SITE SPECIFIC METAL CRITERIA DEVELOPED USING KENTUCKY DIVISION OF WATER PROCEDURES

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ABSTRACT

Alternative limits for Cu, Ni, Pb, and Zn were developed for treated wastewater from four outfalls at a Gaseous Diffusion Plant. Guidance from the Kentucky Division of Water (KDOW) was used to (1) estimate the toxicity of the effluents using water fleas (*Ceriodaphnia dubia*) and fathead minnow (*Pimephales promelas*) larvae; (2) determine total recoverable and dissolved concentrations of Cu, Pb, Ni, and Zn ; (3) calculate ratios of dissolved metal (DM) to total recoverable metal (TRM); and (4) assess chemical characteristics of the effluents. Three effluent samples from each outfall were collected during each of six test periods; thus, a total of 18 samples from each outfall were evaluated for toxicity, DM and TRM. Subsamples were analyzed for alkalinity, hardness, pH, conductivity, and total suspended solids. Short-term (6 or 7 d), static renewal toxicity tests were conducted according to EPA methodology.

Ceriodaphnia reproduction was reduced in one test of effluent from Outfall A, and effluent from Outfall B was acutely toxic to both test species during one test. However, the toxicity was not related to the metals present in the effluents. Of the 18 samples from each outfall, more than 65% of the metal concentrations were estimated quantities. With the exception of two total recoverable Cu values in Outfall C, all metal concentrations were below the permit limits and the federal water quality criteria. Ranges of TR for all outfalls were: Cd, <0.1–0.4 μg/L; Cr, 1.07–3.93 μg/L; Cu, 1.59–7.24 μg/L; Pb, <0.1–3.20 μg/L; Ni, 0.82–10.7 μg/L, Zn, 4.75–67.3 μg/L.

DM:TRM ratios were developed for each outfall. The proportion of dissolved Cu in the effluents ranged from 67 to 82%; the proportion of dissolved Ni ranged from 84 to 91%; and the proportion of dissolved Zn ranged from 74 to 94%. The proportion of dissolved Pb in the effluents was considerably lower (37–51%). TRM and/or DM concentrations of Cu, Ni, Pb, or Zn differed significantly from outfall to outfall but the DM:TRM ratios for Cu, Ni, and Pb did not.

Through the use of the KDOW method, the total recoverable metal measured in an effluent is adjusted by the proportion of dissolved metal present. The resulting alternative total recoverable metal concentration is reported in lieu of the measured total recoverable concentration for determining compliance with permit limits. For example, the monthly average permit limit for Pb in Outfall B (3 μg/L) was exceeded at the Gaseous Diffusion Plant. Through the use of the KDOW method for calculating an alternative total recoverable metal concentration, 4.98 μg Pb/L in Outfall B would be reported as 3.00 μg/L, a difference of > 39%. Thus, the alternative, calculated total recoverable metal concentration provides the discharger with a "cushion" for meeting permit limits.

KEYWORDS

Site specific criteria, metals, toxicity, *Ceriodaphnia*, fathead minnows, *Pimephales*

INTRODUCTION

Water quality criteria (WQC) established by the U.S. Environmental Protection Agency (EPA) to protect aquatic life are estimates of the highest concentration of a pollutant that can be present while still adequately protecting species in an aquatic community. National ambient WQC were derived from laboratory toxicity tests. However, the bioavailability and/or toxicity of most metals is strongly affected by factors such as the types and concentrations of dissolved and particulate organic matter in the water, pH, alkalinity, hardness, temperature, and metal-binding dissolved constituents. These factors are not routinely incorporated into present ambient WQC; therefore, the WQC

may be underprotective or overprotective of aquatic biota.

One issue under debate in the scientific and regulatory communities is whether, and how, to use dissolved metal concentrations or total recoverable metal concentrations in setting water quality standards. In May 1995 the EPA issued a stay of federal water quality criteria for metals (40 CFR Part 131). It is now the policy of the EPA's Office of Water that dissolved metal, rather than total recoverable metal, better approximates the fraction of waterborne metals that are biologically available to aquatic organisms. The use of dissolved metal concentrations is now recommended as the best approach to setting and measuring compliance with water quality standards.

In 1985, the EPA provided guidelines for deriving site-specific water quality criteria (Stephan et al. 1985). Three alternative approaches were identified in these guidelines: (1) the recalculation procedure, which accounts for differences in sensitivity between resident species and species used to derive national criteria; (2) the indicator species procedure [also known as the water-effect ratio (WER) method], which accounts for differences in toxicity in tests conducted in site water vs laboratory water; and (3) the resident species method, which accounts for differences in the sensitivities of resident species and differences in toxicity attributed to water quality factors (Spehar and Carlson 1983).

In 1994, the EPA issued interim guidance on the determination and use of the WER method for deriving site-specific water quality standards (EPA 1994a). The water-effect ratio method is an approach that can be used by dischargers who want higher permit limits for metals. Through the use of the WER method, a site-specific criterion is derived by dividing the toxicity endpoint (i.e., LC_{50} or EC_{50}) obtained by testing with the site water by the endpoint obtained by testing with the laboratory dilution water. Either a total recoverable-metal or a dissolved-metal WER can be calculated. A WER must be determined individually for each metal at each site. In other words, a WER calculated for one metal cannot be extrapolated to another metal, or from one effluent to another, or from one site water to another.

In May 1996, the Kentucky Division of Water (KDOW) issued *Procedures to Facilitate Alternative Metal Limits* as a lower-cost alternative to the WER method for deriving site-specific metals limits. The procedure requires demonstration, through chemical-specific analyses and toxicity testing, that an effluent is not toxic due to the presence of the metal in question. By means of the KDOW method, the amount of total recoverable metal measured in the effluent is adjusted by the dissolved metal:total recoverable metal (DM:TRM) ratio. A DM:TRM ratio is derived for each metal, and at each outfall. The result is the calculated total recoverable metal (TRM) concentration which can be reported in lieu of the measured TRM concentration for a particular metal. This calculated concentration may then be reported for determining compliance with the TRM permit limits. This approach was used to determine whether alternative TRM concentrations for Cd, Cr, Cu, Ni, Pb, and Zn in the effluents from four outfalls located at a Gaseous Diffusion Plant could be calculated (Phipps and Kszos 1996).

METHODS AND MATERIALS

Effluent Samples

Three effluent samples from each outfall (A, B, C, and D) were collected during each of the six test periods (October 1996 to August 1997); thus, over the course of the study, a total of 18 effluent samples from each outfall was evaluated for toxicity and metals concentrations. Samples were collected using automatic portable sampling equipment (ISCO model 3700C). Samples for toxicity tests were collected in 4 gal cubitainers then chilled and stored at $4 \pm 2°C$.

Samples for metals analysis were collected using EPA "clean" sampling and processing techniques within the limitations of the sample collection method (EPA 1995a). Contamination control included (1) decontaminating sampling equipment; (2) replacing equipment tubing; (3) eliminating metal-contact surfaces; (4) using sterilized, pre-rinsed disposable filter units; (5) double-bagging pre-cleaned sampling equipment and sample containers; (6) wearing clean, nontalc vinyl or latex gloves; and (7) filtering and preserving the effluent samples within a designated clean area.

The metals samples were collected in new, clean 125- or 250-mL high-density polyethylene bottles. After collection, the samples were acidified immediately with trace-metals grade HNO_3 to pH<2 and maintained at 4 ± 2°C during storage and shipment to the analytical laboratory.

Analysis of Physico-chemical Parameters

Subsamples of each effluent sample were analyzed for alkalinity, hardness, pH, conductivity, and total suspended solids. Standard EPA-recommended procedures were used to measure pH, conductivity, dissolved oxygen, alkalinity, and hardness (EPA 1979). American Public Health Association (APHA) method 2540D was used for measurements of total suspended solids (TSS).

Metal concentrations were determined by inductively coupled plasma–mass spectrometry (ICP-MS; Method 200.8). The minimum detection limits were 0.1 μg/L for Cd, Pb, and Ni and 1.0 μg/L for Cr, Cu, and Zn.

Toxicity Test Methods

Short-term, static renewal toxicity tests with *Pimephales promelas* and *Ceriodaphnia dubia* were conducted according to standardized technical procedures which are based on EPA methodology (Methods 1002.0, *C. dubia* survival and Reproduction Test and 1000.0, fathead minnow larval survival and growth test; Lewis et al. 1994). Six toxicity tests of the four outfalls were conducted from October 1996 to August 1997. The two toxicity test procedures have been shown to be effective in assessing the toxicity of a variety of pollutants (Mount and Stephan 1969; Benoit and Holcombe 1977; Carlson et al., 1986; Belanger and Cherry 1990; Kszos et al. 1992; Stewart 1996. The *Ceriodaphnia* and fathead minnow tests were conducted concurrently with a series of effluent dilutions—6, 12, 25, 50, and 100%. The toxicity tests were initiated so as not to exceed a sample holding time of 36 h. The results of these tests were used to determine compliance with the Kentucky Pollutant Discharge Elimination System permit toxicity limits.

Ceriodaphnia tests were always initiated with neonates (≤24 h old, all born within 8 h of each other) obtained from cultures maintained by the Aquatic Toxicology Laboratory. The tests were conducted with 30-mL plastic disposable beakers, each containing at least 15 mL of water. Replicate test beakers (10 per effluent dilution) containing one daphnid per replicate were used in every test for each of the five effluent dilutions. A negative control (consisting of dilute mineral water augmented with trace metals) was included with every test. Beakers were randomized at the beginning of the test period by means of a randomizing template derived from a random-numbers table. Neonates were fed 50 μL of a yeast-Cerophyl®-digested trout chow mixture and 100 μL of a suspension of green alga cells (*Selenastrum capricornutum*) daily after water renewal. The beakers were placed in an environmentally controlled chamber to maintain a test temperature of 25 ± 1°C and a photoperiod of 16 h light:8 h dark. Survival was recorded daily, and any dead organisms were removed and noted. When young were produced, they were counted and discarded. Toxicity tests were terminated when ≥60% of the surviving control organisms had produced three broods. For each test, the measured responses were survival and the mean number of young produced per female.

The fathead minnow tests were always initiated with larvae (≤48 h old) obtained from Aquatic BioSystems, Fort Collins, Co. The larvae were acclimated to test temperature (25 ± 1°C) prior their use in a test. Each fathead minnow test used four replicates per effluent dilution, with 10 larvae per replicate. Two groups of five larvae were randomly placed into each test beaker; the beakers were then randomly assigned to positions in a temperature-controlled water bath. An automatically controlled photoperiod of 16 h light:8 h dark was maintained. The minnow larvae were fed 100 μL (approximately 600–900) of newly hatched brine shrimp nauplii (*Artemia*) twice daily. The larvae were allowed to feed at least 2 h before the test water was renewed; they were fed again 5–7 h after water renewal. Uneaten *Artemia*, dead larvae, and other detritus was removed by means of a siphon hose just before water renewal. Live larvae inadvertently removed during the siphoning process were returned to their respective test beaker, and the incident was noted. The number of minnow larvae surviving in each test beaker was recorded daily. At the end of the 7-d test period, the larvae were dried at 100 ± 5°C and weighed to estimate growth.

In an effort to determine if any observed toxicity to fathead minnow larvae or *Ceriodaphnia* could be due to metals, we treated a subsample of full-strength effluent with a complexing ligand, ethylenediaminetetraacetic acid (EDTA). Metals that complex tightly to ligands are generally not readily bioavailable. Thus, such metals are less toxic than their free-metal counterparts to aquatic biota (Allen et al. 1980; Carlson et al. 1986; McCarthy 1989). These EDTA-treated effluent samples were also tested for toxicity through methods described previously. However, the EDTA-treatment toxicity tests with fathead minnow larvae consisted of two replicates, with 10 larvae per replicate, and the *Ceriodaphnia* tests consisted of five replicates, each containing one organism per replicate. Toxicity tests with the EDTA-treated effluent were always conducted concurrently with toxicity tests of the nontreated effluents.

Statistical Analyses

Data reduction

The chemical data for effluent samples collected on October 18, 1996, were rejected on the grounds that for a large number of the metal analyses, the dissolved metal values exceeded the corresponding TRM values by 130% to >1000%. The Cu values for samples from Outfall C collected on February 14, 1997, and April 25, 1997 were excluded as outliers for two reasons: (1) the TR Cu concentrations were well outside the range of remaining TR Cu concentrations from Outfall C, and (2) the DM:TRM ratio for Cu in Outfall C on these two dates was 0.16 and 0.30, respectively. In comparison, the DM:TRM ratio for Cu in all other samples from Outfall C typically ranged from 0.6–1.2. A total of 29 paired observations for Pb were excluded because of the large number of non-detectable values.

Toxicity data

A linear interpolation method was used to calculate the effluent concentration causing a 25% reduction (IC_{25}) in fathead minnow growth or *Ceriodaphnia* reproduction, relative to a control (Norberg-King 1993). If the IC_{25} was <100%, then TUc was computed ($TUc = 100/IC_{25}$) to provide an estimate of the effluent's toxicity to fathead minnows or *Ceriodaphnia*; a higher TUc indicated greater toxicity of the effluent.

Physico-Chemical Data

Descriptive statistics (i.e., mean, standard deviation, minimum and maximum values) summarizing the physico-chemical data were obtained by means of the Statistical Analyses System (SAS®). A SAS analysis of variance (ANOVA) method [general linear models (GLM)] was also used to test for outfall-to-outfall differences in physico-chemical parameters. Tukey's Studentized Range Test was used in conjunction with the GLM procedure to determine (1) within a given outfall, which physico-chemical parameters differed significantly from each other, and (2) for a specific parameter, which outfalls differed from each other. Unless otherwise noted, statements of significance are based on $\alpha \leq 0.05$.

The pH data were transformed to the hydrogen-ion concentration before the statistical analyses were performed. The results (i.e., means and ranges) were transformed back to express pH values in the standard units.

Metals Data

SAS was used to (1) calculate descriptive statistics for the metals data, (2) define the distribution of the data (e.g., normal vs skewed), (3) evaluate variance in the data (e.g., ANOVA), and (4) determine the strength of the association between variables (e.g., correlation). The ratio of DM to TRM for each combination of outfall and metal was calculated assuming the data followed a bivariate normal distribution. Multivariate regression analyses were performed to determine the extent of variation in DM:TRM ratios and in DM concentrations for Cu, Ni, Pb, and Zn.

RESULTS/DISCUSSION

Toxicity Tests

Effluent from Outfalls B or C was not toxic to fathead minnow larvae or *Ceriodaphnia* in any of the six tests. Effluent from Outfall A was not toxic to fathead minnows, but, in the test conducted during October 1996, *Ceriodaphnia* reproduction in effluent from Outfall A was reduced relative to the control. The EDTA-treated effluent from Outfall A did not increase *Ceriodaphnia* reproduction in comparison with the nontreated effluent (P = 0.44). Thus, something other than a metal probably contributed to the effluent's toxicity to *Ceriodaphnia* in this test.

Effluent from Outfall B was toxic to fathead minnows and *Ceriodaphnia* during the February 1997 test period. All of the *Ceriodaphnia* in the full-strength effluent died, and all the minnows in the 50% and 100% concentrations died. Mortality occurred <24 h after test initiation. The mortality coincided with a rapid decline in the pH of the effluent: the pH was 6.89 at test initiation but declined to 3.88 by 24 h later. The drop in pH was suspected to be related to excess loading of sodium thiosulfate. During the chronic test period in February, we conducted a follow-up acute toxicity test of effluent from Outfall B, using fathead minnows. This acute test showed that the effluent was no longer toxic.

Physico-chemical Analyses

Various physico-chemical factors can affect the toxicity and/or bioavailability of metals in an aquatic system. Such factors include pH, hardness, alkalinity, temperature, dissolved oxygen, the presence of chelating agents, and concentrations of dissolved and suspended organic matter (Förstner and Wittman 1979; Borgman 1983; Rand and Petrocelli 1985; McCarthy 1989). The toxicity and uptake of many metals is generally associated with the concentration of free metal ion, not with the total concentration of the metal (Borgmann 1983). From numerous studies, several general observations concerning metal toxicity and/or bioavailability can be made: (1) toxicity increases as pH decreases; (2) increases in hardness reduce the availability of the metal; (3) the presence of organic ligands (such as hydroxides, sulfides, and carbonates), and/or inorganic ligands (such as EDTA) can reduce bioavailability through the formation of metal–ligand complexes; and (4) factors such as temperature, pH, and dissolved oxygen influence the physiology of an organism and, thus, its potential response to a pollutant (Howarth and Sprague 1977; Benoit and Holcombe 1978; Miller and Mackay 1979; Förstner and Wittman 1979; Spehar and Carlson 1984; Carlson et al. 1986).

The physico-chemical characteristics of effluents from the outfalls were inspected by ANOVA through the use of the general linear models (GLM; SAS®) procedure. Tukey's Studentized Range test was used in conjunction with the GLM procedure to (1) determine which physico-chemical characteristics differed between outfalls and (2) which physico-chemical characteristics within a given outfall differed between test periods. Unless otherwise noted, statements of statistical significance are based on $\alpha \leq 0.05$. The mean physico-chemical measurements and the results of Tukey's tests for outfall-to-outfall differences are summarized in **Table 1**

Results of the GLM procedure revealed that significant outfall-to-outfall differences in the physico-chemical characteristics occurred. In general, effluent from Outfall A had a greater hardness and conductivity than the other outfalls. With the exception of TSS, the physico-chemical characteristics of the effluents from Outfalls C and D did not differ much from each other. Mean alkalinity, hardness, and pH in effluent from Outfall B were lower than the other.

Analyses of Metals

A total of 18 effluent samples from each outfall were collected over the course of the study for analysis of TRM and DM. More than 65% of the total number of measured metal concentrations were estimated quantities (i.e., the values were greater than detection limits but less than quantitation limits). All Cd, Cr, and Pb TRM and DM values were estimated quantities. With the exception of two total recoverable Cu values in Outfall C, all metal concentrations were well below the current Kentucky Pollutant Discharge Elimination System permit limits and the federal water quality criteria for each metal (**Figs. 1–4**).

The highest concentration of TR Cd measured in any of the effluent samples was 0.40 μg/L (Outfall C). All

measured values for TR Cd were well below permit limits (4–11 µg/L daily maximum) and the federal WQC (3.7 µg/L acute criterion).

The TR Cr concentrations measured in the effluent samples ranged from 1.07 μg/L (Outfall D) to 3.93 μg/L (Outfall A). No dissolved Cr was detected in effluents from Outfalls A and C, and only one measurable concentration of dissolved Cr was found in Outfall B (1.21 μg/L). All measured values for TR Cr were well below permit limits and the federal WQC.

TR Cu measured in all the outfalls ranged from 2.49 to 9.67 μg/L. Dissolved Cu measured in the outfalls ranged from 1.59 to 7.24 μg/L (**Fig. 1**). With the exception of two TR Cu values (16.0 μg/L and 23.9 μg/L), all measured concentrations for TR Cu were below permit limits (12–26 µg/L monthly average) and the federal WQC (11 µg/L chronic criterion).

The TR permit limits for Pb in Outfall A are 262 μg/L (daily maximum) and 10 μg/L (monthly average). In comparison, the TR concentrations of Pb in Outfall A ranged from <0.1 to 2.71 μg/L. The TR permit limits for Pb in Outfalls B, C, and D are 82 μg/L (daily maximum) and 3 μg/L (monthly average). The amount of TR Pb ranged from <0.1 to 3.20 μg/L at Outfall B, from 0.38 to 2.09 μg/L at Outfall C, and from <0.1 to 2.49 at Outfall D (**Fig. 2**). The range of measurable dissolved Pb in the outfalls was 0.10–0.88 μg/L (**Fig. 2**). The federal WQC for Pb are 65 μg/L (acute criterion) and 2.5 μg/L (chronic criterion) (EPA 1995b). The federal WQC for Pb are expressed as the dissolved metal concentration and are based on a total hardness of 100 mg $CaCO_3$/L (EPA 1995b).

The TR Ni concentrations in all outfalls ranged from 0.82 to 10.70 μg/L, and dissolved Ni ranged from 0.28 to 9.50 μg/L (**Fig. 3**). All measured values for Ni were well below permit limits (1418–3079 µg/L) and the federal WQC (160 µg/L chronic criterion; hardness of 100 mg/L).

The TR Zn concentrations measured in all outfalls ranged from 4.75 to 67.3 μg/L; dissolved Zn ranged from 5.75 to 63.6 μg/L (**Fig. 4**). All measured values for Zn were below permit limits (106–230 µg/L monthly average) and the federal WQC (110 µg/L monthly average; hardness of 100 mg/L).

TRM and DM data were used to derive DM:TRM ratios for Cu, Ni, Pb, and Zn in each of the four outfalls. Cadmium was not detected in >60% of the effluent samples, and Cr was not detected in >75% of the samples. Thus, the DM:TRM ratios for Cd and Cr were not determined.

The proportion of dissolved Cu in the effluents from Outfalls A, B, C, and D ranged from 67 to 82%; the proportion of dissolved Ni ranged from 84 to 91%; and the proportion of dissolved Zn ranged from 74 to 94% (Table 2)). The proportion of dissolved Pb in the effluents was considerably lower (37–51%) than the other metals evaluated (**Table 2**). ANOVAs for the DM:TRM ratios were conducted by means of the GLM procedure (SAS 1985) in conjunction with Tukey's Studentized Range Test. The results of these analyses are summarized in **Table 2**. The analyses of the metals data showed that the DM:TRM ratios for Cu, Ni, or Pb were not significantly different ($P > 0.4$) from each other. The DM:TRM ratio for Zn in Outfall A (0.92) was significantly greater ($P < 0.01$) than that in Outfall D (0.78).

Alternative TRM Concentrations

In accordance with the procedure issued by the Kentucky Division of Water (KDOW 1996), alternative TRM concentrations for Cu, Ni, Pb, and Zn can be calculated for Outfalls A, B, C, and D by using the following equation

$$\begin{matrix}\textit{Metal} \\ \textit{concentration} \\ \textit{reported}\end{matrix} = [TRM \times DM{:}TRM] \times \frac{1}{EPA\ CF}, \qquad \text{Eq. 1}$$

where, TRM is the amount of metal measured in the effluent sample, DM:TRM is the dissolved metal to total recoverable metal ratio, and CF is the EPA's freshwater criteria conversion factor. The result of the equation is the TRM concentration that can be reported in lieu of the measured TRM concentration for a particular metal. This calculated TRM concentration may then be reported to determine compliance with the TRM permit limits.

Freshwater criteria conversion factors for DM were developed by EPA, with final factors for DM published in the Federal Register on May 4, 1995 (EPA 1995b). Metal complexes cannot be considered nontoxic, but they do appear to be substantially less toxic than DM (EPA 1995b). A portion of all DM is adsorbed to or complexed with organic colloids and ligands; this portion may be biologically unavailable. By regulation [40 CFR 122.45(c)], the permit limit, in most cases, must be expressed as the TRM. A hardness-dependent conversion factor is applied to express the criteria as DM, and thereby account for the particulate metal present. Freshwater criteria conversion factors for Cu, Ni, and Zn (**Table 3**) were applied to the KDOW equation (Eq.1).

According to EPA, the conversion factor for Pb can be moderated by total hardness; therefore, the following equation was used to develop site-specific conversion factors for Pb for each outfall (EPA 1995b):

$$Lead\ CF = 1.46203 - [(\ln\ hardness)(0.145712)] \qquad \text{Eq. 2}$$

Mean hardness concentrations from **Table 1** were used in Equation 2 to calculate Pb conversion factors for each outfall (**Table 4**).

Alternative TRM concentrations for Cu, Ni, Pb, and Zn were calculated (**Table 5**). The mean and maximum TRM concentrations measured for each metal in each outfall were used to calculate the corresponding alternative TR concentration. The mean and maximum TRM concentrations measured for each metal in each outfall were used to calculate the corresponding alternative TR concentration (**Table 5**) To evaluate the magnitude of the difference between the measured TRM concentration and the TRM concentration calculated using Equation 1, the percent reduction was also calculated (**Table 5**). For Cu, the percent reduction in calculated TRM concentrations compared with measured TRM concentrations ranged from 14.5% (Outfall C) to 30.3% (Outfall D). The percent reduction for Ni ranged from 8.8 to 15.8%; for Zn, the range was 4.7 to 25.0%. The largest percent reductions occurred for Pb in all outfalls—39.5% (Outfall B) to 54.1% (Outfall C).

The alternative calculated TRM concentration provides the discharger with a "cushion" for meeting permit limits for TRM. For example, the monthly average permit limit for Pb in Outfall B (3 μg/L) was exceeded six times between November 1992 and October 1997. Through the use of the KDOW method for calculating an alternative total recoverable metal concentration, 4.98 μg Pb/L in Outfall B would be reported as 3.00 μg/L, a difference of > 39%. Thus, the alternative, calculated total recoverable metal concentration provides the discharger with a "cushion" for meeting permit limits.

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Table 1. Mean physico-chemical measurements, by outfall, and results of Tukey's tests

Parameter	Outfall A	Outfall B	Outfall C	Outfall D
H^+ (as pH)[b]				
Mean ± SD	7.90 ± 0.51	7.24 ± 0.22	7.78 ± 0.13	7.71 ± 0.12
Range	7.60–9.14	6.89–7.59	7.45–7.96	7.48–7.98
Tukey comparison[a]	B	A	B	B
Alkalinity[c]				
Mean ± SD	37.6 ± 6.5	32.1 ± 10.1	47.2 ± 14.5	39.9 ± 9.1
Range	29–49	17–56	15–73	24–59
Tukey comparison[a]	B,C	C	A	A, B
Hardness[c]				
Mean ± SD	248.8 ± 90.0	68.7 ± 8.9	79.8 ± 14.7	86.8 ± 17.8
Range	70–390	54–90	62–106	66–130
Tukey comparison[a]	A	C	B, C	B
Conductivity[d]				
Mean ± SD	935.5 ± 359.1	334.1 ± 150.1	364.2 ± 293.3	316.6 ± 87.3
Range	233–1485	230–878	201–1418	188–486
Tukey comparison	A	B	B	B
Total suspended solids[f]				
Mean ± SD	21.8 ± 5.9	5.1 ± 2.5	10.0 ± 7.1	23.7 ± 14.7
Range	11.1–30.8	1.6–12.2	3.8–28.2	7.1–59.2
Tukey comparison[a]	A	B	B	A
Flow[g]				
Mean ± SD	2.68 ± 1.07	0.64 ± 0.13	0.29 ± 0.17	0.45 ± 0.22
Range	1.30–4.29	0.43–0.93	0.14–0.63	0.08–0.73
Tukey comparison[a]	A	B	C	B, C

Note: Data collected on 10/18/96 were not included in statistical analyses.
[a]Within a given parameter, mean values sharing the same letter did not differ signficantly from each other. Comparisons of individual parameters were made with Tukey's Studentized Range test; $\alpha \leq 0.05$.
[b]$n = 17$.
[c]Expressed as mg/L as $CaCO_3$ ($n = 17$).
[d]Expressed as μS/cm ($n = 17$).
[e]Expressed as mg C/L ($n = 17$).
[f]Expressed as mg/L ($n = 17$).
[g]Million gallons per day ($n = 15$).

Table 2. Ratios of dissolved metal to total recoverable metal (DM:TRM), by outfall and metal

Metal	Outfall			
	A	B	C	D
Copper				
Mean	0.78	0.79	0.82	0.67
95% C.L.	0.71–0.85	0.74–0.84	0.68–0.97	0.56–0.81
n	17	17	15	17
Tukey comparison[a]	A	A	A	A
Nickel				
Mean	0.87	0.91	0.90	0.84
95% C.L.	0.82–0.93	0.82–1.01	0.82–0.98	0.75–0.97
n	17	17	17	17
Tukey comparison[a]	A	A	A	A
Lead	0.37	0.51	0.38	0.46
Mean	0.23–0.65	0.38–0.63	0.26–0.56	0.33–0.62
95% C.L.	11	11	10	11
n	A	A	A	A
Tukey comparison[a]				
Zinc				
Mean	0.92	0.94	0.74	0.78
95% C.L.	0.84–1.03	0.85–1.03	0.64–0.90	0.67–0.86
n	17	17	17	17
Tukey comparison[a]	A	A,B	A,B	B

[a]Mean values with the same letter were not significantly different. Comparisons of DM:TRM ratios were made using Tukey's Studentized Range test ($\alpha \leq 0.05$).

Table 3. EPA freshwater criteria conversion factors[a]

Metal	Criteria conversion factor[b]
Copper	0.960
Nickel	0.997
Zinc	0.986

[a]From 40 CFR 131(c).
[a]Based on a hardness of 100 mg/L as $CaCO_3$.

Table 4. Hardness-dependent lead conversion factors, by outfall

Outfall	Mean hardness[a] (mg $CaCO_3$/L)	Conversion factor
A	248.8	0.658
B	68.7	0.846
C	79.8	0.824
D	86.8	0.812

[a]Values from Table 1.

Table 5. Alternative total recoverable metal concentrations for Cu, Ni, Pb, and Zn, by outfall

Outfall	Metal	KPDES permit limits[a] (μg/L)		Measured TRM[b] (μg/L)		DM: TRM[c]	CF[d]	Alternative TRM concentration (μg/L)[e]		Percent reduction
		Daily maximum	Monthly average	Mean	Max.			Mean	Max.	
A	Cu	42	26	6.19	9.67	0.78	0.960	5.03	7.86	18.7
	Ni	3079	342	6.00	10.70	0.87	0.997	5.24	9.34	12.7
	Pb	262	10	0.91	2.71	0.37	0.658	0.51	1.52	43.9
	Zn	254	230	11.89	21.9	0.92	0.986	11.09	20.4	6.7
B	Cu	18	12	5.96	80.30	0.79	0.960	4.90	66.08	17.8
	Ni	1418	158	3.18	6.26	0.91	0.997	2.90	5.71	8.8
	Pb	82	3	0.76	3.20	0.51	0.846	0.46	1.93	39.5
	Zn	117	106	20.79	58.5	0.94	0.986	19.82	55.8	4.7
C	Cu	18	12	4.88	23.90	0.82	0.960	4.17	20.41	14.5
	Ni	1418	158	1.54	2.03	0.90	0.997	1.39	1.83	9.7
	Pb	82	3	0.98	2.09	0.38	0.824	0.45	0.96	54.1
	Zn	117	106	16.10	41.9	0.74	0.986	12.08	31.4	25.0
D	Cu	18	12	5.25	8.64	0.67	0.960	3.66	6.03	30.3
	Ni	1418	158	1.65	3.15	0.84	0.997	1.39	2.65	15.8
	Pb	82	3	0.74	2.49	0.46	0.812	0.42	1.41	43.2
	Zn	117	106	27.56	67.3	0.78	0.986	21.80	53.2	20.9

[a]Current KPDES total recoverable metal permit limits.
[b]Mean and maximum total recoverable metal (TRM) data.
[c]Ratio of dissolved metal:total recoverable metal (DM:TRM), from Table 2.
[d]Conversion factor, from Table 3 (Cu, Ni, Zn) or Table 4 (Pb).
[e]Alternative total recoverable concentration calculated by means of the KDOW Equation (1).

Figure 1. Mean (SD) total recoverable and dissolved copper by outfall. Mean total recoverable or dissolved metal values with the same letter were not significantly different based on Tukey's tests ($a < 0.05$). For comparison, the permit limits for Outfall A are 42 mg/L (daily maximum) and 26 mg/L (monthly average), and permit limits for Outfalls B, C, and D are 18 mg/L (daily maximum) and 12 mg/L (monthly average).

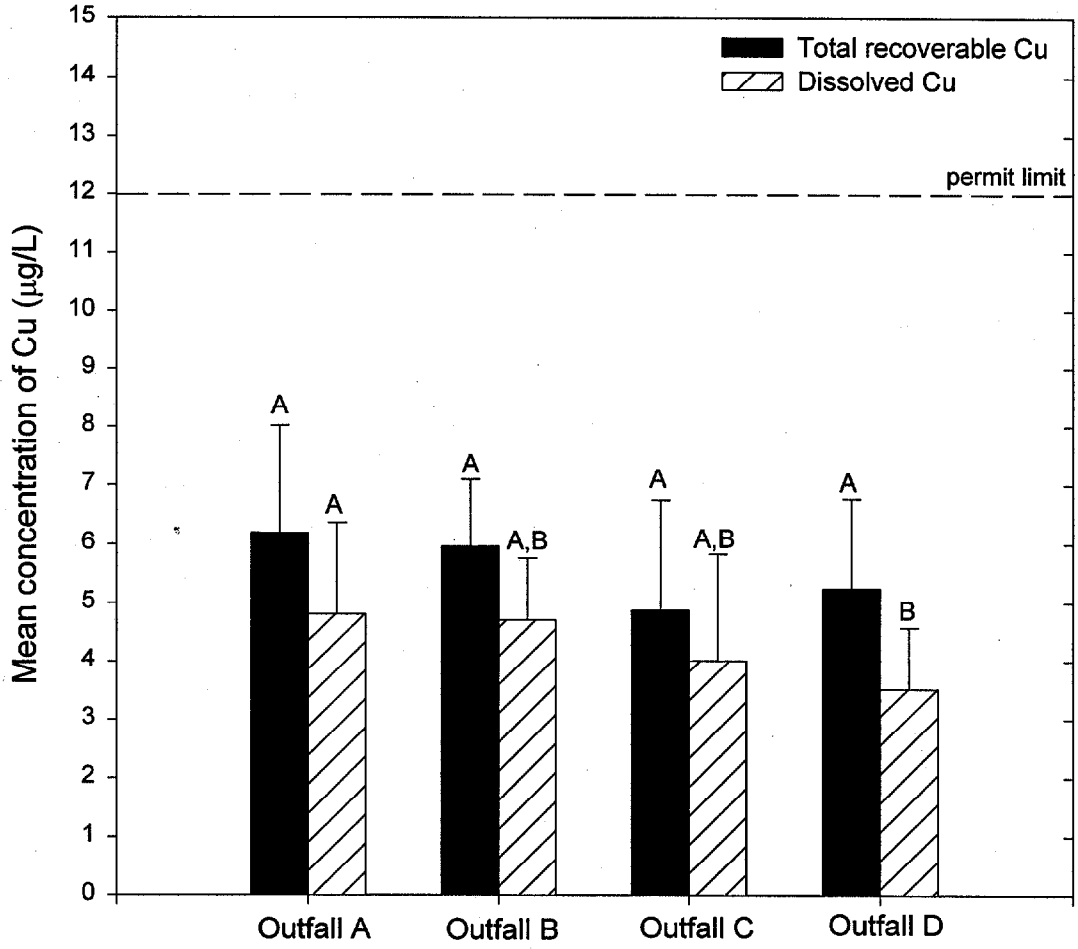

Figure 2. Mean (SD) total recoverable and dissolved lead by outfall. Mean total recoverable or dissolved metal values with the same letter were not significantly different based on Tukey's tests ($a < 0.05$). For comparison, the permit limits for Outfall A are 262 mg/L (daily maximum) and 10 mg/L (monthly average), and permit limits for Outfalls B, C, and D are 82 mg/L (daily maximum) and 3 mg/L (monthly average).

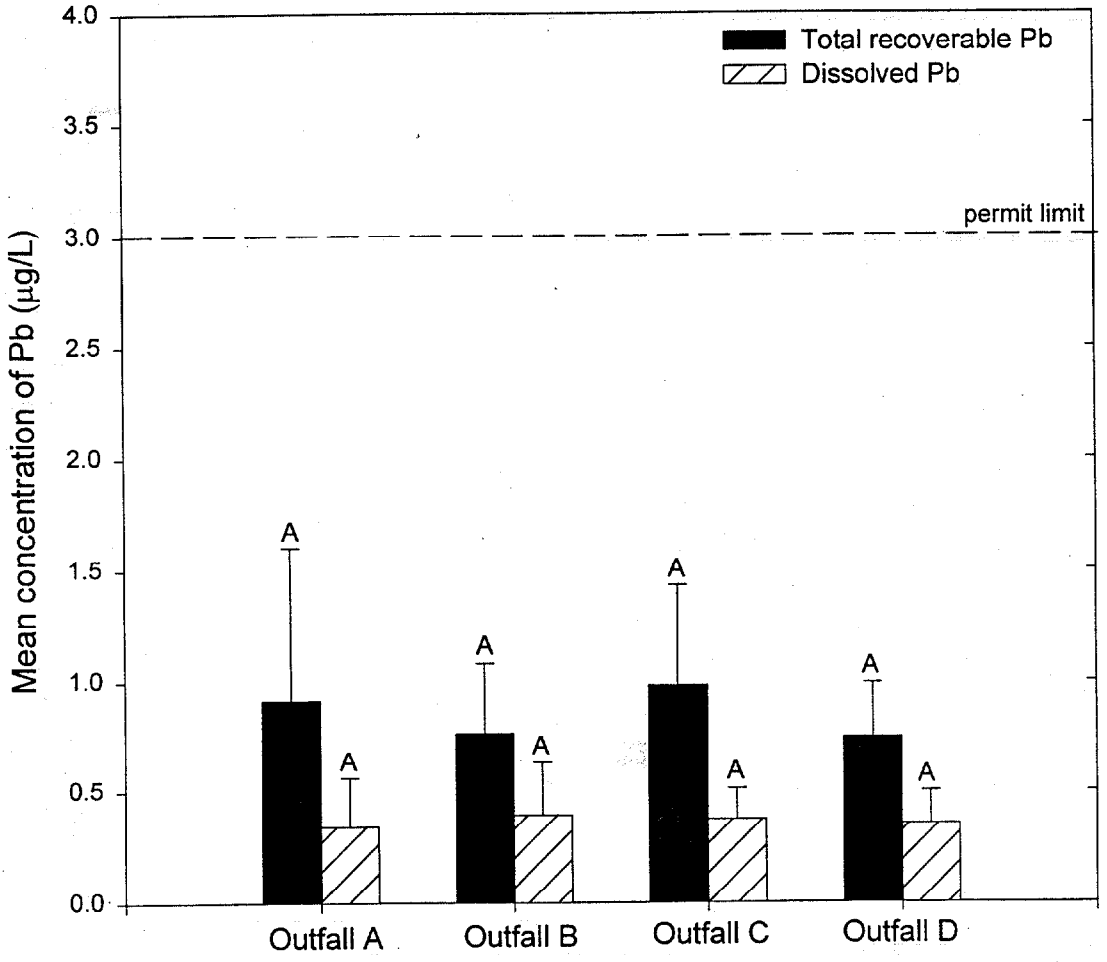

Figure 3. Mean (SD) total recoverable and dissolved nickel by outfall. Mean total recoverable or dissolved metal values with the same letter were not significantly different based on Tukey's tests ($a < 0.05$). For comparison, the permit limits for Outfall A are 3079 mg/L (daily maximum) and 342 mg/L (monthly average), and permit limits for Outfalls B, C, and D are 1418 mg/L (daily maximum) and 158 mg/L (monthly average).

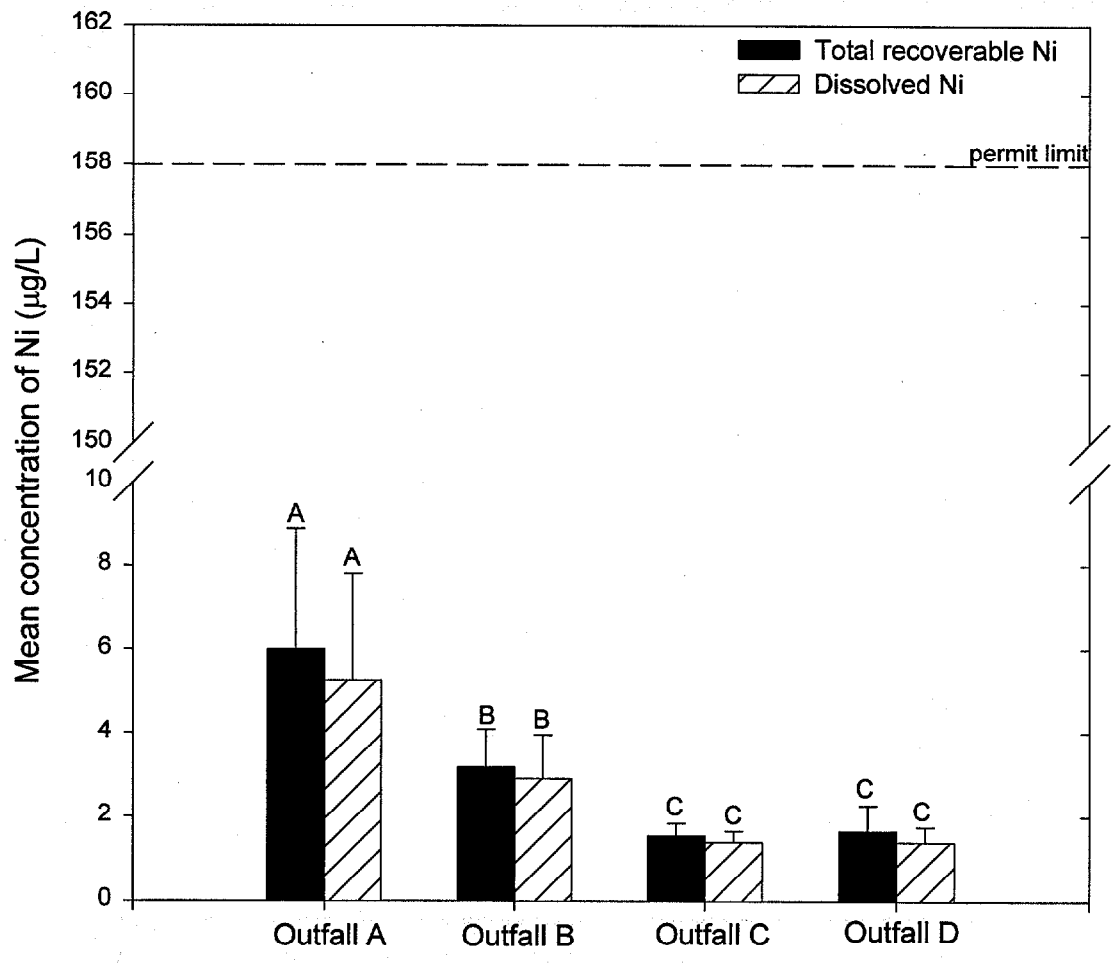

Figure 4. Mean (SD) total recoverable and dissolved zinc by outfall. Mean total recoverable or dissolved metal values with the same letter were not significantly different based on Tukey's tests ($a < 0.05$). For comparison, the permit limits for Outfall A are 254 mg/L (daily maximum) and 230 mg/L (monthly average), and permit limits for Outfalls B, C, and D are 117 mg/L (daily maximum) and 106 mg/L (monthly average).