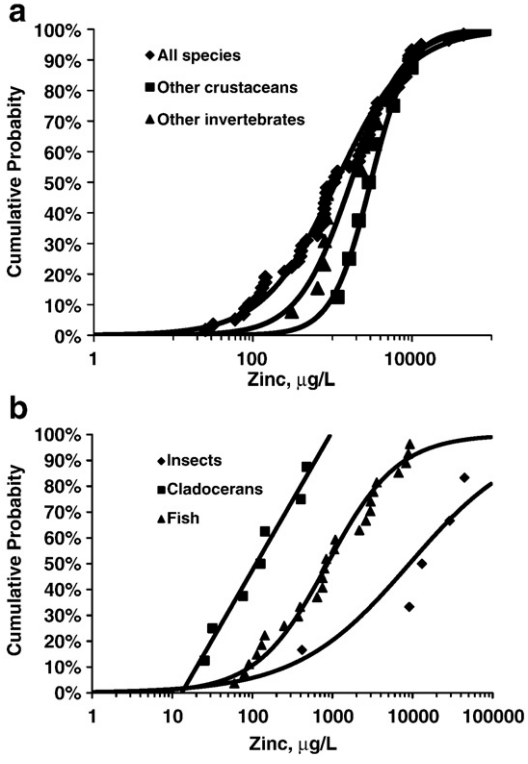

Fig. 2. a. Acute species sensitivity distribution for zinc based on all species, crustaceans (excluding cladocerans), and other invertebrates (excluding crustaceans and insects). All values normalized to a hardness of 50 mg/L and SMAVs are divided by two. b. Acute species sensitivity distribution for zinc based on cladocerans, fish, and insect. All values normalized to a hardness of 50 mg/L and SMAVs are divided by two.

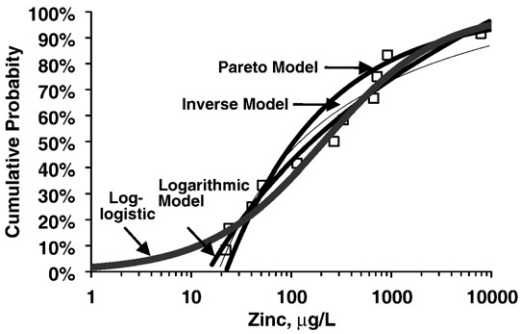

Fig. 3. Comparison of different models for characterizing the chronic SSD.

toxicity in the lower tail. For comparison, other possible models were evaluated. Both inverse and logarithmic functions were found to provide good fits to the chronic toxicity data (r^2 values of 0.95 and 0.97, respectively) and both adequately characterized the threshold response (Fig. 3). For comparison, the chronic WQS, 5th percentile of the log-logistic, Pareto, logarithmic, and inverse models are 4.4, 25, 17, and 21 µg/L, respectively (all normalized to a hardness of 50 mg/L). Overall, the logarithmic model provides the best fit to the relevant range of Zn concentrations for this assessment. Accordingly, it was used for the chronic risk calculations. Chronic Zn toxicity data were available for an insufficient number of species to derive unique SSDs for individual taxonomic groups.

On a sample-by-sample basis, acute and chronic SSDs were adjusted using Zn BLMs that have been developed for *Daphnia magna*, rainbow trout (*Oncorhynchus mykiss*), and fathead minnow (*Pimephales promelas*) (Santore et al., 2002). The BLM version 2.0.0 was used for all calculations (Hydroqual, 2003). Using the BLMs, a water effect ratio (WER) was derived for each sample by estimating the Zn LC50 in a standard synthetic laboratory water and in the sample water using the sample-specific data collected on ionic composition, pH, and DOC.

The ionic composition of the laboratory water was estimated based on the composition of synthetic water defined by USEPA (2002) and adjusted to a hardness matching the sample water. Laboratory water pH was estimated as:

$$pH = 0.4466 \times \ln(hardness\,in\,mg\,/\,L) + 5.8307 \quad (4)$$

This equation was derived from the empirical data on measured laboratory water pH over a hardness range of 10 to 300 mg/L ($r^2 = 0.98$). Alkalinity in the laboratory waters was estimated as the HCO_3 concentration (mg/L) multiplied by 0.82 (Lind, 1979).

The estimated WERs were applied to acute and chronic SSDs by multiplying the individual SMAVs by the WER and deriving a WER-adjusted SSD. Note that the BLMs used for these adjustments are based on models for acute toxicity data. This is necessary because chronic BLMs for Zn, using the USEPA definition of chronic, are currently unavailable. While this introduces uncertainty, use of acute WERs for adjusting chronic AWQC is allowed under the USEPA WER guidance (USEPA, 1994).

5. Risk characterization

5.1. Screening level assessment

The screening level risk characterizations for both surface water and sediment were based on simple hazard quotients (HQs), defined as the ratio of the exposure concentration to the Zn WQS or ESG. Acute surface water HQs were calculated as follows:

$$Acute\ surface\ water\ HQ = \frac{1\text{–}h\ max.\ Zn\ conc.}{Acute\ WQS} \quad (5)$$

For each acute HQ, the WQS was adjusted to the corresponding hardness in the sample. Chronic surface water HQs were calculated in two steps to reflect changes in hardness during the storm:

$$Step\ 1\text{: }Unweighted\ chronic\ surface\ water\ HQ = \frac{1\ h\ max.\ Zn\ conc.}{Chronic\ WQS} \quad (6)$$

$$Step\ 2\text{: }Weighted\ 96\ h\ chronic\ HQ = \frac{HQ_1T_1 + HQ_2T_2 + \ldots + HQ_nT_n}{T_1 + T_2 + \ldots + T_n} \quad (7)$$

Finally, chronic sediment HQs were calculated using pore water data (Eq. (8)) and AVS-SEM data (Eq. (9)):

$$Chronic\ pore\ water\ HQ = \frac{Zn\ pore\ water\ conc.}{Chronic\ WQS} \quad (8)$$

$$Chronic\ sediment\ HQ = \frac{\Sigma SEM\ conc.}{ESG} \quad (9)$$

5.2. Probabilistic assessment

Those stations with acute and/or chronic HQs ≥ 1.0 were further evaluated in a probabilistic assessment (the following only focuses on surface water because, as shown later, pore water and sediment HQs were well below 1.0). In probabilistic risk assessments, probability distributions are typically fitted to the exposure data. However, given the large temporal variability in water quality parameters that modify Zn bioavailability and that these parameters are inputs to BLMs, there is no single hardness-normalized WQS or SSD that is applicable to the entire distribution of exposure concentrations. Therefore, in the acute probabilistic assessment, the Zn concentration in each 1-h composite sample was used to estimate the percent species at risk from the acute SSD. The toxicity data used to derive the SSD were first normalized to the sample hardness and then adjusted by the minimum WER calculated by the BLM models. These calculations result in a distribution of data that describes the percent species at risk for each of the samples analyzed at each station. This distribution can then be used to characterize the cumulative probability (i.e., percent of the time) a given percentage of species is adversely affected at each of the stations.

For the chronic probabilistic risk characterization, the same approach as the acute probabilistic risk characterization was used, with two exceptions. First, the chronic SSD was used. As with the acute SSD, the chronic SSD was normalized for the hardness of each sample and adjusted by the minimum WER derived from the BLMs. Second, after data were adjusted using the BLM, the percentage of species expected to be chronically affected was estimated for each sample and then weighted over 96 h using the same general equation for calculating the time-weighted chronic HQs, resulting in a time-weighted prediction of the percent species chronically affected at each station.

6. Results

6.1. Screening level assessment

Dissolved Zn concentrations from all samples and stations evaluated ranged from <5–385 µg/L while acute WQS for dissolved Zn, based on the varying hardness for each sample, ranged from 12–226 µg/L (Fig. 4a–c). Hardness-normalized chronic water quality standards for dissolved Zn ranged from 11 to 206 µg/L at FT4, 20 to 115 µg/L at FT5, 26 to 183 µg/L at FT8, 12 to 78 µg/L at FT11, and 38 to 166 µg/L at FT13. Maximum acute HQs were ≥1.0 at FT4, FT5, and FT11 for all three storms (Table 1). The 96-h time-weighted average chronic HQs were ≥1.0 at the same stations (Table 1). All acute and chronic HQs at FT8 and FT13 were ≤0.4. Thus, FT4, FT5, and FT11 were carried into the probabilistic assessment.

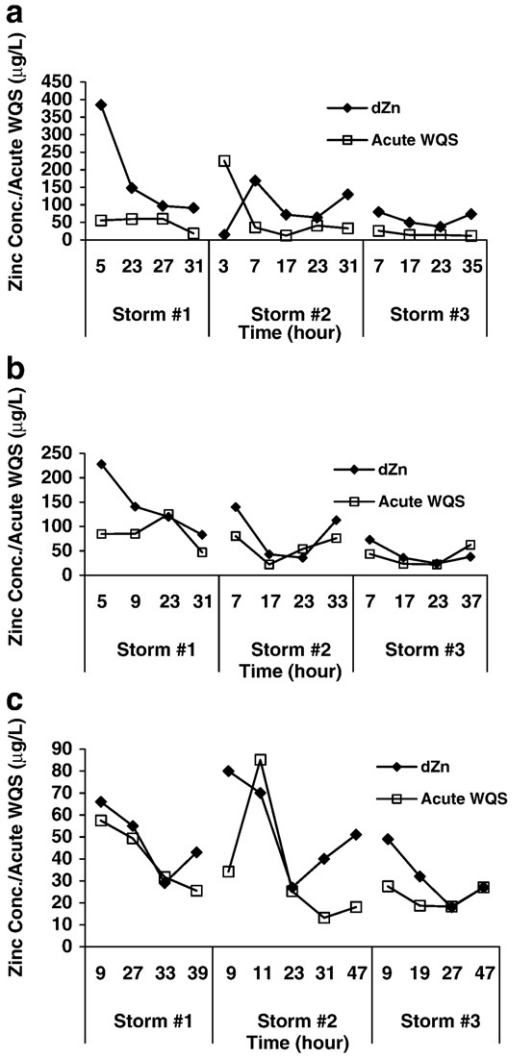

Fig. 4. a. Time series of dissolved Zn concentration and hardness-normalized acute WQS at FT4. b. Time series of dissolved Zn concentration and hardness-normalized acute WQS at FT5. c. Time series of dissolved Zn concentration and hardness-normalized acute WQS at FT11.

Dissolved Zn concentrations in sediment pore water ranged from <5 (not detected) to 7 µg/L. All HQs were ≤0.04 (Table 2), suggesting that bioavailable Zn in sediment is well below levels that may adversely affect benthos. The sediment AVS-SEM data were used as an additional line of evidence for assessing potential Zn risks in sediment. Acid volatile sulfide was only detected at FT17, suggesting the sediment at the remaining stations is highly aerobic. Organic carbon content was also low at these stations with *foc* ranging from 0.003-0.023. The lack of AVS and low *foc* might be expected for most of these stations, which were comprised of a mixed sand/gravel substrate and are subjected to turbulent flows, bedload and potential scouring with each storm event. In comparison, the only station with appreciable AVS and *foc* (FT17) is located in the LRDF, which is a depositional lentic environment with relatively high biological productivity. Because the AVS-SEM based ESG is only applicable to sediments having ≥0.1 µmol AVS/g oc (USEPA, 2000), this evaluation tool was only used at FT17. At this station AVS and ΣSEM were 20.58 and 4.1 µmol/g, indicating all metal would be bound to AVS. This result corroborates with the Zn pore water evaluation for FT17.

For the remaining sediment stations without detectable AVS, we chose to rely solely on the pore water data. Methods exist for estimating conservative sediment criteria using minimum sediment-pore water partition coefficients (K_d) (Ankley et al., 1996), but this was not deemed necessary since measured pore water data were available. Therefore, based on all of the above, benthos are not predicted to be at risk from Zn in sediment.

6.2. Probabilistic assessment

The probabilistic risk assessment estimated the percentage of species acutely and chronically at risk based on the Zn SSDs. This assessment was conducted for those stations with HQs greater than 1.0 (FT4, FT5, and FT11). Both the acute and chronic SSDs were adjusted to reflect WERs derived from Zn BLMs. Estimated WERs ranged from 1.6 to 6.4 across all samples for the three species evaluated. For individual samples, predicted WERs were relatively consistent across species, with a mean coefficient of variation of 11%. To be conservative, the minimum WER from the three models (*Daphnia*, fathead minnow and rainbow trout) was used for each sample (Table 3). The minimum WER was for *P. promelas* in all cases except four, where the minimum WER was associated with *D. magna*.

Based on the SSD for all species, the percentage of species expected to be acutely affected ranged from <1 to 20% for FT4, 2 to 6% for FT5, and 2 to 9% for FT11. The median percentage of species affected is approximately 13, 5, and 3%, for FT4, FT5, and FT11, respectively. To

Table 1
Acute and chronic hazard quotients for surface water.

Station	Acute [a]			Chronic [b]		
	Storm #1	Storm #2	Storm #3	Storm #1	Storm #2	Storm #3
FT4	6.9	5.7	6.3	5.2	1.0	5.8
FT5	2.7	1.9	1.7	1.9	1.6	1.0
FT8	0.1	0.3	0.4	0.2	0.3	0.3
FT11	1.7	3.0	1.8	1.6	2.7	1.3
FT13	0.04	0.2	0.2	0.1	0.1	0.1

[a] Acute HQs based on the maximum one-hour composite concentration.
[b] Chronic HQs based on 96-h time-weighted average.

Table 2
Hazard quotients for sediment pore water and AVS-SEM data.

Station	Pore water data			AVS-SEM data		
	Zn (µg/L)	Hardness (mg/L)	HQ	AVS (µmol/g)	SEM (µmol/g)	AVS-SEM
FT4	5	274	0.02	0	1.81	NA
FT5	7	242	0.03	0	4.33	NA
FT6	<5	202	<0.03	0	1.85	NA
FT7	<5	150	<0.03	0	2.61	NA
FT15	6	135	0.04	0	2.14	NA
FT17	<5	212	<0.03	20.58	4.10	0.2
FT18	<5	156	<0.03	0	0.48	NA

NA = not applicable.

Table 3
Minimum WERs for each sample.

Station	Storm #	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
FT4	1	5.3	4.2	2.5	3.0	NA [a]
	2	1.8	2.4	2.3	2.3	2.1
	3	1.9	1.9	1.5	1.6	NA
FT5	1	3.4	2.7	2.5	2.1	NA
	2	1.9	1.9	2.3	1.8	NA
	3	2.1	1.7	1.9	2.3	NA
FT11	1	2.3	2.8	2.9	3.6	NA
	2	1.9	1.4	2.5	2.0	2.4
	3	2.4	2.1	2.0	2.5	NA

[a] NA = not analyzed, a fifth sample was analyzed only during Storm #2 at a few stations.

evaluate the percentage of time that given levels of acute risk are not exceeded, the acute probabilistic risk estimates from the three storms were pooled. Each risk estimate represented a given number of hours during each storm depending on when it was collected. For example, assuming the beginning of a storm is defined as t_0 (hour 0), samples are collected after 9, 27, 33, and 39 h, and the total duration of interest is 96 h. The time weight of the first sample is 18 h $(9+(27-9))$, the second sample is 12 h $(0.5(27-9)+0.5*(33-27))$, the third sample is 6 h $(0.5(33-27)+0.5(39-33))$, and the time weight of the fourth sample is 60 h $(0.5(39-33)+(96-39))$. This calculation was completed for all three storms for each station and the results combined. The number of hours each sample represented was then divided by the total sampling period for all three storms (3×96 h, or 288 h). Using the results of these calculations, the percentage of time that each acute risk estimate is not exceeded was then determined (Fig. 5). Acute risk estimates are greatest at FT4 with the percent species at risk being greater than 13% over 50% of the time during storm events. In contrast, acute risks at FT5 and FT11 are less than 5 and 7%, respectively, for approximately 90% of the time during storm events. Accordingly, at FT5 and FT11, acute risks, over the majority of time during storm events, are near the level of protection required by WQS (i.e., 95% of species for 100% of the time).

Acute risks to taxonomic groups were also assessed by developing separate SSDs for cladocerans, other crustaceans, insects, other invertebrates, and fish. These risks were also presented as the percentage of time during storms that given levels of acute risk are not exceeded at FT4, FT5, and FT11 (Fig. 6a–c). Results from this analysis indicate cladocerans and fish are the taxonomic groups with the highest risk from Zn. However, as discussed previously, habitat at FT4, FT5, and FT11 is not supportive of zooplankton and fish populations, but is likely supportive of benthic macroinvertebrates, such as insects and small crustaceans. At FT4, a maximum of 10, 8, and 1% of insects, other invertebrates, and other crustaceans, respectively, are estimated to be at risk. At FT5 and FT11, estimated acute Zn risks to benthic invertebrate species are never expected to exceed 5 and 6%, respectively.

Probabilistic chronic risks were also assessed using SSDs adjusted to reflect WERs from the BLMs. The risk estimates were also time-weighted over a 96-h period, analogous to the time-weighted chronic HQs. Using this approach, the estimated percent species at risk from chronic Zn exposure ranged from 42–54% at FT4, 13–29% at FT5, and 18–35% at FT11 for the three storm events (Table 4).

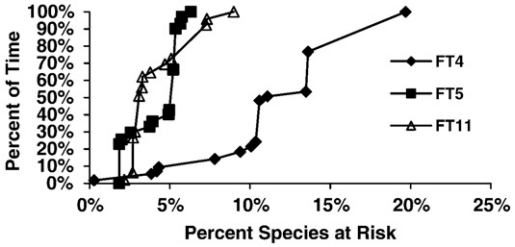

Fig. 5. Percent of time that given levels of acute risk are not exceeded.

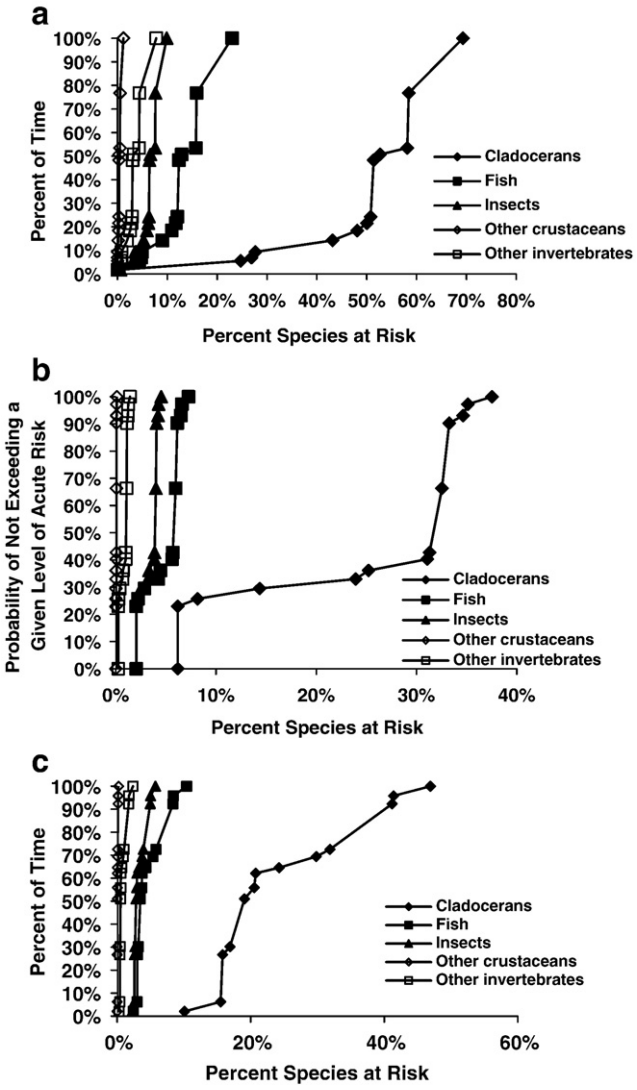

Fig. 6. a. FT4: Percent of time that given levels of acute risk for taxonomic groups are not exceeded. b. FT5: Percentages of time that given levels of acute risk for taxonomic groups are not exceeded. c. FT11: Percent of time that given levels of acute risk for taxonomic groups are not exceeded.

7. Discussion

Overall, this assessment suggests aquatic biota are at risk from exposure to Zn in stormwater at stations FT4, FT5, and FT11. The risks are relatively small for acute (i.e., one hour) exposures, but relatively significant for chronic exposures (4 d). This suggests that despite the relatively high Zn pulses during stormwater events, the risk is driven by longer term exposure to only moderately elevated Zn. There are several key uncertainties that may result in the under- or overestimation of these risk estimates. These are discussed below.

7.1. Aquatic community composition

The aquatic communities at stations FT4, FT5, and FT11 are characterized by limited diversity due to the minimal type and extent of habitat present. Cladocera (water fleas) and fish, which are the two taxonomic groups most sensitive to Zn, have not been observed at these stations and are unlikely to be present due to unsuitable habitat. Both FT4 and FT11 are essentially drainage system outfalls consisting of small, seasonal pools. Habitat in the vicinity of FT5 is an open drainage channel

Table 4
Estimated percent species affected based on chronic exposure scenarios.

Station	Storm #1	Storm #2	Storm #3
FT4	44%	42%	54%
FT5	28%	29%	13%
FT11	18%	35%	19%

that contains little or no baseflow in the dry season. Hence, SSDs and subsequent risk predictions that included these groups, may be overpredicting risk to resident aquatic communities at these locations. We have attempted to improve the risk characterization at these stations by estimating risk to individual taxonomic groups for acute exposures. Indeed, analyzing the risk potential in this manner indicates very minimal risk to biota most likely to naturally occur at these stations.

The same type of assessment cannot be accomplished for chronic exposures because a sufficiently robust chronic toxicity data set is not available. However, it should not be assumed that the large differences in sensitivity between taxonomic groups observed for the acute toxicity would necessarily equate to similarly large differences in chronic sensitivity. In fact, when this type of analysis for Cu was attempted, taxonomic groups shown to have significantly different acute sensitivities were quite comparable in sensitivity under chronic exposure regimes (Brix et al., 2001). Thus the chronic risk assessment may not be affected by differences in species likely or unlikely to be present in the study area.

7.2. Exposure duration

Acute and chronic exposure durations of 1 h and 96 h were characterized in sampling and risk analysis for comparability with the standard exposure durations defined for implementation of AWQC. These default exposure durations are intended to be protective of fast acting toxicants (e.g., ammonia and chlorine) and may not be appropriate for Zn. The acute toxicity data used to develop the SSDs in this assessment were based on 48–96-h exposures and the chronic toxicity data were based on exposures on the order of weeks for invertebrates and months for fish. Pulse exposure toxicity data representative of the storm durations would be required to more accurately assess potential risks.

The effects of Zn pulse exposures have received relatively little study. Brown et al. (1969) conducted one of the first studies by exposing rainbow trout to 2–6 mg/L Zn for alternating periods of 2 and 4 h. Connolly (1985) later developed a model for predicting Zn toxicity based on these data. However, given the very high exposure concentrations (an order of magnitude higher than the exposures measured in this study), it is likely that toxicity was a result of gill damage and corresponding respiratory dysfunction rather than ionoregulatory impairment (Wood, 2001). As a result, these data and the resulting model would not be applicable at lower (<1 mg/L Zn) exposure concentrations typical for stormwater, where ionoregulatory impairment is the primary mode of toxic action.

Brent and Herricks (1998) conducted a study more applicable to the current risk assessment in which *Ceriodaphnia dubia* were exposed to Zn concentrations ranging from 0.15 to 4.8 mg/L for periods of 15 to 240 min. After exposure, organisms were transferred to control water and observed for latent (i.e., post-exposure) toxicity. Observed EC50s (including latent effects) of approximately 200, 225, 650 and 1100 μg/L Zn resulted from pulse exposures of 240, 120, 60, and 30 min, respectively. In comparison, the SMAV for *C. dubia* when adjusted to the same water hardness is 170 μg/L Zn, suggesting the 4-h exposure is approaching the asymptotic EC50. Hence these results suggest an approximate 3-fold difference between the one-hour exposure period assumed in the risk assessment and the 48-h EC50 used in the effects characterization. Further research on the applicability of these types of results across a wide range of exposure concentrations and aquatic organisms is clearly needed.

7.3. Uncertainty in chronic risk estimates

Above and beyond any uncertainty regarding the appropriateness of the 96-h averaging period for chronic risks, there is a potentially significant uncertainty introduced to the risk estimates by the manner in which they were calculated. Specifically, the time-weighted average risk was used as the final risk estimate. To do this, the chronic risk estimates from individual samples were weighted and averaged along with other samples from within a storm. Implicit in this approach is the assumption that each sample component of a chronic risk estimate has a time-weighted proportional impact on the overall 96-h risk estimate.

For example, under this approach a sample representing 1 h of the storm with a bioavailable Zn concentration resulting in a risk estimate of 80% has just as much impact on the final risk estimate as a sample representing 8 h of the storm for which 10% of the species are predicted to be affected. From a toxicological perspective, whether exposure to a Zn concentration imparting 80% risk for 1 h truly has the same consequences as exposure to a Zn concentration imparting 10% risk for 8 h is not known. Data are simply lacking on how variable short-term exposures might affect chronic Zn toxicity.

To assess the potential impact of the approach used, a sensitivity analysis was conducted by comparing the 96-h time-weighted dissolved Zn concentration to chronic Zn SSDs based on the samples with the maximum hardness/WER combination and the minimum hardness/WER combination. This analysis represents the water quality conditions resulting in the lower and upper bounds of Zn bioavailability.

For each station and storm, the range in chronic risk estimates based on minimum and maximum Zn bioavailability conditions were often quite large, with the widest range being a risk of 9–58% for FT4, Storm #2 (Table 5). This wide range is primarily attributed to the extreme variability in hardness measured during this storm 7.4–223 mg/L (as $CaCO_3$). The least variable range in chronic risk estimates was observed at FT11, Storm #1 (12–21%). This analysis demonstrates that there is considerable uncertainty in the chronic risk estimates. However, it also demonstrates that even if the lowest estimated bioavailable Zn concentrations during a storm event were assumed representative of that event, a low level of risk from Zn toxicity would still be present.

7.4. Use of acute BLM for chronic risk estimates

A final uncertainty in the risk estimates was due to the use of the acute BLM for Zn in calculating risk from chronic exposures. It is unknown at this time whether the factors affecting Zn bioavailability in acute exposures will have the same effects in chronic exposures. This uncertainty could result in either under- or overestimation of risk.

8. Conclusion

Overall, we conclude that risk from Zn in stormwater runoff to the detention pond and wetland drainage channels evaluated in this study is relatively limited when issues of bioavailability, exposure duration, and aquatic community composition are considered. We did identify several locations in the forested wetland where aquatic biota are at moderate risk. However, this risk is rapidly attenuated by removal, dilution and reduction in bioavailability as stormwater travels downstream. The net result is that risks are low to negligible ~100 m below the points of discharge.

Table 5
Sensitivity analysis of chronic risk estimates assuming water quality conditions resulting in minimum and maximum Zn bioavailability (value in parentheses represents the weighted mean risk from Table 3).

Station	Storm #1	Storm #2	Storm #3
FT4	24%–53% (44%)	9%–58% (42%)	41%–57% (54%)
FT5	11%–35% (28%)	27%–50% (29%)	7%–35% (13%)
FT11	12%–21% (18%)	17%–47% (35%)	17%–31% (19%)

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