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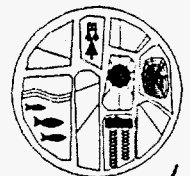
BIOAVAILABILITY STUDY FOR THE PADUCAH GASEOUS DIFFUSION PLANT

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Environmental Sciences Division
Publication No. 4568

August 1996

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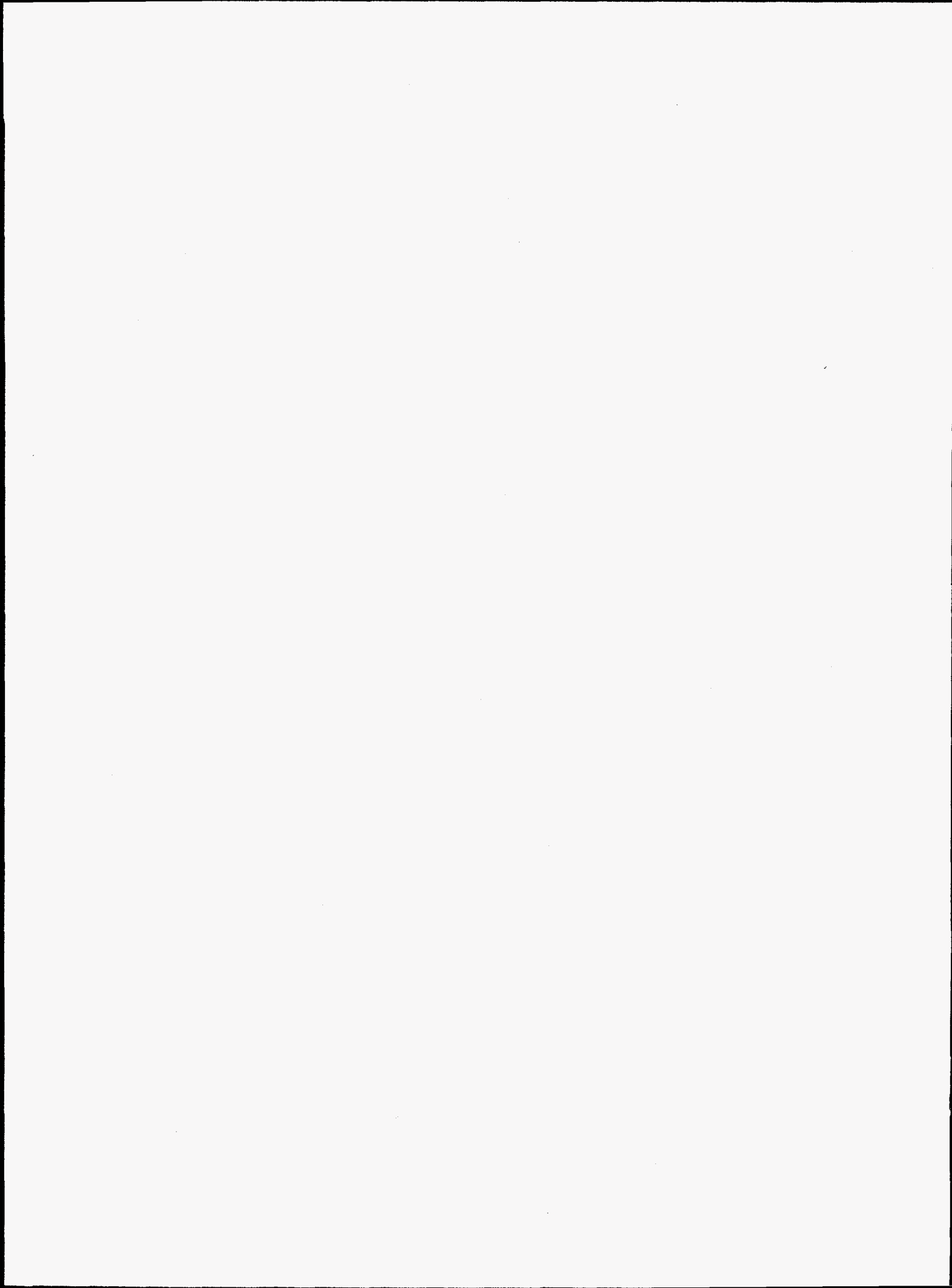
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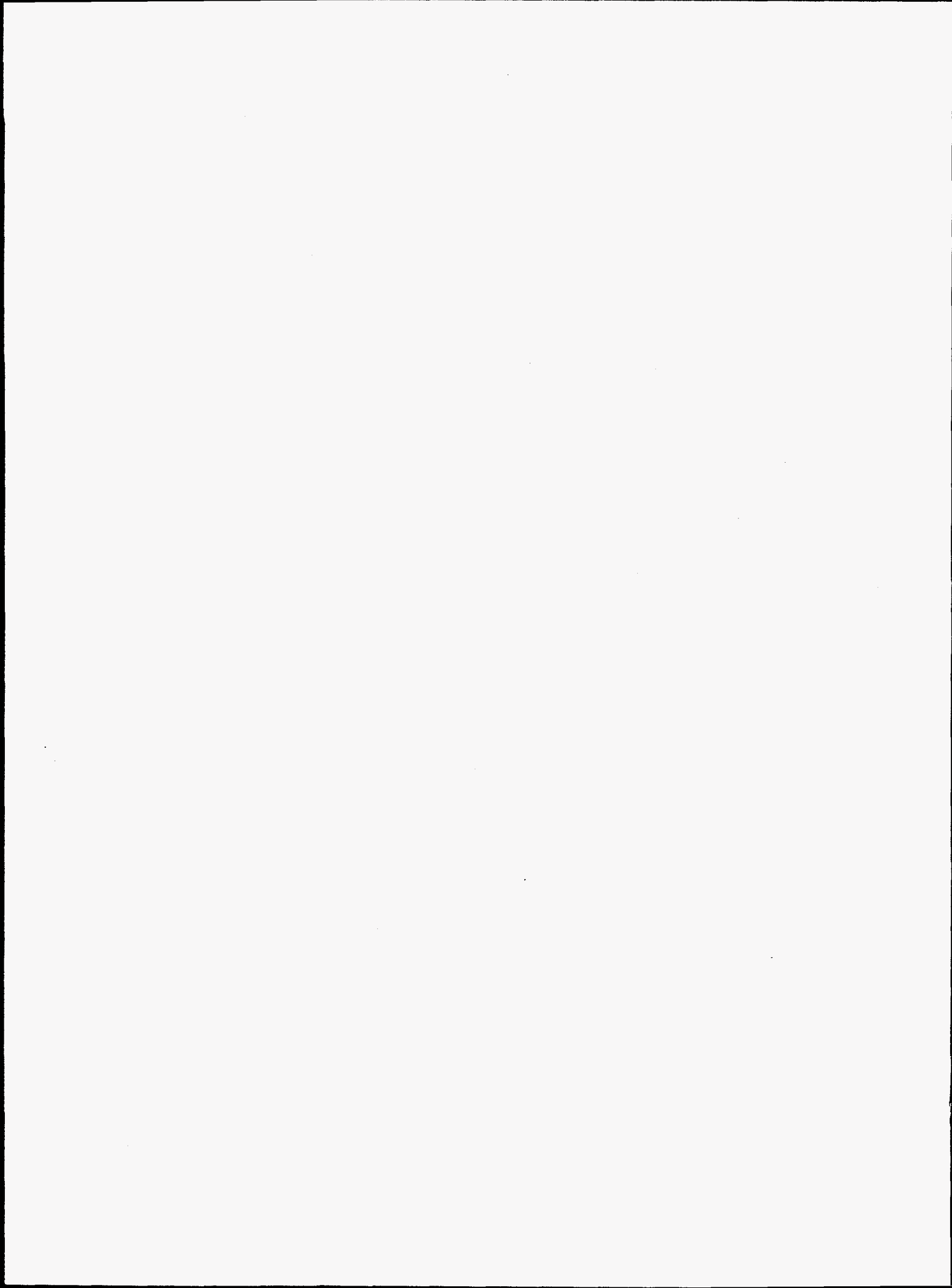
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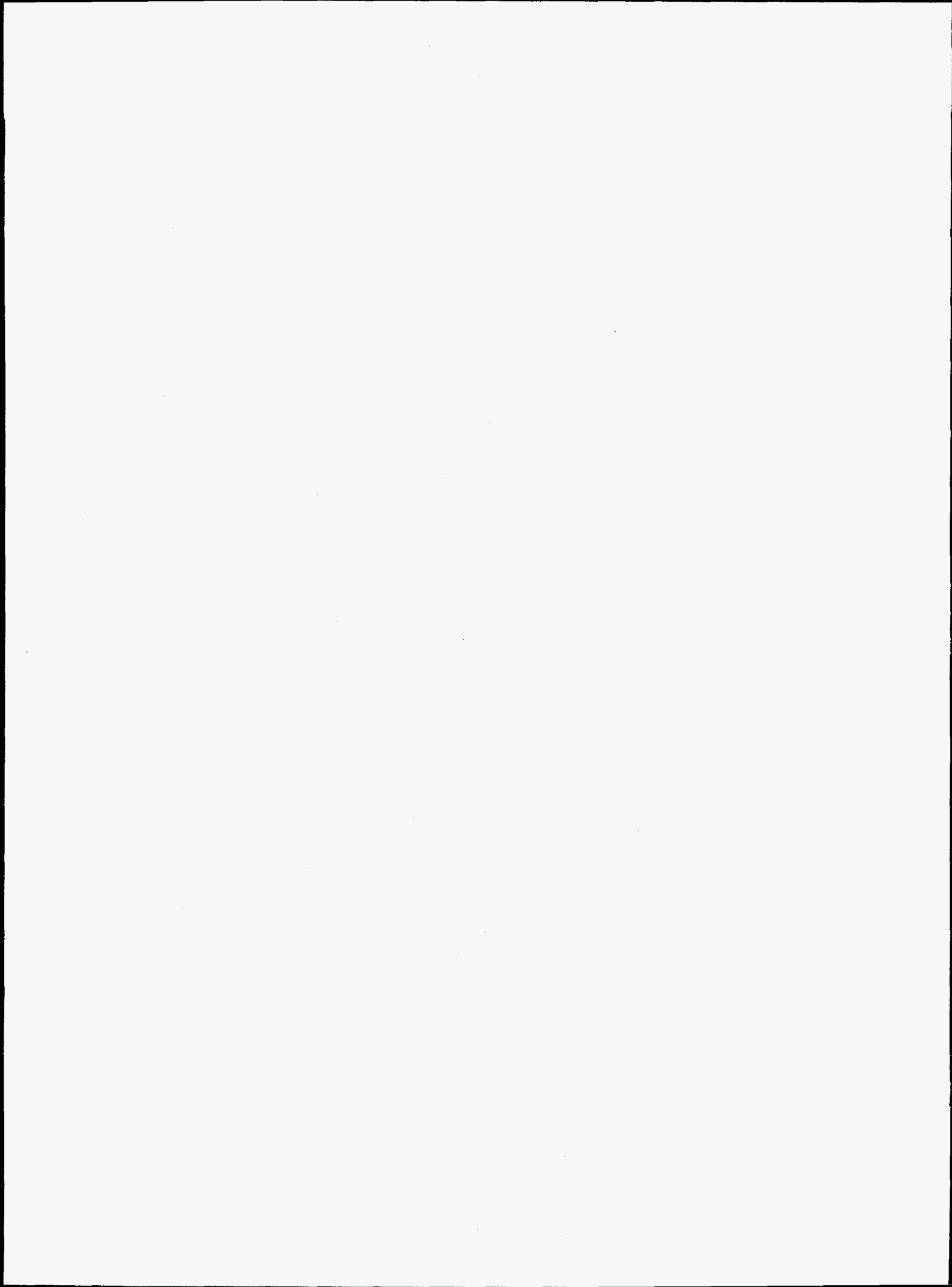
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ACRONYMS

COC	chain-of-custody
DOE	U. S. Department of Energy
EPA	U. S. Environmental Protection Agency
IC	inhibition concentration
KDOW	Kentucky Division of Water
KPDES	Kentucky Pollutant Discharge Elimination System
LMES	Lockheed Martin Energy Systems, Inc.
LMUS	Lockheed Martin Utility Systems, Inc.
MDL	method detection limit
NPDES	National Pollutant Discharge Elimination System
NTR	National Toxics Rule
PGDP	Paducah Gaseous Diffusion Plant
SAP	Sampling and Analysis Plan
TR	total recoverable
TSO	Technical Subcontracting Office
TUc	chronic toxicity unit
USEC	United States Enrichment Corporation
WER	water-effect ratio
WQC	water quality criteria



EXECUTIVE SUMMARY

The overall purpose of this plan is to assess the bioavailability of metals in the continuous and intermittent outfalls. The results may be used to determine alternative metal limits that more appropriately measure the portion of metal present necessary for toxicity to aquatic life. These limits must remain protective of in-stream aquatic life; thus, the highest concentration of metal in the water will be determined concurrently with an assessment of acute or chronic toxicity in laboratory tests.

The Clean Water Act is administered for the Paducah Gaseous Diffusion Plant (PGDP) by the Kentucky Division of Water (KDOW) through the Kentucky Pollutant Discharge Elimination System (KDPES) Wastewater Discharge Permitting Program. The PGDP operates under KPDES Permit No. KY0004049 issued September 29, 1992. The permit became effective November 1, 1992, and is enforced by the KDOW. Metals criteria applied to the KPDES permit are total recoverable metals measured in unfiltered water samples.

On April 5, 1996, the Commonwealth of Kentucky Natural Resources and Environmental Protection Cabinet issued an Agreed Order that required the development of a plan to conduct studies that would identify alternative metal limits for Department of Energy (DOE) and United States Enrichment Corporation (USEC) outfalls 001, 002, 003, 008, 009, 010, 011, 012, 013, 015, 016, 017, and 018. Except during heavy rainfall events, outfalls 002, 010, 011, and 012 will be composited in the C-617 lagoon and discharged from outfall 010. Alternative metal limits may be developed for cadmium, chromium, copper, lead, nickel, and zinc. As stipulated in the Agreed Order, DOE/USEC must demonstrate to the satisfaction of the Cabinet that a more appropriate analytical technique or criteria is available that provides a better measurement of levels of metals present that would be toxic to aquatic life.

In May 1996, the KDOW issued revised *Procedures to Facilitate Alternative Metals Limits*. The revised KDOW procedure provides an alternative method for deriving site-specific metals limits; combining biomonitoring with chemical-specific analyses. The procedure provides an alternative method of measuring compliance to total recoverable metal limits. KDOW developed these procedures to address derivation of alternative metal limits for discharges into zero flow streams. Alternative permit limits are determined by multiplying the total recoverable metal concentration by the dissolved metal:total recoverable (TR) metal ratio. The result is then multiplied by the reciprocal of the U.S. Environmental Protection Agency's (EPA's) freshwater criteria conversion factor for each metal of concern.

$$\text{Metal concentration of effluent} = (\text{TR metal} \times \text{dissolved:TR ratio}) \times 1/\text{EPA criteria conversion factor} \quad \text{Eq. 1}$$

Using the method developed by the KDOW, biomonitoring results and chemical data will be used to recommend alternative metal limits for the outfalls of concern. The data will be used to meet the objectives of the study:

- evaluate the toxicity of continuous outfalls (001, 008, 009, and 010) and intermittent outfalls (003, 013, 015, 016, 017, and 018) at PGDP,
- determine the mean ratio of dissolved to TR metal for Cd, Cr, Cu, Pb, Ni, and Zn in the continuous and intermittent outfalls,

- determine whether the concentration of TR metal discharged causes toxicity to fathead minnows and/or *Ceriodaphnia*, and
- determine alternative metal limits for each metal of concern (Cd, Cr, Cu, Pb, Ni, and Zn).

1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) National Guidelines (Stephan et al. 1985) describe procedures for deriving national water quality criteria (WQC) for the protection of aquatic life. Incorporating national or state WQC into National Pollutant Discharge Elimination System (NPDES) permits assumes that if the aqueous concentration of a material in a body of water is lower than the criterion, the aquatic life in that body of water is unlikely to be affected adversely. Using standardized criteria is more cost-effective than developing site-specific criteria, so standardized criteria have been used since the 1980s. To determine compliance with standardized criteria for metals, the EPA has recommended using measurements of total recoverable (TR) metals. Beginning in 1984, the WQC documents recommended the use of an acid-soluble method for determining concentrations of metals of concern. Either of these methods—TR or acid-soluble—may result in the overestimation of toxicity, because not all of the measured metals are bioavailable.

A major issue in the scientific and regulatory communities is whether, and how, to use dissolved metal concentrations or TR metal concentrations in setting state water quality standards. Under the National Toxics Rule (NTR), the EPA used TR metals to express metals criteria because this approach is more conservative and provides a greater level of protection than dissolved metal measurement. The NTR metals criteria were challenged, and 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 TR metal, better approximates the fraction of waterborne metals that are biologically available to aquatic organisms. Subsequently, the use of dissolved metal is the recommended approach to setting and measuring compliance with water quality standards. One reason for this change is that the bioavailable or dissolved fraction of metal present will more likely be toxic to aquatic organisms.

The bioavailability of most toxic metals is strongly affected by factors such as the types and concentrations of dissolved and particulate organic matter in the water, pH, and metal-binding dissolved constituents, such as sulfide. These factors are not routinely incorporated into present WQC. In May 1992, the EPA issued new guidance for interpreting and implementing WQC for metals in waters of the United States to address issues of bioavailability (EPA 1992). This new guidance document provides new approaches for developing site-specific criteria. These approaches account for the fact that naturally occurring materials in ambient waters can reduce the bioavailability and, thus, lower the toxicity of various metals. In one alternative, measurements of *dissolved* metals in ambient waters are compared to criteria appropriate for *dissolved* metals. In another approach, the toxicity of a metal in ambient water is compared directly to the toxicity of that metal in laboratory water. The national criterion for that metal is then adjusted by the ratio of toxicity in ambient site water to the toxicity in laboratory water. This latter method is referred to as the water-effect ratio (WER).

The EPA has issued guidance for three methodologies that can be used for the development of site-specific criteria: indicator species procedure (WER), recalculation procedure, and resident species procedure (EPA 1994). Use of the WER takes into account differences between toxicity of a metal in laboratory dilution water and its toxicity in site water. Determining the WER is an approach that can be used by dischargers who want higher permit limits. An alternative approach for determining site-specific metals criteria

involves application of the Recalculation Procedure. This method takes into account differences in aquatic species that occur at the site and those species used in the derivation of the national criterion. However, the Recalculation Procedure cannot be used to derive site-specific metals criteria in jurisdictions subject to the NTR.

The EPA method provides guidance for deriving WERs in zero flow streams. The site-specific criterion is derived by dividing the endpoint [e.g., inhibition concentration (IC)₂₅] obtained in the site water by the endpoint obtained in the laboratory dilution water. Either TR metal or dissolved metal WERs can be calculated. Also, WERs are determined individually for each metal at each site; that is, WERs calculated for one metal cannot be extrapolated to another metal, from one effluent to another, or from one site water to another. Several factors need to be considered before determining site-specific criteria using the WER approach:

- Some WERs will be substantially greater than 1.0, some will be approximately 1.0, and some will be less than 1.0.
- The WER approach requires substantial resources.
- More cost-effective methods than determining a WER are available to the discharger.

Several site-specific factors can significantly affect the toxicity of metals and must be considered in the management of metals in an aquatic environment. These factors include toxicity specific to effluent chemistry; toxicity specific to ambient water chemistry; different patterns of toxicity (e.g., increased mortality, reduced fecundity or growth, reduced mobility) for different metals; fate and transport mechanisms; resource limitations for monitoring, analysis, and research; concerns regarding the quality of data currently on record due to possible sample and analytical contamination; and lack of standardized protocols for clean metals analysis.

In May 1996, the Kentucky Division of Water (KDOW) issued *Procedures to Facilitate Alternative Metal Limits* (Appendix A) that could be used in lieu of the WER. This procedure was put forth to allow dischargers to demonstrate "that a form of metal other than TR is the cause of toxicity." In general, the procedure requires demonstration, through chemical-specific analyses and biomonitoring, that an effluent is not toxic as a result of the presence of the metal in question. Language in Kentucky's regulations was recently changed to allow the use of methods other than the TR method to measure attainment of aquatic-life criteria for metals. Based on the Agreed Order signed April 5, 1996, the Department of Energy (DOE) and United States Enrichment Corporation (USEC) may attempt to develop alternative metal limits for Cd, Cu, Pb, Ni, Zn, trivalent chromium [Cr(III)], and hexavalent chromium [Cr(VI)] (Appendix B). A successful demonstration by Paducah Gaseous Diffusion Plant (PGDP) could result in a modification of the permit to incorporate alternative metals limits.

Metals in the environment are usually present in complexed or particulate forms, and only a small fraction of total metal concentration is bioavailable. The changes in physical and chemical forms of certain metals will directly relate to their toxicity toward aquatic organisms. Using the method developed by the KDOW, information obtained from biomonitoring tests as well as analyses of the effluent for TR and dissolved metals will be used to determine whether the concentration of TR metal discharged is toxic to fathead minnows (*Pimephales promelas*) and *Ceriodaphnia dubia*.

2. SCOPE AND OBJECTIVES

The overall purpose of this plan is to assess the bioavailability of metals in the continuous and intermittent outfalls. The results may be used to determine alternative metal limits that more appropriately measure the portion of metal present necessary for toxicity to aquatic life. These limits must remain protective of in-stream aquatic life; thus, the highest concentration of metal in the water will be determined concurrently with an assessment of acute or chronic toxicity in laboratory tests.

2.1 SCOPE

The KDOW administers the Clean Water Act for PGDP through the KPDES Wastewater Discharge Permitting Program. PGDP operates under KPDES Permit No. KY0004049, which was issued September 29, 1992, and became effective November 1, 1992. Biomonitoring tests using aquatic organisms are conducted quarterly for outfalls 001, 006, 008, 009, 010, 013, 015, 016, 017, and 018. (Outfalls 002, 010, 011, and 012 are composited in C-617 and discharged via Outfall 010). Outfalls 001, 006, 008, and 009 discharge continuously to Big Bayou Creek (Fig. 2.1). Outfall 010 discharges continuously to Little Bayou Creek. Outfalls 015, 016, and 017 discharge intermittently to Big Bayou Creek and outfall 018 discharges intermittently to Little Bayou Creek (Fig. 2.1). During heavy rainfall, outfalls 002, 011, and 012 may discharge to Little Bayou Creek.

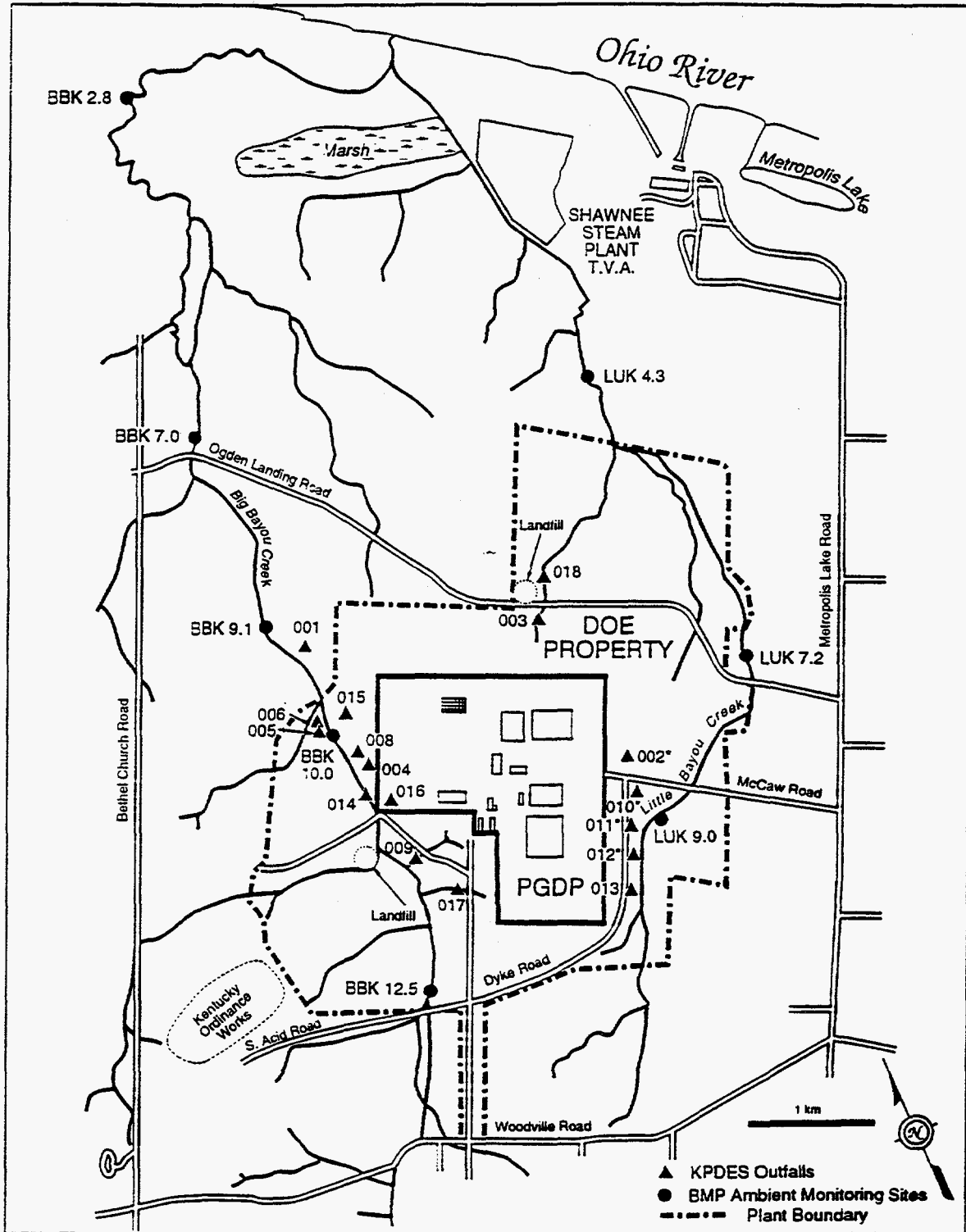
The Environmental Sciences Division (ESD) Aquatic Toxicology Laboratory at Oak Ridge National Laboratory (ORNL) began evaluating the toxicity of continuous and intermittent outfalls at PGDP in October 1991. Quarterly biomonitoring tests are conducted using fathead minnows and/or *C. dubia*. The 25% inhibition concentration (IC25: the concentration that causes a 25% reduction in fathead minnow growth or *Ceriodaphnia* reproduction) was determined for each outfall tested. The compliance endpoint in the permit is expressed as chronic toxicity units (TUC = 100/IC25). The higher the TUC, the more toxic the effluent.

Since October 1991, the monitored outfalls have exhibited periodic toxicity. Table 2.1 summarizes the TUCs for all biomonitoring tests of continuous outfalls conducted October 1991–May 1996. Table 2.2 is a summary of the TUCs for biomonitoring tests of the intermittent outfalls conducted December 1991–April 1996.

The KPDES effluent permit limits for various metals in these effluents are occasionally exceeded. Table 2.3 summarizes, by outfall, the number of permit exceedances for each metal of concern.

In accordance with the Agreed Order, a study to develop alternative metal limits will be conducted for DOE and USEC outfalls 001, 002, 003, 008, 009, 010, 011, 012, 013, 015, 016, 017, and 018. Except during heavy rainfall events, outfalls 002, 010, 011, and 012 are composited in the C-617 lagoon and discharged from Outfall 010.

Although not part of this plan, it is important to recognize that the Biological Monitoring Program will be ongoing during this study. The data from this program will provide additional information concerning the ecological health of the receiving streams, Big Bayou and Little Bayou creeks.



*Combined at C617 pond and discharged through 011/010

Fig. 2.1. Location of KPDES permitted outfalls for the Paducah Gaseous Diffusion Plant.

Table 2.1. Results of effluent biomonitoring tests for continuous outfalls 001, 006, 008, 009, and 010/011

Outfall	Test date	Chronic toxicity units (TUc) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
001	October 1991	ND ^b	<1
	February 1992	<1	<1
	May 1992	ND ^b	4.5
	August 1992	<1	<1
	October 1992	<1	<1
	February 1993	<1	<1
	May 1993	<1	<1
	August 1993	<1	<1
	October 1993	<1	1.09
	March 1994	<1	<1
	May 1994	<1	<1
	August 1994	<1	<1
	October 1994	<1	I ^d
	November 1994	NT ^c	<1
	March 1995	<1	<1
	May 1995	<1	<1
	August 1995	<1	<1
	October 1995	<1	9.18
	November 1995	NT ^c	1.59
	March 1996	<1	<1
May 1996	<1	<1	

Table 2.1 (continued)

Outfall	Test date	Chronic toxicity units (TUC) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
006	October 1991	ND ^b	<1
	February 1992	1.39	1.56
	May 1992	ND ^b	<1
	August 1992	<1	<1
	October 1992	<1	<1
	February 1993	<1	<1
	May 1993	<1	I ^d
	June 1993	NT ^c	<1
	August 1993	<1	<1
	October 1993	<1	<1
	March 1994	5.97	<1
	March 1994	18.32	NT ^c
	April 1994	<1	<1
	August 1994	<1	1.36
	September 1994	NT ^c	<1
	October 1994	<1	<1
	March 1995	<1	<1
	May 1995	<1	<1
	August 1995	<1	NT ^c
	October 1995	<1	NT ^c
	March 1996	2.33	NT ^c
	March 1996	<1	NT ^c
	May 1996	<1	NT ^c

Table 2.1 (continued)

Outfall	Test date	Chronic toxicity units (TUC) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
008	October 1991	ND ^b	<1
	February 1992	9.77	<1
	May 1992	ND ^b	<1
	August 1992	<1	<1
	October 1992	<1	<1
	February 1993	<1	<1
	May 1993	<1	I ^a
	June 1993	NT ^c	<1
	August 1993	<1	<1
	October 1993	4.08	<1
	December 1993	<1	NT ^c
	March 1994	<1	<1
	May 1994	1.3	<1
	June 1994	<1	NT ^c
	August 1994	1.56	<1
	September 1994	<1	NT ^c
	October 1994	<1	<1
	March 1995	<1	<1
	May 1995	<1	<1
	August 1995	<1	NT ^c
October 1995	<1	NT ^c	
March 1996	<1	NT ^c	
May 1996	<1	NT ^c	

Table 2.1 (continued)

Outfall	Test date	Chronic toxicity units (TUC) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
009	October 1991	ND ^b	<1
	February 1992	7.87	<1
	May 1992	<1	<1
	August 1992	<1	<1
	October 1992	2.16	1.05
	February 1993	<1	<1
	May 1993	<1	I ^d
	June 1993	NT ^c	<1
	August 1993	<1	<1
	October 1993	<1	<1
	March 1994	<1	<1
	May 1994	1.09	<1
	June 1994	<1	NT ^c
	August 1994	2.09	<1
	September 1994	<1	NT ^c
	October 1994	10.73	<1
	November 1994	3.38	NT ^c
	March 1995	<1	<1
	May 1995	<1	<1
	August 1995	<1	NT ^c
October 1995	<1	NT ^c	
March 1996	<1	NT ^c	
May 1996	<1	NT ^c	

Table 2.1 (continued)

Outfall	Test date	Chronic toxicity units (TUc) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
011	October 1991	ND ^b	<1
	February 1992	7.69	<1
	May 1992	ND ^b	<1
	August 1992	<1	<1
	October 1992	<1	<1
	February 1993	<1	<1
	May 1993	<1	<1
	August 1993	<1	<1
	October 1993	<1	<1
	March 1994	23.53	<1
	March 1994	32.57	NT ^c
	April 1994	<1	<1
	010	August 1994	<1
October 1994		<1	<1
March 1995		<1	<1
May 1995		<1	<1
August 1995		<1	NT ^c
October 1995		<1	NT ^c
March 1996		8.62	NT ^c
March 1996		<1	NT ^c
May 1996	<1	NT ^c	

^aChronic toxicity unit = 100/IC25; IC25 = the concentration causing a 25% reduction in fathead minnow growth or *Ceriodaphnia* reproduction.

^bND = not determined.

^cNT = not tested.

^dI = invalid test due to low reproduction in the control water.

^eEffluent from the C-617 lagoon was diverted from Outfall 011 to Outfall 010 during June 1994. As a result, effluent from Outfall 010 instead of Outfall 011 was tested after June 1994. Outfall 010 includes discharges from outfalls 002, 011, and 012 during normal plant operations.

Table 2.2. Results of effluent biomonitoring tests for intermittent outfalls 013, 015, 016, 017, and 018

Outfall	Test date	Chronic toxicity units (TUc) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
013	December 1991	<1	<1
	March 1992	5.82	<1
	June 1992	1.02	<1
	September 1992	<1	<1
	November 1992	1.96	<1
	January 1993	<1	6.99
	May 1993	1.3	<1
	September 1993	1.39	<1
	November 1993	<1	<1
	February 1994	11.31	1.04
	April 1994	<1	<1
	September 1994	<1	<1
	November 1994	<1	<1
	January 1995	<1	<1
	April 1995	<1	<1
	July 1995	<1	<1
	November 1995	<1	<1
	January 1996	<1	34.60
	April 1996	<1	NT ^c

Table 2.2 (continued)

Outfall	Test date	Chronic toxicity units (TUc) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
015	December 1991	<1	<1
	March 1992	7.91	<1
	June 1992	<1	<1
	September 1992	<1	ND ^b
	November 1992	<1	<1
	January 1993	1.52	<1
	May 1993	3.62	<1
	September 1993	<1	<1
	November 1993	<1	<1
	February 1994	2.04	<1
	April 1994	11.15	<1
	September 1994	<1	<1
	November 1994	17.54	<1
	January 1995	<1	<1
	April 1995	<1	<1
	July 1995	<1	<1
	October 1995	<1	<1
	January 1996	<1	<1
	April 1996	<1	NT ^c

Table 2.2 (continued)

Outfall	Test date	Chronic toxicity units (TUC) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
016	December 1991	<1	<1
	March 1992	1.74	<1
	September 1992	<1	<1
	November 1992	1.32	<1
	January 1993	2.04	<1
	May 1993	<1	<1
	September 1993	<1	<1
	November 1993	<1	<1
	February 1994	<1	<1
	April 1994	<1	<1
	September 1994	<1	<1
	November 1994	23.47	<1
	January 1995	<1	<1
	April 1995	<1	<1
	July 1995	<1	<1
	November 1995	<1	<1
	January 1996	<1	<1
April 1996	<1	NT ^c	

Table 2.2 (continued)

Outfall	Test date	Chronic toxicity units (TUC) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
017	December 1991	ND ^b	<1
	March 1992	4.54	<1
	June 1992	<1	<1
	September 1992	5.01	<1
	November 1992	<1	<1
	January 1993	<1	<1
	May 1993	23.8	<1
	September 1993	<1	<1
	November 1993	<1	<1
	February 1994	2.83	<1
	April 1994	1.79	<1
	September 1994	<1	<1
	November 1994	66.23	<1
	January 1995	<1	<1
	April 1995	<1	<1
	July 1995	<1	<1
	November 1995	<1	<1
	January 1996	<1	25.91
April 1996	<1	NT ^c	

Table 2.2 (continued)

Outfall	Test date	Chronic toxicity units (TUc) ^a	
		Fathead minnow	<i>Ceriodaphnia</i>
018	December 1991	<1	<1
	March 1992	5.27	<1
	June 1992	<1	<1
	September 1992	<1	<1
	November 1992	1.43	<1
	January 1993	8.47	<1
	May 1993	21.7	<1
	September 1993	<1	<1
	November 1993	<1	<1
	February 1994	<1	<1
	April 1994	1.39	<1
	September 1994	<1	3.47
	November 1994	<1	<1
	January 1995	<1	1.01
	April 1995	1.87	<1
	July 1995	<1	<1
	November 1995	<1	<1
	January 1996	<1	6.73
April 1996	<1	NT ^c	

^aChronic toxicity unit = 100/IC25; IC25 = the concentration causing a 25% reduction in fathead minnow growth or *Ceriodaphnia* reproduction.

^bND = not determined.

^cNT = not tested.

Table 2.3. Number of permit exceedances from the KPDES permit (from Nov. 1, 1992, through Feb. 29, 1996) for PGDP outfalls

Outfall	Metal						Total per outfall
	Cd	Ni	Pb	Zn	Cu	Cr	
Continuous Outfalls							
001	0	0	0	0	0	0	0
006	No permit limits; metal concentrations are report only.						NA
008	2	0	2	0	5	0	9
009	2	0	3	3	5	0	13
010/011 (C-617 discharge)	0	0	5	2	5	0	12
Intermittent Outfalls							
002 ^a	0	0	4	0	7	0	10
003	No discharge since 11/1/92						NA
011 ^a	0	0	0	0	3	0	3
012 ^a	0	0	1	14	4	4	23
013	0	0	2	0	2	0	4
015	0	0	1	0	0	0	1
016	0	0	1	2	0	0	3
017	2	0	2	0	1	0	5
018	0	1	3	0	10	4	18
Total by metal	6	1	23	21	42	8	101

^aStorm water exceedances.

Source: C. C. Travis, LMUS, personal communication.

2.2 OBJECTIVES

EPA policy recommends that the concentration of dissolved (rather than TR) metal be used to set and measure compliance with water quality standards, because dissolved metal more closely estimates the bioavailable fraction of metal in the water column than does TR metal (EPA 1995). The bioavailable or dissolved fraction of metal present will be the most

likely source of toxicity to aquatic animals because dissolved metal is more readily adsorbed at the cellular surfaces (e.g., gill surface). While particle associated metal cannot be considered nontoxic, it does appear to exhibit substantially less toxicity than dissolved metal (EPA 1995). Part of what is measured as dissolved—defined as that which passes through a 0.45- μm filter—is adsorbed to or complexed with organic colloids and ligands; which may be biologically unavailable. By regulation [40 CFR 122.45(c)], the permit limit, in most cases, must be expressed as TR metal. To express the criteria as dissolved metal, a conversion factor is applied to account for the particulate metal present.

Following the KDOW method, effluent samples will be collected concurrently for biomonitoring and chemical analysis to evaluate the protectiveness of the aquatic environment. Biomonitoring of the effluent is required to evaluate potential exposure and effects from contaminants. Analytical data will be used to determine the relationship between the TR and dissolved metal fractions for each metal included in the study. The biomonitoring and analytical data will be used to meet the objectives of this study:

1. Evaluate the toxicity of continuous and intermittent outfalls at PGDP.
2. Determine whether the concentration of TR metal discharged is toxic to fathead minnows and/or *Ceriodaphnia*.
3. Determine the mean ratio of dissolved to TR metal in the continuous and intermittent outfalls.
4. Recommend alternative metal limits for each metal of concern.

While the KDOW method (developed to determine alternative metal limits) will be followed, PGDP reserves the right to develop alternative metal limits for its permitted outfalls using the EPA water-effect ratio approach. Data collected for this study may be used to evaluate the appropriateness of determining the WER for each outfall of concern.

3. SITE DESCRIPTION

The PDGP is owned by DOE. In July 1993, DOE leased the plant production operations facilities, which are managed by Lockheed Martin Utility Systems, Inc. (LMUS), to USEC. Under this lease, USEC has assumed responsibility for compliance activities directly associated with uranium enrichment operations. The environmental restoration and waste management activities are managed by Lockheed Martin Energy Systems, Inc. (LMES). Construction of the plant was completed in 1954, although production of uranium began in 1952. PGDP is an active uranium enrichment facility consisting of a diffusion cascade and extensive support facilities. The uranium enrichment gaseous diffusion process involves more than 1800 stages with operations housed in 5 buildings covering ~300 ha. Including support facilities, the plant has ~30 permanent buildings located on a 1385-ha site. Support facilities include a steam plant, four electrical switchyards, four sets of cooling towers, a chemical cleaning and decontamination facility, water and wastewater treatment plants, a chromium reduction facility, and maintenance and laboratory facilities. Several inactive facilities are also located on the site. Currently, the Paducah cascade processes are being used for the

enrichment of uranium to 2% ^{235}U . This product is then transferred to the Portsmouth (Ohio) Gaseous Diffusion Plant for further enrichment. Most of the uranium produced is used commercial reactors in the United States or abroad (Kszos 1996).

4. TECHNICAL SPECIFICATIONS

The work plan is designed to follow guidance from the KDOW for determining alternative metal limits and thus will require collection of data on effluent toxicity and concentrations of TR and dissolved metals.

4.1 MONITORING SCHEDULE

Sampling and analysis will be conducted in two phases. Alternative metals limits for the continuously discharging outfalls (001, 008, 009, and 010) will be determined in Phase I and for the intermittently discharging outfalls (003, 013, 015, 016, 017, and 018) in Phase II. If, prior to implementation of the schedules set forth, KDOW issues to PGDP a new KPDES permit that includes metals limits, and such limits are not challenged by PGDP, then all activities scheduled to be completed in Phase II will be canceled and PGDP will meet the limits established in the new KPDES permit. In each phase, samples will be evaluated for toxicity and TR and dissolved metals will be measured.

Phase I activities will be initiated no later than 60 days following approval of the work plan by KDOW.

4.2 MONITORING DURATION

During Phase I, six biomonitoring tests of each continuous outfall will be conducted over a period of one year. This schedule will assure that temporal variations in the chemical properties of the effluent and other environmental conditions are taken into account.

The physico-chemical properties of the effluent (e.g., temperature, pH, alkalinity, dissolved oxygen, hardness, and total suspended solids) will determine the fraction of metal that is dissolved and the fraction that is in particulate form. Biomonitoring tests of intermittent outfalls will be conducted following a similar schedule. Phase II sampling activities will not begin until completion of Phase I and approval by PGDP and KDOW.

4.3 SAMPLE COLLECTION AND PROCESSING

For this study, samples for biomonitoring tests and chemical analyses will be collected concurrently from each effluent. Under Phase I, three 24-h composite samples from outfalls 001, 008, 009, and 010 or 011 (whichever is running) will be collected during each 7-d test period. A total of 18 samples from each continuous outfall will be collected and evaluated for toxicity and for determination of mean metals concentrations. Under Phase II, one grab sample from intermittent outfalls that exhibit metals or toxicity problems will be collected and

evaluated for toxicity and for measuring metals concentrations. A total of six samples will be used to determine the mean ratio of dissolved to TR metal in the intermittent outfalls.

Collection procedures must not alter the effluent sampled. The potential for contamination during sample collection and sample processing will be minimized by use of EPA "clean" techniques and by minimizing sample handling. Studies have shown that metals concentrations in EPA and U. S. Geological Survey databases and in effluent discharges may be largely the result of sample contamination rather than actual sample concentration. The use of clean techniques have resulted in fewer noncompliances (EPA 1996).

Samples will be collected in acid-cleaned or precleaned plastic containers, such as high-density polyethylene or polypropylene. Unnecessary exposure of the sample to the atmosphere will be avoided to reduce the potential for contamination from atmospheric particulates.

Any sampling devices used will be constructed of nonmetallic material or, at a minimum, all water contact surfaces will be constructed of nonmetallic material.

Until analysis by the analytical laboratory, any metals concentrations in the samples must be maintained as close as possible to the same levels as they were in the environment from which they were collected. For dissolved metal determinations, samples must be filtered through a 0.45- μm membrane or capsule filter. To minimize exposure, field preservation and filtration will be performed inside a field-portable glove bag or in a designated clean area. Effluent samples for TR and dissolved metals analyses will be preserved with 10% HNO_3 to $\text{pH} < 2$.

A minimum two-person sampling team is required. All sampling personnel must wear clean, non-talc gloves and may need to wear disposable nylon coveralls or windsuits to prevent sample contamination.

At the time of sample collection, the flow from the outfalls will be measured and recorded. Testing of the effluents will be initiated within 36 h of sample collection. Samples collected for metals analyses will be segregated from samples used to conduct biomonitoring tests. Preserved samples will be stored and shipped on ice to the analytical laboratory. Samples for toxicity testing will be packed in coolers with sufficient ice to keep the samples at approximately $4 \pm 2^\circ\text{C}$ and shipped to the Aquatic Toxicology Laboratory.

The sampling team may modify the sampling techniques described in the Sampling and Analysis Plan (SAP) to improve performance or reduce sampling costs, provided that samples and blanks are not contaminated or altered. Any modifications to procedures contained in the SAP must be documented and approved by the Project Manager.

4.4 SAMPLE CUSTODY

Each sample will be shipped with chain-of-custody (COC) forms generated by the field sampling personnel, documenting custody of each sample. Samples will be received in the Aquatic Toxicology Laboratory and analytical laboratory with appropriate COC documents and analysis request forms. Upon receipt, the Aquatic Toxicology Laboratory will immediately store the samples in the dark at $4 \pm 2^\circ\text{C}$. Chain of custody will be maintained by the Toxicology Laboratory until final disposition of the samples.

4.5 BIOMONITORING

Chronic, static-renewal biomonitoring tests using fathead minnow (*P. promelas*) larvae and *C. dubia* will be conducted according to technical procedures described in the Toxicology Laboratory Quality Assurance Program manual (Kszos et al. 1989). Toxicity test procedures are based on EPA methodology (Methods 1000.0, Fathead Minnow Larval Survival and Growth Test, and 1002.0, *C. dubia* Survival and Reproduction Test) (Lewis 1994).

The fathead minnow test will consist of four replicates per test concentration with 10 larvae per replicate. The number of larvae surviving will be recorded daily. At the end of the test period (7 d), the larvae will be dried and weighed to estimate growth. The *Ceriodaphnia* test will consist of 10 replicates per test concentration with one animal per replicate. Survival and the number of offspring will be recorded daily for each animal.

Any toxic effects will include the synergistic, antagonistic, and additive effects of all chemical and physical components of the effluent which adversely affect the physiological and biochemical functions of the test organisms.

All biomonitoring tests will be conducted by qualified personnel in the Aquatic Toxicology Laboratory

4.6 LABORATORY ANALYSIS OF TOTAL RECOVERABLE AND DISSOLVED METALS

To achieve low detection limits, the EPA recommends that trace metals analyses be performed using inductively coupled plasma/mass spectrometry (ICP/MS) (EPA 1994b). Therefore, concentrations of TR and dissolved Cd, Cu, Cr, Pb, Ni, and Zn in each outfall will be determined using ICP/MS (EPA Method 200.8). Based on compliance history for Outfall 001, analysis of hexavalent chromium will not be included in the work plan.

All metals of interest—Cd, Cu, Cr, Pb, Ni, and Zn—can be analyzed simultaneously from a single effluent sample using ICP/MS. The target Method Detection Limits (MDLs) should be one third of the regulatory compliance limit.

Metals analyses will be performed by competent analysts using clean techniques. The analytical laboratory should meet the requirements established under the EPA Contract Laboratory Program (CLP). The laboratory must be able to demonstrate capability to perform method 200.8. Inadvertent contamination could be introduced during sample preparation and analysis, therefore, the laboratory should have a trace metal clean room. The basic requirements for a trace metal clean room are: (1) metal free work surfaces and hoods, (2) positive pressure with HEPA-filtered air, and (3) ultrapure water. Laboratory qualifications will be evaluated and determined by the Technical Subcontracting Office (TSO).

4.7 ADDITIONAL PHYSICAL/CHEMICAL ANALYSES

The chemical properties of the effluent will determine the fraction of the metal that is in the dissolved and particulate phases. Different factors influence the dissolved to TR metal ratio such as water temperature, pH, total hardness, concentrations of metal binding sites (i.e., concentrations of total suspended solids), dissolved organic carbon, as well as concentrations of other metals and organic compounds that compete with metal ions for binding sites (EPA 1995a). A portion of each effluent sample will be saved for measurement

of total suspended solids. Measurement of dissolved organic carbon will not be performed initially; a decision to include this analysis will be made after reviewing initial testing and metals data.

Analysis of pH, conductivity, alkalinity, hardness, and dissolved oxygen will be made in the high, middle, and low toxicity test concentrations for each new effluent sample. Dissolved oxygen and pH will also be measured each day before test water renewal.

4.8 MEASUREMENT ENDPOINTS

Using the method developed by the KDOW, data collected and analyzed for this study will be used to recommend alternative metals limits for the outfalls. The measurement endpoints for this study are as follows:

- Measurement endpoint 1: determine the inhibition concentration (i.e., IC_{25} ; the concentration that causes a 25% reduction in fathead minnow growth or *Ceriodaphnia* reproduction).
- Measurement endpoint 2: determine the chronic toxicity unit (TUc) derived ($TUc = 100/IC_{25}$) to evaluate effluent toxicity to fathead minnows or *Ceriodaphnia*.
- Measurement endpoint 3: determine the TR and dissolved metal concentrations for each outfall sampled.
- Measurement endpoint 4: determine the mean dissolved:TR ratio for each metal of concern in each outfall.
- Measurement endpoint 5: use the following equation (from KDOW method) to evaluate whether measured metal concentrations would comply with permit limits expressed as TR:

$$\text{Metal concentration of effluent sampled} = (\text{TR metal of effluent} \times \text{dissolved:TR ratio}) \times 1/\text{EPA criteria conversion factor for dissolved metals}$$

Criteria conversion factors for dissolved metals were developed by the EPA. Final factors were published in the Federal Register on May 4, 1995 (EPA 1995c). For this study, the EPA freshwater chronic conversion factors in Table 4.1 will be applied to measurement endpoint 5. Chronic conversion factors for any hardness can be calculated using the following equations (EPA 1995c):

$$\text{Cadmium: } CF = 1.101672 - [(\ln \text{ hardness})(0.041838)]$$

$$\text{Lead: } CF = 1.46203 - [(\ln \text{ hardness})(0.145712)]$$

Table 4.1. EPA freshwater chronic conversion factors

Metal	Chronic conversion factor
Cadmium	0.909 ^a
Chromium VI	0.962
Copper	0.960
Lead	0.791 ^a
Nickel	0.997
Zinc	0.986

^aConversion factors are hardness dependent. The values shown are for a hardness of 100 mg/L as CaCO₃.

5. QUALITY ASSURANCE/QUALITY CONTROL

The QA objectives for the bioavailability study data are the following:

- Scientific data generated will withstand scientific scrutiny,
- Data will be gathered using controlled, approved procedures for field sampling, chain-of-custody, and laboratory analyses, and
- Data will be of known precision and accuracy.

The QA objective for all data collected for the bioavailability study is to obtain measurements that are reproducible, precise, and accurate and are consistent with the intended use of the data and the limitations of the sampling and analytical methods used. The objective for completeness—the amount of valid data obtained from the sampling and analytical process—is 95% of the planned samples. Completeness of sample collection will be measured by comparing the number of samples planned versus the number collected and submitted for analysis. Completeness—for field QC purposes—will be made by comparing samples submitted for a particular analysis with samples rejected because of errors in collection, processing, preservation, or other field or laboratory related activities.

The sampling and analysis of effluent samples will be performed following approved procedures to ensure the highest quality, accountability, and traceability of data in sampling, analysis, and reporting activities. Quality assurance is achieved through management, planning and control of work processes, establishing performance criteria, assessing achievement of quality criteria, evaluating technical capabilities, and ensuring the traceability of data.

5.1 QUALITY CONTROL SAMPLE CHECKS

Quality control (QC) sample checks are used to (1) monitor sample collection and sample handling techniques; (2) evaluate sampling equipment and sample container decontamination

procedures; (3) assess the sensitivity of the test organisms and the credibility of the test system; (4) measure the precision of analytical methods; (5) evaluate contamination introduced during sample collection, processing, and analysis; and (6) document equipment calibration. These checks may include, but are not limited to, field blanks, field duplicates, replicates, controls, equipment rinse blanks, matrix spikes, preservative blanks, and certified reference standards for equipment calibration.

5.1.1 Field Data Quality

Field QC includes, but is not limited to sample collection, custody, processing, preservation, container selection, transport, and field record keeping. These activities will be performed following procedures contained in the ESD Toxicology Laboratory Quality Assurance Program Plan, the work plan, or in the SAP.

Sample custody will be established by the sampling personnel at the time of sample collection through the use of chain-of-custody forms. Custody will be maintained throughout sample processing and delivery to the analytical laboratory.

Quality control samples will be collected to address field quality as it relates to precision, representativeness, comparability, and completeness. Field QC samples will include field splits, equipment rinse blanks, field rinse water blanks, and filter blanks, as appropriate. Field QC samples will be treated identically to routine samples in terms of sample identification, sample custody, sample processing, request for analytical services, and data processing.

- Field splits will be collected for analysis of TR or dissolved metals at the rate of one per sampling location per test period. These samples will be used to evaluate the precision of the laboratory analysis. The level of precision will be judged acceptable if the relative percent difference (RPD) is $\leq 20\%$.
- Equipment rinse blanks will be collected from each automatic sampler unit before the first effluent sample from each location is collected. These samples will be used to evaluate the adequacy of the decontamination process.
- Presterilized filter units will be used to process field collected samples for analysis of dissolved metals. Filter (field) blanks will be collected at the rate of one per lot used or one per sampling location, whichever is less.
- Rinse water blanks will consist of ASTM Type II water or equivalent. This water will be used to collect filter blanks, equipment rinse blanks, sampler unit bottle blanks, and for rinsing automatic sampler unit bottles between sample collection. A rinse water sample will be collected at the rate of one per batch of water used.

5.1.2 Analytical Data Quality

Quality control requirements for the analytical laboratory are Level 3. Level 3 QC provides low detection limits, a range of calibrated analytes, laboratory process control

information, and known precision and accuracy. Laboratory control samples should include, but not be limited to, method blanks, matrix spikes, and matrix spike duplicates.

- Method blanks will be evaluated to assess contamination introduced during different phases of sample processing and analysis. Blanks may include calibration blanks and laboratory blanks.
- The accuracy of the analytical method and potential matrix effects will be assessed by analyzing matrix spikes (MS) and matrix spike duplicates (MSD). At least one MS/MSD will be analyzed per sample batch (samples collected from the same site during each test period).

Method detection limits for each analyte will be determined according to the procedure in 40 *CFR* 136, Appendix B, using the apparatus, reagents, and standards that will be used in Method 200.8. MDLs should be determined when a new analyst begins work or, in the judgment of the analyst, when a change in instrument hardware or operating conditions would dictate that they be redetermined. At a minimum, the MDL will be one-third of the lowest regulatory compliance limit for each metal of concern.

Sample holding times will begin on the day of sample collection. Holding time ends when the analysis, resulting in reportable data, has been initiated. The maximum allowable holding time is 180 d for preserved samples.

Additional Level 3 QA requirements may include, but are not limited to, the evaluation of the following:

- Initial and continuing instrument calibration. The instrument should be calibrated a minimum of three points for each analyte to be determined. The correlation coefficient should be > 0.990 .
- ICP interference checks. Interference sample checks should be run at the beginning and at the end of each sample analysis run. The results should be within $\pm 20\%$ of the true value.
- Initial and ongoing precision and recovery. Aliquots of reagent grade water will be spiked with the metal(s) of interest. These samples will be subjected to all steps in the analytical process, including digestion, extraction, and concentration, as applicable. The average percent recovery and the standard deviation of the recovery for each metal should be reported.

The TSO is responsible for the procurement and approval of subcontractors for direct analytical support. TSO approval covers analytical methods, QA/QC requirements, deliverables, appropriateness of the laboratory to accomplish the work, and any other requirements of the analytical plan. The TSO is responsible for assessing the laboratory to ensure compliance with quality and technical standards.

5.1.3 Toxicity Data Quality

Reference toxicant tests will be conducted to assess the sensitivity of the test organisms and the overall credibility of the test method. The tests will use the same organisms and control media and be performed under the same conditions as the biomonitoring tests commonly performed by the testing laboratory. Reference toxicant tests using fathead minnow larvae and *C. dubia* will be conducted monthly.

Additional data quality and test requirements are specified in the ESD Toxicology Laboratory Quality Assurance Program Plan, in standard operating procedures, and in the EPA test methods. These requirements include, but are not limited to, instrument calibration and verification, test temperature, food volumes, feeding intervals, and test organism age.

Any variations in the test method will be documented in accordance with the ESD Toxicology Laboratory Quality Assurance Program Plan.

5.2 ANALYTICAL DATA DELIVERABLES

Data deliverables from the analytical laboratory will be Level 3. Both hard copy and electronic data transmission will be required. The turnaround time for data deliverables is 30 days from sample receipt. The data set deliverables should include the following information, as appropriate.

- Sample identification numbers,
- Batch number identifiers,
- Holding time information,
- Digestion date(s),
- Analysis date(s),
- Discussion of laboratory analysis (including problems encountered and corrective actions taken),
- Results of laboratory control samples,
- Sample results (reported in $\mu\text{g/L}$),
- Initial and continuing calibration (including dates of analyses, calibration curves, and correlation coefficients),
- Analysis of method blanks,
- ICP interference checks, and
- Sample spike recovery.

5.3 INCORPORATION OF EPA "CLEAN" TECHNIQUES

Because metals data are used to estimate effluent concentrations (i.e., daily maximums and monthly averages) and determine compliance with permit limits, the quality of the data is an important issue. Therefore the EPA recommends the use of "clean" techniques for collecting and analyzing samples for metals analyses.

EPA Method 1669 (EPA 1995b) was developed for the collection and filtration of ambient water samples for determination of TR and dissolved metals at levels substantially below the ambient WQC. This method, however, was not intended for use in the determination of metals at concentrations that are normally found in treated and untreated

industrial discharges. Metal concentrations in ambient water are normally in the low parts-per-trillion (ppt) to low parts-per-billion (ppb) range; whereas, metal concentrations in industrial effluents are normally found in the high ppb range.

Every effort will be made to avoid contamination by incorporating "clean" techniques within the limitations of the sampling and analytical methods. The general principles of contamination control, as they apply to this bioavailability study, include the following:

- Using non-talc gloves during sample collection and processing activities for handling sampling equipment and sample bottles.
- Using preclean, disposable, or acid-cleaned sample containers and filter units.
- Decontaminating sampling equipment prior to initial sample collection.
- Using reagent grade, trace-metals-free preservatives.
- Properly storing cleaned sampling equipment and sample bottles to prevent exposure to atmospheric particulates.
- Using ASTM II Type water or equivalent (i.e., deionized distilled water).
- Using metal free work surfaces and fume hoods.
- Maintaining clean work surfaces and work areas.

Specific instructions for controlling contamination will be contained in the SAP for field sampling and field processing activities. Instructions for contamination control, as they apply to the analytical laboratory, will be identified in the analytical Statement of Work.

Results of the analysis of quality control samples will be used to assess the effectiveness of contamination control measures and the overall impact on sample results.

6. TOXICITY IDENTIFICATION EVALUATION

According to the *KDOW Procedures to Facilitate Alternative Metals Limits*, a toxicity identification evaluation (TIE) will be required in the event of failure of two biomonitoring tests.

Effluent toxicity may be caused by certain cationic metals (e.g., copper, lead, nickel, zinc). The addition of a chelating agent to an effluent sample may provide information concerning the category of toxicant present if toxicity is observed; therefore, a subsample of full-strength effluent used to conduct the biomonitoring tests will be treated with ethylenediaminetetraacetate (EDTA). The EDTA-treated samples will be evaluated using fathead minnow larvae and *Ceriodaphnia*. Data obtained from the EDTA-treated effluent biomonitoring tests as well as chemical analyses may be used as part of a TIE.

7. SCHEDULE OF DELIVERABLES

The schedule in Table 7.1 allows for completion of 7-d biomonitoring tests and chemical analyses for each phase of the study. Data in the final reports will be used to recommend alternative metal limits for the outfalls.

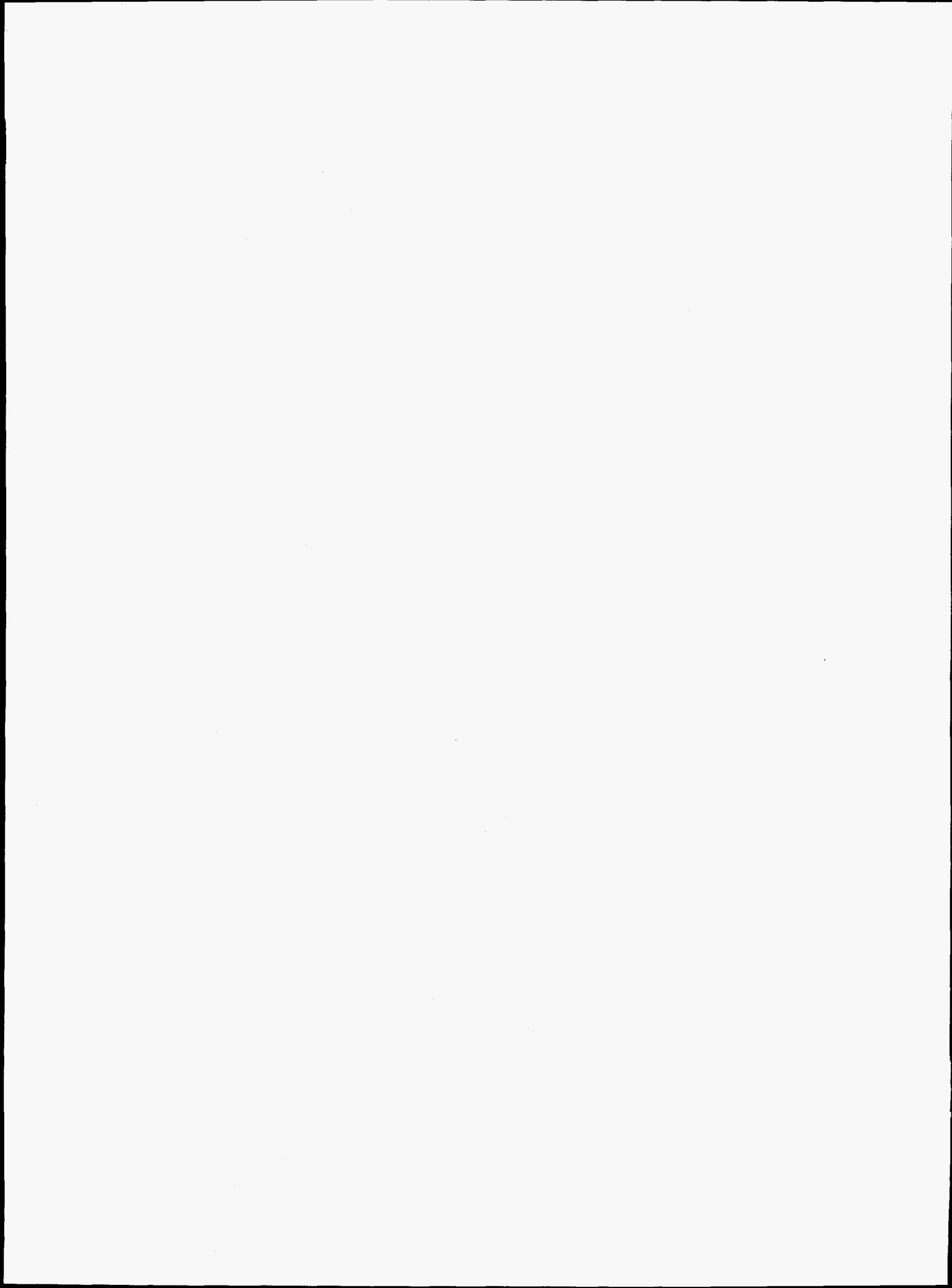
Table 7.1. Deliverables for study

Activity	Status
Initiation of Phase I	No later than 60 days following approval of the work plan by the State.
Completion of Phase I	No later than 12 months following initiation of Phase I activities.
Draft Report - Phase I	Submitted to PGDP no later than 60 days following results of Phase I sampling and analytical activities.
Final Report - Phase I	Submitted to KDOW no later than 30 days following receipt of comments on the Phase I draft report.
Initiation of Phase II ^a	No later than 60 days following approval of the Phase I draft report by KDOW.
Completion of Phase II	No later than 12 months following initiation of Phase II activities.
Draft Report - Phase II	Submitted to PGDP no later than 60 days following results of Phase II sampling and analytical activities.
Final Report - Phase II	Submitted to KDOW no later than 30 days following receipt of comments on the Phase II draft report.

^aIf, prior to implementation of the schedule set forth, KDOW issues to PGDP a new KPDES permit that includes metals limits and such limits are not challenged by PGDP, then all activities scheduled to be completed in Phase II will be canceled and PGDP will meet the limits established in the new KPDES permit.

8. REFERENCES

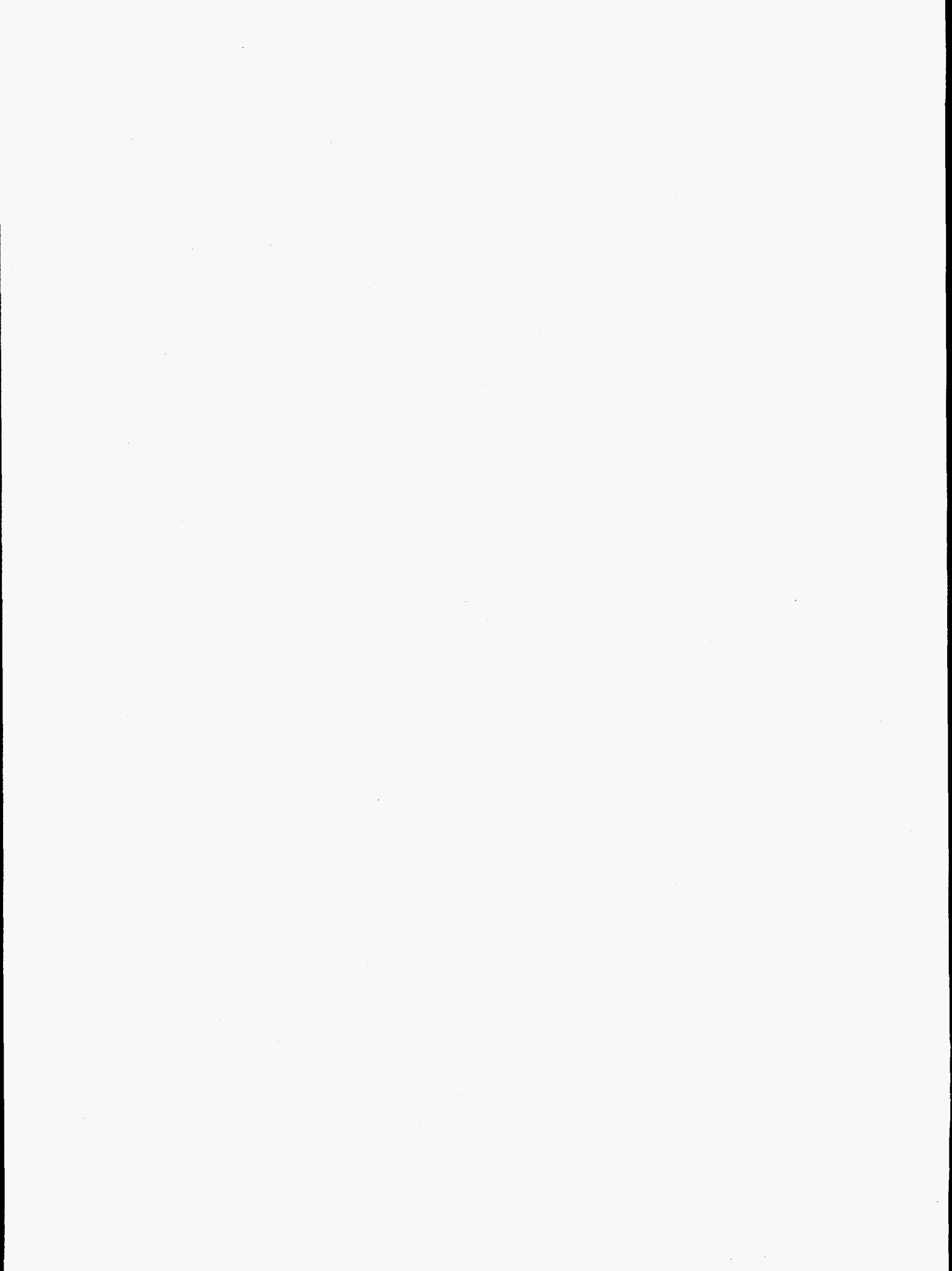
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Appendix A

**KENTUCKY DEPARTMENT OF ENVIRONMENTAL PROTECTION
KENTUCKY DIVISION OF WATER**

Procedures to Facilitate Alternative Metals Limits

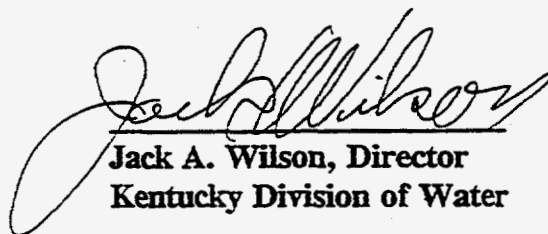


Procedures to Facilitate Alternative Metals Limits

**Kentucky Department of Environmental Protection
Kentucky Division of Water
Frankfort, Kentucky**

May, 1996

This report has been approved for release.


**Jack A. Wilson, Director
Kentucky Division of Water**

May 14, 1996
Date

Procedures to Facilitate Alternative Metals Limits Kentucky Division of Water

Introduction

Language in Kentucky's Warmwater Aquatic Habitat Criteria of the Surface Water Standards contained in 401 KAR 5:031 states that a demonstration may be performed to prove that a form of metal other than total recoverable (TR) is the cause of toxicity. This alternative to TR metal criteria was made in response to comments received during the 1992 triennial review of water quality standards and is consistent with recent EPA guidance (Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria, USEPA 1993), which recognizes that TR metal criteria are often overly conservative.

The procedures outlined below, developed by the Kentucky Division of Water (Division), provide a straightforward manner in which permit applicants can demonstrate that alternative means of measuring compliance with TR metal limits are appropriate. Measuring dissolved metal in the wastewater (in cases where no instream dilution is available), or instream after mixing with receiving waters, and comparing it to dissolved metal permit limits would be a simple and generally conservative approach, but both Federal and State regulations require TR metal limits to be placed on permits. 401 KAR 5:065 Section 3(3) states that TR must be used unless another form of the metal is specified in the CWA or the analytical procedure measures another form of the metal (e.g. hexavalent chromium).

EPA issued Interim Guidance on Determination and Use of Water-Effect Ratios for Metals in February 1994 (EPA-823-B-94-001). The water effect ratio (WER) guidance suggested three levels of increasing complexity that could be used in interpreting aquatic life criteria: (1) TR metal (as Kentucky has historically done); (2) dissolved metal, using dissolved metal criteria; or (3) either of the above combined with a water-effects ratio that compares metal toxicity in stream water to that in lab make-up water.

The Division allows either the WER or its own procedures to be used in the alternative metal demonstration. Kentucky's procedures were originally drafted to address discharges into zero 7Q10 flow streams that early WER methods did not adequately address. Although the latest WER methodology now accounts for these situations, Kentucky's methods offer the applicant a second alternative that may be easier to apply in certain instances.

Metals that are eligible for alternative limits are: arsenic, beryllium, cadmium, trivalent and hexavalent chromium, copper, iron, lead, nickel, silver, and zinc. Because of "free-from" narrative language in Section 2 of 5:031, it is also possible that a metal other than those with numerical criteria in Section 4 could be involved.

Mercury and selenium are not eligible for the alternative procedures. The divalent mercury cation, Hg(II), whether introduced directly or resulting from the oxidation of elemental mercury,

can be transformed in the aquatic environment to methylmercury, which is both more toxic and more readily bioaccumulated. (The chronic criterion is based on levels in fish tissue and the resultant impact on human health, and the acute criterion is based on toxicity to aquatic organisms). Therefore, the mercury criteria should remain in TR form. The criteria for selenium were derived from field studies that related toxic effects to biomagnification of the metal, not toxic effects at the gill surface resulting from the availability of dissolved metal as is the case for most metals.

Procedures

The applicant must demonstrate through chemical-specific analyses and biomonitoring that an effluent does not exhibit metal toxicity. A six-month testing period is necessary to account for effluent variability, without imposing undue testing or time constraints. Chemical analyses will be performed on the effluent on a monthly basis for the dissolved and TR forms of metals for which the applicant is seeking alternative limits. Because of recent controversy regarding quality assurance of dissolved metal results, care should be taken to reduce potential sample contamination both in the field and the laboratory by using "clean" techniques. These techniques are described by the U.S. Geological Survey¹ and U.S. EPA².

Biomonitoring requirements (acute or chronic, availability of instream dilution) will be determined by the Division on a case-by-case basis according to the applicant's discharge and receiving stream characteristics. Definitive toxicity tests will be performed every month on the water flea Ceriodaphnia dubia and the fathead minnow Pimephales promelas, as specified by Division biomonitoring protocol. Samples for biomonitoring and chemical analysis must be collected concurrently from the effluent.

Failure of two biomonitoring tests requires a toxicity identification evaluation (TIE) to determine if the metals in question were the cause of toxicity. Chemical data from these tests should be determined on samples used for the toxicity identification evaluation. If the TIE determines that metals are causing or contributing to toxicity, those metals are not eligible for alternative limits. The corresponding chemical data will assist in determining which metals are present in high enough concentrations to be contributing to the toxicity. Analytical results are used to determine the relationship between the TR and dissolved metal fractions. The ratio is initially developed with results from the six monthly samples, supplemented by earlier data if available. The ratio should be updated in subsequent years as the number of observations increases from continued dissolved and TR metal sampling.

Permit limits are based on the most stringent of the following: (1) the dissolved fraction cannot exceed Kentucky's aquatic life criteria multiplied by EPA factors that convert TR criteria

¹A Protocol for the Collection and Processing of Surface- Water Samples for Subsequent Determination of Trace Elements, Nutrients, and Major Ions in Filtered Water, Office of Water Quality Technical Memorandum 94.09

²Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, EPA 821-R-95-034.

to dissolved criteria (see Table 1); 2) the total recoverable form of the metal cannot exceed human health criteria for fish consumption or domestic water supply, while accounting for any available dilution of the receiving water; or (3) the dissolved, total recoverable, or other specified form of the metal cannot exceed a technology-based limit as found in effluent guidelines. Also, for nondegradation purposes as described in 401 KAR 5:030, a discharge into a High Quality Water will receive limits twice as stringent as in a Use Protected Water. The dissolved:TR ratio is used to determine sample compliance with total recoverable permit limits in (1) above in the following manner. The TR metal concentration of the effluent is first multiplied by the dissolved:TR ratio found from the six-month testing. This results in a "dissolved" concentration. As permit limits must be expressed as TR metal, the result must then be multiplied by the reciprocal of EPA's criteria conversion factor (see Table 1). For example, assume that a chronic TR copper criterion is 0.010 mg/l, and that sampling of 100% effluent (to a stream with a low flow of zero) has shown that the dissolved:TR ratio is 0.5. Compliance sampling by the permittee shows TR levels of 0.020 mg/l in the effluent. Applying the ratio of 0.5 results in a dissolved level of 0.010 mg/l. The result then must be multiplied by the reciprocal of EPA's criteria conversion factor (1/0.96 = 1.04) to properly compare it to the permit limit expressed as TR.

Metal concentration of effluent reported by permittee =
 (TR metal of effluent X Dissolved:TR metal ratio of effluent) X
 1/EPA criteria conversion factor

Continued biomonitoring will be required once the alternative metal procedures are in place to account for the potential for different ratios of dissolved to TR metal or higher levels of metal. Biomonitoring frequency will be as stipulated in the permit if the permit already contains toxicity monitoring, or at least semiannually if the permit does not already contain toxicity monitoring.

New facilities present different situations than existing dischargers. Upon receiving the application, the Division will inform the applicant of its options. However, a demonstration cannot be made until a permit has been issued and the facility built. Therefore, if a TR limit initially is given, the limit could be modified once the demonstration has been successfully completed.

As a result of the metals demonstration, facilities not normally subject to biomonitoring requirements may find that toxicity is present. The Division may then decide whether or not to place biomonitoring limits on the permit.

Table 1. Criteria Conversion Factors for Dissolved Metals^a

<u>Metal</u>	<u>Acute</u>	<u>Chronic</u>
Arsenic	1.000	1.000
Cadmium ^b	0.944	0.909
Chromium III	0.316	0.860
Chromium VI	0.982	0.962
Copper	0.960	0.960
Lead ^b	0.791	0.791
Nickel	0.998	0.997
Silver	0.85	NA
Zinc	0.978	0.986

^aSource: USEPA, Federal Register Vol. 60, No. 86, May 4, 1995, p. 22231, Table 2

^bConversion factors are hardness-dependent. The values shown are with a hardness of 100 mg/l as CaCO₃. Conversion factors (CF) for any hardness can be calculated using the following equations:

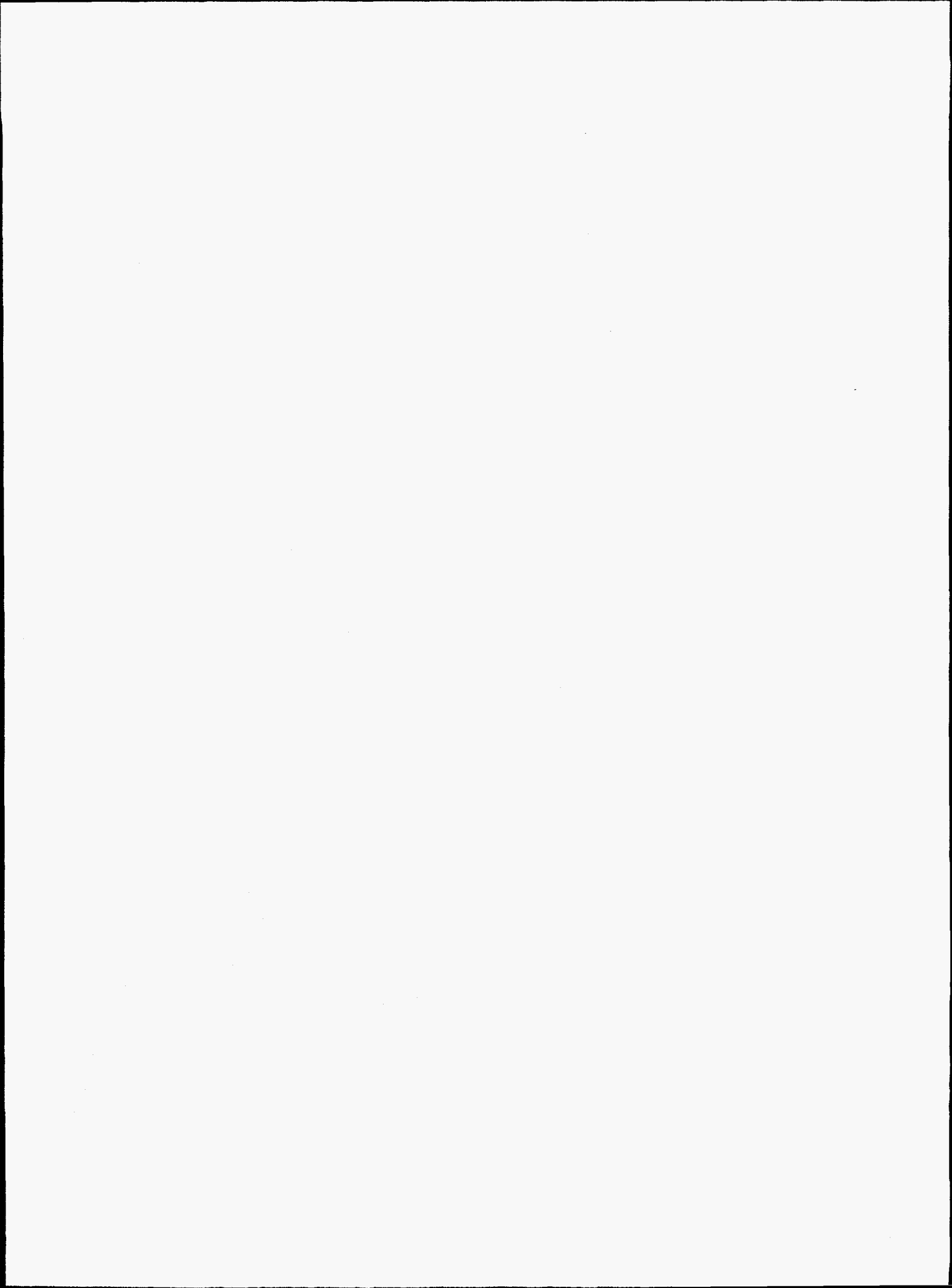
Cadmium

Acute: $CF = 1.136672 - [(\ln \text{ hardness})(0.041838)]$

Chronic: $CF = 1.101672 - [(\ln \text{ hardness})(0.041838)]$

Lead

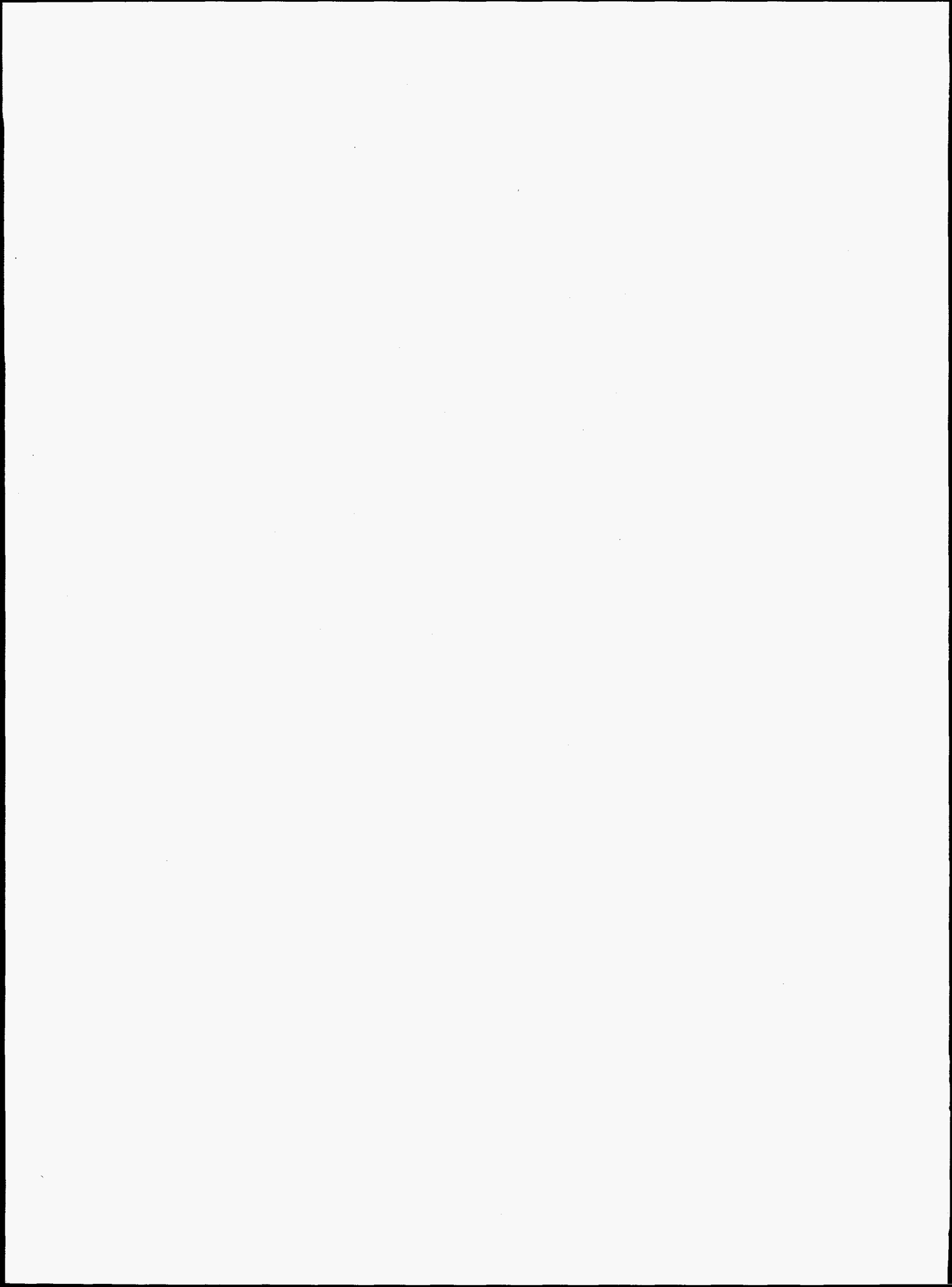
Acute and Chronic: $CF = 1.46203 - [(\ln \text{ hardness})(0.145712)]$



Appendix B

AGREED ORDER OF DISMISSAL

(File No. DOW-20277-056)



February 1, 1996

COMMONWEALTH OF KENTUCKY
NATURAL RESOURCES AND
ENVIRONMENTAL PROTECTION CABINET
FILE NO. DOW-20277-056

UNITED STATES DEPARTMENT OF ENERGY,
PADUCAH GASEOUS DIFFUSION PLANT

PETITIONER

VS.

AGREED ORDER OF DISMISSAL

NATURAL RESOURCES AND
ENVIRONMENTAL PROTECTION CABINET

RESPONDENT

WHEREAS, the parties to this Agreed Order, the Natural Resources and Environmental Protection Cabinet (hereinafter "Cabinet") and United States Department of Energy, Paducah Gaseous Diffusion Plant (hereinafter "DOE") and the United States Enrichment Corporation (hereinafter "USEC"), state:

1. The Paducah Gaseous Diffusion Plant (PGDP), located approximately ten (10) miles west of Paducah, Kentucky, is a uranium enrichment facility owned by the United States Department of Energy (DOE).

2. DOE and USEC discharge wastewater to the Big Bayou and Little Bayou Creeks. The facility was operated from October 12, 1987, through October 31, 1992, pursuant to an Agreed Order issued October 12, 1987, relating to the challenge of a Kentucky Pollutant Discharge Elimination System (KPDES) Permit Number KY0004049 issued to the DOE October 22, 1986 by the Kentucky Division of Water (KDOW).

3. Pursuant to Title IX of the Energy Policy Act of 1992, the USEC was established as a wholly owned government corporation. In accordance with the Energy Policy Act, the USEC and DOE entered into an agreement pursuant to which USEC is leasing portions of PGDP effective as of July 1, 1993. At the non-leased premises of PGDP, DOE continues to perform various activities including decontamination, decommissioning, and environmental response actions and corrective actions. DOE conducts its activities at PGDP primarily through Lockheed Martin Energy Systems, Inc., a wholly owned subsidiary of Lockheed Martin Technologies, Inc. USEC conducts its activities at PGDP through an operating contractor, Lockheed Martin Utility Services, Inc., also a wholly owned subsidiary of Lockheed Martin Technologies, Inc.

4. Since 1987, DOE has performed a comprehensive biological monitoring program assessing the biological impacts to Big Bayou and Little Bayou Creeks.

5. On May 9, 1991, DOE made an application for a KPDES permit.

6. On September 29, 1992, the Cabinet reissued KPDES Permit Number KY0004049 to DOE as a final action. The permit, by its terms, became effective on November 1, 1992, and requires compliance with the new and more stringent effluent limitations on and after that date. In September 1993, USEC was added to the permit to discharge under the KPDES system, thereby authorizing USEC to discharge from PGDP to certain receiving waters. The effective date of this addition to KPDES Permit No. KY0004049 was November 1, 1992.

7. On October 21, 1992, DOE petitioned the Cabinet for a hearing requesting relief from certain limits in KPDES Permit No. KY0004049. These limits are copper, cadmium, chromium, lead, nickel, zinc, temperature, phosphorous, pH, and chronic toxicity.

8. On October 21, 1992, DOE requested that the Cabinet issue a stay of these specified limits contained in KPDES Permit No. KY0004049.

9. On October 28, 1992, the Cabinet's Office of Administrative Hearings issued an Order granting a stay of certain permit conditions.

10. PGDP submitted a Plan for Development of Alternative Temperature Limit to the KDOW under cover letter dated August 8, 1994.

Now, therefore, in the interest of settling the issues involved in this challenge to the KPDES permit, the parties agree as follows:

11. DOE and USEC shall meet the KPDES permit limit for phosphorus upon entry of this final Agreed Order.

12. The KPDES permit limits for all other parameters except lead, chromium, cadmium, copper, nickel, zinc (hereinafter metals), temperature and pH, shall be final and remain in effect upon entry of this final Agreed Order. The KPDES permit limits for lead, cadmium, chromium, copper, nickel, zinc, temperature and pH shall be governed by this Agreed Order until the Cabinet makes its final determinations on these parameters under this order. At that time, DOE and USEC shall have twenty (20) days to request a stay of the final limits or comply with the determination.

13. TEMPERATURE: DOE and USEC shall conduct the temperature study as described in paragraph 10 and approved by KDOW September 27, 1994 for outfalls 001, 008, and the effluent from C-617 lagoon whether it be discharged from outfall 010 or 011 for the purpose of determining the variability in temperature of the effluent discharges in Big Bayou Creek and Little Bayou Creek. The interim temperature limit shall be 95° Fahrenheit at a monthly average, 100° Fahrenheit daily maximum until the interim limit is terminated in accordance with this Agreed Order. DOE and

USEC shall submit the results of the study to the Kentucky Division of Water on or before April 1, 1996. The parties agree that any data collected as part of this study will not be included in the Discharge Monitoring Reports. At the end of the study and after review of the study results the Cabinet shall notify DOE and USEC of its final determination regarding alternative temperature limits. DOE and USEC shall retain the right to petition for hearing pursuant to KRS 224.10-420(2) or may make application for a new permit decision depending upon the Cabinet's determination. Compliance with this paragraph shall constitute compliance with the temperature requirements of the permit. All other outfalls shall meet the KPDES Permit limit for temperature upon entry of this Agreed Order. If the Cabinet determines that the temperature limits should be less than the interim limits contained in this Agreed Order then DOE and USEC, within thirty (30) days of receiving the Cabinet's notice, shall submit to the Cabinet a plan and schedule for coming into compliance with such new temperature limits. Upon approval by the Cabinet, DOE and USEC shall comply with the approved plan and schedule to come into compliance with such new temperature limits.

14. pH: DOE and USEC shall submit a proposal to conduct instream monitoring for pH in Big Bayou Creek and Little Bayou Creek to evaluate the impact of effluents with pH greater than 9.0 on ambient water quality. The study will focus on impacts of effluents from outfalls 001, 006, 008, 009, and the effluent from the C-617 lagoon whether it be discharged from outfall 010 or 011. A draft proposal shall be submitted as soon as possible but in no case later than three (3) months following the entry of this Agreed Order. Monitoring of instream pH will commence thirty (30) days after the Cabinet grants approval of the monitoring plan. After the completion of twelve (12) months of monitoring, a comprehensive review of the monitoring data shall be conducted by DOE and USEC and the Kentucky Division of Water to determine the impact of the discharges from the

outfall(s) in questions. Based on the findings of this review, DOE and USEC shall, within one (1) year, install pH control systems at any outfall whose effluent causes Big Bayou Creek or Little Bayou Creek to exceed the warm water quality standard of 9.0 pH. For the outfalls studied for any outfall whose effluent does not cause Big Bayou Creek or Little Bayou Creek to exceed the warm water quality standard of 9.0 pH, final effluent limits shall be based upon that pH discharge limit which is found not to cause environmental harm, not to exceed a maximum of 10.5 pH. DOE and USEC shall retain the right to petition for hearing pursuant to KRS 224.10-420(2) to contest the question of whether or not the Cabinet's final determination as to pH was proper. An interim limit of 6.0 to 10.5 pH shall apply to outfalls 001, 006, 008, 009, and the effluent from the C-617 lagoon, whether it be discharged from outfall 010 or 011, until these interim limits are terminated by this Agreed Order. All other outfalls not subject to the pH studies shall meet the KPDES permit limit for pH upon entry of this Agreed Order. DOE and USEC reserve the right to petition the Cabinet for an exception to criteria as provided for in 401 KAR 5:031, Section 9. Compliance with this paragraph shall constitute compliance with the pH requirements of the permit. Data collected in stream will be reported but will not be included on Discharge Monitoring Reports.

15. METALS: 401 KAR 5:031 sets the water quality criteria for certain metals. Pursuant to 401 KAR 5:031, metals criteria applied to the KPDES permit are "total recoverable metals" to be measured in an unfiltered sample unless it can be demonstrated to the satisfaction of the Cabinet that a more appropriate analytical technique or criteria is available which provides a better measurement of that portion of the metals present which causes toxicity to aquatic life. DOE and USEC shall conduct studies to develop alternative metal limits pursuant to the above regulations for DOE and USEC outfalls 001, 002, 003, 008, 009, 010, 011, 012, 013, 015, 016, 017, and 018 (except during

heavy rainfall events outfalls 002, 010, 011, and 012 shall be composited in the C-617 lagoon, dechlorinated and discharged from outfall 010 or outfall 011). All other outfalls shall meet the KPDES permit limit for metals upon entry of this Agreed Order. A draft plan shall be submitted to the Cabinet for review as soon as possible but no later than three (3) months following the entry of this Agreed Order, with a final report submitted to the Cabinet in accordance with the schedule outlined in the approved plan. DOE and USEC may attempt to develop alternative metal limits for cadmium, chromium, copper, lead, nickel, and zinc. If pursuant to 401 KAR 5:031, DOE and USEC prove to the satisfaction of the Cabinet that a more appropriate analytical technique or criteria is available which provides a better measurement of that portion of the metals present which causes toxicity to aquatic life, the Cabinet will propose to modify the permit to incorporate these alternative metals limits and will issue a final KPDES permit determination as authorized by KRS 224 and 401 KAR Chapter 5. Until the process is complete, DOE and USEC shall monitor for cadmium, chromium, nickel, lead, copper and zinc and report the results. The data collected as a part of this study and reported pursuant to the previous section shall not be included in the discharge monitoring reports. In lieu of metals limits, DOE and USEC shall comply with the requirements specified in Part III, Sections E and F of KPDES Permit No. KY0004049 issued September 29, 1992. This section establishes a whole effluent toxicity limit of 1 TU₅ for outfalls 001, 006, 008, 009, and the effluent from the C-617 lagoon (composited 002, 010, 011, 012) discharged from outfall 010 or 011 and requires testing of these outfalls to be conducted quarterly. Outfalls 013, 015, 016, 017, and 018 will also be tested quarterly for toxicity and the results reported on the Discharge Monitoring Reports. DOE and USEC retain all rights to petition for hearing pursuant to KRS 224.10-420(2) to contest the question of whether or not the final determination of the Cabinet regarding alternative

metals limits was proper. Compliance with this paragraph shall constitute compliance with the cadmium, chromium, nickel, lead, copper and zinc requirements of the permit. DOE and USEC reserve the right to petition the Cabinet for an Exception to Criteria as provided for in 401 KAR 5:031, Section 9.

16. Those conditions of the permit not specifically addressed in this Agreed Order are final and shall remain in effect. Monitoring frequencies for all parameters shall be as required in KPDES Permit No. KY0004049 unless otherwise specified in this Agreed Order. Any previous Agreed Orders between the parties involving DOE and USEC's KPDES permit are expressly terminated. The interim limits for temperature and pH provided in this Agreed Order shall terminate no later than (a) if no application for permit is timely filed, the expiration date of the permit October 31, 1997 or (b) if an application for a permit is timely filed, the date a subsequent KPDES permit is issued.

17. The DOE and USEC agree that this Agreed Order only resolves the permit challenge to KPDES Permit No. KY0004049 filed in action number DOW 20277-56. The DOE and USEC agree there are other matters with the Cabinet, not related to this Agreed Order, that this Agreed Order does not address. To the extent any interim limits are deemed by DOW to satisfy water quality standards, these limits will be considered when the permit is reissued.

18. DOE shall use its best efforts and take all necessary steps to obtain timely funding to meet the obligations under this Agreed Order. It is DOE's position that any requirement for the payment or obligation of funds to perform required studies under this Agreed Order is subject to the availability of appropriated funds and that no provision of this Agreed Order should be interpreted to require obligation for payment of funds in violation of the Anti-Deficiency Act, 31 U.S.C. Section

1341, as amended. It is the Cabinet's position that the Act or any other defense based on the lack of appropriations or funding does not apply to the activities and requirements of this Agreed Order and that DOE's obligations under this Agreed Order are not affected by its failure to obtain adequate funds or appropriations from Congress. The parties reserve their respective rights, positions, and defenses on the issue. Failure to obtain adequate funds or appropriations from Congress does not in any way release DOE from its ultimate obligation to comply with the effective terms and conditions of KPDES Permit No. KY0004049. Subject to the terms of this Agreed Order, if DOE maintains adequate funds are not available to fulfill its obligations under this Agreed Order, the parties agree to meet to determine if new dates requiring the payment or obligations of such funds can be agreed upon. If the parties are unable to resolve their differences on these issues, the Cabinet reserves the right to initiate any other remedy that it would have absent this Agreed Order.

19. This Agreed Order is a final order in action DOW 20277-56 and this action is hereby dismissed.

20. The Cabinet does not, by its consent to the entry of this Agreed Order, warrant in any manner that DOE and USEC's complete compliance with this Agreed Order will result in compliance with the provisions of all statutes under the Cabinet's jurisdiction and any regulations adopted pursuant thereto. Notwithstanding the Cabinet's review and approval of any plans formulated pursuant to this Agreed Order, DOE and USEC shall remain solely responsible for compliance with the terms of any statute under the Cabinet's jurisdiction and the regulations adopted pursuant thereto, this Agreed Order and any other permit requirements.

21. The Cabinet enters this Agreed Order based on information provided by the DOE and USEC. Nothing contained herein shall be construed to waive or to limit any remedy or cause of

action by the Cabinet based on statutes or regulations under its jurisdiction and DOE and USEC reserves their defenses thereto. The Cabinet expressly reserves its right at any time to issue administrative orders and to take any other action it deems necessary, including the right to order all necessary remedial measures, assess penalties for violations, or recover all response costs incurred, and DOE and USEC reserves their defenses thereto. This Agreed Order shall not prevent the Cabinet from issuing, reissuing, renewing, modifying, revoking, suspending, denying, terminating, or reopening any permit to DOE and USEC. DOE and USEC reserves their defenses thereto, except that DOE and USEC shall not use this Agreed Order as a defense.

22. This Agreed Order may not be amended except by a written order of the Cabinet's Secretary. DOE and USEC may request an amendment by writing the Cabinet and stating the reasons for the request. If granted, the amended Agreed Order shall not affect any provision of this Agreed Order unless expressly provided in the amended Agreed Order. Upon receipt of a written request, the Cabinet may, in its sole discretion, accord DOE and USEC an extension of time reasonably needed for DOE and USEC to complete their performance under the terms of this Agreed Order. Such extension must be by Agreed Order and the request shall be tendered prior to the time performance is due. Such a request shall be submitted directly to the Director of the Division of Water, 14 Reilly Road, Frankfort, Kentucky 40601. DOE and USEC retain all rights to petition for hearing to contest the Cabinet's decision on any request for an amendment to this Agreed Order. Except as provided for in paragraph 18 of this Agreed Order, economic factors shall not be considered as grounds for an extension.

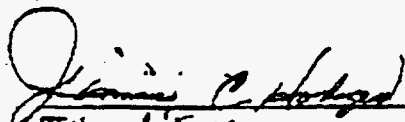
23. The parties recognize that any major modification to this permit will require the Cabinet to abide by the public notification and public hearing requirements of 401 KAR Chapter 5.

24. The provisions of this Agreed Order shall apply to and be binding upon the parties to this action, their officers, directors, agents, successors, assigns, and all persons, firms and corporations in active concert or participation with them. DOE and USEC shall give notice of this Agreed Order to any successors in interest prior to the transfer of ownership and/or operation of any part of their now existing facility and shall notify the Natural Resources and Environmental Protection Cabinet that such notice has been given and follow all statutory and regulatory requirements for such a transfer.

25. This Agreed Order shall be of no force and effect unless and until it is entered by the Secretary or his designee as evidenced by his signature thereon.

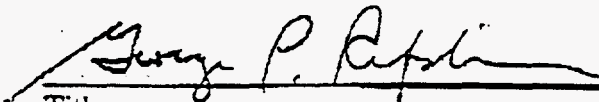
AGREED TO BY:

Authorized Representative for the United States Department of Energy, Paducah Gaseous Diffusion Plant


 Title Site Manager

3-7-96
 Date

Authorized Representative for the United States Enrichment Corporation


 Title Executive V.P.

2/04/96
 Date

FROM: LUSE

301-664-3210

1996.05-07

15:18

#011 P.12/14

FILE NO. DOW-20277-056

APPROVAL RECOMMENDED BY:

Jack A. Wilson
Jack A. Wilson, Director
Division of Water

3-19-96
Date

Brenda Gail Lowe
Brenda Gail Lowe, Attorney
Natural Resources and Environmental
Protection Legal Branch

Mar 15, 96
Date

Kathryn M. Hargraves
Kathryn M. Hargraves, Branch Manager
Natural Resources and Environmental
Protection Cabinet

3-31-96
Date

Glenna Jo Curry
Glenna Jo Curry, General Counsel
Office of Legal Services

3-3-96
Date

Steve Blanton
Steve Blanton, Hearing Officer
Office of Administrative Hearings

4/3/96
Date

ORDER

WHEREFORE, the forgoing Agreed Order is entered as the final Order of the Natural Resources and Environmental Protection Cabinet this 5th day of April, 1996.

NATURAL RESOURCES AND
ENVIRONMENTAL PROTECTION CABINET

James E. Bickford
JAMES E. BICKFORD, SECRETARY

FROM TUSEP

301-564-3210

1996.06-07

15119

#011 P.13/14

50

CERTIFICATE OF SERVICE

I hereby certify that a true and accurate copy of the foregoing AGREED ORDER OF DISMISSAL was, on this 5th day of April, 1996, mailed by first-class mail, postage prepaid to:

HON. TERRI SLACK
HON. RACHEL BLUMENFELD
U.S. DEPARTMENT OF ENERGY
P.O. BOX 2001
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T. MIKE TAIMI
ASSISTANT GENERAL COUNSEL
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HON. DANE A. BARTLETT
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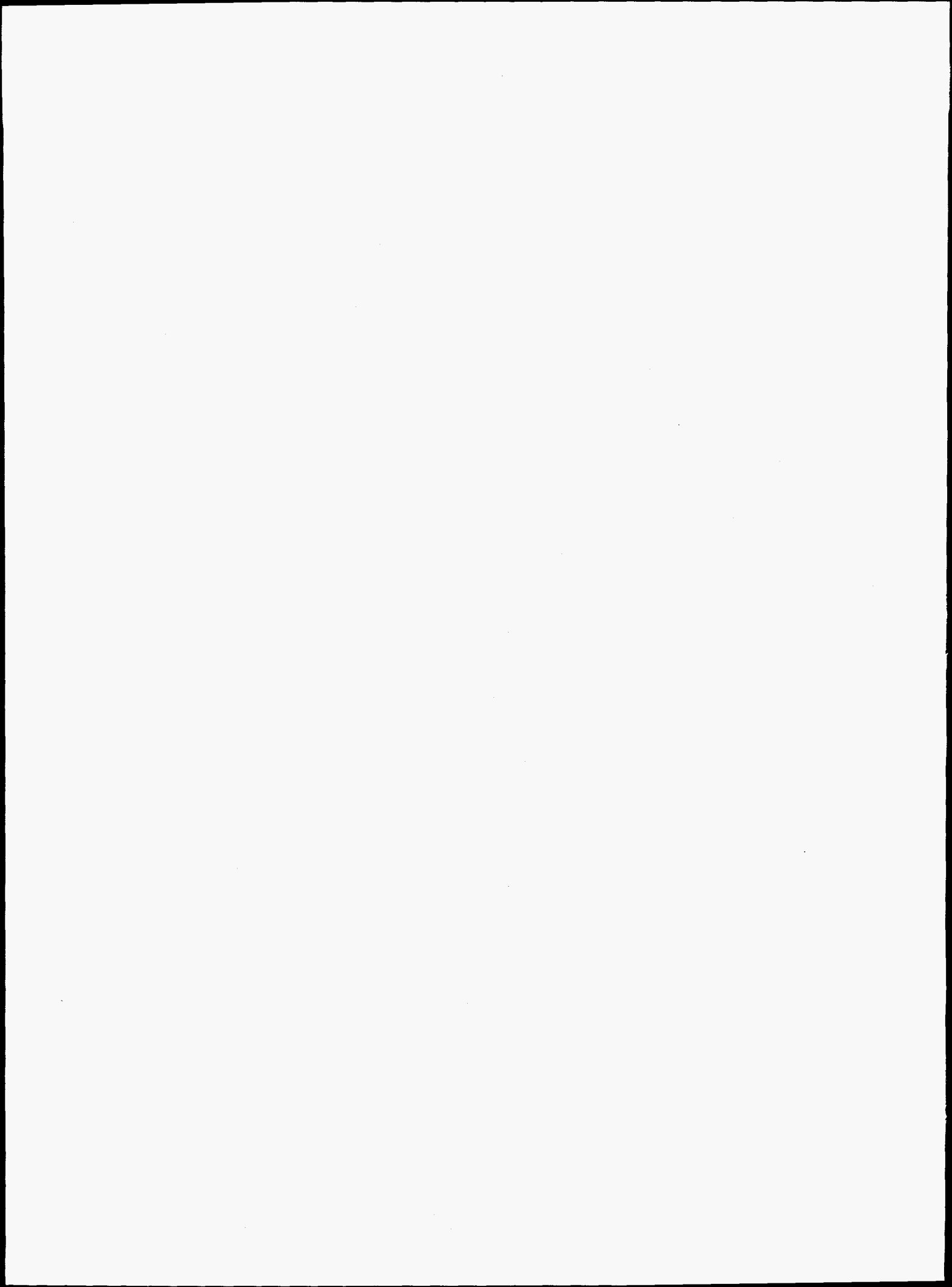
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Hon. Michael Williamson
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Natural Resources and
Environmental Protection Cabinet
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