September 25, 2019



Ms. Susan Braley Mr. Chad Brown Washington State Department of Ecology Water Quality Program P.O. Box 47600 Olympia, WA 98504-7600

Re: Comments on Washington's Draft Rule Implementation Plan Chapter 173-201A WAC (revisions) Water Quality Standards for Surface Waters of the State of Washington

Dear Ms. Braley and Mr. Brown:

The purpose of this letter is to provide comments on Washington's Draft Rule Implementation Plan Chapter 173-201A WAC (revisions) Water Quality Standards for Surface Waters of the State of Washington released August, 2019.

The proposed addition to Washington's Water Quality Standard, Section WAC 173-201A-240 Toxic Substances, Toxic Substances Criteria Table 240, Footnote dd requires adjusted site specific criteria to be incorporated into the State's Water Quality Standard and be approved by the U.S. Environmental Protection Agency (EPA). The Port of Seattle (Port) Seattle-Tacoma International Airport (STIA) NPDES Permit WA-0024651 copper and zinc effluent limits were calculated by an adjusted site specific criteria. The copper and zinc adjusted site specific criteria established through a rigorous process incorporating EPA and Ecology guidelines and requirements.

The Port requests the site specific water quality objectives (SSWQOs) and respective copper and zinc effluent limitations established for STIA NPDES Permit #WA-0024651 be incorporated into Chapter 173-201A WAC (revisions) Water Quality Standards for Surface Waters of the State of Washington and approved by the U.S. Environmental Protection Agency (EPA), as stated in Section WAC 173-201A-240 Toxic Substances, Toxic Substances Criteria Table 240, Footnote dd.

Robust methodology and strict QA/QC standards were applied to derive the STIA zinc and copper SSWQOs for Des Moines, Walker, and Miller Creek. A conservative scientific approach was applied to ensure STIA site discharges are protective of the aquatic environment. As an additional measure to the SSWQOs, STIA implements a comprehensive instream monitoring program conducting fall and spring *insitu* toxicity testing to confirm there are no adverse impacts of site discharges to the respective receiving waters.

These comments are provided in support of the Port STIA SSWQOs derived for copper and zinc in streams draining specifically to Walker, Des Moines and Miller Creeks. Of note, Miller and Des Moines Creeks originate upstream of STIA and receive inputs from urban and commercial sources associated with those reaches. The SSWQOs were developed in close consultation with Washington

Department of Ecology staff as well as local community stakeholders, with the intent of establishing site-specific concentrations that would be protective of local aquatic organisms.

The overall approach was based on guidance published by the US Environmental Protection Agency and Washington Department of Ecology (USEPA 1994 and 2001; WDOE 1999), and involved performing parallel toxicity tests on metals of interest in laboratory and site waters. The ratios of the respective median lethal concentrations (LC50s) were then used as measures of the difference in toxicity between site and laboratory waters. Thus, this ratio (i.e., "water effect" or WER) characterized the extent to which site-specific water chemistry conditions affected toxicity relative to laboratory water and could be applied to the generic water quality criterion to derive a site-specific objective that would reflect local conditions. Of note, this basic approach was augmented by additional procedures to ensure that the process was robust and that the site-specific values were consistent with the protection of aquatic life in the receiving environment. The derived values were then used to establish effluent limits for associated stormwater discharges based on conservative assumptions including no provision for dilution.

The process was designed to incorporate seasonal variability in water chemistry that might affect bioavailability and toxicity. Consequently, a minimum of 4 samples were collected from each creek to ensure that the seasonal range of local water quality conditions was characterized, with an additional sample collected during summer low flows to ensure that this critical period was appropriately represented. Individual samples were then spiked with different concentrations of each metal and toxicity determined with the sensitive invertebrate *Ceriodaphnia dubia*, which is widely used in regulatory programs to evaluate aquatic toxicity. Supplemental testing was also conducted with rainbow trout to ensure that results obtained with *C. dubia* were protective of salmonids. Ultimately, a preliminary estimate of the "water effect" was derived from the combined results of the seasonal tests for each site and then compared back to the results from the individual tests. If necessary, the preliminary value was then adjusted appropriately to ensure that it would be protective in all cases. As noted above, the site-specific objectives for each site were then used to derive effluent discharge limits for associated outfalls. The results of these studies were submitted to Ecology in 2008, and subsequently incorporated into STIA's NPDES permit.

While the laboratory-based approach was designed to be comprehensive with respect to identifying appropriate and protective site-specific objectives, it was recognized that it could not capture all possible combinations of water quality variables that might affect toxicity. Consequently, implementation of the SSWQOs and associated discharge limits included a rigorous monitoring plan to ensure that aquatic life in the receiving environment was protected. This plan, the most extensive in Washington State, was subsequently incorporated into STIA's NPDES permit and includes wet and dry weather monitoring in each of the creeks using *in situ* studies initiated with eyed rainbow trout embryos and continuing through the swim-up fry stage. This approach provides an extended exposure period (e.g., approximately 25-30 days, depending on temperature) in the receiving environment and measures the cumulative effects of multiple precipitation events and environmental conditions across a series of developmental stages. Moreover, it incorporates an experimental design that consistently results in the ability to detect the presence of acute and sublethal effects with a level of sensitivity comparable to laboratory-based toxicity tests (Chalmers *et al*, 2014).

This testing program has been conducted for nearly 10 years and has not indicated any metals-related impacts downstream of STIA inputs. These instream monitoring results are consistent with results of toxicity tests conducted on the discharges from the outfalls themselves which are also tested on a regular basis and have generally indicated no evidence of toxicity.

In summary, the SSWQOs derived for copper and zinc for streams associated with STIA property were developed with a high degree of rigor to ensure protection of aquatic life in local waters. Moreover, their implementation was coupled with a comprehensive monitoring program that included *in situ* exposures of sensitive salmonid life history stages, as well as acute and sublethal tests on associated stormwater discharges, to ensure that the objectives were indeed protective. Of note, results from nearly a decade of monitoring support the successful implementation of the objectives developed.

The Port is requesting the STIA NPDES Permit WA-0024651 copper and zinc adjusted site specific criteria be incorporated into the State's Water Quality Standard and be approved by the U.S. Environmental Protection Agency (EPA). The information provided in this letter and the Ecology approved derivation reports detail the conservative approach implemented to ensure the adjusted criteria are protective to aquatic habitat.

Enclosed are the STIA Ecology approved derivation reports for site specific water quality objectives for copper and zinc. If you have any questions concerning the contents of this letter or attachment, please contact me at (206) 787-7137.

Sincerely,

Sarah Cup

Sarah Cox Senior Environmental Program Manager Port of Seattle Seattle-Tacoma International Airport PO Box 68727 Seattle, WA 98168 Phone: (206) 787-47137 Email: cox.sarah@portseattle.org

Cc: Bobb Nolan – Department of Ecology Arlyn Purcell – Port of Seattle Elizabeth Black – Port of Seattle

Enclosure:

Derivation of Site-Specific Water Quality Objectives and Effluent Limits for Copper in Stormwater Derivation of Site-Specific Water Quality Objectives and Effluent Limits for Zinc in Stormwater



June 23, 2008

Mr. Ed Abbasi, P.E. Department of Ecology Water Quality Program 3190 160th Avenue S.E. Bellevue, WA 98008

RE: Site-Specific Studies for Copper and Zinc Seattle-Tacoma International Airport NPDES Permit No. WA-002465-1, Part II Condition S9C

Dear Mr. Abbasi,

Part II Condition S9C of the Airport's NPDES permit requires the Port of Seattle to prepare a Site-Specific Study, e.g., water effects ratio, as required by Condition J.2 of the Airport's and §401 Water Quality Certification 1996-4-02325-2 Condition J.2.a. Attached for your review and approval are two copies the site-specific study reports for copper and zinc. These reports have been revised from earlier versions in accordance with clarifying comments provided to Ecology on May 28, 2008.

Please call me if you have any questions or concerns.

Sincerely;

Bob Duffner Aviation Environmental, Water Resources Manager

- Cc: Gary Bailey, Ecology Randy Marshall, Ecology
- Enclosure: Derivation of Site-Specific Water Quality Objectives and Effluent Limits for Copper in Stormwater. Derivation of Site-Specific Water Quality Objectives and Effluent Limits for Copper in Stormwater.

Seattle-Tacoma International Airport P.O. Box 68727 Seattle, WA 98168 U.S.A. TELEX 703433 FAX (206) 431-5912



Date: June 23, 2008

TRANSMITTAL FORM

401 Water Quality Certification No. 1996-4-02325 (Amended-2) Submittal

Certification Condition: 401 J - Operational Stormwater Requirements

Task Name: 2 (a) - Complete WER (Water Effects Ratio) and SSA (Site Specific Analysis) prior to operation of 3 R/W

Port Task Manager: Robert Duffner

Sent By: Port of Seattle

Agency Task Manager: Ed Abbasi

To: Alice Kelly

Ed Abbasi

Ecology's NW Regional Planner Washington State Department of Ecology Northwest Regional Office 3190 160th Avenue SE Bellevue, WA 98008-5452

We are transmitting 3 sets of the following materials:

- Deviation of Site-Specific Water Quality Objectives and Effluent Limits for Copper in Stormwater - Revised June 23, 2008
- Deviation of Site-Specific Water Quality Objectives and Effluent Limits for Zinc in Stormwater - Revised June 23, 2008

Item sent by Email, U.S. Mail; Review and approval requested by 7/23/2008

Item sent by Email, U.S. Mail; Review and approval requested by 7/23/2008

Questions regarding this submittal should be directed to Robert Duffner (206) 988-5528.

Copies: Abbasi, Ed - Department of Ecology Kordik, Robin - POS AV/ENV (form only) Leavitt, Elizabeth - POS AV/ENV (form only) 401 File (Debbie Bradford), POS AV/ENV)

Sincerely

Robert Duffner or Robin Kordik for the Port of Seattle



Derivation of Site-Specific Water Quality Objectives and Effluent Limits for Copper in Stormwater

Final report date: June 23, 2008

Prepared for:

Port of Seattle – Aviation Division Seattle-Tacoma International Airport Seattle, WA

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EXECUTIVE SUMMARY

This report presents the development of site-specific water quality objectives (SSWQOs) for copper in streams that receive stormwater discharges from the Seattle-Tacoma International Airport (STIA). On the basis of these objectives, potential SSWQO-based discharge limits for copper were also derived. This report includes the background for the study, the methods and materials used to achieve the objectives of the study, the data used to derive the site-specific objectives, as well as the actual derivation of specific objectives and effluent limits.

The overall approach was based on guidelines promulgated by the U.S. Environmental Protection Agency and the Washington State Department of Ecology (Ecology), and consisted of water-effect ratio studies (WERs) conducted with *Ceriodaphnia dubia*. Strict QA/QC standards were applied to ensure that a rigorous approach was used and that data quality objectives were met. A minimum of five WER comparisons were used to derive a final WER for each site; this number exceeds the minimum required by USEPA and Ecology, and further ensures that the final WER is a robust measure of the bioavailability of copper in each stream. Supplemental comparisons were also conducted with rainbow trout (*Oncorhynchus mykiss*) to ensure that the site-specific objectives derived from data obtained with *C. dubia* were also protective of salmonids. Finally, the calculated values were then compared with the original dataset to confirm that they were, indeed, appropriate.

Water-effect ratios were determined for sites located in the Des Moines, Miller and Walker Creek drainages. The water-effect ratios varied between sites, and ranged from 1.79 to 4.90, based on dissolved copper. SSWQOs were calculated by multiplying the generic water quality criterion for copper (based on hardness) by the WER appropriate for each site.

Typically, the need for effluent limits is determined based on the outcome of a reasonable potential analysis. Reasonable potential and mixing zone analyses have not been completed at this time due to lack of sufficient data representing post-retrofit conditions. STIA has recently completed a comprehensive retrofit of its stormwater treatment and flow control facilities. These new facilities are expected to significantly decrease pollutant loading. Stormwater facilities associated with Third Runway associated outfalls will be completed in the near future in conjunction with that project's

completion. In the interim, this study determined potential discharge limits for each of the stormwater outfalls on the basis of the corresponding SSWQO, with no consideration of dilution. Since SSWQOs are derived on the basis of dissolved copper, and discharge limits are expressed as total copper at a specific hardness, the discharge limits were further adjusted to reflect the ratio of dissolved to total copper and 10th percentile hardness at each site.

The Port recognizes uncertainties associated with projected removal efficiencies in the stormwater treatment system, as well as in derivation of SSWQOs. Consequently, a robust and comprehensive monitoring program will continue to be applied to the discharges, as well as the receiving environment, to ensure that beneficial uses are protected.

1. INTRODUCTION

1.1. Historical Background

The Port of Seattle ("the Port") owns and operates the Seattle-Tacoma International Airport (STIA), and currently discharges stormwater run-off from a number of locations at STIA. These existing stormwater discharges are permitted by the Washington Department of Ecology ("Ecology") under individual NPDES Permit No. WA-002465-1, the most recent version of which was issued in 2003 and which was subsequently modified in 2005, and again in 2007. In addition, the Port is in the process of a major expansion called the Master Plan Update (MPU), which includes a Third Runway and related facilities. As a part of the permitting for the MPU, Ecology issued a §401 Water Quality Certificate No. 1996-4-02325 in 2001. The terms of the original Certificate were subsequently amended as a result of a settlement agreement, a decision by the Pollution Control Hearings Board in 2002 and a decision by the Washington Supreme Court in 2004. The new outfalls that are being constructed to handle stormwater from the MPU are identified in the current permit as "future outfalls" and will be included as part of the Port's permit application for the next NPDES permit, which will be issued in late 2008.

Condition J.2 of the §401 Certification (as amended) states that "no stormwater generated by operation of new pollution generating impervious surfaces of ... [MPU projects] (excluding surfaces not to be included in the airport NPDES permit...) shall be discharged to state receiving waters until a site-specific study, e.g., a Water Effects Ratio Study (WERS) has been completed and approved by Ecology and appropriate limitations and monitoring requirements have been established in the Port's NPDES permit. The study may use existing impervious surfaces as a surrogate for future new impervious surfaces, and it shall be submitted to Ecology for review and approval. The Port shall consult with Ecology's Northwest Regional Office Water Quality Program's SeaTac NPDES Manager to determine an appropriate time for submittal of the WERS." In turn, the NPDES permit (Part II, Condition S9C.1) requires the Port to comply with Condition J.2 of the §401 Certification, and specifically states that the Port must: "[c]onduct a site specific study, e.g., Water Effect Ratio, which is a criteria adjustment factor accounting for the effect of site specific water characteristics of pollutants bioavailability and toxicity to aquatic life ... By December 31, 2007, the Permittee shall submit to the Department for review and approval a report documenting the results of the site specific study." On December 7, 2007, the Port requested and was verbally granted an extension of the report submittal date to February 29, 2008. The copper report was initially submitted to Ecology on February 29, 2008. Based on discussions with Ecology, clarifying responses were submitted on May 28, 2008. This report has been revised in accordance with those clarifying responses. All of the information contained within this document has been prepared to satisfy both the NPDES and §401 requirements.

1.2. Technical Background

As a result of contact with metallic surfaces and metal-bearing particulates (metal roofing material and particulate wear from brake linings, for example), run-off may contain elevated concentrations of dissolved metals, particularly copper and zinc. The Port has implemented an extensive best management practice (BMP) based program to control concentrations of these metals in stormwater discharges. Although the BMP program meets Ecology-approved AKART for STIA, it is expected that some amount of metal contamination will continue to be discharged to State receiving waters.

A number of factors may influence the bioavailability of metals, and consequently influence their toxicity under different conditions. These factors include hardness, pH and dissolved organic carbon (DOC; primarily comprised of humic and fulvic acids), as well as the balance of other inorganic ions present. The effect of hardness on toxicity has been widely documented, and the USEPA incorporated hardness into the derivation of historical water quality objectives for a number of metals including zinc and copper (USEPA 1994). Most recently, the biotic ligand model (BLM) has been used to derive site-specific criteria for copper by incorporating selected water quality parameters in addition to hardness (Di Toro *et al.* 2001), and similar applications are being developed for other metals, as well. Indeed, the BLM has been incorporated into the most recent version of the USEPA copper criteria document (USEPA 2007).

The interest in developing site-specific criteria or objectives for metals originates in the fact that most of the original toxicity studies that led to the development of metals criteria were conducted in laboratory water, which typically does not contain constituents (e.g., DOC) that have the capacity to reduce the bioavailability of the metals. Thus, metals toxicity in site waters is typically lower than observed in laboratory tests or predicted simply on the basis of differences in hardness between laboratory water tests

and site water. Conversely, it is possible that site-specific characteristics of certain parameters (e.g., pH) might increase toxicity compared with that predicted on the basis of laboratory toxicity tests conducted in laboratory water.

Due to uncertainties in predicting toxicity purely on the basis of models (such as the BLM) in the absence of site validation, site-specific evaluations of toxicity are generally conducted to obtain empirical comparisons between tests conducted in laboratory water and in the site water of interest. The ratio between the toxicity observed in site water and that observed in laboratory water provides a measure of the effect of site water on the bioavailability of the contaminant of interest. This ratio is referred to as the water-effect ratio (WER), and can be used to adjust the water quality criterion as appropriate on a site-specific basis.

USEPA has published two guidance documents related to deriving WERs. The first document (USEPA 1994) provided the initial guidance, whereas the second document (USEPA 2001) is focused on copper and incorporates a revised approach that reflects more recent developments in the field. For example, in the more recent document (USEPA 2001), fewer comparative tests are required to derive a WER. In addition, only a single species is used to derive a WER in USEPA (2001), whereas USEPA (1994) calls for a primary and a secondary species. In this instance, USEPA (2001) notes that the use of a second species was not found to substantively improve or alter the interpretation of the results obtained with the primary species. Some of the 2001 document's implicit assumptions (e.g., continuous point-source discharge, and samples collected under low-flow conditions) need to be modified when applying the procedures to situations that reflect different conditions (e.g., stormwater discharges) associated with a variety of loadings, sources and flow.

Ecology also provides guidance for conducting and implementing WER studies in their Permit Writer's Manual (1999). Prior to initiating a WER, the permittee must conduct an evaluation of options for reducing metals concentrations in the discharge, and implement practices and technologies that meet the cost test for reasonableness (WDOE 1999). To achieve this objective, the Port conducted an engineering study to optimize outfall design and identify the known and reasonable technologies (AKART) that could be applied (R.W. Beck and Parametrix 2005). The guidance document also requires that a preliminary study be conducted using clean sampling and analytical techniques to confirm that there is a reasonable potential for exceedences to occur, and that a study plan for conducting the WER studies be submitted and approved by Ecology. Consequently, a preliminary study report documenting metals concentrations in various outfalls and receiving environment samples was prepared and submitted to Ecology (Ecotox and Parametrix 2002), and a work plan for developing site-specific water standards for both copper and zinc submitted and approved by Ecology (Brix and Deforrest 2004). Other considerations for WER studies include use of standard and approved toxicity testing techniques by certified laboratories and submittal of all data in the final report (WDOE 1999).

Because of the variety of receiving environments, with potentially unknown possibilities for interactions that might affect toxicity, Ecology decided during the §401 Certification process that the most appropriate approach for determining site-specific copper objectives and corresponding discharge limits would be to perform WER studies on each of the potentially affected receiving environments. The actual approach was designed to be robust. It not only exceeds the minimum requirements specified by USEPA, but was further intended to provide sufficient numbers of samples to fully characterize variability in the receiving environments. The general technical approach was described in the original Workplan (Brix and Deforest 2004), which was approved by Ecology in advance of initiating this testing program. Subsequently, minor modifications to the approach were made in consultation with Ecology.

Briefly, the approach involved testing a minimum of five discrete samples from instream sites. Samples were collected from a total of seven in-stream sites (see Figure 1), representing the Miller, Des Moines and Walker Creek drainages.

The samples represented all four seasons, including the critical summer low-flow period identified in the Workplan (Brix and DeForest 2004), which was represented by two samples to provide additional "weight" to this period in subsequent calculations. The Workplan noted that historical sampling suggested that copper and zinc concentrations tended to be higher between July and September than other months, and longer periods between storms would likely increase accumulation of metal particulates during this period. In addition, baseflows in the creeks would tend to be lowest during this period, with most run-off absorbed by pervious surfaces which would tend to be more saturated during wet months.

In general, the samples were spiked with copper, and their toxicity compared with concurrent toxicity tests performed with copper in laboratory water. Thus, the ratios between LC50s obtained in the laboratory and site water are measures of the relative bioavailability of copper in site water compared with laboratory water. The primary test organism was the invertebrate *Ceriodaphnia dubia*, with supplemental testing with rainbow trout (*Oncorhynchus mykiss*). WERs were calculated for each event, and the geometric mean determined for each site. These values were then applied to Washington State's generic water quality criterion for copper as an adjustment factor to derive a site-specific objective for each site.

2. METHODS

2.1. Sampling Sites

Surface run-off from the STIA typically flows into two major watersheds – Miller and Des Moines Creeks (see Figure 1). The STIA comprises approximately 2.5 and 20% of the Miller and Des Moines Creek watersheds, respectively. In addition, the STIA also plans to discharge stormwater into Walker Creek, as part of their ongoing expansion efforts. The locations of the sampling sites and outfall points were described in detail in the Workplan (Brix and DeForest 2004). A sampling point at the outlet of Lake Reba (RBOut) was subsequently added following discussions with Ecology. Briefly, sampling sites RBOut, Miller Creek, and MC8th provide information relevant to the Miller Creek drainage, and sites DME, Bowdown and NPOut provide information relevant to the Des Moines Creek watershed. Stormwater discharges from areas associated with the Third Runway will also enter Walker Creek, a tributary of Miller Creek, as well as Miller Creek itself. Consequently, samples were also collected from Walker Creek to derive a sitespecific objective for this watershed.

2.2. Sampling Methods

Ecology and the Port determined that a minimum of five acceptable WERs, representing each of the four seasons, as well as one additional value corresponding to the critical summer low-flow period, would comprise an acceptable database for each site. In addition to season, the criteria for identifying sampling events included at least 0.2 inches of rain, preceded by not more than 0.1 inches of rain over the previous 24 hr, and separation of sampling events by at least 3 weeks (Brix and DeForest 2004). Samples were 48-hr composites collected over the first 48 hrs of any given rain event. The samples were collected at mid-channel using an ISCO sampler (Model 3700 or 6712). Subsamples making up the composite were comprised of 450 mL aliquots collected at 30-min intervals over the 48-hr period, and stored on ice until completion of the sampling event. A portion (approximately 500 mL) of the composited sample was then taken for chemical analysis. The split samples were transported on ice to the toxicity testing and analytical laboratories. The sample containers were polyethylene, and Teflon tubing was used in the sampler.

2.3. Toxicity Tests

Acute toxicity tests with *C. dubia* were conducted in two laboratories, Nautilus Environmental (Nautilus), Tacoma, WA, and ENSR, Fort Collins, CO, using procedures consistent with USEPA acute toxicity test methods (USEPA 2002). The general methods were similar between laboratories, and are summarized in Table 2.1. Toxicity tests with rainbow trout were conducted by Nautilus, and the methods are summarized in Table 2.2. Water quality and background copper and zinc concentrations in the laboratory water associated with each of WER tests are summarized in Table 2.3.

Test organism	Ceriodaphnia dubia
Test organism source	In-house cultures
Test organism age at initiation	< 24 hours
Test duration	48 hours
Test solution renewal	None
Feeding	None
Test chamber	30 ml plastic cup
Test solution volume	15 mL
Test temperature	20 ° or 25 ° ± 1°C
Dilution water	Moderately Hard Synthetic Water or Site Water
Number of organisms/chamber	5
Number of replicates	4
Photoperiod	16 hours light/8 hours dark
Aeration	None
Test Protocol	EPA-821-R-02-012 (USEPA, 2002)
Test acceptability criterion for controls	\geq 90% survival
Reference toxicant	Copper chloride

	Table 2.1. Sum	mary of acute	e toxicity test	methods for	<i>C</i> .	dubia.
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^a ENSR ^b Nautilus

Table 2.2. Summary of acute toxicity test methods for rainbow trout.

Test organism	Oncorhynchus mykiss
Test organism source	Troutlodge, Sumner WA
Test organism age at initiation	10 - 25 days post swim up
Pre-test acclimation time	5 days minimum
Test duration	96 hours
Test solution renewal	80% at 48 hr (no renewal for Bowdown, DME,
	MC8th, Miller Creek) ^a
Feeding	None
Test chamber	8-L plastic tank
Test solution volume	4 L
Test temperature	12 ± 1°C
Dilution water	Moderately Hard Synthetic Water or Site Water
Number of organisms/replicate	10
Number of replicates	3
Photoperiod	16 hours light/8 hours dark
Aeration	None
Test Protocol	EPA-821-R-02-012 (USEPA, 2002)
Test acceptability criterion for controls	\geq 90% survival
Reference toxicant	Copper chloride

^a Insufficient sample was collected to conduct a renewal at 48 hr

Test Initiation Date	Samples Tested	Hardness (mg/L)	Alkalinity (mg/L)	pН	DOC (mg/L)	Copper (mg/L) Total/Diss	Zinc (mg/L) Total/Diss
29 Mar 04	DME, BOWDOWN, MC8th, Miller Creek, NPOut	88	61	7.3	<0.250	<0.002/<0.002	<0.005/<0.005
29 May 04	BOWDOWN, MC8th, Miller Creek, NPOut	92	64	7.0	<0.250	<0.001/<0.001	<0.005/<0.005
10 Aug 04	DME, MC8tn, Miller Creek, NPOut	96	62	7.1	<0.250	0.0027/<0.002	<0.005/<0.005
12 Oct 04	DME, Miller Creek, MC8th	90	58	8.1	<0.250	<0.002/<0.002	<0.005/<0.005
22 Mar 05	DME, BOWDOWN, MC8th, Miller Creek	90	57	8.0	<0.250	<0.002/<0.002	0.006/<0.005
11 Jul 05	DME, BOWDOWN, Miller Creek	90	59	8.2	<0.250	<0.002/<0.002	<0.005/<0.005
30 Aug 05	RBOut	87	60	8.25	<0.250	<0.002/<0.002	<0.005/<0.005
17 Oct 05	Miller Creek, NPOut, RBOut	84	56	8.2	<0.250	<0.002/<0.002	<0.005/<0.005
19 Jan 06	DME, MC8th, BOWDOWN, Miller Creek, NPOut, RBOut	88	64	8.09	<0.250	<0.002/<0.002	<0.005/<0.005
16 Apr 06	DME, NPOut, RBOut	84	52	8.08	<0.250	<0.002/<0.002	0.008/0.005
17 Sept 06	NPOut, RBOut	100	76	8.37	< 0.250	<0.002/<0.002	0.017/0.017
12 Jun 07	Walker Creek	84	64	8.18	< 0.250	<0.002/<0.002	<0.005/<0.005
7 Sep 07	NPOut, Walker Creek	84	68	8.13	<0.250	<0.002/<0.002	<0.005/<0.005
2 Oct 07	Walker Creek	80	64	8.23	< 0.250	<0.002/<0.002	0.006/0.007
12 Nov 07	Walker Creek	88	60	8.21	< 0.250	<0.002/<0.002	<0.005/<0.005
29 Nov 07	Walker Creek	88	60	8.01	< 0.250	<0.002/<0.002	0.006/0.006
	Mean	88.3	61.6	7.97	<0.250		
	St. dev.	4.9	5.4	0.43	na		

Table 2.3. Water Quality for Laboratory Water

The toxicity of copper in site waters was determined by spiking the site waters with CuCl₂, and preparing serial dilutions using a dilution factor of 0.6 – 0.7. Concentrations were allowed to equilibrate for 2 - 3 hrs prior to taking water quality measurements and adding the test organisms. Subsamples of each dilution were also taken for determinations of dissolved and total copper at the beginning of the test, and dissolved copper again at 48 hrs (total and dissolved at this time point for rainbow trout) and, in the case of rainbow trout, also at 96 hr. Survival and water quality were monitored at 24-hr intervals, and LC50s determined based on survival at test termination. LC50 calculations were made on the basis of the initial total concentrations, as well as the average dissolved concentrations, using the trimmed Spearman-Karber method (CETIS vers. 1.025B-1.6.3revG).

Copper toxicity in laboratory water was determined similarly. However, since the laboratory water was tested at only one hardness, it was necessary to extrapolate the LC50 estimate to that which would be predicted for laboratory water at the hardness of each test sample (i.e., site water) to facilitate comparisons between site and laboratory waters. This estimate of toxicity in laboratory water at the hardness of the test sample was obtained using the USEPA equation for adjusting copper toxicity based on hardness (USEPA 2001):

Adjusted LC50_{lab water} =
$$LC50_{lab water} x$$
 (Hardness_{site water} / Hardness_{lab water})^{0.9422} Eq. 1

The WER for a given sample and event was then calculated as the ratio between the LC50 in site water, and the LC50 for laboratory water, adjusted to the hardness of the site water. Thus, a WER greater than 1 was a measure of the extent to which the receiving environment sample reduced toxicity compared with that which would be expected simply on the basis of a difference in hardness between the laboratory and site waters. Conversely, a WER <1 would suggest that some factor in the site water was contributing to an increase in toxicity greater than would be expected just on the basis of a change in hardness alone.

2.4. Site-Specific Water Quality Objective

Deriving a site-specific water quality objective for copper is relatively straightforward. Once the individual WER values have been calculated, the dataset for the site is evaluated to determine if any of the values appear inconsistent with the rest of the dataset. Assuming that the WERs are reasonably distributed, with no extremely large or small values, a final WER is calculated as the geometric mean of the individual WERs. This value is then multiplied by the Washington State water quality criterion (*see* WAC 173-201A-240) for copper to obtain a site-specific objective.

3. QUALITY ASSURANCE

Results from each toxicity test were evaluated to determine the following:

- Did the test procedures follow the appropriate guidelines?
- Did the tests meet control acceptability criteria?
- Did the tests exhibit a reasonably consistent dose-response?
- Did the tests exhibit acceptable water quality parameters?
- Were the tests initiated within an appropriate time-frame?
- Were the proper controls performed?
- Did the test concentrations exhibit acceptable stability over the exposure period?

Each of these measures of test validity was compared against the criteria set forth in the original Workplan (Brix and DeForest 2004), which cited USEPA (1993, 1994, and 2001) and WDOE (1999 and 2001) as technical support documents. Potential issues were deemed minor if they were not likely to affect the results or conclusions (e.g., change a calculated LC50 significantly). Major issues were those in which the calculated LC50 or WER might be affected (e.g., atypical dose-response), or situations in which test procedures or acceptability criteria might have been altered to the point where the results might be considered suspect (e.g., excessive control mortalities, significant exceedences of holding time, or dissipation of the test chemical).

This QA evaluation was performed approximately half-way through the program and again at the end of the program. At the interim evaluation point, each of the data anomalies identified was critically evaluated with respect to its ultimate inclusion in the dataset and, if necessary, additional sampling events were scheduled to replace rejected datasets. In addition, "gray" areas in which different protocols provided different guidance were identified and resolved with Ecology. The final evaluation confirmed that a sufficient number of samples representing a broad spectrum of temporal conditions were obtained, and that all of the datasets were acceptable.

The following guidelines were used to evaluate whether data were acceptable for proceeding with calculating site-specific water quality objectives:

- Control acceptability criteria
 - Were appropriate and concurrent controls used (Brix and DeForest 2004; USEPA 1994 and 2001)?
 - Was control survival at least 90 percent (USEPA 1993 and 2002)?
- Appropriate test procedures and water quality
 - Was the dilution factor between 0.65 and 0.90? A dilution factor of 0.6 (USEPA 2001) was allowed for tests initiated prior to the interim review, but a higher dilution factor was considered desirable for subsequent tests (USEPA 1994; Brix and DeForest 2004).
 - Did water quality (e.g., dissolved oxygen) remain within acceptable ranges (USEPA 1993 and 2002)?
- Acceptable holding times
 - ≤36 hr was considered desirable (USEPA 1994); 96 hr was considered maximum, based on an analysis that indicated no relationship between holding time and toxicity. This maximum holding time is also consistent with USEPA guidance for conducting streamlined copper WERs (USEPA 2001).
- Acceptable toxicant stability
 - At least 50% of the test material measured initially must be present at the end of the test (USEPA 1994);
 - A test was considered acceptable if only one concentration exhibited excessive dissipation of the toxicant;
 - A test was considered unacceptable if more than one concentration exhibited excessive dissipation of the toxicant.
- Acceptable dose-response for estimating a valid LC50 (USEPA 1993)?
- Did the data provide sufficient temporal coverage?
 - Were a minimum of 5 valid data points available for the site? This level of temporal coverage exceeds the requirements of both USEPA WER guidance documents (USEPA 1994 and 2001).
 - Was the critical summer dry period represented by 2 samples?

4. ANALYTICAL CHEMISTRY

Analytical chemistry support for this study was provided by Aquatic Research Inc, Seattle, WA. Analytical parameters measured in samples used for the WER tests included: total and dissolved silver, arsenic, calcium, cadmium, chromium, copper, iron, potassium, lead, magnesium, manganese, nickel, sodium, zinc, total suspended solids, total organic carbon, dissolved organic carbon, hardness, alkalinity, pH, sulfate and chloride. In addition, dilutions of the water samples spiked with copper were measured for total copper at test initiation, and dissolved copper at test initiation and at termination. These actual measured values were used in calculation of the LC50s that resulted in the WERs.

5. RESULTS

5.1. Sampling Events

A total of five to eight samples collected from each of the sampling sites resulted in definitive WERs that met the QA criteria. Samples were collected between March 2004 and September 2006 from the Des Moines and Miller Creek watersheds, and between June and November 2007 from Walker Creek. The sampling dates, total rainfall over the 48-hr sampling period and general water chemistry parameters, including background zinc and copper concentrations, associated with each of the sampling events and sites are summarized in Table 5.1.

	Dainfall	TT	A 11 11 11.		DOC^{2}	Copper ²	Zinc ²
Sampling Site	(in)	(ma/I)	(ma/I)	pH^1	(ma/I)	(mg/L)	(mg/L)
	(111.)	(iiig/ L)	(mg/ L)		(IIIg/L)	Total/Diss.	Total/Diss.
DME							
26 Mar 04	0.80	30	24	6.9	5.63	0.012/0.006	0.057/0.043
8 Aug 04	0.66	38	32	7.0	12.60	0.021/0.017	0.105/0.031
10 Oct 04	1.04	32	29	7.5	7.39	0.007/0.007	0.033/0.017
21 Mar 05	0.44	34	28	7.5	5.79	0.009/0.005	0.058/0.048
10 Jul 05	0.33	32	27	7.6	10.10	0.008/0.006	0.037/0.019
21 Jan 06	0.62	23	24	6.9	3.03	0.005/0.004	0.030/0.023
15 Apr 06	0.85	28	26	7.0	4.28	0.008/0.005	0.051/0.027
Bowdown							
26 Mar 04	0.80	28	22	6.9	5.45	0.010/0.007	0.039/0.033
27 May 04	1.05	30	30	6.6	7.50	0.015/0.007	0.049/0.014
21 Mar 05	0.44	30	24	7.3	5.66	0.008/0.005	0.049/0.051
10 Jul 05	0.33	28	27	7.6	10.40	0.016/0.005	0.040/0.015
16 Oct 05	0.35	42	42	7.6	10.20	0.005/0.004	0.023/<0.005
21 Jan 06	0.62	20	14	6.8	3.41	0.004/0.004	0.027/0.024
MC8th							
26 Mar 04	0.80	76	69	7.5	7.17	0.007/0.004	0.021/0.013
27 May 04	1.05	94	85	7.4	6.93	0.005/0.003	0.033/<0.005
8 Aug 04	0.66	70	62	6.8	9.40	0.004/0.005	0.014/<0.005
10 Oct 04	1.04	64	59	7.2	7.01	0.022/0.003	0.025/0.006
21 Mar 05	0.44	96	87	8.0	6.06	<0.002/<0.002	0.024/0.017
18 Jan 06	0.62	48	41	7.2	5.60	0.003/0.003	0.021/0.007
Miller Creek							
26 Mar 04	0.80	70	65	7.8	7.12	0.007/0.004	0.043/0.024
27 May 04	1.05	90	88	7.1	6.97	0.006/0.002	0.030/<0.005
8 Aug 04	0.66	76	71	7.2	9.75	0.005/0.004	0.210/<0.005
10 Oct 04	1.04	56	52	7.8	6.74	0.006/0.004	0.022/0.008
21 Mar 05	0.44	90	88	7.9	6.17	0.003/<0.002	0.022/0.023
10 July 05	0.33	84	84	8.0	7.16	0.004/0.003	0.015/0.007
16 Oct 05	0.35	92	96	7.6	6.24	0.005/0.003	0.025/<0.005
18 Jan 06	0.62	44	40	7.1	6.46	0.005/0.004	0.052/0.008
NPOut							
26 Mar 04	0.80	92	90	7.6	6.53	0.006/0.004	0.014/<0.005
28 May 04	1.05	88	94	7.4	6.96	0.005/0.004	0.010/<0.005
8 Aug 04	0.66	112	124	7.2	8.75	<0.002/<0.002	<0.005/<0.005
17 Oct 05	0.35	92	95	7.6	7.05	0.006/0.002	0.005/0.013
21 Jan 06	0.62	46	40	6.9	4.86	0.006/0.006	0.016/0.015
15 Apr 06	0.85	75	77	7.6	5.28	0.008/0.005	0.016/0.010
16 Sep 06	0.43	139	111	7.4	9.65	<0.002/<0.002	0.025/0.018

 Table 5.1. Summary of rainfall and general water chemistry parameters associated with samples used to derive WERs.

Sampling Site and Date	Rainfall (in.)	Hardness (mg/L)	Alkalinity (mg/L)	pH1	DOC ² (mg/L)	Copper ² (mg/L) Total/Diss.	Zinc ² (mg/L) Total/Diss.
RBOut							
30 Aug 05	0.19	150	161	8.0	6.78	0.002/<0.002	0.013/0.012
17 Oct 05	0.35	113	124	7.6	5.65	0.004/0.003	0.014/<0.005
18 Jan 06	0.62	63	62	7.2	5.92	0.004/0.004	0.023/0.005
15 Apr 06	0.85	92	97	7.7	5.20	0.005/0.003	0.018/0.011
16 Sep 06	0.43	135	106	7.4	7.89	<0.002/<0.002	0.023/0.016
Walker Creek							
11 June 07	0.25	134	97	7.7	2.55	<0.002/<0.002	0.009/0.005
6 Sep 07	1.08	124	122	7.7	7.43	0.003/0.002	0.031/0.009
1 Oct 07	1.44	108	98	7.8	7.36	0.002/0.002	0.009/0.008
11 Nov 07	0.32	132	86	7.6	11.5	0.003/0.003	0.015/0.015
28 Nov 07	0.49	112	118	7.8	4.11	<0.002/0.002	0.028/0.008

Table 5.1, continued.

¹pH measured at lab at time of receipt; ²metals and DOC measured at analytical lab Note: pH values as measured in samples at the laboratory have been shown to be higher than pH measured in-stream.

Rainfall ranged from 0.19 to 1.44 inches over a 48-hr period associated with the different sampling events. Hardness ranged from a low of 20 mg/L to a high of 150 mg/L, as CaCO₃. Alkalinity ranged between 14 and 161 mg/L, as CaCO₃. pH ranged from 6.6 to 8.0, and DOC measured in the samples ranged from 2.55 to 12.60 mg/L, compared with <0.25 mg/L in laboratory water. Total copper measured from <0.002 mg/L to 0.022 mg/L, and dissolved copper ranged from <0.002 mg/L to 0.017 mg/L. Total zinc concentrations ranged between 0.005 and 0.210 mg/L, compared with a range of <0.005 to 0.051 mg/L for dissolved zinc.

5.2. Water-Effect Ratios

LC50 estimates, based on total and dissolved copper for the laboratory and site waters, and the associated WER values for each of the sampling locations and events are shown in Table 5.2.

	Total	Copper (µg/I	L)	Dissolved Copper (μ g/L)		
Sample Date	Site Water LC50	Lab Water LC 50	WER	Site Water LC 50	Lab Water LC 50	WER
DME						
26 Mar 04	39.80	2.36	16.87	24.56	2.41	10.21
8 Aug 04	74.92	2.00	37.39	56.08	1.69	33.11
10 Oct 04	66.75	1.86	35.93	49.43	1.76	28.05
21 Mar 05	40.11	1.92	20.95	26.43	2.32	11.41
10 Jul 05	87.60	2.67	32.78	43.05	2.37	18.19
21 Jan 06	21.12	1.51	14.00	21.70	1.05	20.67
15 Apr 06	30.70	3.60	8.53	27.60	2.90	9.52
Bowdown						
26 Mar 04	38.96	2.21	17.63	28.40	2.24	12.70
27 May 04	64.18	1.36	47.30	32.90	1.10	30.02
21 Mar 05	37.19	1.70	21.85	28.37	2.06	13.78
10 Jul 05	87.07	2.36	36.96	40.68	2.09	19.49
16 Oct 05	40.5	3.67	11.0	40.50	1.80	22.50
21 Jan 06	22.75	1.63	13.9	22.90	1.10	20.82
MC8th						
26 Mar 04	80.14	5.56	14.15	58.86	5.78	10.19
27 May 04	65.12	3.98	16.36	38.20	3.22	11.80
8 Aug 04	105.80	3.58	29.50	48.83	2.84	17.21
10 Oct 04	95.45	3.57	26.73	48.74	3.32	14.69
21 Mar 05	95.14	5.09	18.66	51.66	6.16	8.39
18 Jan 06	69.04	2.57	26.86	51.36	1.91	26.89
Miller Creek						
26 Mar 04	79.56	5.30	15.01	49.94	5.31	9.41
27 May 04	89.63	3.82	23.46	53.97	3.09	17.48
8 Aug 04	84.24	3.85	21.88	47.44	3.26	14.57
10 Oct 04	77.55	3.15	24.63	48.58	2.93	16.61
21 Mar 05	81.69	4.79	17.05	53.04	5.80	9.15
10 July 05	107.2	6.63	16.16	71.12	5.88	12.11
16 Oct 05	48.9	7.22	6.8	35.4	3.50	10.11
18 Jan 06	61.4	2.28	26.9	52.6	1.70	30.94

Table 5.2. Summary of LC50 estimates, based on total and dissolved copper, and associated WERs for each of the sampling events.

Lab water LC50s are adjusted to correspond to the hardness of each sample.

Nautilus Environmental

Comunito Dista	Total	Copper (µg/]	L)	Dissolved Copper (μ g/L)			
Sample Date	Site Water LC 50	Lab Water LC 50	WER	Site Water LC 50	Lab Water LC 50	WER	
NPOut							
26 Mar 04	88.60	6.86	12.92	74.69	6.86	10.88	
28 May 04	64.55	3.74	17.25	56.51	3.02	18.69	
8 Aug 04	95.78	5.57	17.19	48.45	4.42	10.97	
17 Oct 05	62.4	7.34	8.5	42.00	3.50	12.00	
2 1 Jan 06	NC	na	na	40.10	1.88	21.33	
15 Apr 06	53.47	9.28	5.8	49.40	7.46	6.6	
16 Sep 06	84.7	6.10	13.9	62.3	8.05	7.7	
RBOut							
30 Aug 05	53.7	5.25	10.2	31.1	6.2	5.02	
17 Oct 05	39.2	8.81	4.4	25.8	4.30	6.00	
18 Jan 06	79.81	3.27	24.41	60.45	2.43	24.88	
15 Apr 06	53.19	11.28	4.72	48.05	9.07	5.30	
16 Sep 06	75.50	6.06	12.46	52.90	8.00	6.61	
Walker Creek							
11 Jun 07	27.9	7.66	3.64	22.4	4.90	4.57	
6 Sep 07	150.0	10.40	14.42	133.0	4.92	27.04	
1 Oct 07	58.0	6.50	8.92	49.3	5.44	3.13	
11 Nov 07	90.6	6.92	13.10	88.7	6.11	14.51	
28 Nov 07	74.9	10.28	7.29	67.9	8.30	8.18	

Table 5.2, continued.

NC = not calculated due to anomalous analytical values.

na = not applicable (see above).

DME

Based on total copper, LC50 estimates ranged between 1.51 and 3.60 μ g/L in laboratory water, following adjustment to the hardness of the test samples. Conversely, LC50 estimates in site waters ranged between 21.12 and 87.60 μ g/L, based on total copper. The ratio between maximum and minimum LC50 estimates was 2.38 in lab water and 4.15 in site water. Based on dissolved copper, LC50 estimates ranged between 1.05 and 2.90 μ g/L in laboratory water, compared with a range of 21.70 to 56.08 μ g/L in site water. Similar ranges were observed between the maximum and minimum LC50 estimates for dissolved copper in both laboratory and site waters; i.e., ranges encompassing factors of 2.8 and 2.6, respectively.

Bowdown

Based on total copper, LC50 estimates ranged between 1.36 and 3.67 μ g/L in laboratory water, following adjustment to the hardness of the test samples. Conversely, LC50 estimates in site waters ranged between 22.75 and 87.07 μ g/L, based on total copper. The ratio between maximum and minimum LC50 estimates was 2.70 in lab water and 3.83 in site water. Based on dissolved copper, LC50 estimates ranged between 1.10 and 2.24 μ g/L in laboratory water, compared with a range of 22.90 to 40.68 μ g/L in site water. Similar ranges were observed between the maximum and minimum LC50 estimates for both laboratory and site waters; i.e., ranges encompassing factors of 2.04 and 1.78, respectively.

MC8th

Based on total copper, LC50 estimates ranged between 2.57 and 5.56 μ g/L in laboratory water, following adjustment to the hardness of the test samples. Conversely, LC50 estimates in site waters ranged between 65.12 and 105.80 μ g/L, based on total copper. The ratio between maximum and minimum LC50 estimates was 2.16 in lab water and 1.62 in site water. Based on dissolved copper, LC50 estimates ranged between 1.91 and 6.16 μ g/L in laboratory water, compared with a range of 38.20 to 58.86 μ g/L in site water. Similar ranges were observed between the maximum and minimum LC50 estimates for both laboratory and site waters; i.e., ranges encompassing factors of 3.23 and 1.54, respectively.

Miller Creek

Based on total copper, LC50 estimates ranged between 2.28 and 7.22 µg/L in laboratory water, following adjustment to the hardness of the test samples. Conversely, LC50 estimates in site waters ranged between 48.9 and 107.20 µg/L, based on total copper. The ratio between maximum and minimum LC50 estimates was 3.17 in lab water and 2.19 in site water. Based on dissolved copper, LC50 estimates ranged between 1.70 and 5.88 µg/L in laboratory water, compared with a range of 35.40 to 71.12 µg/L in site water. Similar ranges were observed between the maximum and minimum LC50 estimates for both laboratory and site waters; i.e., ranges encompassing factors of 3.5 and 2.0, respectively.

NPOut

Based on total copper, LC50 estimates ranged between 3.74 and 9.28 μ g/L in laboratory water, following adjustment to the hardness of the test samples. Conversely, LC50 estimates in site waters ranged between 53.47 and 95.78 μ g/L, based on total copper. The ratio between maximum and minimum LC50 estimates was 2.48 in lab water and 1.79 in site water. Based on dissolved copper, LC50 estimates ranged between 1.88 and 8.05 μ g/L in laboratory water, compared with a range of 40.10 to 74.69 μ g/L in site water. Similar ranges were observed between the maximum and minimum LC50 estimates for both laboratory and site waters; i.e., ranges encompassing factors of 4.28 and 1.86, respectively.

RBOut

Based on total copper, LC50 estimates ranged between 3.27 and 11.28 μ g/L in laboratory water, following adjustment to the hardness of the test samples. Conversely, LC50 estimates in site waters ranged between 39.2 and 79.81 μ g/L, based on total copper. The ratio between maximum and minimum LC50 estimates was 3.45 in lab water and 2.04 in site water. Based on dissolved copper, LC50 estimates ranged between 2.43 and 9.07 μ g/L in laboratory water, compared with a range of 25.80 to 60.45 μ g/L in site water. Similar ranges were observed between the maximum and minimum LC50 estimates for both laboratory and site waters; i.e., ranges encompassing factors of 3.73 and 2.34, respectively.

Walker Creek

For total copper, LC50 estimates ranged between 6.50 and 10.40 ug/L in laboratory water, following adjustment to the hardness of the test samples, and between 27.9 and 150.0 ug/L in site waters. The ratios between the lowest and highest LC50s were 1.6 and 5.4 in laboratory and site waters, respectively. Based on dissolved copper, LC50 estimates ranged between 4.90 and 8.30 ug/L in laboratory water, and between 22.4 and 133.0 in site water. The associated ratios were 1.7 and 5.9, respectively.

Collectively, the range of responses (i.e., the ratio between the minimum and maximum values) was comparable between site waters and laboratory waters. Moreover, the range of values observed within each of the sites falls within that typically associated with intralaboratory variability observed with tests conducted with the same material over time (Chapman 1995; USEPA 2002), suggesting that none of the values were atypically

small or large. Consequently, on a preliminary basis, all of the values were considered representative and appropriate for further analysis.

5.3. Calculation of Site-Specific Water Quality Objectives

Although the national water quality criterion is calculated on the basis of total copper, a conversion is applied to achieve a final value that is stated in terms of dissolved copper, because it is generally recognized that toxicity is largely associated with the dissolved form of the metal. Thus, in calculating a site-specific water quality objective (SSWQO), the dissolved WER is applied to the generic criterion. For example, in this study, the dissolved WERs for DME ranged between 9.5 and 33.1, with a geometric mean (i.e., final WER) of 16.86, which would then be used to adjust the generic water quality criterion to account for site-specific differences in bioavailability. Thus, for DME, Washington State's freshwater acute copper criterion:

Acute dissolved copper criterion =
$$e^{(0.9422(\ln(hardness))-1.464)}$$
 Eq. 2

would be multiplied by 16.86 to achieve a site-specific objective. [Note that the 0.96 USEPA dissolved-to-total factor was deleted from Eq. 2 because the WER data are already in dissolved form, and do not have to be converted from total.]

To complete this analysis, the SSWQOs derived for each site were then compared against the actual test data to determine if the site-specific numbers would, in fact, be protective. For example, substituting the lowest hardness observed at DME during the WER study (i.e., 23 mg/L) into Eq. 2, above, results in a generic acute criterion of 4.44 μ g/L which, when multiplied by the site-specific WER for DME (i.e., 16.86), results in a value of 74.9 μ g/L, as dissolved copper. Comparison of this SSWQO against the site water LC50 estimates for dissolved copper in Table 5.2 (between 21.12 and 87.60 μ g/L) suggests that all of the samples from DME would have exhibited toxicity at the calculated objective. Similar results were obtained with data from the other sites, suggesting that these calculated SSWQOs would not be considered protective.

The primary reason for this apparent discrepancy is that the WER values calculated for this study were obtained using laboratory data that exhibited comparatively high sensitivity to copper compared with the national water quality dataset, which is based on the geometric mean of a much larger number of data sets obtained from a number of different laboratories and dilution waters. The USEPA has recognized that this is an issue in their updated guidance on WER studies with copper (USEPA 2001). Indeed, the Agency has noted that most of the LC50 data from tests in laboratory water submitted in support of site-specific WERs were lower than values in the national database and, consequently, introduced a bias into the site-specific derivation process. The Agency's solution to this problem was to substitute the species mean acute value (SMAV) derived from the USEPA database into WER calculations in instances where the laboratory-derived LC50 values (adjusted for hardness) were less than the SMAV. With this approach, the calculated WER will have a direct relationship to the existing database and the associated national water quality criterion derivation process.

Using the USEPA SMAV for *C. dubia* as the denominator in the WER calculations results in a geometric mean (i.e., final WER) of 4.60 for DME (see Table 5.3). This number would then be applied to Eq. 2 to derive a SSWQO for DME. To verify the validity of this revised approach, the site-specific objective was re-calculated at a hardness of 23 mg/L. This calculation results in a SSWQO of 20.4 μ g/L (i.e., 4.60 x 4.44 μ g/L), which would be considered protective when compared against the acute toxicity values shown for DME in Table 5.2. Using the same reasoning, WERs were calculated similarly for the remaining sites (Table 5.3), using the SMAV and similarly validated against the actual toxicity data.

	Dissolved Copper (µg/L)			
Sample Date	Site Water Lab Water			
	LC50	LC50	WER	
DME				
26 Mar 04	24.56	7.11	3.45	
8 Aug 04	56.08	8.89	6.31	
10 Oct 04	49.43	7.56	6.54	
21 Mar 05	26.43	8.00	3.30	
10 Jul 05	43.05	7.56	5.70	
21 Jan 06	21.70	5.54	3.92	
15 Apr 06	27.60	6.67	4.14	
Geometric Mean	-	-	4.60	
<u>Bowdown</u>				
26 Mar 04	28.40	6.67	4.26	
27 May 04	32.90	7.11	4.63	
21 Mar 05	28.37	7.11	3.99	
10 Jul 05	40.68	6.67	6.10	
16 Oct 05	40.50	9.33	4.34	
21 Jan 06	22.90	3.47	6.61	
Geometric Mean	-	-	4.90	
MC8th				
26 Mar 04	58.86	17.08	3.45	
27 May 04	38.20	20.86	1.83	
8 Aug 04	48.83	15.80	3.09	
10 Oct 04	48.74	14.52	3.36	
21 Mar 05	51.66	21.28	2.43	
18 Jan 06	51.36	11.08	4.64	
Geometric Mean	-	-	3.01	
Millor Crook				
26 Mar 04	49 94	15.80	3 16	
20 May 04	53.97	20.03	2 70	
$\frac{27 \operatorname{Way} 04}{8 \operatorname{Aug} 04}$	17 AA	20.05	2.70	
$10 \Omega_{c} + 01$	48 58	17.00	2.70	
21 Mar 05	-10.00 53 0 <i>1</i>	20.02	2.79	
21 1v1ar 05 10 I11 1 v 05	71 19	20.05	2.05	
16 July 05 16 Oct 05	25 1	20.77	1 72	
10 Oct 00 18 Jan 06	50. 4 50.6	20. 44 0.00	1.73 5 97	
Geometric Mean	52.0	2.22	2.00	
Geometric Ivieun	-	-	5.09	

Table 5.3 Summary of LC50 estimates and associated WERs for each sampling event, incorporating USEPA SMAV for C. dubia.

The Lab Water LC50s represent the USEPA SMAV for C. dubia exposed to copper,

adjusted to correspond to the hardness of each sample.

Nautilus Environmental

	Dissolved Copper (μ g/L)			
Sample Date	Site Water LC50	Lab Water LC50	WER	
NPOut				
26 Mar 04	74 69	20.44	3 65	
28 May 04	56.51	19.61	2.88	
8 Aug 04	48.45	24.61	1.97	
17 Oct 05	42.00	20.65	2.03	
21 Jan 06	40.10	10.42	3.85	
15 Apr 06	49.40	16.87	2.93	
16 Sep 06	62.3	30.16	2.07	
Geometric Mean	-	-	2.68	
RBOut				
$30 \operatorname{Aug} 05$	31.1	30.98	1.00	
17 Oct 05	25.8	24.82	1.04	
18 Jan 06	60.45	14.52	4.16	
15 Apr 06	48.05	20.44	2.35	
16 Sep 06	52.90	29.34	1.80	
Geometric Mean	-	-	1.79	
Walker Creek				
11 Jun 07	22.4	29.14	0.77	
6 Sep 07	133.0	27.14	0.77 4 91	
1 Oct 07	493	23.78	2.07	
11 Nov 07	88 7	28.73	3.09	
28 Nov 07	67.9	24.61	2 76	
Geometric Mean	-		2.32	

Table 5.3, continued.

5.4. Conversion from Dissolved to Total Copper

Given that effluent permit limits are based on total copper, rather than dissolved, the dissolved SSWQO needs to be adjusted appropriately to reflect the site-specific ratio of the dissolved fraction to total copper present. There are two potential methods to derive this site-specific metals "translator"; one is to use the average ratio of dissolved to total copper measured in samples from a particular site, and the other is to use the ratio between LC50s calculated on the basis of dissolved and total copper. The former approach is typically used in the absence of toxicity data (USEPA 1996) but, since toxicity data is available for this study, it is potentially more justified to use the latter

approach because it represents the actual biological response to the bioavailable fraction. Values calculated using both approaches are included in Table 5.4 for comparison, but the ratio between LC50s calculated on the basis of dissolved and total copper was used to derive the final adjustment factor.

Using DME again as an example, the mean of the ratios of the dissolved and total LC50s shown in Table 5.4 is 0.74. This "metals translator" can be blended with the final WER (i.e., 4.60/0.74 = 6.22) to obtain a value that can be multiplied by Eq. 2 to calculate an effluent limit directly for any given hardness. A similar approach was used to derive translators for the remaining sites; all of the data are summarized below in Table 5.4.

Site	Final WER	Dissolv Tra	ved/Total nslator	Final Adjustment Factor
		LC50	Analytical	
DME	4.60	0.74	0.65	6.22
Bowdown	4.90	0.70	0.61	6.99
MC8th	3.01	0.62	0.63	5.02
Miller Creek	3.09	0.60	0.62	4.98
NPOut	2.68	0.78	0.53	3.44
RBOut	1.79	0.79	0.88	2.27
Walker Creek	2.32	0.89	0.93	2.62

 Table 5.4. Summary of parameters used to derive site-specific adjustments for total copper.

5.5. Consideration of a Second Species

Although the effectiveness of using a second species as part of the process of developing a SSWQO has been largely discounted in USEPA's more recent WER guidance (USEPA 2001), local concerns over potential impacts to salmonids suggests that such an evaluation may be appropriate. In general, the literature indicates that salmonids, including rainbow trout, are substantially less sensitive to copper than *C. dubia*, and this conclusion is consistent with the data obtained in this study. For example, one WER test was conducted with copper on DME using rainbow trout as part of this study. This test resulted in a WER of 6.1, when compared with laboratory water. Regardless, for this particular sample from DME, the calculated LC50 (as dissolved copper) obtained with

rainbow trout was 145.1 μ g/L at a hardness of 40 mg/L. By way of comparison, the SSWQO for DME at this hardness would be 34.4 μ g/L, suggesting that the SSWQO derived with *C. dubia* should protect beneficial uses associated with salmonids.

Similar results were obtained with the other sites tested, and are summarized in Table 5.5, along with the results for DME. As the data suggest, the SSWQOs were all several-fold lower than their respective LC50s obtained with rainbow trout, suggesting that the individual SSWQOs should be protective of salmonids. Note that NPOut was not tested with rainbow trout, but the consistency of the results obtained with the other sites suggests that there is no reason to suspect that the SSWQO derived for this site would not be similarly protective.

 Table 5.5. Toxicity data and WERs obtained with rainbow trout compared with SSWQOs derived for *C. dubia* at same hardness.

Site	Sample Date	Hardness (mg/L)	LC50 (µg/L, as dissolved Cu)	WER	SSWQO (µg/L, as dissolved Cu)
DME	12 Sep 04	40	145.1	6.1	34.4
Bowdown	12 Sep 04	44	133.1	5.1	40.0
MC8th	23 Aug 04	84	208.3	5.1	45.3
Miller Creek	23 Aug 04	100	206.9	4.3	54.7
RBOut	30 Aug 05	143	282.0	3.1	44.5
Walker Creek	1 Oct 07	108	>208.8	13.2	44.2

6. SSWQO-BASED EFFLUENT LIMITS FOR STORMWATER DISCHARGES FROM SEATTLE-TACOMA INTERNATIONAL AIRPORT

As noted in Section 1.1, the §401 Certification for the Master Plan Update Projects requires that "appropriate limitations and monitoring requirements" be established in the Port's NPDES permit. The need for appropriate effluent limits on specific outfalls is typically determined based on the outcome of a reasonable potential analysis (RPA). A critical component of an RPA is a mixing zone factor. Reasonable potential and mixing zone analyses have not been completed at this time due to lack of sufficient data representing post-retrofit conditions. The STIA has recently completed a comprehensive stormwater treatment and flow control facility retrofits in four of its non-Third Runway subbasins. These new facilities are expected to significantly decrease pollutant loading. However, as most evident in SDE4, major construction and changes to Airport infrastructure continues in these retrofitted subbasins (e.g., North Expressway Relocation Project). The remaining six outfalls are integrated into the Third Runway Project and will not be discharging representative runoff until November 2009, after project completion. As such it is not possible to fully assess pollutant loadings and actual BMP performance before the NPDES permit is to be renewed.

As described in the previous paragraph, STIA's stormwater discharge facilities are still in various stages of development and implementation, which has implications for deriving effluent limits from a regulatory perspective. Specifically, Ecology (1999) states that:

• Ecology will only authorize the highest WER that allows a permittee to fall below the reasonable potential threshold...

In general, the STIA's stormwater outfalls, subbasins and BMPs are still at various stages of completion. Indeed, outfalls associated with the Third Runway Expansion will not be discharging until November 2009. Thus, representative data are not available with which to conduct a RPA. Consequently, the STIA proposes that the WER values presented in Table 5.4 be used to establish SSWQO-based effluent limits on an interim basis until such time as the discharge basins and associated BMPs are fully operational and sufficient data are available to conduct RPAs. Following such an analysis, the applied WERs may be modified as appropriate to establish final effluent limits.

Additional conditions (Ecology 1999) for applying a WER to a discharge limit are noted below, along with specific comments related to each:

- The WER shall be re-evaluated during year 5 of the wastewater discharge permit, or sooner...This condition is an operational constraint that is part of the permit, but does not impact the derivation of SSWQOs or associated effluent limits.
- *WET testing will be required in the permit...*This condition is part of the current permit, and is acknowledged in Section 7 of this report as part of the STIA's recommended overall monitoring strategy to support implementation of SSWQOs and associated effluent limits.
- A receiving water bioassessment may be required... This condition is acknowledged in Section 7 of this report as part of the STIA's recommended overall monitoring strategy to support implementation of SSWQOs and associated effluent limits.

In the interim, this study determined potential discharge limits for each of the stormwater outfalls on the basis of the corresponding SSWQO, with no consideration of dilution. Site-specific water quality objectives were calculated by multiplying the generic water quality criterion for copper (based on hardness) by the WER appropriate for each site. Since SSWQOs are derived on the basis of dissolved copper, and discharge limits are expressed as total copper, the discharge limits were further adjusted to reflect the ratio of dissolved to total copper at each site.

6.1. Background

This section describes the process of deriving preliminary interim water quality-based stormwater discharge limits from the site-specific water quality objectives (SSWQOs) for copper, using an approach consistent with Ecology's Permit Writer's Manual (1999). As discussed in detail above, the SSWQOs were derived from a comprehensive evaluation of water-effect ratios (WERs) for each site. A final WER was then calculated for each site, and used to adjust the State's water quality criterion for copper to reflect differences in bioavailability associated with each site. A metals translator, based on the ratio of dissolved to total copper (as expressed by the ratio of the respective LC50s), was then used to express the site-specific objective in terms of total metal (this process is detailed in Sections 5.3 and 5.4 of this report).

These SSWQOs were subsequently used to calculate effluent limits for each of the sites in terms of total metal at a specific hardness characteristic of each site. The hardness
used to calculate effluent limits is typically identified as the 10th percentile of all the hardness values available from a given site. This approach is commonly used to establish limits in NPDES permits for point-source discharges. However, because only four of the ten stormwater detention facilities to be constructed have only recently come on line it is currently impossible to characterize mixing zones associated with the discharges. In addition, the small sizes of the receiving streams, and the large variation in stormwater discharge flows, antecedent conditions and storm profiles, make it problematic to identify appropriate mixing zones that fully represent the associated complexities. Therefore, the calculated effluent limits presented below assume no dilution for the discharge in the receiving environment. Mixing zone analyses may need to be completed before final effluent limits can be established.

In addition to this water quality based approach, consideration could be given to calculating the effluent limits based on available analytical data (i.e., apply a technology or performance-based approach). However, applying this approach to STIA stormwater is not appropriate because the Port's stormwater BMPs are still being implemented, their efficiencies are largely projections based on modeling, and the §401 Master Plan expansion is still in progress. In addition, the STIA, as will all urban basins in Puget Sound, will see continually increased use of its facilities as the population grows resulting in ever increasing pollutant loading. Consequently, the existing analytical data do not reflect conditions associated with a complete build-out of STIA stormwater drainage facilities and their performance under a wide range of storm conditions.

6.2. SSWQO-Based Effluent Limit Derivation

6.2.1. General Considerations

Stormwater has historically been collected in a number of sub-basins (Figure 1) prior to discharge. Numerous source controls, as well as treatment methodologies, have been implemented to control copper concentrations in run-off from all of the sub-basins. The Ecology-approved Stormwater AKART Analysis Report (January 2005) determined that "basic treatment" generally meets the requirement for AKART at STIA. However, a higher level of treatment for dissolved metals (i.e., enhanced) is AKART for stormwater discharges from the SDE4 sub-basin, which in routine NPDES monitoring has historically contained the highest concentrations of copper.

The historic STIA sub-basins, along with associated impervious and pervious areas are summarized in Table 6.1. Detailed information on each of the sub-basins, as well as associated contaminant sources, BMPs, control technologies and anticipated removal efficiencies is presented in the Stormwater Engineering Report prepared for the Port (R.W. Beck and Parametrix 2006).

Sub-basin	Impervious	Pervious	Total
SDS1	11.60	1.80	12.68
SDE4	106.75	45.30	152.05
SDS3	249.53	213.48	463.01
SDS4	24.51	41.92	66.44
SDS5	4.97	13.45	18.42
SDS6	5.26	37.43	42.68
SDS7	2.56	1.74	4.30
SDN1	10.70	3.82	14.51
SDN2 ^b	31.80	10.52	42.32
SDN3	28.62	36.21	64.83
SDN4	12.97	28.44	41.41

Table 6.1. Areas (in acres) of pervious and impervious areas associated with each subbasin.^a

 ^a Subbasin areas are those in existence in 2003 and as reported in the Stormwater Engineering Report (RW Beck, March 2006).
 Although basin areas will remain approximately the same, individual subbasin areas will vary with completion of the stormwater system retrofit.

^b SDN2 is typically diverted to IWS, and only discharges when rainfall exceeds the 6-month, 24-hr design criterion.

The sub-basins shown in Table 6.1 represent the basins present at the time the Stormwater Engineering Report was prepared. A variety of source control, water quality treatment and flow control BMPs were historically in place, and the Stormwater Engineering Report considered these as baseline in its analyses. Considerable upgrades to the STIA stormwater drainage system were subsequently identified in the Stormwater Engineering Report and other planning documents in order to effectively meet the 401 Certification, and NPDES flow control, water quality AKART and enhanced treatment

requirements. As a result of these changes, a number of sub-basins are directed to single flow control or water quality treatment facilities. The final drainage configuration, including sub-basins that will be combined prior to discharge are shown in Table 6.2. Table 6.2 also shows the Instream Station (i.e., receiving environment) most closely associated with each of the sub-basin configurations. The sub-basin outfalls and associated in-stream stations are shown on Figure 1.

Discharging Retrofit	In-Stream
Sub-basins	Station
SDS1 + SDE4	DME
SDS3 + SDS5	NPOut
SDS4	NPOut
SDS6 + SDS7	NPOut
SDN1	RBOut
SDN2 + SDN3 + SDN4	RBOut

Table 6.2. Retrofit sub-basins discharging stormwater, and associated receiving environment stations used to establish site-specific water quality objectives.

Brief descriptions of the final configurations of the different sub-basins are summarized below. The summaries also include additional projected removals of copper (beyond what is currently being achieved) that are anticipated from BMPs that have recently been or will be put into place (R.W. Beck and Parametrix 2006).

- Stormwater from SDS1 pollution generating surfaces (PGS) is currently treated with bioswales; additional bioswales are projected to further reduce copper concentrations by 11%. The flow then combines with SDE4, and the combined flow is treated by additional bioswale prior to release. This bioswale is expected to further reduce copper concentrations, but the amount was not estimated.
- Stormwater from the entire SDE4 sub-basin is treated by extended detention basin and media filtration, with a projected removal efficiency of 44%. The flow then combines with that from SDS1 and pass through additional bioswale prior to release. As noted above, the amount of removal associated with this additional bioswale was not estimated.

- Stormwater from SDS3 PGS is currently effectively treated by filter strips; there is a small opportunity to improve their effectiveness, but the estimated additional reduction in copper concentrations is only 1%. In addition to existing filter strips, media catch basin inserts were installed in select locations. However, removal estimates are not available for this experimental BMP. Flows from the SDS3 sub-basin combine with those from SDS5 in the SDS3 Level 1 detention vault prior to discharge through the existing S3 outfall. No additional pollutant removal from the Level 1 vault was characterized, but some may occur.
- Stormwater from SDS5 PGS has historically received partial treatment by a filter strip. Filter strip improvements and conversion of limited areas to IWS are anticipated to reduce copper concentrations by an additional 5%. Treated water has been combined with SDS3 in the S3 detention vault prior to discharge through the existing S3 outfall. No additional pollutant removal from the Level 1 vault was characterized, but some may occur.
- Stormwater from the entire SDN1 sub-basin has been directed to a wet pond (N1 pond) prior to entering Lake Reba. It is anticipated that this will reduce copper concentrations by 57%.
- Stormwater from the entire SDN2 sub-basin is pumped to IWS, except in cases where storm events exceed the design criterion of a 6-month 24-hr storm. Under those circumstances, excess flows will receive extended detention in Pond M prior to discharge to Lake Reba in combination with flows from SDN3 and SDN4, which are also directed to Pond M prior to release.
- Sub-basins SDN3 and SDN4 both currently meet AKART through use of filter strip BMPs. Discharge flows will be further directed to Pond M which will provide Level 2 detention prior to discharge to Lake Reba. The level of copper removal associated with detention in Pond M was not estimated.
- SDS4 currently meets AKART, however, flows have been directed to a Level 1 detention pond prior to discharge. No additional pollutant removal from the Level 1 vault was characterized, but some may occur.
- The SDS6 and SDS7 sub-basins are currently being combined as part of the Third Runway redevelopment effort. Additional filter strips and bioswales are anticipated to further reduce copper concentrations by 12

and 61% for SDS6 and SDS7, respectively. No additional pollutant removal from the Level 1 vault was characterized, but some may occur.

In addition to the historical sub-basins described above, stormwater will also be discharged into both Walker and Miller Creeks as part of the Third Runway expansion. The related sub-basins are summarized in Table 6.3, along with the associated receiving waters. Stormwater from each of these sub-basins will be treated with Level 2 ponds, and discharges are anticipated to begin in November 2009.

Sub-basin	Impervious (acres)	Pervious (acres)	Total (acres)	Receiving Water
SDN3A	7.2	24.3	31.5	Miller Creek
SDW1A	25.6	44.5	70.1	Miller Creek
SDW1B	23.2	49.1	72.3	Miller Creek
SDW2	10.3	27.2	37.5	Walker Creek

Table 6.3. Areas (in acres) of pervious and impervious areas associated with each of
the new sub-basins.

6.2.2. SSWQO-Based Effluent Limit Calculations

Selection of Appropriate Hardness – In Table 6.4, below, the 10th percentile hardness is presented for each of the relevant receiving environment sites. Note that MC8th was selected as the most appropriate site on Miller Creek because it is located downstream of the anticipated outfall locations that are projected for activation in 2009. The hardness values were taken from data provided by the Port, as well as from the WER studies; in general, multiple values obtained from a site within a given day were averaged, as were the values for a given month in a given year, resulting in a single value for that month. Exceptions to this procedure are noted in discussions of the specific outfalls below.

Site	10 th Percentile Hardness
	(mg/L)
DME	21.2
NPOut	50.8
RBOut	69.3
MC8th	64.9
Walker Creek	103.8

Table 6.4. Summary of the 10th percentile hardness for each of the receiving environment sites

Preliminary effluent limits are calculated below on the basis of the 10th percentile hardness values, and the dissolved / total translator based on the ratio of the dissolved and total LC50 estimates.

Combined SDS1 and SDE4 – A site-specific water quality objective (SSWQO) for copper (as dissolved) was derived for DME using a WER (4.60) calculated from 7 samples. Based on these same samples, the ratio of dissolved to total copper was 0.74, ultimately resulting in a multiplier of 6.22 that can be used to adjust the generic Washington State copper criterion and set a limit based on total copper. Note that these data are presented in Table 5.4.

To calculate an SSWQO-based effluent limit, hardness concentrations measured in samples collected from DME between March 2004 and December 2007 (n=27) were evaluated, and the 10th percentile hardness concentration was 21.2 mg/L, as CaCO₃. Substituting this hardness value into site-specific equation for copper results in a SSWQO-based effluent limit value of 25.6 ug/L Cu (i.e., the generic criterion of 4.11 ug/L at a hardness of 21.2 mg/L X 6.22).

SDS4, Combined SDS3 and SDS5, and Combined SDS6 and SDS7 – The SSWQO for copper determined for NPOut was based on a WER of 2.68 and a translator of 0.78, resulting in a multiplier of 3.44 that can be used to adjust Washington's generic copper criterion. Inspection of hardness values collected from NPOut between March 2004 and December 2007 (n=28) indicated that the 10th percentile hardness was 50.8 mg/L. At this hardness level, the SSWQO-based effluent limit would be 32.2 ug/L total Cu (the generic criterion of 9.36 ug/L at a hardness of 50.8 mg/L X 3.44).

SDN1 and Combined SDN2, SDN3 and SDN4 – The SSWQO for copper at RBOut was derived from a WER of 1.79 and a translator of 0.79, resulting in a multiplier of 2.27. Hardness values were available from 30 samples collected between May 2004 and December 2007; the 10th percentile value was 69.3 mg/L. At this hardness, the SSWQO-based effluent limit would be 28.5 ug/L total copper (the generic criterion of 12.54 at a hardness of 69.3 mg/L X 2.27).

SDN3A, SDW1A and SDW1B (Projected Discharges to Miller Creek) - The SSWQO for MC8th was derived from a WER of 3.01 and a translator of 0.60, resulting in a final multiplier of 5.02. The 10th percentile hardness was 64.9 mg/L, based on 10 samples collected between March 2004 and December 2007, and 10 additional samples collected from storm events between March and May 2008. At this hardness, the SSWQO-based effluent limit would be 59.7 ug/L total copper (the generic criterion of 11.77 at a hardness of 64.9 mg/L X 5.02).

SDW2 (Projected Discharge to Walker Creek) – The SSWQO for copper at Walker Creek was derived from a WER of 2.32 and a translator of 0.89, resulting in a multiplier of 2.62. Hardness values were available from 14 samples collected between March 2004 and November 2007, and from 10 additional samples collected between March and May 2008. The 10th percentile value was 103.8 mg/L. At this hardness, the SSWQO-based effluent limit would be 48.1 ug/L total copper (the generic criterion of 18.35 at a hardness of 103.8 mg/L X 2.62). Note that the WER (0.77) obtained for the 11 June 2007 sample from Walker Creek is clearly an outlier compared with the other WERs from this site (range: 2.07 to 4.91; p<0.05). However, it was retained in the calculation of SSWQO to meet the minimum requirement of 5 samples. Therefore, it may be desirable to obtain another sample from this site in the future.

6.2.3. Projected Compliance

Where possible, these preliminary SSWQO-based effluent limits for copper were used to estimate the approximate level of compliance that the Port would be expected to achieve given current and projected levels of copper reduction with AKART and additional treatment. Probability distributions were constructed that show the copper concentrations in samples collected from the various sub-basins based on NPDES data collected between October 2003 and November 2006. Note that the data used for SDN1

and SDE4 were collected from December 2004 through November 2006, and are considered more representative of existing water quality conditions in these sub-basins following a number of source-control activities such as rooftop painting and gutter cleaning (R.W. Beck and Parametrix, 2006). These distributions were then compared against the preliminary effluent limits to estimate the percentage of samples that would be expected to meet the limits.

The probability distributions for each of the sub-basins are summarized in figures that show the associated SSWQO-based effluent limits, as well as the 2005 benchmark effluent limit for copper (i.e., 63.6 ug/L) contained in the Port's current NPDES permit, which is identical to the benchmark provided in USEPA's 2000 Multi-Sector General Permit. Finally, each figure also shows the projected copper concentrations assuming the additional removal efficiencies associated with the BMPs in place when redevelopment is completed (see Section 6.2.1 and the Engineering Report). Note that the removal efficiencies were considered conservative estimates, and may also vary depending on actual copper concentration, duration of storm event, intervals between storms, and so on. Again, the reader is referred to the Engineering Report for detailed analysis and projections of removal efficiencies (R.W. Beck and Parametrix 2006).

Combined SDS1 and SDE4 will discharge into East Des Moines Creek upstream of DME. Based on existing data, SDS1 would have historically met the SSWQO-based effluent limit (25.6 ug/L) approximately 85% of the time. Full implementation of AKART is expected to further reduce copper concentrations by an estimated 11%, which will result in a modest improvement in compliance (Figure 2). With no additional treatment, SDE4 would have historically met the SSWQO-based effluent limit approximately 70% of the time, but implementation of enhanced treatment is expected to reduce copper concentrations by 44%, achieving compliance approximately 95% of the time (Figure 3). Overall compliance of the combined discharge will be affected by differences in sizes of each of the sub-basins, and their relative contributions during individual storm events. In addition, concentrations in the combined discharge should be further reduced by flow through a vegetated swale prior to discharge, although the associated reduction has not been estimated and is not included in this compliance analysis.

Combined SDS3 and SDS5 will discharge into Des Moines Creek through Northwest Ponds. Based on existing data, SDS3 would have historically met the SSWQO-based effluent limit of 32.2 ug/L 85% of the time; full implementation of AKART will provide

an estimated 1% additional reduction in copper, and a marginal improvement in compliance (Figure 4). Copper concentrations are significantly lower in SDS5, and should be in compliance virtually all the time (Figure 5). Overall compliance of the combined discharge will be affected by relative contributions of each sub-basin during individual storm events, but should still be at least 85%, based on the performance of SDS3 alone.

SDS4 will discharge into Des Moines Creek through Northwest Ponds. Based on existing data, SDS4 would have historically met the SSWQO-based effluent limit at least 95% of the time (Figure 6). Since, no additional BMPs are being constructed, the basin is expected achieve a similar level of compliance in the future.

Combined SDS6 and SDS7 will also discharge into Des Moines Creek via Northwest Ponds. Based on existing data, SDS6 runoff would have historically met the SSWQObased effluent limit virtually all of the time (Figure 7), as would SDS7 (Figure 8). BMPs incorporated into the Third Runway reconstruction of the SDS6 and 7 sub-basins are expected to reduce copper concentrations by 12% and 61%, respectively. Given that both of the individual discharges are currently well-within the proposed SSWQO-based effluent limit, the combined discharges should reflect a similar level of compliance.

SDN1 will continue to discharge into Lake Reba. Based on existing data, SDN1 would have historically met the SSWQO-based effluent limit of 28.5 ug/L approximately 75% of the time. However, the estimated additional reduction in copper concentrations associated with detention in the N1 Level 2 pond prior to discharge should improve compliance to over 95% (Figure 9).

Combined SDN2, SDN3 and SDN4 will discharge into Lake Reba. Based on existing data, SDN3 would have historically met the SSWQO-based effluent limit of 28.5 ug/L essentially all of the time (Figure 10). Copper concentrations are somewhat higher in SDN4, but still would have achieved compliance approximately 85% of the time (Figure 11). Both of these sites are already essentially compliant with AKART, but these numbers do not reflect any additional removals associated with the detention pond, which should further reduce copper concentrations. Ultimately, the combined discharges should still be in compliance at least 85% of the time, based on the performance of the individual discharges. The impact of SDN2 on the quality of the combined discharge is more difficult to predict. Copper concentrations tend to be

higher at SDN2 (Figure 12) than at SDN3 or SDN4, but flows from SDN2 will be discharged through the combined outfall only during storm events that exceed the water quality design criteria (i.e., 6-month 24-hr storm), and then only after passing through Pond M. In addition, the SDN2 sub-basin is smaller than the combined SDN3 and SDN4 sub-basins, which will minimize its impact on the overall discharge. Given these uncertainties, it is problematic to predict the effect of SDN2 on the combined discharge, but it is expected to be small given the relative infrequency of events and low discharge volume. For example, during a 38-month period between October 2003 and November 2006, SDN2 discharged a total of 20 times, with a median volume of 3500 gallons.

One important observation that can be made from the figures is the comparison of the SSWQO-based effluent limits and the benchmark-based effluent limit for copper contained in the Port's current NPDES permit. In all cases, the SSWQO-based limits are substantially lower than the Port's current benchmark-based effluent limit for discharges contributing to DME, NPOut and Lake Reba (RBOut). Thus, the SSWQO-based limits described above are more protective than the current Permit.

6.2.4. Alternative Limit Calculation

In the above approach, the 10th percentile hardness was used to derive effluent limits and estimate the approximate level of compliance that the Port would be expected to achieve given current and projected levels of copper reduction with AKART and additional treatment. However, that approach seems unnecessarily restrictive in that the 10th percentile hardness is not representative of seasonal variations in hardness that occur as a function of stormwater discharges. Under these circumstances, the Port could be found in violation if they were discharging at higher hardness, even though the copper concentrations were not exceeding the site-specific objective at that particular hardness. Thus, the Port could be in violation at 90% of the hardness values (i.e., samples), even though there would not be any exceedences of the actual objective, and no associated environmental risk.

To address this issue, the Port proposes that the actual effluent limits be set with flexible hardness. Using this approach, seasonal hardness values or hardness at each of the instream sites would be measured at the same time samples are collected for copper analysis, and compliance would be determined on the basis of total copper measured and the hardness at the time the sample was collected. This approach will ensure that environmental concerns are addressed by not exceeding the respective site-specific objectives, while avoiding inappropriate violations that do not reflect actual exceedences that could result in impairment.

7. MONITORING AND FOLLOW-UP ACTIVITIES

Although the above analysis suggests that the Port should be able to comply with the proposed SSWQO-based effluent limits on a consistent basis, the Port notes that there is uncertainty associated with projecting the efficiency of BMPs designed to treat stormwater, as well as predicting how well the new systems will work under a variety of storm conditions once build-out is complete. Consequently, monitoring will continue to be used as a tool for verifying the performance of the Port's stormwater program, as well as ensuring that the receiving environment is properly protected.

Currently, the Port has a robust well-tailored stormwater monitoring program in place. Program elements include monitoring concentrations of constituents of concern in the discharges, and conducting acute toxicity tests on the discharges and sublethal toxicity tests on samples from the receiving environment, with provision for conducting Toxicity Identification Evaluations if samples exhibit toxicity. In addition, the benthic macroinvertebrate community is currently being monitored in the receiving environment as part of the CRWS and 401 Certification program. An enhancement to this current program would be to substitute *in situ* early life stage tests with salmonids at receiving environment stations during fall and spring for the current laboratory-based rainbow trout embryo sublethal toxicity test. This component would directly address the current level of public and regulatory concerns regarding potential impacts of stormwater on salmonids.

8. SUMMARY

USEPA guidance was used to develop site-specific water quality objectives (SSWQOs) for copper at several sites that receive stormwater drainage from STIA facilities. Using the water-effect ratio approach, WERs were derived for each of the sites, and used to adjust the generic State of Washington copper criterion to achieve SSWQOs for each site. A comparison of species sensitivity between *C. dubia* and rainbow trout suggested that the SSWQOs derived from data obtained with *C. dubia* should be protective of salmonids. SSWQO-based effluent limits (as total copper) were subsequently derived

using an approach that assumed no dilution, but incorporating a site-specific ratio of dissolved-to-total copper, and the 10th percentile hardness associated with the nearest receiving environment station. A comparison of these limits with historic and projected copper discharge concentrations suggests that the Port should be in compliance most of the time. Nonetheless, these limits should be considered as interim until sufficient data have been obtained to evaluate the performance of the associated BMPs, some of which are still to be implemented, and a mixing zone analysis is completed if found necessary. In addition, use of the 10th percentile hardness presents an unnecessary constraint in that most of the samples will have higher hardness, and could have higher copper levels without exceeding the SSWQO. In these cases, the Port would be in violation without actually causing impairment. Consequently, the Port proposes that the effluent limits incorporate variable hardness, as represented by actual values associated with each storm/sampling event. Thus, actionable violations would be associated with exceedences potentially associated with environmental harm, rather than artifacts of variability in hardness characteristic of stormwater events. Finally, implementation of a robust and comprehensive monitoring program focused on the discharges and the receiving environment will provide a means of assessing the performance of the SSWQOs, as well as STIA's stormwater discharge program.

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FIGURES







SDE4-Copper, Total





SDS3 Copper, Total



Figure 5

SDS5 Copper, Total

SDS4 Copper, Total





SDS6 Copper, Total







Figure 9









SDN2 Copper, Total



APPENDIX A

Hardness Values

Common Site	Hardness		Common Site	Hardness		Common Site Hardness		; 0. – .
Name	(mg/L)	Storm Date	Name	(mg/L)	Storm Date	Name	(mg/L)	Storm Date
DME	30.0	3/26/2004	NP-Out	92.0	3/26/2004	REBA-Out	112.0	5/27/2004
DME	40.0	5/27/2004	NP-Out	98.0	5/28/2004	REBA-Out	60.0	11/1/2004
DME	38.0	8/8/2004	NP-Out	112.0	8/8/2004	REBA-Out	128.0	1/6/2005
DME	40.0	9/12/2004	NP-Out	52.0	11/1/2004	REBA-Out	87.2	5/10/2005
DME	32.0	10/10/2004	NP-Out	80.0	1/6/2005	REBA-Out	128.0	7/10/2005
DME	48.0	12/6/2004	NP-Out	72.0	7/10/2005	REBA-Out	135.6	8/29/2005
DME	36.0	1/6/2005	NP-Out	107.0	9/10/2005	REBA-Out	125.0	9/10/2005
DME	34.0	3/21/2005	NP-Out	102.0	10/6/2005	REBA-Out	127.5	10/6/2005
DME	42.0	7/10/2005	NP-Out	57.9	11/2/2005	REBA-Out	109.5	11/2/2005
DME	37.0	9/10/2005	NP-Out	72.0	12/3/2005	REBA-Out	99.7	12/1/2005
DME	31.9	10/6/2005	NP-Out	36.0	1/21/2006	REBA-Out	75.8	1/4/2006
DME	26.3	11/2/2005	NP-Out	94.0	2/23/2006	REBA-Out	137.0	2/23/2006
DME	31.9	12/1/2005	NP-Out	67.9	3/8/2006	REBA-Out	110.5	3/8/2006
DME	17.7	1/5/2006	NP-Out	99.8	4/8/2006	REBA-Out	110.0	4/8/2006
DME	32.6	2/23/2006	NP-Out	107.8	5/21/2006	REBA-Out	170.0	5/21/2006
DME	27.1	3/8/2006	NP-Out	40.3	6/2/2006	REBA-Out	70.0	6/1/2006
DME	22.6	4/8/2006	NP-Out	138.0	9/13/2006	REBA-Out	157.0	9/13/2006
DME	22.7	5/21/2006	NP-Out	101.0	10/14/2006	REBA-Out	144.6	10/14/2006
DME	24.0	10/14/2006	NP-Out	67.0	11/13/2006	REBA-Out	62.7	11/13/2006
DME	33.7	11/13/2006	NP-Out	65.6	12/11/2006	REBA-Out	97.6	12/11/2006
DME	19.1	12/11/2006	NP-Out	85.0	2/7/2007	REBA-Out	44.6	1/6/2007
DME	15.4	1/6/2007	NP-Out	140.0	4/17/2007	REBA-Out	112.6	2/14/2007
DME	28.0	2/7/2007	NP-Out	48.0	3/26/2007	REBA-Out	160.0	4/17/2007
DME	64.0	4/17/2007	NP-Out	91.0	5/22/2007	REBA-Out	79.0	3/25/2007
DME	48.0	6/10/2007	NP-Out	78.0	9/5/2007	REBA-Out	135.0	5/22/2007
DME	68.4	11/15/2007	NP-Out	64.0	10/2/2007	REBA-Out	115.0	8/21/2007
DME	50.7	12/2/2007	NP-Out	85.2	11/15/2007	REBA-Out	160.0	9/19/2007
			NP-Out	99.0	12/15/2007	REBA-Out	132.0	10/19/2007
						REBA-Out	129.8	11/15/2007
						REBA-Out	117.0	12/15/2007
10th percentile	21.2		10th percentile	50.8		10th percentile	69.3	
median	32.6		median	85.1		median	116.0	
n	27.0		n	28.0		n	30.0	

Common Site	Hardness	Storm Date	Common Site	Hardness	Storm Date
	(IIIg/L) 104	6/11/07	MC9th	(mg/L) 76	2/26/2004
	134	0/11/07		76	3/20/2004
walker Ck	124	9/6/07		94	5/27/2004
Walker Ck	108	10/1/07	MC8th	11	8/8/2004
Nalker Ck	132	11/11/07	MC8th	64	10/10/2004
Nalker Ck	112	11/28/07	MC8th	96	3/21/2005
Nalker Ck	102	3/26/2004	MC8th	48	1/18/2006
Valker Ck	116	5/27/2004	MC8th	84	3/25/2007
Nalker Ck	114	8/8/2004	MC8th	87	5/22/2007
Walker Ck	108	8/23/2004	MC8th	122	9/19/2007
Valker Ck	108	10/10/2004	MC8th	102.3	12/15/2007
Valker Ck	112	3/21/2005	MC8th	98	3/13/2008
Nalker Ck	114	7/10/2005	MC8th	70	3/23/2008
Nalker Ck	72	1/21/2006	MC8th	90	3/25/2008
Valker Ck	114	5/22/2007	MC8th	65	3/26/2008
Nalker Ck	120	3/13/2008	MC8th	75	3/28/2008
Nalker Ck	110	3/23/2008	MC8th	110	4/4/2008
Nalker Ck	130	3/25/2008	MC8th	120	4/14/2008
Valker Ck	120	3/26/2008	MC8th	88	4/28/2008
Valker Ck	94	3/28/2008	MC8th	130	5/13/2008
Valker Ck	120	4/4/2008	MC8th	120	5/20/2008
Valker Ck	130	4/14/2008			
Valker Ck	120	4/28/2008			
Nalker Ck	130	5/13/2008			
Valker Ck	120	5/20/2008			
10th porceptile	102.0			64.0	

10th percentile	103.8	10th percentile	64.9
median	115.0	median	89.0
n	24.0	n	20.0



Derivation of Site-Specific Water Quality Objectives and Effluent Limits for Zinc in Stormwater

Report date: June 23, 2008

Prepared for: Port of Seattle – Aviation Division Seattle-Tacoma International Airport Seattle, WA

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EXECUTIVE SUMMARY

This report presents the development of site-specific water quality objectives (SSWQOs) for zinc in streams that receive stormwater discharges from the Seattle-Tacoma International Airport (STIA). On the basis of these objectives, SSWQO-based discharge limits for zinc were also derived. This report includes the background for the study, the methods and materials used to achieve the objectives of the study, the data used to derive the site-specific objectives, as well as the actual derivation of specific objectives and effluent limits.

The overall approach was based on guidelines promulgated by the U.S. Environmental Protection Agency and the Washington State Department of Ecology (Ecology), and consisted of water-effect ratio studies (WERs) conducted with *Ceriodaphnia dubia*. Strict QA/QC standards were applied to ensure that a rigorous approach was used and that data quality objectives were met. At least four WER comparisons were used to derive a final WER for each site; this number exceeds the minimum required by USEPA and Ecology, and further ensures that the final WER is a robust measure of the bioavailability of zinc in each stream. Supplemental comparisons were also conducted with rainbow trout (*Oncorhynchus mykiss*) to ensure that the site-specific objectives derived from data obtained with *C. dubia* were also protective of salmonids. Finally, the calculated values were then compared with the original dataset to confirm that they were, indeed, appropriate.

Water-effect ratios were determined for sites located in the Des Moines, Miller and Walker Creek drainages. The water-effect ratios varied between sites, and ranged from 0.91 to 3.86, based on dissolved zinc and correcting for changes in pH that occurred during the laboratory exposures. Site-specific water quality objectives were then calculated by multiplying the generic water quality criterion for zinc (based on hardness) by the WER calculated for each site.

Typically, the need for effluent limits is determined based on the outcome of a reasonable potential analysis. Reasonable potential and mixing zone analyses have not been completed at this time due to lack of sufficient data representing post-retrofit conditions. STIA has recently completed a comprehensive retrofit of its stormwater treatment and flow control facilities, and these new facilities are expected to significantly decrease pollutant loading. Stormwater facilities associated with Third Runway associated outfalls will be completed in the near future in conjunction that project's completion. In the interim, this study determined potential discharge limits for each of the stormwater outfalls on the basis of the corresponding SSWQO,

Nautilus Environmental

with no consideration of dilution. Since SSWQOs are derived on the basis of dissolved zinc, and discharge limits are expressed as total zinc at a specific hardness, the discharge limits were further adjusted to reflect the ratio of total to dissolved zinc and 10th percentile hardness at each site.

While the calculated effluent limits for zinc were based on procedures consistent with USEPA and Ecology guidelines, there is some uncertainty associated with the derived values, including an adjustment for pH effects that occurred as part of the laboratory exposures. In addition, many of the WERs overlapped "1", suggesting that the existing water quality objective (WQO) for zinc appropriately characterizes the bioavailability of zinc in local streams that receive stormwater discharges from the STIA. Finally, the calculated limits generally exceed the current limit of 117 ug/L. Given that the calculated limits do not significantly alter the Port's anticipated ability to comply with the limits, the Port proposes that the existing limit be retained on an interim basis until the STIA's stormwater treatment and discharge system is fully operational and sufficient data are available to characterize the concentration profiles associated with the different discharge points.

The Port recognizes uncertainties associated with projected removal efficiencies in the stormwater treatment system, as well as in derivation of SSWQOs. Consequently, a robust and comprehensive monitoring program will continue to be applied to the discharges, as well as the receiving environment, to ensure that beneficial uses are protected.

1. INTRODUCTION

1.1. Historical Background

The Port of Seattle ("the Port") owns and operates the Seattle-Tacoma International Airport (STIA), and currently discharges stormwater run-off from a number of locations at STIA. These existing stormwater discharges are permitted by the Washington Department of Ecology ("Ecology") under individual NPDES Permit No. WA-002465-1, the most recent version of which was issued in 2003 and which was subsequently modified in 2005, and again in 2007. In addition, the Port is in the process of a major expansion called the Master Plan Update (MPU), which includes a Third Runway and related facilities. As a part of the permitting for the MPU, Ecology issued a §401 Water Quality Certificate No. 1996-4-02325 in 2001. The terms of the original Certificate were subsequently amended as a result of a settlement agreement, a decision by the Pollution Control Hearings Board in 2002 and a decision by the Washington Supreme Court in 2004. The new outfalls that are being constructed to handle stormwater from the MPU are identified in the current permit as "future outfalls" and have been included as part of the Port's permit application for the next NPDES permit, which will be issued in late 2008.

Condition J.2 of the §401 Certification (as amended) states that "no stormwater generated by operation of new pollution generating impervious surfaces of ... [MPU projects] (excluding surfaces not to be included in the airport NPDES permit...) shall be discharged to state receiving waters until a site-specific study, e.g., a Water Effects Ratio Study (WERS) has been completed and approved by Ecology and appropriate limitations and monitoring requirements have been established in the Port's NPDES permit. The study may use existing impervious surfaces as a surrogate for future new impervious surfaces, and it shall be submitted to Ecology for review and approval. The Port shall consult with Ecology's Northwest Regional Office Water Quality Program's SeaTac NPDES Manager to determine an appropriate time for submittal of the WERS." In turn, the NPDES permit (Part II, Condition S9C.1) requires the Port to comply with Condition J.2 of the §401 Certification, and specifically states that the Port must: "[c]onduct a site specific study, e.g., Water Effect Ratio, which is a criteria adjustment factor accounting for the effect of site specific water characteristics of pollutants bioavailability and toxicity to aquatic life ... By December 31, 2007, the Permittee shall submit to the Department for review and approval a report documenting the results of
the site specific study." All of the information contained within this document has been prepared to satisfy both the NPDES and §401 requirements. On December 7, 2007, the Port requested and was verbally granted an extension of the report submittal date to February 29, 2008. The zinc report was initially submitted to Ecology on March 3, 2008. Based on discussions with Ecology, clarifying responses were submitted on May 28, 2008. This report has been revised in accordance with those clarifying responses.

1.2. Technical Background

As a result of contact with metallic surfaces and metal-bearing particulates (metal roofing material and particulate wear from brake linings, for example), run-off may contain elevated concentrations of dissolved metals, particularly copper and zinc. The Port has implemented an extensive best management practice (BMP) based program to control concentrations of these metals in stormwater discharges. Although the BMP program meets Ecology-approved AKART for STIA, it is expected that some amount of metal contamination will continue to be discharged to State receiving waters.

A number of factors may influence the bioavailability of metals, and consequently influence their toxicity under different conditions. These factors include hardness, pH and dissolved organic carbon (DOC; primarily comprised of humic and fulvic acids), as well as the balance of other inorganic ions present. The effect of hardness on toxicity has been widely documented, and the USEPA incorporated hardness into the derivation of historical water quality objectives for a number of metals including zinc and copper (USEPA 1994). Most recently, the biotic ligand model (BLM) has been used to derive site-specific criteria for copper by incorporating selected water quality parameters in addition to hardness (Di Toro *et al.* 2001), and similar applications are being developed for other metals, as well. Indeed, the BLM has been incorporated into the most recent version of the USEPA copper criteria document (USEPA 2007).

The interest in developing site-specific criteria or objectives for metals originates in the fact that most of the original toxicity studies that led to the development of metals criteria were conducted in laboratory water, which typically does not contain constituents (e.g., DOC) that have the capacity to reduce the bioavailability of the metals. Thus, metals toxicity in site waters is typically lower than observed in laboratory tests or predicted simply on the basis of differences in hardness between laboratory water tests and site water. Conversely, it is possible that site-specific characteristics of certain

parameters (e.g., pH) might increase toxicity compared with that predicted on the basis of laboratory toxicity tests conducted in laboratory water.

Due to uncertainties in predicting toxicity purely on the basis of models (such as the BLM) in the absence of site validation, site-specific evaluations of toxicity are generally conducted to obtain empirical comparisons between tests conducted in laboratory water and in the site water of interest. The ratio between the toxicity observed in site water and that observed in laboratory water provides a measure of the effect of site water on the bioavailability of the contaminant of interest. This ratio is referred to as the water-effect ratio (WER), and can be used to adjust the water quality criterion as appropriate on a site-specific basis.

USEPA has published two guidance documents related to deriving WERs. The first document (USEPA 1994) provided the initial guidance, whereas the second document (USEPA 2001) is focused on copper and incorporates a revised approach that reflects more recent developments in the field. For example, in the more recent document (USEPA 2001), fewer comparative tests are required to derive a WER. In addition, only a single species is used to derive a WER in USEPA (2001), whereas USEPA (1994) calls for a primary and a secondary species. In this instance, USEPA (2001) notes that the use of a second species was not found to substantively improve or alter the interpretation of the results obtained with the primary species. Some of the 2001 document's implicit assumptions (e.g., continuous point-source discharge, and samples collected under low-flow conditions) need to be modified when applying the procedures to situations that reflect different conditions (e.g., stormwater discharges) associated with a variety of loadings, sources and flow.

Ecology also provides guidance for conducting and implementing WER studies in their Permit Writer's Manual (1999). Prior to initiating a WER, the permittee must conduct an evaluation of options for reducing metals concentrations in the discharge, and implement practices and technologies that meet the cost test for reasonableness (WDOE 1999). To achieve this objective, the Port conducted an engineering study to optimize outfall design and identify the known and reasonable technologies (AKART) that could be applied (R.W. Beck and Parametrix 2006). The guidance document also requires that a preliminary study be conducted using clean sampling and analytical techniques to confirm that there is a reasonable potential for exceedences to occur, and that a study plan for conducting the WER studies be submitted and approved by Ecology. Consequently, a preliminary study report documenting metals concentrations in various outfalls and receiving environment samples was prepared and submitted to Ecology (Ecotox and Parametrix 2002), and a work plan for developing site-specific water standards for both copper and zinc submitted and approved by Ecology (Brix and Deforrest 2004). Other considerations for WER studies include use of standard and approved toxicity testing techniques by certified laboratories and submittal of all data in the final report (WDOE 1999).

Because of the variety of receiving environments, with potentially unknown possibilities for interactions that might affect toxicity, Ecology decided during the §401 Certification process that the most appropriate approach for determining site-specific zinc objectives and corresponding discharge limits would be to perform WER studies on each of the potentially affected receiving environments. The actual approach was designed to be robust. It not only exceeds the minimum requirements specified by USEPA, but was further intended to provide sufficient numbers of samples to fully characterize variability in the receiving environments. The general technical approach was described in the original Workplan (Brix and Deforest 2004), which was approved by Ecology in advance of initiating this testing program. Subsequently, minor modifications to the approach were made in consultation with Ecology.

Briefly, the approach involved testing a minimum of five discrete samples from seven in-stream sites (see Figure 1), representing the Miller, Walker and Des Moines Creek drainages. The samples represented all four seasons, including the critical summer lowflow period identified in the Workplan (Brix and DeForest 2004), which was represented by two samples to provide additional "weight" to this period in subsequent calculations. The Workplan noted that historical sampling suggested that copper and zinc concentrations tended to be higher between July and September than other months, and longer periods between storms would likely increase accumulation of metal particulates during this period. In addition, baseflows in the creeks would tend to be lowest during this period, with most run-off absorbed by pervious surfaces which would tend to be more saturated during wet months.

In general, water-effect ratios were determined by spiking the water samples with zinc, and comparing their toxicity to concurrent toxicity tests performed with zinc in laboratory water. Thus, the ratios between LC50s obtained in the laboratory and site water are direct measurements of the relative bioavailability of zinc in site water

compared with laboratory water. The primary test organism was the invertebrate *Ceriodaphnia dubia*, with supplemental testing with rainbow trout (*Oncorhynchus mykiss*). WERs were calculated for each event, and the geometric mean subsequently determined for each site. These values were then applied to Washington State's generic water quality criterion for zinc as an adjustment factor to derive a site-specific objective for each site.

2. METHODS

2.1. Sampling Sites

Surface run-off from the Airport typically flows into two major watersheds – Miller and Des Moines Creeks (see Figure 1). The STIA comprises approximately 2.5 and 20% of the Miller and Des Moines Creek watersheds, respectively. In addition, STIA also plans to discharge stormwater into Walker Creek, as part of their ongoing expansion program. The locations of the sampling sites and outfall points are described in detail in the Workplan (Brix and DeForest 2004). A sampling point at the outlet of Lake Reba (RBOut) was subsequently added following discussions with Ecology. Briefly, sampling sites RBOut, Miller Creek, and MC8th provide information relevant to the Miller Creek drainage, and sites DME, and NPOut provide information relevant to the Des Moines Creek watershed. Stormwater discharges from areas associated with the Third Runway will also enter Walker Creek, a tributary of Miller Creek, as well as Miller Creek itself. Consequently, samples were also collected from Walker Creek to derive a site-specific objective for this watershed.

2.2. Sampling Methods

Ecology and the Port determined that a minimum of five acceptable WERs, representing each of the four seasons, as well as one additional value corresponding to the critical summer low-flow period, would comprise an acceptable database for each site. In addition to season, the criteria for identifying sampling events included at least 0.2 inches of rain, preceded by not more than 0.1 inches of rain over the previous 24 hr, and separation of sampling events by at least 3 weeks (Brix and DeForest 2004).

Samples were 48-hr composites collected over the first 48 hrs of any given rain event. The samples were collected at mid-channel using an ISCO sampler (Model 3700 or 6712). Subsamples making up the composite were comprised of 450 mL aliquots collected at 30-min intervals over the 48-hr period, and stored on ice until completion of the sampling event. A portion (approximately 500 mL) of the composited sample was then taken for chemical analysis. The split samples were transported on ice to the toxicity testing and analytical laboratories. The sample containers were polyethylene, and Teflon tubing was used in the sampler.

2.3. Toxicity Tests

Acute toxicity tests with *C. dubia* were conducted in two laboratories, Nautilus Environmental (Nautilus), Tacoma, WA, and ENSR, Fort Collins, CO, using procedures consistent with USEPA acute toxicity test methods (USEPA 2002). The general methods were similar between laboratories, and are summarized in Table 2.1. Toxicity tests with rainbow trout were conducted by Nautilus, and the methods are summarized in Table 2.2. Water quality and background copper and zinc concentrations in the laboratory water associated with each of WER tests is summarized in Table 2.3.

Test organism	Ceriodaphnia dubia
Test organism source	In-house cultures
Test organism age at initiation	< 24 hours
Test duration	48 hours
Test solution renewal	One at 24 hr
Feeding	None
Test chamber	30 ml plastic cup
Test solution volume	15 mL
Test temperature	20 ° or 25 ° ± 1°C
Dilution water	Moderately Hard Synthetic Water or Site Water
Number of organisms/chamber	5
Number of replicates	4
Photoperiod	16 hours light/8 hours dark
Aeration	None
Test Protocol	EPA-821-R-02-012 (USEPA, 2002)
Test acceptability criterion for controls	\geq 90% survival
Reference toxicant	Copper chloride

Table 2.1. Summary of acute toxicity test methods for *C. dubia*.

^a ENSR ^b Nautilus

Table 2.2. Summary of acute toxicity test methods for rainbow trout.

Test organism	Oncorhynchus mykiss
Test organism source	Troutlodge, Sumner WA
Test organism age at initiation	10 - 25 days post swim up
Pre-test acclimation time	5 days minimum
Test duration	96 hours
Test solution renewal	80% at 48 hr (no renewal for Bowdown, DME,
	MC8th, Miller Creek) ^a
Feeding	None
Test chamber	8-L plastic tank
Test solution volume	4 L
Test temperature	12 ± 1°C
Dilution water	Moderately Hard Synthetic Water or Site Water
Number of organisms/replicate	10
Number of replicates	3
Photoperiod	16 hours light/8 hours dark
Aeration	None
Test Protocol	EPA-821-R-02-012 (USEPA, 2002)
Test acceptability criterion for controls	\geq 90% survival
Reference toxicant	Copper chloride

^a Insufficient sample was collected to conduct a renewal at 48 hr

Test Initiation Date	Samples Tested	Hardness (mg/L)	Alkalinity (mg/L)	pН	DOC (mg/L)	Copper (mg/L) Total/Diss	Zinc (mg/L) Total/Diss
						,	•
29 Mar 04	DME	88	61	7.3	< 0.250	<0.002/<0.002	<0.005/<0.005
10 Aug 04	DME, Miller Creek, NPOut	96	62	7.1	<0.250	0.0027/<0.002	<0.005/<0.005
25 Aug 04	MC8th	82	60	7.8	< 0.250	<0.002/<0.002	0.006/<0.005
14 Sep 04	DME	82	60	7.8	< 0.250	<0.002/<0.002	0.007/<0.005
12 Oct 04	DME, Miller Creek, MC8th	90	58	8.1	<0.250	<0.002/<0.002	<0.005/<0.005
22 Mar 05	DME, Miller Creek	90	57	8	<0.250	<0.002/<0.002	0.006/<0.005
27 Mar 07	Miller Creek, MC8th, RBOut, NPOut	88	64	8.18	<0.250	<0.002/<0.002	<0.005/<0.005
12 Jun 07	Walker Creek	84	64	8.18	< 0.250	<0.002/<0.002	<0.005/<0.005
22 Aug 07	RBOut	96	60	7.97	< 0.250	<0.002/<0.002	0.014/<0.005
7 Sep 07	NPOut, Walker Creek	84	68	8.13	<0.250	<0.002/<0.002	<0.005/<0.005
19 Sep 07	Miller Creek, MC8th, RBOut	88	64	8.19	<0.250	<0.002/<0.002	<0.005/<0.005
19 Oct 07	RBOut	80	60	8.12	< 0.250	<0.002/<0.002	<0.005/<0.005
12 Nov 07	Walker Creek	88	60	8.21	< 0.250	<0.002/<0.002	<0.005/<0.005
29 Nov 07	Walker Creek	88	60	8.01	< 0.250	<0.002/<0.002	0.006/0.006
17 Dec 07	MC8th, RBOut, NPOut	88	60	8.00	<0.250	<0.002/<0.002	0.006/0.006
	Mean	86.9	61.2	7.94	<0.250		
	St. dev.	5.0	2.8	0.33	na		

Table 2.3. Water Quality for Laboratory Water

The toxicity of zinc in site waters was determined by spiking the site waters with ZnCl₂, and preparing serial dilutions using a dilution factor of 0.6 – 0.7. Because of potential dissipation of zinc during the exposures, static renewal test procedures were used, with fresh test solutions prepared at 24-hr intervals, or at 48 hrs for rainbow trout. Test concentrations were allowed to equilibrate for 2 - 3 hrs prior to taking water quality measurements and adding the test organisms. In the *Ceriodaphnia* tests, subsamples of each dilution were taken for determinations of total and dissolved zinc on fresh solutions prepared at the beginning of the test and at 24 hrs. Dissolved zinc was also measured in the "old" solutions at 24 hrs when the test solutions were renewed, and at 48 hrs at test termination. In the case of the rainbow trout tests, samples were taken for analysis of total and dissolved zinc from freshly prepared solutions at the beginning of

exposure, and at the 48-hr renewal. Composite samples were also taken for dissolved zinc on "old" solutions at the 48-hr renewal, and at 96 hr when the tests were terminated. Survival and water quality were monitored at 24-hr intervals, and LC50s determined based on survival at test termination. LC50s were calculated separately on the basis of average total and dissolved concentrations using the trimmed Spearman-Karber method (CETIS vers. 1.025B-1.6.3revG).

Zinc toxicity in laboratory water was determined similarly. However, since the laboratory water was tested at only one hardness, it was necessary to extrapolate the LC50 estimate to that which would be predicted for laboratory water at the hardness of each test sample (i.e., site water) to facilitate comparisons between site and laboratory waters. This estimate of toxicity in laboratory water at the hardness of the test sample was obtained using the USEPA equation for adjusting zinc toxicity based on hardness (USEPA 2001):

The WER for a given sample and event was then calculated as the ratio between the LC50 in site water, and the LC50 for laboratory water, adjusted to the hardness of the site water. Thus, a WER greater than 1 was a measure of the extent to which the receiving environment sample reduced toxicity compared with that which would be expected simply on the basis of a difference in hardness between the laboratory and site waters. Conversely, a WER <1 would suggest that some factor in the site water was contributing to an increase in toxicity greater than would be expected just on the basis of a change in hardness alone.

2.4. Site-Specific Water Quality Objective

Deriving a site-specific water quality objective for zinc is relatively straightforward. Once the individual WER values have been calculated, the dataset for the site is evaluated to determine if any of the values appear inconsistent with the rest of the dataset. Assuming that the WERs are reasonably distributed, with no extremely large or small values, a final WER is calculated as the geometric mean of the individual WERs. This value is then multiplied by the Washington State water quality criterion (*see* WAC 173-201A-240) for zinc to obtain a site-specific objective.

3. QUALITY ASSURANCE

Results from each toxicity test were evaluated to determine the following:

- Did the test procedures follow the appropriate guidelines?
- Did the tests meet control acceptability criteria?
- Did the tests exhibit a reasonably consistent dose-response?
- Did the tests exhibit acceptable water quality parameters?
- Were the tests initiated within an appropriate time-frame?
- Were the proper controls performed?
- Did the test concentrations exhibit acceptable stability over the exposure period?

Each of these measures of test validity was compared against the criteria set forth in the original Workplan (Brix and DeForest 2004), which cited USEPA (1993, 1994, 2001) and WDOE (1999 and 2001) as technical support document. Potential issues were deemed minor if they were not likely to affect the results or conclusions (e.g., change a calculated LC50 significantly). Major issues were those in which the calculated LC50 or WER might be affected (e.g., atypical dose-response), or situations in which test procedures or acceptability criteria might have been altered to the point where the results might be considered suspect (e.g., excessive control mortalities, significant exceedences of holding time, or dissipation of the test chemical).

This QA evaluation was performed approximately half-way through the program and again at the end of the program. At the interim evaluation point, each of the data anomalies identified was critically evaluated with respect to its ultimate inclusion in the dataset and, if necessary, additional sampling events were scheduled to replace rejected datasets. In addition, "gray" areas in which different protocols provided different guidance were identified and resolved with Ecology. The final evaluation confirmed that a sufficient number of samples representing a broad spectrum of temporal conditions were obtained, and that all of the datasets were acceptable.

The following guidelines were used to evaluate whether data were acceptable for proceeding with calculating site-specific water quality objectives:

• Control acceptability criteria

- Were appropriate and concurrent controls used (Brix and DeForest 2004; USEPA 1994 and 2001)?
- Was control survival at least 90 percent (USEPA 1993 and 2002)?
- Appropriate test procedures and water quality
 - Was the dilution factor between 0.65 and 0.90? A dilution factor of 0.6 (USEPA 2001) was allowed for tests initiated prior to the interim review, but a higher dilution factor was considered desirable for subsequent tests (USEPA 1994; Brix and DeForest 2004).
 - Did water quality (e.g., dissolved oxygen) remain within acceptable ranges (USEPA 1993 and 2002)?
- Acceptable holding times
 - <36 hr was considered desirable (USEPA 1994); 96 hr was considered maximum, based on an analysis that indicated no relationship between holding time and toxicity. This maximum holding time is also consistent with USEPA guidance for conducting streamlined copper WERs (USEPA 2001).
- Acceptable toxicant stability
 - At least 50% of the test material measured initially must be present at the end of the test (USEPA 1994);
 - A test was considered acceptable if only one concentration exhibited excessive dissipation of the toxicant;
 - A test was considered unacceptable if more than one concentration exhibited excessive dissipation of the toxicant.
- Acceptable dose-response for estimating a valid LC50 (USEPA 1993)?
- Did the data provide sufficient temporal coverage?
 - Were a minimum of 5 valid data points available for the site? This level of temporal coverage exceeds the requirements of both USEPA WER guidance documents (USEPA 1994 and 2001).
 - Was the critical summer dry period represented by 2 samples?

4. ANALYTICAL CHEMISTRY

Analytical chemistry support for this study was provided by Aquatic Research Laboratory, Seattle, WA. Analytical parameters measured in samples used for the WER tests included: total and dissolved silver, arsenic, calcium, cadmium, chromium, copper, iron, potassium, lead, magnesium, manganese, nickel, sodium, zinc, total suspended solids, total organic carbon, dissolved organic carbon, hardness, alkalinity, pH, sulfate and chloride. In addition, dilutions of the water samples spiked with zinc were measured for total zinc on fresh solutions prepared at test initiation and when solutions were renewed. Dissolved zinc was measured on freshly prepared test solutions, as well as on "old" solutions prior to renewal. The actual measured values were used in calculation of the LC50s that resulted in the WERs.

5. RESULTS

5.1. Sampling Events

A minimum of five samples collected from each of the sampling sites resulted in definitive WERs that met the QA criteria. The sampling dates, total rainfall over the 48-hr sampling period and general water chemistry parameters, including background zinc and copper concentrations, associated with each of the sampling events and sites are summarized in Table 5.1.

		-				Copper ²	Zinc ²
Sampling Site	Rainfall	Hardness	Alkalinity	$\mathcal{D}H^1$	DOC ²	(mg/L)	(mg/L)
and Date	(in)	(mg/L)	(mg/L)	r	(mg/L)	Total/Diss	Total/Diss
DME						,	,
26 Mar 04	0.80	30	24	7.0	5.63	0.012/0.006	0.057/0.043
8 Aug 04	0.66	38	32	7.0	12.60	0.021/0.017	0.105/0.031
12 Sep 04	1.17	40	40	7.6	10.80	0.012/0.005	0.027/0.021
10 Oct 04	1.04	32	29	7.6	7.39	0.007/0.007	0.033/0.017
21 Mar 05	0.44	34	28	7.7	5.79	0.009/0.005	0.058/0.048
Miller Creek							
8 Aug 04	0.66	76	69	7.4	9.75	0.005/0.004	0.210/<.005
10 Oct 04	1.04	56	52	7.8	6.74	0.006/0.004	0.022/0.008
21 Mar 05	0.44	90	87	7.6	6.17	0.003/<.002	0.022/0.023
25 Mar 07	1.34	62	67	7.6	5.77	0.005/<.002	0.028/0.015
18 Sep 07	0.42	140	136	7.8	5.14	0.003/0.003	0.013/0.008
MC8th							
23 Aug 04	0.59	84	80	7.8	8.33	0.005/0.005	0.014/0.009
10 Oct 04	1.04	64	59	7.6	7.01	0.022/0.003	0.025/0.006
26 Mar 07	1.34	84	72	7.7	5.70	0.004/<.002	0.019/0.010
22 May 07	0.85	87	92	7.8	5.55	0.006/0.002	0.061/0.017
19 Sep 07	0.42	122	122	7.9	5.07	0.003/<.002	0.006/0.008
15 Dec 07	0.42	102	94	7.6	4.67	0.002/0.002	0.013/0.014
<u>RBOut</u>							
25 Mar 07	1.34	79	88	7.6	3.96	0.005/0.004	0.018/0.012
22 May 07	0.85	135	145	7.8	4.00	<.002/<.002	0.021/0.012
21 Aug 07	0.63	115	118	8.0	3.41	<.002/<.002	0.016/0.007
19 Sep 07	0.42	160	169	8.0	3.40	<.002/<.002	0.007/0.008
19 Oct 07	0.81	132	135	7.5	4.40	0.003/0.002	0.009/<.005
15 Dec 07	0.42	130	120	7.3	4.30	<.002/<.002	0.014/0.014
<u>NPOut</u>							
8 Aug 04	0.66	112	122	7.6	8.75	<.002/<.002	<.005/<.005
26 Mar 07	1.34	48	50	7.4	3.14	0.007/0.002	0.012/0.009
22 May 07	0.85	91	105	7.7	5.90	0.007/0.005	0.028/0.006
5 Sep 07	1.08	78	73	7.7	5.85	0.028/0.005	0.055/0.008
2 Oct 07	1.44	64	57	7.2	4.37	0.046/0.004	0.095/0.008
15 Dec 07	0.42	99	82	7.3	5.55	0.003/0.004	0.011/0.010
<u>Walker Creek</u>							
22 May 07	0.85	114	116	7.9	4.13	0.002/<.002	0.026/0.014
11 Jun 07	0.25	134	97	7.8	2.55	<.002/<.002	0.009/0.005
6 Sep 07	1.08	124	122	8.0	7.43	0.003/0.002	0.031/0.009
1 Oct 07	1.44	108	98	7.8	7.36	0.002/0.002	0.009/0.008
11 Nov 07	0.32	132	86	7.5	11.5	0.003/0.003	0.015/0.015
28 Nov 07	0.49	113	118	7.8	4.11	<.002/0.002	0.028/0.008

Table 5.1. Summary of rainfall and general water chemistry parameters associated with samples used to derive WERs.

¹pH measured at lab at time of receipt; ²metals and DOC measured at analytical lab Note: pH values as measured in samples at the laboratory have been shown to be higher than pH measured in-stream. See Section 7.0 for additional information.

Rainfall ranged from 0.25 to 1.44 inches over a 48-hr period associated with the different sampling events. Hardness ranged from a low of 30 mg/L to a high of 160 mg/L, as CaCO₃. Alkalinity ranged between 24 and 169 mg/L, as CaCO₃. pH ranged from 7.0 to 8.0, and DOC measured in the samples ranged from 2.55 to 12.60 mg/L, compared with <0.25 mg/L in laboratory water. Total copper measured from <0.002 mg/L to 0.046 mg/L, and dissolved copper ranged from <0.002 mg/L to 0.017 mg/L. Total zinc concentrations ranged from <0.005 to 0.210 mg/L, compared with a range of <0.005 to 0.048 mg/L for dissolved zinc.

5.2. Water-Effect Ratios

LC50 estimates, based on total and dissolved zinc for the laboratory and site waters, and the associated WER values for each of the sampling locations and events are shown in Table 5.2.

Commis Data	Tota	Total Zinc (µg/L)			Dissolved Zinc (μ g/L)		
Sample Date	Site Water LC50	Lab Water LC 50	WER	Site Water LC 50	Lab Water LC 50	WER	
DME							
26 Mar 04	405.0	88.7	4.57	361.3	114.6	3.15	
8 Aug 04	337.2	122.6	2.75	265.7	121.7	2.18	
12 Sep 04	267.9	97.4	2.75	173.4	88.7	1.96	
10 Oct 04	240.8	146.6	1.64	209.6	143.3	1.46	
21 Mar 05	438.2	175.3	2.50	298.3	163.2	1.83	
Geometric Mean			2.69			2.05	
Miller Creek							
8 Aug 04	400.7	220.5	1.82	183.5	219.0	0.84	
10 Oct 04	395.9	235.6	1.68	255.3	230.3	1.11	
21 Mar 05	285.1	400.0	0.71	157.0	372.4	0.42	
25 Mar 07	106.3	107.4	0.99	99.4	118.3	0.84	
18 Sep 07	115.0	142.6	0.81	36.5	90.6	0.40	
Geometric Mean			1.12			0.67	
MC8th							
23 Aug 04	188.2	188.0	1.00	160.2	124.1	1.29	
10 Oct 04	299.2	263.8	1.13	145.7	257.8	0.57	
26 Mar 07	213.0	141.2	1.51	102.1	155.6	0.66	
22 May 07	94.3	256.5	0.37	40.7	171.4	0.24	
19 Sep 07	72.4	126.9	0.57	36.3	80.7	0.45	
15 Dec 07	119.0	245.8	0.48	123.0	262.4	0.47	
Geometric Mean			0.75			0.54	
<u>RBOut</u>							
26 Mar 07	116.7	134.1	0.87	103.1	147.7	0.70	
22 May 07	84.4	372.3	0.23	30.3	248.7	0.12	
21 Aug 07	64.2	239.0	0.27	26.2	167.1	0.16	
19 Sep 07	54.4	159.7	0.34	24.2	101.5	0.24	
19 Oct 07	97.8	183.0	0.53	51.0	107.4	0.47	
15 Dec 07	183.0	299.4	0.61	161.0	319.6	0.50	
Geometric Mean			0.43			0.30	

Table 5.2. Summary of initial LC50 estimates, based on total and dissolved zinc, and associated WERs for each of the sampling events. Lab water LC50s are adjusted to correspond to the hardness of each sample.

Commis Data	Tot	al Zinc (µg/L)		Dissolved Zinc (µg/L)		
Sample Date	Site Water LC 50	Lab Water LC 50	WER	Site Water LC 50	Lab Water LC 50	WER
NPOut						
8 Aug 04	367.2	306.2	1.20	203.6	304.2	0.67
26 Mar 07	144.9	87.9	1.65	128.0	96.8	1.32
22 May 07	117.0	266.5	0.44	32.9	178.0	0.18
5 Sep 07	236.0	177.2	2.01	81.5	75.5	1.08
2 Oct 07	105.2	46.3	2.27	42.1	29.9	1.41
15 Dec 07	183.0	238.8	0.77	172.0	255.0	0.67
Geometric Mean			1.20			0.74
Walker Creek						
22 May 07	61.5	322.6	0.19	28.8	215.5	0.13
11 Jun 07	51.3	NC	na	45.3	213.2	0.21
6 Sep 07	115.0	173.5	0.66	68.5	111.8	0.61
1 Oct 07	77.0	72.1	1.07	51.4	46.6	1.10
11 Nov 07	137.0	417.2	0.33	115.0	265.9	0.43
28 Nov 07	80.5	198.0	0.41	63.8	198.0	0.32
Geometric Mean			0.45			0.37

Table 5.2, continued.

NC = not calculated due to anomalous analytical values. na = not applicable (see above).

Analysis of the Toxicity Data

In general, the range between the minimum and maximum LC50 estimates obtained for lab water and site waters varied within a factor of 5 to 6, and occasionally exceeded a factor of ten. This level of variation (i.e., the ratio between the minimum and maximum values) exceeded that typically associated with intralaboratory variability observed with tests conducted under controlled conditions with the same material over time (Chapman 1995; USEPA 2002), but is not unexpected given that these samples varied in both hardness and pH. Moreover, the overall variability associated with the site waters was similar to that associated with laboratory water, suggesting that none of the values were atypically small or large. Consequently, on a preliminary basis, all of the values were considered representative and appropriate for further analysis.

However, inspection of the calculated WER values revealed that many of them were less than "1" and, in some cases, substantially so. In general, one would not expect zinc to exhibit significantly greater toxicity in site waters than in laboratory waters, unless there were obvious and considerable differences in water chemistry. Since differences in water chemistry (e.g., hardness) did not appear sufficient to account for observed differences in bioavailability, we suspected that they were related to an unidentified artifact associated with either the laboratory testing process, or the method used to adjust the LC50s in laboratory water to the hardness of the test samples.

Typically, in generating WERs, laboratory water is tested only at one hardness, and the resulting LC50 is adjusted to reflect the different hardnesses associated with the site waters tested concurrently. This adjustment uses an equation based on the relationship between zinc toxicity and hardness derived by the USEPA. Consequently, we evaluated the possibility that the USEPA equation for estimating the toxicity of zinc as a function of hardness might not provide a good fit of the hardness:toxicity relationship within the range of hardnesses of interest in this study (i.e., between 10 and 100 mg/L). In other words, because the USEPA equation is designed to predict toxicity across a much wider range of hardnesses, it is possible that achieving a good fit across a wide range of values might be at the cost of not having as good a fit within the lower range of the curve.

To evaluate this hypothesis, we ran a series of acute toxicity tests with zinc at different hardnesses over the range of 10 - 100 mg/L, and found that increasing the hardness did not have the expected result of consistently reducing toxicity as the hardness increased. Moreover, review of the data suggested that pH might be a confounding factor, as pH increased as hardness increased. Thus, if increasing pH increased the toxicity of zinc, it would counter the expected decrease in toxicity as hardness increased. This factor is particularly relevant in that this study found that the pH of site water increased from instream conditions through testing (see Section 7.0).

To eliminate the effect of pH, we performed a subsequent study in which pH was held constant using a CO_2 atmosphere over the test containers, and compared the observed relationship between hardness and toxicity to the relationship predicted by the USEPA equation. With the pH held at approximately 7.0, the toxicity data exhibited a strong linear relationship with hardness (R² = 0.92), suggesting that toxicity was closely related to hardness. Moreover, comparing our results with those predicted by the USEPA equation resulted in similar values, generally within 10% across the range of hardnesses tested. This result suggested that refining the USEPA hardness equation would do little to improve our ability to predict the toxicity of zinc, and indicated that the relationship between hardness and toxicity is robust, provided that pH is controlled.

Based on the evidence that pH is a major factor controlling toxicity, the next step was to determine if we could incorporate pH into a predictive equation. This was a bit more complicated than it might first appear because the degree of effect appeared to increase sharply as the pH approaches 8, instead of being constant for a given incremental change in pH. Thus, the relationship between pH and toxicity appeared to be an exponential function, with toxicity increasing more rapidly as pH increases beyond 8. Using the relationship between hardness and toxicity to establish an "expected" level of toxicity (with toxicity being characterized as an LC50), we then used the ratio between the expected and actual LC50 values to characterize the departure from expected. Assuming that pH was responsible for the departure from expected value, we would expect to see larger ratios associated with higher pH values, and should be able to describe the ratios as a function of pH. This procedure resulted in an equation that describes the ratio between expected and actual LC50 values as an exponential function of pH; the R² for the equation is 0.91, which suggests that increasing pH is strongly associated with increasing departure from the expected relationship between hardness and the toxicity of zinc.

To validate the relationship between pH and hardness and the toxicity of zinc, the "pH adjustment" described in the paragraph above was used to modify LC50 values that would be expected on the basis of hardness alone, and very close agreement was obtained between the expected and actual LC50s ($R^2 = 0.94$). For comparison, the fit of this relationship was much better than the predictive relationship between hardness and toxicity with no compensation for pH ($R^2 = 0.54$). Thus, the data suggest that the toxicity of zinc can be described as a function of hardness and pH, and that pH exerts an increasingly strong effect as it rises above 8.

Finally, this finding further suggested that it was appropriate to refine our estimates of toxicity (i.e., LC50s) to reflect changes in pH of the samples that occurred during testing. Under these circumstances, samples typically increased to pH 8 or more subsequent to sampling due to the small test volumes and agitation that occurred during mixing and water quality measurements. The results of these studies were submitted to Ecology in August 2006, in a summary paper titled: *"Relationships Between Zinc Toxicity, Hardness and pH, and Their Effect in Calculating Water-Effect Ratios"*. This document is also included in Appendix B.

Adjusting the LC50 estimates to compensate for the changes in pH associated with laboratory testing artifacts results in the data shown in Table 5.3. In general, the WERs more closely approximate or exceed "1". In addition, the data exhibit less overall variability, which suggests that accounting for the variability in pH removed much of the variability associated with the laboratory results. The exception to this observation are the WERs obtained during the May 2007 sampling event. In this event, samples were collected from MC8th, RBOut, NPOut and Walker Creek. In all cases, the May samples resulted in the lowest WERs obtained for these sites, generally substantially lower than other samples collected from each site. Because this appeared to be a non-random occurrence (different watersheds were all affected in the same event), we were suspicious that this result was a function of a testing or analytical artifact. Consequently, additional samples were collected from these sites (November and December 2007) to aid in evaluating these results.

The data from these additional samples provided additional evidence that the May samples were not representative; moreover, the data from the May event did not respond particularly well to pH adjustment, further suggesting that the associated results were not related to general water chemistry or test procedures. Further evaluation of the data provided no evidence that other factors (e.g., DOC) could account for the suspiciously low WERs. Consequently, based on the atypically low WERs, the lack of any relationship between the WERs and water chemistry, and the consistency of the low values across different watersheds, we concluded that the results were most likely due to an artifact and not to any intrinsic property of the individual samples. Therefore, the May results were not included in further calculations.

Additional datapoints that might be considered anomalous include the October 1-2, 2007 data for NPOut and Walker Creek. In both sites, these samples resulted in the highest WERs obtained, which appear to be a function of the extremely low values obtained for zinc in laboratory water (see Table 5.3). The low laboratory values would tend to result in higher WERs; however, these values appear to be atypical compared with the rest of the dataset. Consequently, WERs associated with these events were also not included in any additional calculations. This action reduces the number of acceptable WERs available for NPOut and Walker Creek to four, which is less than the desired number of testing events (i.e., 5 WERs per site), but the consistency of the remaining values suggests a representative characterization has been obtained.

	Dis	ssolved Zinc (µg/L)	
Sample Date	Site Water	Lab Water	
	LC50	LC50	VV LIX
DME			
26 Mar 04	580.9	114.6	5.07
8 Aug 04	601.7	121.7	4.94
12 Sep 04	274.0	88.7	3.09
10 Oct 04	399.9	143.3	2.79
21 Mar 05	647.2	163.2	3.97
Geometric Mean	-	-	3.86
Miller Creek			
8 Aug 04	537.2	219.0	2.45
10 Oct 04	454.9	230.3	1.98
21 Mar 05	459.6	372.4	1.23
25 Mar 07	210.2	118.3	1.78
18 Sep 07	98.1	90.6	1.08
Geometric Mean	-	-	1.63
MC8th			
23 Aug 04	362.8	124.1	2.92
10 Oct 04	391.5	257.8	1.52
26 Mar 07	239.3	155.6	1.54
22 May 07	92.2	171.4	0.54
19 Sep 07	101.8	80.7	1.26
15 Dec 07	290.7	262.4	1.11
Geometric Mean	-	-	1.57
<u>RBOut</u>			
26 Mar 07	254.3	147.7	1.72
22 May 07	79.4	248.7	0.32
21 Aug 07	75.4	167.1	0.45
19 Sep 07	72.1	101.5	0.71
19 Oct 07	137.1	107.4	1.28
15 Dec 07	451.6	319.6	1.41
Geometric Mean	-	-	1.00

Table 5.3. Summary of LC50 estimates (incorporating pH adjustment) and associated WERs for each site. Lab water LC50 estimates are from Table 5.2. Note that the results from the May 2007 and October 2007 sampling event are not included in calculation of the geometric mean WER.

	Dis	ssolved Zinc (µg/L)	
Sample Date	Site Water LC50	Lab Water LC50	WER
NPOut			
8 Aug 04	770.6	304.2	2.53
26 Mar 07	257.1	96.8	2.65
22 May 07	84.7	178.0	0.48
5 Sep 07	169.4	75.5	2.24
2 Oct 07	97.8	29.9	3.27
15 Dec 07	446.7	255.0	1.75
Geometric Mean	-	-	2.27
Walker Creek			
22 May 07	84.3	215.5	0.39
11 Jun 07	132.6	213.2	0.62
6 Sep 07	184.1	111.8	1.65
1 Oct 07	157.1	46.6	3.37
11 Nov 07	229.0	265.9	0.86
28 Nov 07	152.1	198.0	0.77
Geometric Mean	-	-	0.91

Table 5.3, continued.

Values in gray were not included in the geometric mean, see above text for discussion.

5.3. Calculation of Site-Specific Water Quality Objectives

Although the national water quality criterion is calculated on the basis of total zinc, a conversion is applied to achieve a final value that is stated in terms of dissolved zinc, because it is generally recognized that toxicity is largely associated with the dissolved form of the metal. Thus, in calculating a site-specific water quality objective (SSWQO), the dissolved WER is applied to the generic criterion. For example, in this study, the dissolved WERs for DME ranged between 2.79 and 5.07, with a geometric mean (i.e., final WER) of 3.86, which would then be used to adjust the generic water quality criterion to account for site-specific differences in bioavailability. Thus, for DME, Washington State's freshwater acute zinc criterion:

Acute dissolved zinc criterion =
$$e^{(0.8473(\ln(hardness))+0.8604)}$$
 Eq. 2

would be multiplied by 3.86 to achieve a site-specific objective. [Note that the 0.978 USEPA dissolved-to-total factor was deleted from Eq. 2 because the WER data are already in dissolved form, and do not have to be converted from total.]

To complete this analysis, the SSWQOs derived for each site were then compared against the actual test data to determine if the site-specific numbers would, in fact, be protective. For example, substituting the lowest hardness observed at DME during the WER study (i.e., 30 mg/L) into Eq. 2, above, results in a generic acute criterion of 42.2 μ g/L which, when multiplied by the site-specific WER for DME (i.e., 3.86), results in a value of 162.8 μ g/L, as dissolved zinc. Comparison of this SSWQO against the site water LC50 estimates for dissolved zinc in Table 5.3 (between 274.0 and 647.2 μ g/L) suggests that the calculated SSWQO would be protective.

5.4. Conversion from Dissolved to Total Zinc

Given that effluent permit limits are based on total zinc, rather than dissolved, the dissolved SSWQO needs to be adjusted appropriately to reflect the site-specific ratio of the dissolved fraction to total zinc present. There are two potential methods to derive this site-specific metals "translator"; one is to use the average ratio of dissolved to total zinc measured in samples from a particular site, and the other is to use the ratio between LC50s calculated on the basis of dissolved and total zinc. The former approach is typically used in the absence of toxicity data (USEPA 1996) but, since toxicity data is available for this study, it is potentially more justified to use the latter approach because it represents the actual biological response to the bioavailable fraction. Values calculated using both approaches are included in Table 5.4 for comparison, but the ratio between LC50s calculated on the basis of dissolved and total zinc was used to derive the final adjustment factor. Note that this approach is more protective than using the translator based on analytical measurements, since it results in lower overall concentrations of zinc when expressed as "total zinc".

Using DME as an example, the mean of the ratios of the dissolved and total LC50s shown in Table 5.2 is 0.78. This "metals translator" can be blended with the final WER (i.e., 3.86/0.78 = 4.95) to obtain a value that can be multiplied by Eq. 2 to calculate an effluent limit (as total zinc) directly for any given hardness. A similar approach was used to derive translators for the remaining sites; all of the data are summarized below in Table 5.4.

Site	Final WER	Dissolv Trai	ved/Total nslator	Final Adjustment
		LC50	Analytical	Factor
DME	3.86	0.78	0.59	4.95
Miller Creek	1.63	0.58	0.38	2.81
MC8th	1.57	0.63	0.47	2.49
RBOut	1.00	0.58	0.48	1.72
NPOut	2.27	0.57	0.59	3.98
Walker Creek	0.91	0.71	0.53	1.28

 Table 5.4.
 Summary of parameters used to derive site-specific adjustments for total zinc.

5.5. Consideration of a Second Species

Although the effectiveness of using a second species as part of the process of developing a SSWQO has been largely discounted in USEPA's more recent WER guidance (USEPA 2001), local concerns over potential impacts to salmonids suggests that such an evaluation may be appropriate. In general, the literature indicates that salmonids, including rainbow trout, are substantially less sensitive to zinc than *C. dubia*, and this conclusion is consistent with the data obtained in this study. For example, one WER test was conducted with zinc on DME using rainbow trout as part of this study. This test resulted in a WER of 1.24, based on dissolved zinc, when compared with laboratory water. For this particular sample, the calculated LC50 (as dissolved zinc) obtained with rainbow trout was 299.1 μ g/L at a hardness of 40 mg/L. By way of comparison, the SSWQO for DME at this hardness would be 207.7 μ g/L, suggesting that the SSWQO derived with *C. dubia* should protect beneficial uses associated with salmonids.

Similar results were obtained with the other sites tested, and are summarized in Table 5.5, along with the results for DME. As the data suggest, the SSWQOs were generally lower than their respective LC50s obtained with rainbow trout, suggesting that the individual SSWQOs should be protective of salmonids. The exception was Miller Creek for which the rainbow trout LC50 was virtually identical to the SSWQO.

Site	Sample Date	Hardness (mg/L)	LC50 (µg/L, as dissolved Zn)	WER	SSWQO (µg/L, as dissolved Zn)
DME	12 Sep 04	40	299.1	1.2	207.7
Miller Creek	23 Aug 04	100	190.7	0.9	190.6
MC8th	23 Aug 04	84	188.6	1.1	158.4
RBOut	21 Aug 07	115	261.0	0.8	131.7
NPOut	6 Sep 07	78	350.0	1.1	215.1
Walker Creek	6 Sep 07	125	755.0	1.6	128.6

Table 5.5.Toxicity data and WERs obtained with rainbow trout compared with SSWQOs derived for *C. dubia* at same hardness.

6. SSWQO-BASED EFFLUENT LIMITS FOR STORMWATER DISCHARGES FROM SEATTLE-TACOMA INTERNATIONAL AIRPORT

As noted in Section 1.1, the §401 Certification for the Master Plan Update Projects requires that "appropriate limitations and monitoring requirements" be established in the Port's NPDES permit. The need for appropriate effluent limits on specific outfalls is typically determined based on the outcome of a reasonable potential analysis (RPA). A critical component of an RPA is a mixing zone factor. Reasonable potential and mixing zone analyses have not been completed at this time due to lack of sufficient data representing post-retrofit conditions. The STIA has recently completed a comprehensive stormwater treatment and flow control facility retrofits in four of its non-Third Runway subbasins. These new facilities are expected to significantly decrease pollutant loading. However, as most evident in SDE4, major construction and changes to STIA infrastructure continues in these retrofitted subbasins (e.g., North Expressway Relocation Project). The remaining six outfalls are integrated into the Third Runway Project and will not be discharging representative runoff until November 2009, after project completion. As such it is not possible to fully assess pollutant loadings and actual BMP performance before the NPDES permit is to be renewed.

As described in the previous paragraph, STIA's stormwater discharge facilities are still in various stages of development and implementation, which has implications for deriving effluent limits from a regulatory perspective. Specifically, Ecology (1999) states that:

• Ecology will only authorize the highest WER that allows a permittee to fall below the reasonable potential threshold...

In general, the STIA's stormwater outfalls, subbasins and BMPs are still at various stages of completion. Indeed, outfalls associated with the Third Runway Expansion will not be discharging until November 2009. Thus, representative data are not available with which to conduct a RPA. Consequently, the STIA proposes that if SSWQO-based effluent limits are to be incorporated into the Port's upcoming renewed permit, they should be based on the WER values presented in Table 5.4 on an interim basis until such time as the discharge basins and associated BMPs are fully operational and sufficient data are available to conduct RPAs. Following such an analysis, the WERs may be modified as appropriate to establish final effluent limits.

Additional conditions (Ecology 1999) for applying a WER to a discharge limit are noted below, along with specific comments related to each:

- The WER shall be re-evaluated during year 5 of the wastewater discharge permit, or sooner...This condition is an operational constraint that is part of the permit, but does not impact the derivation of SSWQOs or associated effluent limits.
- *WET testing will be required in the permit...*This condition is part of the current permit, and is acknowledged in Section 8 of this report as part of the STIA's recommended overall monitoring strategy to support implementation of SSWQOs and associated effluent limits.
- A receiving water bioassessment may be required... This condition is acknowledged in Section 8 of this report as part of the STIA's recommended overall monitoring strategy to support implementation of SSWQOs and associated effluent limits.

In the interim, this study determined potential discharge limits for each of the stormwater outfalls on the basis of the corresponding SSWQO, with no consideration of dilution. Site-specific water quality objectives were calculated by multiplying the generic water quality criterion for zinc (based on hardness) by the WER appropriate for each site. Since SSWQOs are derived on the basis of dissolved zinc, and discharge limits are expressed as total zinc, the discharge limits were further adjusted to reflect the ratio of total to dissolved zinc at each site.

6.1. Background

This section describes the process of deriving preliminary interim water quality-based stormwater discharge limits from the site-specific water quality objectives (SSWQOs) for zinc, using an approach consistent with Ecology's Permit Writer's Manual (1999). As discussed in detail above, the SSWQOs were derived from a comprehensive evaluation of water-effect ratios (WERs) for each site. A final WER was then calculated for each site, and used to adjust the State's water quality criterion for zinc to reflect differences in bioavailability associated with each site. A metals translator, based on the ratio of dissolved to total zinc (as expressed by the ratio of the respective LC50s), was then used to express the site-specific objective in terms of total metal (this process is detailed in Sections 5.3 and 5.4 of this report).

These SSWQOs were subsequently used to calculate effluent limits for each of the sites in terms of total metal at a specific hardness characteristic of each site. The hardness used to calculate effluent limits is typically identified as the 10th percentile of all the hardness values available from a given site. This approach is commonly used to establish limits in NPDES permits for point-source discharges. However, because only four of the ten stormwater detention facilities to be constructed have only recently come on line it is currently impossible to characterize mixing zones associated with the discharges. In addition, the small sizes of the receiving streams, and the large variation in stormwater discharge flows, antecedent conditions and storm profiles, make it problematic to identify appropriate mixing zones that fully represent the associated complexities. Therefore, the calculated effluent limits presented below assume no dilution for the discharge in the receiving environment. Mixing zone analyses may need to be completed before final effluent limits can be established.

In addition to this water quality based approach, consideration could be given to calculating the effluent limits based on available analytical data (i.e., apply a technology or performance-based approach). However, applying this approach to STIA stormwater is not appropriate because the Port's stormwater BMPs are still being implemented, their efficiencies are largely projections based on modeling, and the §401 Master Plan expansion is still in progress. In addition, the STIA, as will all urban basins in Puget Sound, will see continually increased use of its facilities as the population grows resulting in ever increasing pollutant loading. Consequently, the existing analytical data

do not reflect conditions associated with a complete build-out of STIA stormwater drainage facilities and their performance under a wide range of storm conditions.

6.2. SSWQO-Based Effluent Limit Derivation

6.2.1. General Considerations

Stormwater has historically been collected in a number of sub-basins (Figure 1) prior to discharge. Numerous source controls, as well as treatment methodologies, have been implemented to control zinc concentrations in run-off from all of the sub-basins. The Ecology-approved Stormwater AKART Analysis Report (January 2005) determined that "basic treatment" generally meets the requirement for AKART at STIA. However, a higher level of treatment for dissolved metals (i.e., enhanced) is required for stormwater discharges from the SDE4 sub-basin, which in routine NPDES monitoring has historically contained the highest concentrations of zinc.

The historic STIA sub-basins, along with associated impervious and pervious areas are summarized in Table 6.1. Detailed information on each of the sub-basins, as well as associated contaminant sources, BMPs, control technologies and anticipated removal efficiencies is presented in the Stormwater Engineering Report prepared for the Port (R.W. Beck and Parametrix 2006).

Sub-basin	Impervious	Pervious	Total
SDS1	11.60	1.80	12.68
SDE4	106.75	45.30	152.05
SDS3	249.53	213.48	463.01
SDS4	24.51	41.92	66.44
SDS5	4.97	13.45	18.42
SDS6	5.26	37.43	42.68
SDS7	2.56	1.74	4.30
SDN1	10.70	3.82	14.51
SDN2 ^b	31.80	10.52	42.32
SDN3	28.62	36.21	64.83
SDN4	12.97	28.44	41.41

 Table 6.1. Areas (in acres) of pervious and impervious areas associated with each subbasin.^a

^a Subbasin areas are those in existence in 2003 and as reported in the Stormwater Engineering Report (RW Beck, March 2006). Although basin areas will remain approximately the same, individual subbasin areas will vary with completion of the stormwater system retrofit.

^b SDN2 is typically diverted to IWS, and only discharges when rainfall exceeds the 6-month, 24-hr design criterion.

The sub-basins shown in Table 6.1 represent the basins present at the time the Stormwater Engineering Report was prepared. A variety of source control, water quality treatment and flow control BMPs were historically in place, and the Stormwater Engineering Report considered these as baseline in its analyses. Considerable upgrades to the STIA stormwater drainage system were subsequently identified in the Stormwater Engineering Report and other planning documents in order to effectively meet the 401 Certification, and NPDES flow control, water quality AKART and enhanced treatment requirements. As a result of these changes, a number of sub-basins are directed to single flow control or water quality treatment facilities. The final drainage configuration, including sub-basins that will be combined prior to discharge are shown in Table 6.2. Table 6.2 also shows the Instream Station (i.e., receiving environment) most closely associated with each of the sub-basin configurations. The sub-basin outfalls and associated in-stream stations are shown on Figure 1.

Discharging Retrofit	In-Stream
Sub-basins	Station
SDS1 + SDE4	DME
SDS3 + SDS5	NPOut
SDS4	NPOut
SDS6 + SDS7	NPOut
SDN1	RBOut
SDN2 + SDN3 + SDN4	RBOut

Table 6.2. Retrofit sub-basins discharging stormwater, and associated receiving environment stations used to establish site-specific water quality objectives.

Brief descriptions of the final configurations of the different sub-basins are summarized below. The summaries also include additional projected removals of zinc (beyond what is currently being achieved) that are anticipated from BMPs still being put into place (R.W. Beck and Parametrix 2006).

- Stormwater from SDS1 pollution generating surfaces (PGS) is currently treated with bioswales; additional bioswales are projected to further reduce zinc concentrations by 9%. The flow will then combine with SDE4, and the combined flow treated by additional bioswale prior to release. This bioswale is expected to further reduce zinc concentrations, but the amount was not estimated.
- Stormwater from the entire SDE4 sub-basin is treated by extended detention basin and media filtration, with a projected removal efficiency of 77%. The flow then combines with that from SDS1 and pass through additional bioswale prior to release. As noted above, the amount of removal associated with this additional bioswale was not estimated.
- Stormwater from SDS3 PGS is currently effectively treated by filter strips; there is a small opportunity to improve their effectiveness, but the estimated additional reduction in zinc concentrations is only 1%. In addition to existing filter strips, media catch basin inserts were installed in select locations. However, removal estimates are not available for this experimental BMP. Flows from the SDS3 sub-basin combine with those from SDS5 in the SDS3 Level 1 detention vault prior to discharge through

the existing S3 outfall. No additional pollutant removal from the Level 1 vault was characterized, but some may occur.

- Stormwater from SDS5 PGS has historically received partial treatment by a filter strip. Filter strip improvements and conversion of limited areas to IWS are anticipated to reduce zinc concentrations by an additional 3%. Treated water has been combined with SDS3 in the S3 detention vault prior to discharge through the existing S3 outfall. No additional pollutant removal from the Level 1 vault was characterized, but some may occur.
- Stormwater from the entire SDN1 sub-basin has been directed to a wet pond (N1 pond) prior to entering Lake Reba. It is anticipated that this will reduce zinc concentrations by 71%.
- Stormwater from the entire SDN2 sub-basin is pumped to IWS, except in cases where storm events exceed the design criterion of a 6-month 24-hr storm. Under those circumstances, excess flows will receive extended detention in Pond M prior to discharge to Lake Reba in combination with flows from SDN3 and SDN4, which are also directed to Pond M prior to release.
- Sub-basins SDN3 and SDN4 both currently meet AKART through use of filter strip BMPs. Discharge flows will be further directed to Pond M which will provide Level 2 detention prior to discharge to Lake Reba. The level of zinc removal associated with detention in Pond M was not estimated.
- SDS4 currently meets AKART, however, flows have been directed to a Level 1 detention pond prior to discharge. No additional pollutant removal from the Level 1 vault was characterized, but some may occur.
- The SDS6 and SDS7 sub-basins are currently being combined as part of the Third Runway redevelopment effort. Additional filter strips and bioswales are anticipated to further reduce zinc concentrations by 14% and 54% for SDS6 and SDS7, respectively. No additional pollutant removal from the Level 1 vault was characterized, but some may occur.

In addition to the historical sub-basins described above, stormwater will also be discharged into both Walker and Miller Creeks as part of the Third Runway expansion. The related sub-basins are summarized in Table 6.3, along with the associated receiving

waters. Stormwater from each of these sub-basins will be treated with Level 2 ponds, and discharges are anticipated to begin in November 2009.

Sub-basin	Impervious (acres)	Pervious (acres)	Total (acres)	Receiving Water
SDN3A	7.2	24.3	31.5	Miller Creek
SDW1A	25.6	44.5	70.1	Miller Creek
SDW1B	23.2	49.1	72.3	Miller Creek
SDW2	10.3	27.2	37.5	Walker Creek

 Table 6.3. Areas (in acres) of pervious and impervious areas associated with each of the new sub-basins.

6.2.2. SSWQO-Based Effluent Limit Calculations

Selection of Appropriate Hardness – In Table 6.4, below, the 10th percentile hardness is presented for each of the relevant receiving environment sites. Note that MC8th was selected as the most appropriate site on Miller Creek because it is located downstream of the anticipated outfall locations that are projected for activation in 2009. The hardness values were taken from data provided by the Port, as well as from the WER studies; in general, multiple values obtained from a site within a given day were averaged, as were the values for a given month in a given year, resulting in a single value for that month. Exceptions to this procedure are noted in discussions of the specific outfalls below.

Cita	10 th Percentile Hardness	
Site	(mg/L)	
DME	21.2	
MC8th	64.9	
RBOut	69.3	
NPOut	50.8	
Walker Creek	103.8	

Table 6.4. Summary of the 10th percentile hardness for each of the receiving environment sites.

Preliminary effluent limits are calculated below on the basis of the 10th percentile hardness values, and the dissolved / total translator based on the ratio of the dissolved and total LC50 estimates.

Combined SDS1 and SDE4 – A SSWQO for zinc (as dissolved) was derived for DME using a WER (3.86) calculated from 5 samples. Based on these same samples, the ratio of dissolved to total zinc was 0.78, ultimately resulting in a multiplier of 4.95 that can be used to adjust the generic Washington State zinc criterion and set a limit based on total zinc. Note that these data are presented in Table 5.4.

To calculate an SSWQO-based effluent limit, hardness concentrations measured in samples collected from DME between March 2004 and December 2007 (n=27) were evaluated, and the 10th percentile hardness concentration was 21.2 mg/L, as CaCO₃. Substituting this hardness value into the site-specific equation for zinc results in a SSWQO-based effluent limit value of 155.6 ug/L total Zn (i.e., the generic criterion of 31.43 ug/L at a hardness of 21.2 mg/L X 4.95).

SDS4, Combined SDS3 and SDS5, and Combined SDS6 and SDS7 – The SSWQO for zinc determined for NPOut was based on a WER of 2.27 and a translator of 0.57, resulting in a multiplier of 3.98 that can be used to adjust Washington's generic zinc criterion. Inspection of hardness values collected from NPOut between March 2004 and December 2007 (n=28) indicated that the 10th percentile hardness was 50.8 mg/L. At this hardness level, the SSWQO-based effluent limit would be 262.3 ug/L total Zn (the generic criterion of 65.9 ug/L at a hardness of 50.8 mg/L X 3.98).

SDN1 and Combined SDN2, SDN3 and SDN4 – The SSWQO for zinc at RBOut was derived from a WER of 1.00 and a translator of 0.58, resulting in a multiplier of 1.72. Hardness values were available from 23 samples collected between May 2004 and December 2007; the 10th percentile value was 69.3 mg/L. At this hardness, the SSWQO-based effluent limit would be 147.4 ug/L total Zn (the generic criterion of 131.7 at a hardness of 69.3 mg/L X 1.72).

SDN3A, SDW1A and SDW1B (Projected Discharges to Miller Creek) - The SSWQO for MC8th was derived from a WER of 1.57 and a translator of 0.63, resulting in a final multiplier of 2.49. The 10th percentile hardness was 64.9 mg/L, based on 10 samples collected between March 2004 and December 2007, and 10 additional samples collected

from storm events between March and May 2008. At this hardness, the SSWQO-based effluent limit would be 201.9 ug/L total Zn (the generic criterion of 81.1 at a hardness of 64.9 mg/L X 2.49).

SDW2 (*Projected Discharge to Walker Creek*) – The SSWQO for zinc at Walker Creek was derived from a WER of 0.91 and a translator of 0.71, resulting in a multiplier of 1.28. Hardness values were available from 14 samples collected between March 2004 and November 2007, and from 10 additional samples collected between March and May 2008. The 10th percentile value was 103.8 mg/L. At this hardness, the SSWQO-based effluent limit would be 154.5 ug/L total Zn (the generic criterion of 120.72 at a hardness of 103.8 mg/L X 1.28).

6.2.3. Projected Compliance

Where possible, these SSWQO-based effluent limits for zinc were used to estimate the approximate level of compliance that the Port would be expected to achieve given current and projected levels of zinc reduction with AKART and additional treatment. Probability distributions were constructed that show the zinc concentrations in samples collected from the various sub-basins based on NPDES data collected between October 2003 and November 2006. Note that the data used for SDN1 and SDE4 were collected from December 2004 through November 2006, and are considered more representative of existing water quality conditions in these sub-basins following a number of source-control activities such as rooftop painting and gutter cleaning (R.W. Beck and Parametrix 2006). These distributions were then compared against the preliminary effluent limits to estimate the percentage of samples that would be expected to meet the limits.

The probability distributions for each of the sub-basins are summarized in figures that show the associated SSWQO-based effluent limits, as well as the 2005 benchmark effluent limit for zinc (i.e., 117 ug/L) contained in the Port's current NPDES permit, which is identical to the benchmark provided in USEPA's 2000 Multi-Sector General Permit and the Washington State's current Industrial Stormwater General Permit. Finally, each figure also shows the projected zinc concentrations assuming the additional removal efficiencies associated with the BMPs in place when redevelopment is completed (see Section 6.2.1 and the Engineering Report). Note that the removal efficiencies were considered conservative estimates, and may also vary depending on actual zinc concentration, duration of storm event, intervals between storms, and so on. Again, the reader is referred to the Engineering Report for detailed analysis and projections of removal efficiencies (R.W. Beck and Parametrix 2006).

Combined SDS1 and SDE4 will discharge into East Des Moines Creek upstream of DME. Based on existing data, SDS1 would have historically met the SSWQO-based effluent limit (155.6 ug/L) approximately 80% of the time. Full implementation of AKART is expected to further reduce zinc concentrations by an estimated 9%, which will result in a modest improvement in compliance (Figure 2). With no additional treatment, SDE4 would have historically met the SSWQO-based effluent limit approximately 80% of the time, but implementation of enhanced treatment is expected to reduce zinc concentrations by 77%, achieving compliance at least 95% of the time (Figure 3). Notably, enhanced treatment will also bring SDE4 into compliance with the current effluent limit (i.e., 117 ug/L) approximately 95% of the time. Overall compliance of the combined discharge will be affected by differences in sizes of each of the sub-basins, and their relative contributions during individual storm events. In addition, concentrations in the combined discharge should be further reduced by flow through a vegetated swale prior to discharge, although the associated reduction has not been estimated and is not included in this compliance analysis.

Combined SDS3 and SDS5 will discharge into Des Moines Creek through Northwest Ponds. Based on existing data, SDS3 would have historically met the SSWQO-based effluent limit of 262.3 ug/L all of the time; notably, SDS3 historically met the current limit of 117 ug/L, as well. Full implementation of AKART will provide an estimated 1% additional reduction in zinc, and a marginal improvement in compliance (Figure 4). Zinc concentrations are similar in SDS5, and should be in compliance with both the SSWQO-based and current effluent limits virtually all the time (Figure 5). Overall compliance of the combined discharge will be affected by relative contributions of each sub-basin during individual storm events, but should still approach 100%, based on the historical performance of each of the discharges.

SDS4 will discharge into Des Moines Creek through Northwest Ponds. Based on existing data, SDS4 would have historically met the both the historical and SSWQO-based effluent limits virtually all of the time (Figure 6). Since, no additional BMPs are being constructed, the basin is expected achieve a similar level of compliance in the future.

Combined SDS6 and SDS7 will also discharge into Des Moines Creek via Northwest Ponds. Based on existing data, SDS6 runoff would have historically met the current and SSWQO-based effluent limits virtually all of the time (Figure 7). Based on historical data, SDS7 would have met the SSWQO-based effluent limit essentially all of the time, and met the existing limit approximately 95% of the time (Figure 8). BMPs incorporated into the Third Runway reconstruction of the SDS6 and 7 sub-basins are expected to reduce zinc concentrations by 14% and 54%, respectively. The projected reduction in zinc concentrations should bring SDS7 into 100% compliance with both the historical and SSWQO-based effluent limits. Given that the expected performance of both of the individual discharges is well-within the proposed current and SSWQO-based effluent limits, the combined discharges should reflect a similar level of compliance.

SDN1 will continue to discharge into Lake Reba. Based on existing data, SDN1 would have historically met the SSWQO-based effluent limit of 147 ug/L approximately 70% of the time, and the current limit about 60% of the time. However, the estimated additional reduction in zinc concentrations associated with detention in the N1 Level 2 pond prior to discharge should improve compliance with both limits to virtually 100% (Figure 9).

Combined SDN2, SDN3 and SDN4 will discharge into Lake Reba. Based on existing data, SDN3 would have historically met the SSWQO-based effluent limit of 147 ug/L, as well as the current limit, between 90 and 95% all of the time (Figure 10). Historical zinc concentrations were substantially lower in SDN4, and would have achieved compliance with both limits essentially all of the time (Figure 11). Both of these sites are already essentially compliant with AKART, but these numbers do not reflect any additional removals associated with the detention pond, which should further reduce zinc concentrations. Ultimately, the combined discharges should still be in compliance virtually all of the time, based on the performance of the individual discharges. The impact of SDN2 on the quality of the combined discharge is more difficult to predict. Zinc concentrations tend to be higher at SDN2 (Figure 12) than at SDN3 or SDN4, but flows from SDN2 will be discharged through the combined outfall only during storm events that exceed the water quality design criteria (i.e., 6-month 24-hr storm), and then only after passing through Pond M. In addition, the SDN2 sub-basin is smaller than the combined SDN3 and SDN4 sub-basins, which will minimize its impact on the overall discharge. Given these uncertainties, it is problematic to predict the effect of SDN2 on the combined discharge, but it is expected to be small given the relative infrequency of events and low discharge volume. For example, during a 38-month period between October 2003 and November 2006, SDN2 discharged a total of 20 times, with a median volume of 3500 gallons.

One important observation that can be made from the figures is a comparison of the projected zinc concentrations with the SSWQO-based effluent limits and the benchmark value for zinc contained in the Port's current NPDES permit. In all cases, the SSWQO-based limits are higher than the Port's current benchmark for zinc in discharges contributing to DME, NPOut and RBOut. Moreover, the expected level of compliance is not significantly different regardless of whether the current or SSWQO-based limit is applied.

6.2.4. Alternative Limit Calculation

In the above approach, the 10th percentile hardness was used to derive SSWQO-based effluent limits and estimate the approximate level of compliance that the Port would be expected to achieve given current and projected levels of zinc reduction with AKART and additional treatment. However, that approach seems unnecessarily restrictive in that the 10th percentile hardness is not representative of seasonal variations in hardness that occur as a function of stormwater discharges. Under these circumstances, the Port could be found in violation if they were discharging at higher hardness, even though the zinc concentrations were not exceeding the site-specific objective at that particular hardness. Thus, the Port could be in violation at 90% of the hardness values (i.e., samples), even though there would not be any exceedences of the actual objective, and no associated environmental risk.

To address this issue, the Port proposes that the SSWQO-based effluent limits be set with flexible hardness. Using this approach, seasonal hardness values or instream hardness (e.g., at DME, NPOut and RBOut) would be measured at the same time samples are collected for zinc analysis, and compliance would be determined on the basis of total zinc measured and the hardness at the time the sample was collected. This approach will ensure that environmental concerns are addressed by not exceeding the respective site-specific objectives, while avoiding inappropriate violations that do not reflect actual exceedences that could result in impairment.

7. OBSERVATIONS ON DEVELOPMENT OF SSWQOS AND ASSOCIATED EFFLUENT LIMITS FOR ZINC

Development of SSWQOs for zinc was more complex than with copper. This was due to somewhat greater variability in the results, as well as the interaction between pH and toxicity. Since the WERs tended to be smaller than those observed with copper, these factors made it problematic to clearly identify site-specific differences in bioavailablility. The following discussion is aimed at placing these factors into proper context.

Since the WERs tended to be relatively small compared with the copper data, and in some cases, were even <1, it is important to consider these results in the context of variability typically associated with toxicity tests and analytical chemistry results. Conversely, because the copper WERs tended to be greater, they subsumed variability associated with analytical and toxicological testing. To help place the zinc results in context, Table 7.1 below summarizes data from zinc toxicity tests conducted in moderately hard (hardness: 80 to 100 mg/L) laboratory water in one laboratory. Based on 16 test results, the LC50s ranged between 36.1 and 299.1 ug/L, with an average of 130.9 ug/L. All values were based on measured dissolved zinc concentrations, so the results also reflect analytical variability, as well as intra-laboratory test variability.

Parameter	Value
Mean LC50 (ug/L)	130.9
Std. Dev. (ug/L)	73.6
CV (%)	56.2
Max (ug/L)	299.1
Min (ug/L)	36.1

Table 7.1. Zinc toxicity tests in moderately hard water within one laboratory

In general, values would be expected to fall within one standard deviation of the mean (plus or minus) between 60 and 70 percent of the time, and outside of that range approximately 35 percent of the time. Thus, using the data in the above table as an example, +/- 1SD around the average LC50 would give WERs ranging from approximately 0.4 to 1.6; i.e., from somewhat less to somewhat greater than "1". Using this as an example, most of the copper WERs exceeded the upper limit of this range,
implying that there is a clear site-specific decrease in bioavailability associated with the streams tested. Conversely, most of the zinc WERs were within this range, suggesting no difference between bioavailability in laboratory or site water. Alternatively, if the WERs were consistently below this range, the data would imply that toxicity was greater in the site waters, and a more protective standard would be appropriate. Thus, in evaluating these data, the inherent level of variability between the LC50s, as well as the central tendency, is key to assessing whether the data support development of a site-specific criterion, or whether they merely reflect oscillations (variability) around the existing norm (i.e., a WER of "1"). Given that the WERs tended to be either within this range, or slightly higher, these data suggest that the existing criterion is an appropriate measure of bioavailability and toxicity in the streams tested.

pH turned out to be a confounding factor with respect to the toxicity of zinc. It was demonstrated that increases in pH contributed strongly to the toxicity of zinc, particularly as the pH approached and exceeded 8. Typically, the pH of site water samples tended to drift higher over time, beginning with the time they were actually sampled. While the potential for change in pH is a function of water chemistry, the actual degree of change is affected by site-specific or laboratory test conditions. In the laboratory, the increase in pH reflects surface to volume relationships in the test containers, sample agitation to achieve mixing and equilibration of gases, and overall simplified conditions associated with laboratory exposures. Conversely, actual receiving environments exist in dynamic conditions, with much different surface to volume relationships than observed in laboratory studies, and also with continuing inputs from substrate chemistry, natural decay and respiration processes, and groundwater inputs that would act to maintain a lower pH.

As part of this study, equations were developed to adjust the toxicity values (i.e., LC50s) to compensate for the increase in pH that occurred in the samples over time. As shown in Table 7.2 below, the lowest pH values were observed as the samples were collected, typically increased at sample receipt, and tended to be slightly higher in the test containers after 24 hr of exposure compared with the time the dilutions were prepared.

	Site	Date	Sample	Nautilus	Fresh Test	Old Test
			Collection	Receipt	Solutions	Solutions
	Miller Creek	3/25/07	6.78	7.65	7.7-7.9	7.8-7.9
	MC8th	3/26/07	6.83	7.67	7.7-7.9	7.8-8.0
	RBOut	3/26/07	6.90	7.56	7.6-7.9	8.0-8.1
	NPOut	3/25/07	7.13	7.40	7.5-7.6	7.8-7.9
	Walker Creek	11/11/07	7.19	7.81	8.1-8.2	7.9-8.0

Table 7.2. pH values from sample collection time to test renewal/completion

From the perspective of environmental relevance, it is important to place the increase in pH into context with actual receiving environment conditions. In other words, is the increase in pH a laboratory artifact, or is it a factor that needs to be taken into consideration when developing SSWQOs? The pH data at the time of sample collection presented above are all approximately pH 7, suggesting that lower pH values are more representative of actual environmental conditions. This observation is supported by the following field data collected downstream of STIA outfalls as part of the NPDES monitoring program; mean pH values were: RBOut: 6.9 (n=25); NPOut: 7.0 (n=40); DME: 7.1 (n=56); Miller Creek: 7.2 (n=23); Walker Creek: 7.2 (n=53).

Overall, these data suggest that observations made under laboratory conditions need to be validated under actual receiving environment conditions. In this case, pH measured in the receiving environment tends to be much lower than the values attained in the laboratory exposures. Other contaminants, most notably ammonia, also exhibit pHsensitive responses with respect to toxicity, and typically need to be considered in the context of field pH values before concluding that laboratory measures of toxicity are valid and representative of potential adverse effects in the receiving environment.

In considering implementation of interim effluent limits, the limits derived in Section 6.2.2 are all greater than the current limit of 117 ug/L total zinc. In addition, despite some variation from outfall to outfall, discharge concentrations of zinc have generally been at or below this current limit (see Section 6.2.3), so having higher limits does not appreciably alter the Port's probability of compliance. These data suggest that it may be worthwhile to consider applying the current limit (i.e., the 117 ug/L benchmark) as an

interim value until future outfalls become fully operational and conditions associated with existing subbasins stabilize.

8. MONITORING AND FOLLOW-UP ACTIVITIES

Although the preceding analysis suggests that the Port should be able to comply with both the proposed SSWQO-based effluent limits, as well as the current effluent limit on a consistent basis, the Port notes that there is uncertainty associated with projecting the efficiency of BMPs designed to treat stormwater, as well as predicting how well the new systems will work under a variety of storm conditions once build-out is complete. Consequently, monitoring will continue to be used as a tool for verifying the performance of the Port's stormwater program, as well as ensuring that the receiving environment is properly protected.

Currently, the Port has a robust well-tailored stormwater monitoring program in place. Program elements include monitoring concentrations of constituents of concern in the discharges, and conducting acute toxicity tests on the discharges and sublethal toxicity tests on samples from the receiving environment, with provision for conducting Toxicity Identification Evaluations if samples exhibit toxicity. In addition, the benthic macroinvertebrate community is currently being monitored in the receiving environment as part of the CRWS and 401 Certification program. An enhancement to this current program would be to substitute *in situ* early life stage tests with salmonids at receiving environment stations during fall and spring for the current laboratory-based rainbow trout embryo sublethal toxicity test. This component would directly address the current level of public and regulatory concerns regarding potential impacts of stormwater on salmonids.

9. SUMMARY

USEPA and Ecology guidance was used to develop site-specific water quality objectives (SSWQOs) for zinc at several sites that receive stormwater drainage from STIA facilities. Using the water-effect ratio approach, WERs were derived for each of the sites, and used to adjust the generic State of Washington zinc criterion to achieve SSWQOs for each site. A comparison of species sensitivity between *C. dubia* and rainbow trout suggested that the SSWQOs derived from data obtained with *C. dubia* should generally be protective of salmonids, but the level of protection is not as great as observed with copper. SSWQO-

based effluent limits (as total zinc) were subsequently derived using an approach that assumed no dilution, but incorporated a site-specific ratio of dissolved-to-total zinc and the 10th percentile hardness associated with the nearest receiving environment station. A comparison of these limits with historic and projected zinc discharge concentrations suggests that the Port should be in compliance most of the time. Moreover, the level of compliance is essentially the same for the SSWQO-based limits as with the zinc limit currently in place, which is lower than the calculated site-specific limits. However, use of the 10th percentile hardness presents an unnecessary constraint in that most of the samples will have higher hardness, and could have higher zinc levels without actually causing impairment. Consequently, the Port proposes that the effluent limits incorporate variable hardness, as represented by actual values associated with each storm/sampling event. Thus, actionable violations would be associated with exceedences potentially associated with environmental harm, rather than artifacts of variability in hardness characteristic of stormwater events. Finally, implementation of a robust and comprehensive monitoring program focused on the discharges and the receiving environment will provide a means of assessing the performance of the SSWQOs, as well as STIA's stormwater discharge program.

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FIGURES





Figure 2

Nautilus Environmental























→ SDN1 ZN → 71% Reduction

Figure 9











APPENDIX A

Hardness Values

Nautilus Environmental August 2006

Common Site Hardness Storm Name (mg/L)			Common Site Hardness			Common Site Hardness		
		Storm Date	Name	(mg/L)	Storm Date	Name	(mg/L)	Storm Date
DME	30.0	3/26/2004	NP-Out	92.0	3/26/2004	REBA-Out	112.0	5/27/2004
DME	40.0	5/27/2004	NP-Out	98.0	5/28/2004	REBA-Out	60.0	11/1/2004
DME	38.0	8/8/2004	NP-Out	112.0	8/8/2004	REBA-Out	128.0	1/6/2005
DME	40.0	9/12/2004	NP-Out	52.0	11/1/2004	REBA-Out	87.2	5/10/2005
DME	32.0	10/10/2004	NP-Out	80.0	1/6/2005	REBA-Out	128.0	7/10/2005
DME	48.0	12/6/2004	NP-Out	72.0	7/10/2005	REBA-Out	135.6	8/29/2005
DME	36.0	1/6/2005	NP-Out	107.0	9/10/2005	REBA-Out	125.0	9/10/2005
DME	34.0	3/21/2005	NP-Out	102.0	10/6/2005	REBA-Out	127.5	10/6/2005
DME	42.0	7/10/2005	NP-Out	57.9	11/2/2005	REBA-Out	109.5	11/2/2005
DME	37.0	9/10/2005	NP-Out	72.0	12/3/2005	REBA-Out	99.7	12/1/2005
DME	31.9	10/6/2005	NP-Out	36.0	1/21/2006	REBA-Out	75.8	1/4/2006
DME	26.3	11/2/2005	NP-Out	94.0	2/23/2006	REBA-Out	137.0	2/23/2006
DME	31.9	12/1/2005	NP-Out	67.9	3/8/2006	REBA-Out	110.5	3/8/2006
DME	17.7	1/5/2006	NP-Out	99.8	4/8/2006	REBA-Out	110.0	4/8/2006
DME	32.6	2/23/2006	NP-Out	107.8	5/21/2006	REBA-Out	170.0	5/21/2006
DME	27.1	3/8/2006	NP-Out	40.3	6/2/2006	REBA-Out	70.0	6/1/2006
DME	22.6	4/8/2006	NP-Out	138.0	9/13/2006	REBA-Out	157.0	9/13/2006
DME	22.7	5/21/2006	NP-Out	101.0	10/14/2006	REBA-Out	144.6	10/14/2006
DME	24.0	10/14/2006	NP-Out	67.0	11/13/2006	REBA-Out	62.7	11/13/2006
DME	33.7	11/13/2006	NP-Out	65.6	12/11/2006	REBA-Out	97.6	12/11/2006
DME	19.1	12/11/2006	NP-Out	85.0	2/7/2007	REBA-Out	44.6	1/6/2007
DME	15.4	1/6/2007	NP-Out	140.0	4/17/2007	REBA-Out	112.6	2/14/2007
DME	28.0	2/7/2007	NP-Out	48.0	3/26/2007	REBA-Out	160.0	4/17/2007
DME	64.0	4/17/2007	NP-Out	91.0	5/22/2007	REBA-Out	79.0	3/25/2007
DME	48.0	6/10/2007	NP-Out	78.0	9/5/2007	REBA-Out	135.0	5/22/2007
DME	68.4	11/15/2007	NP-Out	64.0	10/2/2007	REBA-Out	115.0	8/21/2007
DME	50.7	12/2/2007	NP-Out	85.2	11/15/2007	REBA-Out	160.0	9/19/2007
			NP-Out	99.0	12/15/2007	REBA-Out	132.0	10/19/2007
						REBA-Out	129.8	11/15/2007
						REBA-Out	117.0	12/15/2007
10th percentile	21.2		10th percentile	50.8		10th percentile	69.3	
median	32.6		median	85.1		median	116.0	
n	27.0		n	28.0		n	30.0	

Common Site Hardness Name (mg/L)		Storm Date	Common Site Name	Hardness (mg/L)	Storm Date	
Walker Ck	134	6/11/07	MC8th	76	3/26/2004	
Walker Ck	124	9/6/07	MC8th	94	5/27/2004	
Walker Ck	108	10/1/07	MC8th	77	8/8/2004	
Walker Ck	132	11/11/07	MC8th	64	10/10/2004	
Walker Ck	112	11/28/07	MC8th	96	3/21/2005	
Walker Ck	102	3/26/2004	MC8th	48	1/18/2006	
Walker Ck	116	5/27/2004	MC8th	84	3/25/2007	
Walker Ck	114	8/8/2004	MC8th	87	5/22/2007	
Walker Ck	108	8/23/2004	MC8th	122	9/19/2007	
Walker Ck	108	10/10/2004	MC8th	102.3	12/15/2007	
Walker Ck	112	3/21/2005	MC8th	98	3/13/2008	
Walker Ck	114	7/10/2005	MC8th	70	3/23/2008	
Walker Ck	72	1/21/2006	MC8th	90	3/25/2008	
Walker Ck	114	5/22/2007	MC8th	65	3/26/2008	
Walker Ck	120	3/13/2008	MC8th	75	3/28/2008	
Walker Ck	110	3/23/2008	MC8th	110	4/4/2008	
Walker Ck	130	3/25/2008	MC8th	120	4/14/2008	
Walker Ck	120	3/26/2008	MC8th	88	4/28/2008	
Walker Ck	94	3/28/2008	MC8th	130	5/13/2008	
Walker Ck	120	4/4/2008	MC8th	120	5/20/2008	
Walker Ck	130	4/14/2008				
Walker Ck	120	4/28/2008				
Walker Ck	130	5/13/2008				
Walker Ck	120	5/20/2008				

10th percentile	103.8	10th percentile	64.9
median	115.0	median	89.0
n	24.0	n	20.0

APPENDIX B

Relationships Between Hardness, pH and the Toxicity of Zinc

Relationships Between Zinc Toxicity, Hardness and pH, and Their Effect on Calculating Water Effect Ratios

Background

As part of the process of developing site-specific objectives for zinc, comparisons are made between the toxicity of zinc in site water and toxicity observed in laboratory water. Up to this point, laboratory water has been tested only at one hardness, and that value extrapolated to different hardnesses, depending on the hardnesses of the site water tested. This extrapolation uses an equation based on the relationship between zinc toxicity and hardness derived by the USEPA. However, the WER values obtained have been inconsistent and do not necessarily correspond with the expected relationship between hardness and toxicity. Initially, two hypotheses were developed to explain this discrepancy. The first hypothesis considered the possibility that the USEPA equation might not provide a good fit of the hardness:toxicity relationship within the range of hardnesses of interest in this study (i.e., between 10 and 100 mg/L). In other words, the USEPA equation is designed to predict toxicity across a much wider range of hardnesses, and it is possible that achieving a good fit across a wide range of values might be at the cost of not having as good a fit within smaller areas of the curve. An alternative hypothesis was that another water quality parameter was affecting the toxicity of zinc and, in the process, reducing the effect of hardness. Based on a review and analysis of test results, this parameter was tentatively identified as pH.

EVALUATION OF HARDNESS EQUATION

To evaluate the first hypothesis, we ran a series of tests at different hardnesses (10 - 100 mg/L), but found that increasing hardness did not have the expected result of consistently reducing toxicity as the hardness increased. However, review of the data suggested that pH might be a confounding factor, as pH increased as hardness increased. Thus, if increasing pH increased the toxicity of zinc, it would counter the expected decrease in toxicity as hardness increased.

To eliminate the effect of pH, we performed a subsequent study in which pH was held constant using a CO_2 atmosphere over the test containers, and compared the observed relationship between hardness and toxicity to the relationship predicted by the USEPA equation. With the pH held at approximately 7.0, the toxicity data exhibited a strong linear relationship with hardness ($R^2 = 0.92$), suggesting that toxicity was closely related to hardness (Figure 1). Moreover, comparing our results with those predicted by the USEPA equation resulted in similar values, generally within 10% across the range of hardnesses tested.

The similarity in results between the two equations suggests that refining the USEPA hardness equation will do little to improve our ability to predict the toxicity of zinc, and provides further evidence that pH is a major factor controlling toxicity. Moreover, the fact that the two hardness equations provided similar results is encouraging in that it indicates that the relationship between hardness and toxicity is robust, provided that pH is controlled.



Figure 1. Relationship between hardness and toxicity with the pH held constant.

EFFECT OF PH

The next step was to determine if we could incorporate pH into a predictive equation. This is a bit more complicated than it might first appear in that the degree of effect appears to increase sharply as the pH approaches 8, instead of being constant for a given incremental change in pH. Thus, the relationship between pH and toxicity appears to be an exponential function, with toxicity increasing more rapidly as pH increases beyond 8. Using the relationship between hardness and toxicity to establish an "expected" level of toxicity (with toxicity being characterized as an LC50), we then used the ratio between the expected and actual LC50 values to characterize the departure from expected. Assuming that pH was responsible for the departure from expected value, we would expect to see larger ratios associated with higher pH

values, and should be able to describe the ratios as a function of pH. This process resulted in an equation that describes the ratio between expected and actual LC50 values as an exponential function of pH; the R² for that equation is 0.91, which suggests that increasing pH is strongly associated with increasing departure from the expected relationship between hardness and the toxicity of zinc. These data are shown in Figure 2.



Figure 2. Relationship between pH and the ratio of the predicted and observed LC50 values.

If the "pH adjustment" is used to further adjust the LC50 values that would be expected based on hardness, we get very close agreement with the expected and actual LC50 values obtained ($R^2 = 0.94$). The fit of this relationship can be compared with the predictive relationship between hardness and toxicity with no adjustment or control of pH ($R^2 = 0.54$). These relationships are shown in Figures 3 and 4.



Figure 3. Comparison of actual LC50s and LC50s predicted as a function only of hardness.



Figure 4. Comparison of actual LC50s and LC50s predicted as a function of hardness and pH.

Summary

These data suggest that the toxicity of zinc can be described as a function of hardness and pH, and that pH exerts an increasingly strong effect as it rises above 8. This finding

further suggests that we should be able to refine our predictions of toxicity in laboratory water to incorporate the pH of the samples. In addition, it will important to perform the laboratory tests in a way that minimizes pH changes beyond what might occur in the actual receiving environment.