

Attachment B

Water Quality-Based Effluent Limits

Coal Combustion Waste Impoundments

I. Background

Recent Coal Combustion Residual Impoundment Spills

On December 22, 2008, a coal combustion residual (CCR) ash impoundment dam collapsed at the TVA Fossil plant located at Kingston, Tennessee. The breach released 5.4 million cubic yards of coal combustion residuals into tributaries of the Tennessee River, the Clinch and Emory Rivers, as well as surrounding areas. A second incident at a CCR impoundment at the TVA Widows Creek plant on January 9, 2009, added further attention to this issue. At 10,000 gallons, that second spill was dwarfed by the Kingston spill; however, the two incidents, as well as others that have occurred, highlighted the need for better management of CCR impoundments and the potential water quality impacts associated with the discharges. This document discusses potential water quality impacts associated with discharges from CCR impoundments and provides guidance on the methods to control them through water quality analysis and permit conditions.

Waste Streams and Wastewater Discharges

The Steam Electric Power Generating Category Effluent Limitations Guidelines (ELGs) found at 40 CFR Part 423 contain technology-based limits for most wastewater streams expected at facilities subject to that guideline. The ELGs apply to discharges from generating units located at establishments primarily engaged in the generation of electrical power for distribution and sale. The ELGs do not address discharges from steam electric generating units at facilities that are not primarily engaged in the production of electricity for distribution or sale. Steam electric facilities not covered by the ELGs typically supply electricity to industrial facilities such as paper mills. The waste streams discharged by either type of coal-fired steam electric plant include: fly ash and bottom ash transport water, metal cleaning wastes, once through cooling water, cooling tower blowdown, coal pile runoff, and low volume waste (a broadly-defined term that includes wastes such as boiler feedwater treatment waste water and flue gas desulfurization (FGD) wastewater). Discharges from both types of coal fired steam electric facilities are covered by this guidance. This guidance does not address other process related pollutants that are discharged from the industrial generating facilities described above. For those industrial facilities, permit writers must examine the specific process related waste streams and determine the need for permit limits applicable to the industry being regulated.

Treatment of wastewater at coal fired steam electric facilities varies significantly from plant to plant. Coal pile runoff is typically treated in settling ponds and is often segregated from other waste streams. In addition to fly ash and/or bottom ash, ash ponds often contain commingled wastes such as cooling tower blowdown, metal cleaning wastes, coal pile runoff, and low volume waste (including treated or untreated FGD wastewater).

Point Source Discharges of Seepage

In addition to traditional coal combustion effluent discharges, facilities with combustion waste impoundments are likely to discharge wastewater via seepage. Seepage can be collected via seepage interception systems that may be built into impoundments and are intended to manage seepage and prevent internal erosion of the structure. Wastewater from these systems is either pumped back into the impoundment or discharged. If the seepage is discharged directly to waters of the U.S., it is likely discharged via a discrete conveyance and thus is a point source discharge. Seepage discharges are expected to be relatively minor in volume compared to other discharges at a facility and could be inadvertently overlooked by permitting authorities. Although little data are available, seepage consists of CCRs including fly ash and bottom ash transport water and FGD wastewater and is likely to contain the same pollutants found in bottom ash and fly ash transport water and FGD wastewater. If seepage is discharged directly via a point source to a water of the U.S., the discharge must be addressed under the NPDES permit for the facility.

Permitting authorities will need to conduct a reasonable potential analysis and develop appropriate permit limits and other conditions similar to discharges from the ash pond and other sources at the facility as discussed below. Seepage discharges to surface water through a shallow ground water hydrologic connection have been controlled in a number of cases through NPDES permit requirements to either use lined impoundments to prevent seepage or to install seepage interception systems. Permitting authorities should examine the need for these types of requirements for hydrologically connected discharges that cannot be regulated through traditional NPDES outfalls. If effluent pollutant data for point source discharges of seepage are not included in the permit application, permitting authorities will need to request information from permittees.

II. Pollutants Present in CCR Impoundments

Application reporting requirements

The current NPDES application form 2C requires permittees to submit data for metals, GC/MS volatile and acid fraction compounds, and other parameters, such as nitrogen compounds that could be present in coal combustion effluent. Permittees typically submit this required data once every five years when they apply for permit renewal. For most parameters only one sample is collected and analyzed. However, permittees are required to provide daily maximum, monthly average and long term average data in the application for pollutants required to be monitored in the permit. Long term monitoring data for CCR discharges are required for pollutants including Total Suspended Solids (TSS) and Oil and Grease, which are limited by the ELG. Other long term monitoring data are required in the application if water quality based limits and/or monitoring requirements were included in the previous permit.

Effluent data

Effluent data shown below in Appendix A were collected by EPA as part of the ELG detailed study of steam electric plants. EPA began a detailed review of steam electric facilities in 2005 as a result of the Clean Water Act section 304(m) review process.

Effluent Variability and Pollutants of Concern

As shown below in Appendix A, effluent pollutant concentrations vary significantly between dischargers. The pollutant concentration variability is the result of factors such as the type of coal used. Note that none of the plants listed in Table 1 utilizes air emissions controls specific for mercury. Implementation of additional emissions controls for mercury or other pollutants would likely result in increased concentrations of those pollutants in CCR and the associated discharges. The current degree of effluent variability and the increasing use of emissions controls provide additional evidence supporting the need for permitting authorities to require site specific effluent data as part of permit applications.

III. Water Quality Permitting Issues

Pollutants Potentially Exceeding Water Quality Criteria

Appendix A shows that metals in CCR effluent are variable and have the potential to exist in relatively high concentrations. For reference, selected national recommended water quality criteria are shown in Appendix A. Based on information presented in Table 1, the following pollutants may be expected to be found in CCR effluent at concentrations that are greater than water quality criteria: Aluminum, Arsenic, Cadmium, Chromium, Copper, Iron, Manganese, Nickel, Selenium, Thallium, Chloride, and Nitrate/Nitrite. Barium, Lead, Mercury, and Silver also can exceed water quality criteria as measured at internal outfalls; however, due to dilution received through mixing the CCR waste stream with other effluents, they do not appear to exceed the criteria at the final outfall. Although water quality criteria were shown to be exceeded, the reasonable potential for a discharge to cause or contribute to an excursion of applicable Water Quality Standards in the receiving water will depend on site-specific conditions, the amount of in-stream dilution available, and the in-stream ambient pollutant concentration, as discussed below. While this comparison does not indicate that there is reasonable potential to exceed applicable water quality standards for each such discharge, it does demonstrate the need to collect data required by the application form 2C and to conduct a reasonable potential analysis for such discharges and establish water quality-based effluent limits where appropriate.

Other parameters shown in Table 1, such as Total Dissolved Solids and Sulfate are present in concentrations which could potentially cause or contribute to water quality impacts. Those parameters are not required to be monitored for the permit application Form 2C. Many states have not established numeric water quality criteria for parameters such as Total Dissolved Solids or Sulfate. Permit writers should be aware of this potential impact on the achievement of applicable narrative water quality criteria and may need to require that effluent data are submitted so that such impacts can be appropriately addressed by the permit. While permitting

authorities have the option of requiring monitoring in the permit to obtain such data, it is preferable to request the information during the permit reissuance process. In cases where the reissued permit requires data to be collected, actions to address impairments may be unnecessarily delayed until the subsequent permit is issued. In cases where the previous permit did not require whole effluent toxicity testing, the permitting authority should consider requesting that data also be submitted with the application.

Determining the Need for Water Quality Based Permit Limits

Permitting authorities need to examine the impacts of a discharge relative to both numeric and narrative criteria. Most States have adopted implementation guidance to address the reasonable potential (RP) for a discharge to cause or contribute to an exceedance of numeric criteria. That guidance includes statistical tools and methods for permit writers to determine the RP for a discharge to exceed Water Quality Standards (WQS). A reasonable potential determination as to whether a discharge causes or contributes to an excursion of applicable water quality criteria is required for every discharge (see 40 CFR 122.44(d)).

Most State permitting authorities derived their specific implementation plan for determining RP and establishing water quality based permit limits using EPA's Technical Support Document for Water Quality Based Toxics Control (TSD) (EPA 1991). In general, RP analysis compares the reasonable maximum in-stream pollutant concentration with water quality criteria to determine the need for effluent limits.

An initial part of the RP process is the determination of available in-stream dilution. Methods used to determine dilution in the mixing zone vary by state and are prescribed by WQS and the State's mixing zone policy.

Using the available dilution, permitting authorities make a statistical comparison of in-stream effluent pollutant concentrations after mixing and water quality criteria to determine whether there is a reasonable potential to exceed the criteria. This is typically done by comparing the calculated 95th or 99th percentile of the effluent data with criteria. The TSD includes methodology that can be used to conduct that analysis and to derive the resulting permit limits.

Examination of the potential for a discharge to exceed the narrative criteria is a more difficult task that is complicated by a lack of clearly prescribed implementation guidance. CCR can contain fairly high concentrations of parameters that have the potential to impact water quality, such as Total Dissolved Solids, Sulfate, and Calcium that can cause excursions of narrative water quality standards. Since most states have not established numeric criteria for those parameters, permit writers must rely on narrative criteria when addressing potential water quality impacts. One tool states commonly use to address narrative criteria is whole effluent toxicity (WET) monitoring and limits. Chronic WET testing, which include measurement of sub-lethal effects of growth and fecundity, is used in most cases. However, in situations where a discharge is made to a larger waterbody permitting authorities often require acute WET testing based on an acute to chronic ratio. Most states have adopted procedures to determine which test methods and species are used as part of their implementation plans. The TSD also includes

guidance that is intended to assist with implementation of water quality based permit limits. WET testing measures the toxic effects of the complete mix of pollutants in a discharge and is a useful tool for measuring the impacts to aquatic life. Permit writers also have the option of requiring bioassessments to determine whether discharges are causing impacts and understand the specific causes. Another option is for the permitting authority to target CCR discharges in their stream surveillance activities and address impacts under the Total Maximum Daily Load program. State stream assessment programs may also utilize other tools to analyze the water quality of surface waters. State established tools that are used to translate narrative standards based on numeric data may be useful to permit writers attempting to protect water quality.

Use of Ambient Pollutant Data

Permit limits that fully protect water quality cannot be developed without taking into account the ambient pollutant concentration, also known as the background concentration. However, permit writers typically do not have access to defensible ambient pollutant data. In the absence of data, permit writers have often established water quality based permit limits using the assumption that the background concentration is zero.

The equation used to calculate waste load allocations for water quality based limits follows, as shown in the NPDES permit Writers Manual (EPA 1996)

$$(Q_d C_d + Q_s C_s) / Q_r = C_r$$

Where:

Q_d = waste discharge flow in million gallons per day (mgd) or cubic feet per second (cfs)

C_d = pollutant concentration in waste discharge in milligrams per liter (mg/l)

Q_s = background stream flow in mgd or cfs above point of discharge

C_s = background in-stream pollutant concentration in mg/l

Q_r = resultant in-stream flow, after discharge in mgd or cfs

C_r = resultant in-stream pollutant concentration in mg/l in the stream reach (after complete mixing occurs)

This equation or a variation thereof is used by permitting authorities as part of the process to derive water quality based limits. If a value of zero is used for the ambient concentration for a pollutant (C_s) in the equation, the permit writer would be able to establish a limit that would give the entire pollutant allocation to the discharger. The resulting limit would not account for any upstream discharges or any natural background concentration of the pollutant, and it would not protect the Water Quality Standard. Since it is highly unlikely that the background concentration is ever zero, the limit would not prevent an in-stream excursion of criteria.

Since it is not realistic to assume that the ambient pollutant concentration is zero, permit writers must develop a method to adequately protect water quality. A number of options exist for that task. Some states have adopted a policy of assuming that the ambient concentration is equal to one half of the water quality criteria when no ambient data exist. While this is a

somewhat conservative approach, the permittee could be given the opportunity to collect data during the comment period for the permit if they believed that the approach resulted in an overly stringent limit. Other options available to the permitting authority include requiring submittal of ambient data with permit applications, developing permit requirements to collect data, or establishing default ambient concentrations using literature values. Any approach chosen by the permitting authority to estimate background pollutant concentrations will result in more realistic water quality based limits and improved compliance with state standards.

IV. Use of Sufficiently Sensitive Analytical Test Methods

The use of sufficiently sensitive analytical methods is critically important to detecting, identifying and measuring the concentrations of pollutants in CCW wastestreams. For further discussion of sufficiently sensitive methods, see Part V of Attachment A of this memo, and the memo on Analytical Methods for Mercury in NPDES Permit, dated August 23, 2007 in Appendix C.

V. Disclaimer

This guidance document does not change or substitute for any legal requirements, though it does provide clarification of some regulatory requirements. While EPA has made every effort to ensure the accuracy of the discussion in this document, the obligations of the regulated community are determined by the relevant statutes, regulations, or other legally binding requirements. This guidance document is not legally enforceable and does not confer legal rights or impose legal obligations upon any member of the public, EPA, states, or any other agency. In the event of a conflict between the discussion in this document and any statute or regulation, this document would not be controlling. The word “should” as used in this guidance document does not connote a requirement, but does indicate EPA’s strongly preferred approach to assure effective implementation of legal requirements. This guidance may not apply in a particular situation based upon the circumstances, and EPA, states and Tribes retain the discretion to adopt approaches on a case-by-case basis that differ from the recommendations of this guidance document where appropriate. Permitting authorities will make each permitting decision on a case-by-case basis and will be guided by the applicable requirements of the CWA and implementing regulations, taking into account comments and information presented at that time by interested persons regarding the appropriateness of applying these recommendations to the particular situation. In addition, EPA may decide to revise this guidance document to reflect changes in EPA’s approach to implementing the regulations or to clarify and update text.

VI. References

- USEPA. 2009. *Steam Electric Power Generating Point Source Category: Final Detailed Study Report*. USEPA Engineering and Analysis Division, Office of Water. EPA 821-R-09-008. Washington, DC. October, 2009. Available online at: <http://www.epa.gov/waterscience/guide/steam/finalreport.pdf>
- USEPA. 1996. *USEPA NPDES Permit Writers Manual*. USEPA Office of Water. EPA 833-B-96-003. Washington, DC. December, 1996. Available online at: http://cfpub.epa.gov/npdes/writermanual.cfm?program_id=45

USEPA. 1991. *Technical Support Document for Water Quality Based Toxics Control*. USEPA Office of Water Enforcement and Permits. Washington, DC. March, 1991. Available online at: <http://www.epa.gov/npdes/pubs/owm0264.pdf>

Appendix A: Steam Electric 2007/2008 Detailed Study Report. Ash Pond Effluent Concentrations, USEPA 2009)

Analyte	Method	Unit	Homer City – Effluent from Bottom Ash Pond ^a	Widows Creek – Effluent from Combined Ash Pond ^a	Mitchell – Effluent from Fly Ash Pond ^a	Cardinal – Effluent from Fly Ash Pond ^{a, b}
Routine Metals - Total						
Aluminum	200.7	ug/l	323	1,070	404	344
Antimony	200.7	ug/l	ND (20.0)	ND (20.0)	24.6	21.2
Arsenic	200.7	ug/l	ND (10.0)	38.2	150	77.6
Barium	200.7	ug/l	101	227	133	165
Beryllium	200.7	ug/l	ND (5.00)	ND (5.00)	ND (5.00)	ND (5.00)
Boron	200.7	ug/l	396	2,210	2,350	1,100
Cadmium	200.7	ug/l	ND (5.00)	ND (5.00)	ND (5.00)	ND (5.00)
Calcium	200.7	ug/l	186,000	58,500	115,000	88,400
Chromium	200.7	ug/l	ND (10.0)	13.5	15.9	ND (10.0)
Cobalt	200.7	ug/l	ND (50.0)	ND (50.0)	ND (50.0)	ND (50.0)
Copper	200.7	ug/l	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)
Iron	200.7	ug/l	355	144	ND (100)	ND (100)
Lead	200.7	ug/l	ND (50.0)	ND (50.0)	ND (50.0)	ND (50.0)
Magnesium	200.7	ug/l	31,800	6,680	21,000	17,900
Manganese	200.7	ug/l	128	ND (15.0)	ND (15.0)	64.7
Mercury	245.1	ug/l	ND (0.200)	ND (0.200)	ND (0.200)	ND (0.200)
Molybdenum	200.7	ug/l	19.7	143	359	361
Nickel	200.7	ug/l	ND (50.0)	ND (50.0)	ND (50.0)	ND (50.0)
Selenium	200.7	ug/l	6.02	16.2	177	44.5
Sodium	200.7	ug/l	106,000	21,300	526,000	70,800
Thallium	200.7	ug/l	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)
Titanium	200.7	ug/l	ND (10.0)	14.5	ND (10.0)	12.6
Vanadium	200.7	ug/l	ND (20.0)	68.5	110	104
Yttrium	200.7	ug/l	ND (5.00)	ND (5.00)	ND (5.00)	ND (5.00)
Zinc	200.7	ug/l	21.6	ND (10.0)	ND (10.0)	ND (10.0)

Analyte	Method	Unit	Homer City – Effluent from Bottom Ash Pond a	Widows Creek – Effluent from Combined Ash Pond a	Mitchell – Effluent from Fly Ash Pond a	Cardinal – Effluent from Fly Ash Pond a, b
Routine Metals - Dissolved						
Aluminum	200.7	ug/l	231	357	241	130 L
Antimony	200.7	ug/l	ND (20.0)	ND (20.0)	23.9	20.9
Arsenic	200.7	ug/l	ND (10.0)	30.1	138	74.6
Barium	200.7	ug/l	106	206	128	157
Beryllium	200.7	ug/l	ND (5.00)	ND (5.00)	ND (5.00)	ND (5.00)
Boron	200.7	ug/l	397	2,200	2,290	1,090
Cadmium	200.7	ug/l	ND (5.00)	ND (5.00)	ND (5.00)	ND (5.00)
Calcium	200.7	ug/l	192,000	55,400	113,000	87,200
Chromium	200.7	ug/l	ND (10.0)	11.9	14.1	ND (10.0)
Hex. Chromium	D1687-92	ug/l	ND (2.00)	12.0	7.00	<3.50
Cobalt	200.7	ug/l	ND (50.0)	ND (50.0)	ND (50.0)	ND (50.0)
Copper	200.7	ug/l	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)
Iron	200.7	ug/l	106	ND (100)	ND (100)	ND (100)
Lead	200.7	ug/l	ND (50.0)	ND (50.0)	ND (50.0)	ND (50.0)
Magnesium	200.7	ug/l	32,600	6,430	20,300	17,700
Manganese	200.7	ug/l	129	ND (15.0)	ND (15.0)	42.9
Mercury	245.1	ug/l	ND (0.200)	ND (0.200)	ND (0.200)	ND (0.200)
Molybdenum	200.7	ug/l	20.2	136	330	352
Nickel	200.7	ug/l	ND (50.0)	ND (50.0)	ND (50.0)	ND (50.0)
Selenium	200.7	ug/l	6.10 L	15.3	162	43.8
Sodium	200.7	ug/l	106,000	20,000	514,000	70,300
Thallium	200.7	ug/l	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)
Titanium	200.7	ug/l	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)
Vanadium	200.7	ug/l	ND (20.0)	64.7	108	99.9
Yttrium	200.7	ug/l	ND (5.00)	ND (5.00)	ND (5.00)	ND (5.00)
Zinc	200.7	ug/l	35.2	ND (10.0)	ND (10.0)	ND (10.0)

Analyte	Method	Unit	Homer City – Effluent from Bottom Ash Pond ^a	Widows Creek – Effluent from Combined Ash Pond ^a	Mitchell – Effluent from Fly Ash Pond ^a	Cardinal – Effluent from Fly Ash Pond ^{a, b}
Low-Level Metals - Total						
Antimony	1638	ug/l	1.09	4.39	25.8	21.9
Arsenic	1638	ug/l	6.52	34.9	142	69.8
Cadmium	1638	ug/l	ND (0.500)	ND (0.500)	1.32	1.14
Chromium	1638	ug/l	ND (4.00)	13.5 L	20.4	4.64 L
Copper	1638	ug/l	2.37	1.49	5.47	2.98
Lead	1638	ug/l	ND (0.250)	0.490	0.580	0.420
Mercury	1631E	ug/l	0.00511	0.00157	0.00212	0.00125
Nickel	1638	ug/l	10.7	ND (5.00)	11.0	10.7
Selenium	1638	ug/l	5.74	17.1	191	45.8
Thallium	1638	ug/l	1.32	1.46	1.72	2.84
Zinc	1638	ug/l	24.2	ND (2.50)	10.1	5.98
Low-Level Metals - Dissolved						
Antimony	1638	ug/l	0.990	4.45	22.5	22.4
Arsenic	1638	ug/l	5.00	29.0	131	68.9
Cadmium	1638	ug/l	ND (0.500)	ND (0.500)	1.17	1.11
Chromium	1638	ug/l	ND (4.00)	12.6 L	16.0	4.49 L
Hex. Chromium	1636	ug/l	3.01	14.7	17.4	3.96
Copper	1638	ug/l	2.08	ND (1.00)	4.54	2.27
Lead	1638	ug/l	ND (0.250)	ND (0.250)	ND (0.250)	ND (0.250)
Mercury	1631E	ug/l	0.00141	ND (0.000500)	ND (0.000500)	ND (0.000500)
Nickel	1638	ug/l	10.4	ND (5.00)	9.57	10.6
Selenium	1638	ug/l	5.16	15.6	161	45.0
Thallium	1638	ug/l	1.31	1.49	1.42	2.87
Zinc	1638	ug/l	15.0	ND (2.50)	9.51	4.15

Analyte	Method	Units	Homer City – Effluent from Bottom Ash Pond ^a	Widows Creek – Effluent from Combined Ash Pond ^a	Mitchell – Effluent from Fly Ash Pond ^a	Cardinal – Effluent from Fly Ash Pond ^{a, b}
Ammonia As Nitrogen (NH ₃ -N)	4500-NH ₃ F	mg/l	0.340	0.160	0.150	0.205
Nitrate/Nitrite (NO ₃ -N + NO ₂ -N)	353.2	mg/l	37.0	0.230	0.730	4.73 ^E
Total Kjeldahl Nitrogen (TKN)	4500-N,C	mg/l	1.36	3.39	ND (0.100)	<0.785 ^L
Biochemical Oxygen Demand (BOD)	5210B	mg/l	ND (2.00)	4.00	2.00	ND (2.00)
Chloride	4500-CL-C	mg/l	90.0	20.0	240	60.0
Hexane Extractable Material (HEM)	1664A	mg/l	ND (5.00)	6.00	ND (5.00)	10.0
Silica Gel Treated HEM (SGT-HEM)	1664A	mg/l	NA	ND (5.00)	NA	ND (4.00)
Sulfate	D516-90	mg/l	1,290	80.7	1,110	494
Total Dissolved Solids (TDS)	2540 C	mg/l	1,250	281	2,050	673
Total Phosphorus	365.3	mg/l	1.09	0.250 ^E	0.200	0.0870
Total Suspended Solids (TSS)	2540 D	mg/l	5.00	12.0 ^E	15.0	6.00

Source: [ERG, 2008l; ERG, 2008m; ERG, 2008k; ERG, 2008o].

Note: EPA used several analytical methods to analyze for metals during the sampling program. For the purposes of sampling program, EPA designated some of the analytical methods as “routine” and some of them as “low-level.” EPA designated all of the methods that require the use of clean hands/dirty hands sample collection techniques (i.e., EPA Method 1669 sample collection techniques) as “low-level” methods. Note that although not required by the analytical method, EPA used clean hands/dirty hands collection techniques for all low-level and routine metals samples.]

^a – The concentrations presented have been rounded to three significant figures.

^b – The ash pond effluent results represent the average of the ash pond effluent and the duplicate of the ash pond effluent analytical measurements.

< – Average result includes at least one non-detect value. (Calculation uses the report limit for non-detected results).

^E – Sample analyzed outside holding time.

^L – Sample result between 5x and 10x blank result.

NA – Not analyzed.

ND – Not detected (number in parenthesis is the report limit). The sampling episode reports for each of the individual plants contains additional sampling information, including analytical results for analytes measured above the detection limit, but below the reporting limit (i.e., J-values).

Appendix B: National Recommended Water Quality Criteria

EPA National Recommended Water Quality Criteria ¹

Analyte	2006 National Recommended Water Quality Criteria			
	Freshwater Acute (ug/l)	Freshwater Chronic (ug/l)	Human Health (Water + Organism) (ug/l)	Human Health (Organism only) (ug/l)
Aluminum	750	87		
Antimony			5.6	640
Arsenic	340	150	0.018	0.14
Barium			1000	
Cadmium	2	0.25		
Hexavalent Chromium	16	11		
Copper	13	9	1,300	
Lead	65	2.5		
Manganese			50	100
Mercury	1.4	0.77		
Nickel	470	52	610	4,600
Selenium		5	170	4,200
Silver	3.2			
Thallium			0.24	0.47
Zinc	120	120	7,400	26,000
Nitrate/Nitrite			10,000	

¹ <http://www.epa.gov/waterscience/criteria/wqctable/index.html>

Appendix C: Mercury Analytic Test Method Memorandum



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
WATER

signed: August 23, 2007

MEMORANDUM

SUBJECT: Analytical Methods for Mercury in National Pollutant Discharge Elimination System (NPDES) Permits

FROM: James A. Hanlon, Director
Office of Wastewater Management

TO: Water Division Directors, Regions 1 – 10

The purpose of this memorandum is to inform you of EPA's March 12, 2007, approval of Method 245.7 for measurement of mercury and modified versions of approved analytical methods for mercury as well as the impact of their approval on the NPDES permitting process. While several different methods are currently approved under 40 CFR Part 136 for the analysis of mercury, some of these methods have much greater sensitivities and lower quantitation levels than others. This memorandum clarifies and explains that, in light of existing regulatory requirements for NPDES permitting,¹ only the most sensitive methods such as Methods 1631E and 245.7 are appropriate in most instances for use in deciding whether to set a permit limitation for mercury and for sampling and analysis of mercury pursuant to the monitoring requirements within a permit.

BACKGROUND

Section 301 of the Clean Water Act (CWA) requires NPDES permits to include effluent limitations that are as stringent as necessary to meet water quality standards. Thus, under the Act and EPA regulations, each permit must include, as necessary, requirements in addition to or more stringent than technology-based effluent limitations established under section 301 of the CWA in order to achieve water quality standards. 40 C.F.R. § 122.44(d)(1). The regulations require limitations to control all pollutants that the NPDES program director determines are or may be discharged at a level that "will cause, have the reasonable potential to cause, or contribute to an excursion above any state water quality standard," including both narrative and

¹ This memorandum is based on existing legal requirements and authorities. It does not impose any new, legally binding requirements on EPA, states, or the regulated community.

numeric criteria. 40 C.F.R. § 122.44(d)(1)(i). If the program director determines that a discharge has the reasonable potential to cause or contribute to such an excursion, the permit must contain water quality-based effluent limitations for the pollutant. 40 C.F.R. § 122.44(d)(1)(iii). Thus, a prospective permittee may need to measure various pollutants in its effluent at two stages: first, at the permit application stage so that the program director can determine whether “reasonable potential” exists and establish appropriate permit limits; and second, where a permit limit has been established, to meet the monitoring requirements within the permit. The following discussion explains which analytical methods permit applicants and permittees should use to make these measurements when mercury is the pollutant at issue.

Approved Analytical Methods

Measurements included on NPDES permit applications and on reports required to be submitted under the permit must generally be made using analytical methods approved by EPA under 40 CFR Part 136. See 40 CFR 136.1, 136.4, 136.5, 122.21(g)(7), and 122.41(j). For mercury, there are three methods commonly used in the NPDES program that EPA has approved under Part 136: Method 245.1, Method 245.2, and Method 1631E. Methods 245.1 and 245.2 were approved by EPA in 1974 and can achieve measurement of mercury down to 200 parts per trillion (ppt). Additionally, EPA approved Method 1631 Revision E in 2002. Method 1631E has a quantitation level of 0.5 ppt, making it 400 times more sensitive than Methods 245.1 and 245.2. In fact, the sensitivity of Methods 245.1 and 245.2 are well above the water quality criteria now adopted in most states (as well as the criteria included by EPA in the Final Water Quality Guidance for the Great Lakes System) for the protection of aquatic life and human health, which generally fall in the range of 1 to 50 ppt.² In contrast, Method 1631E, with a quantitation level of 0.5 ppt, does support the measurement of mercury at these low levels.

In addition to Methods 245.1, 245.2, and 1631E listed above, EPA approved Method 245.7 as well as modified versions of other EPA-approved methods on March 12, 2007. See 72 FR 11200. Method 245.7 has a quantitation level of 5.0 ppt, making it 40 times more sensitive than Methods 245.1 and 245.2. Additionally, modified versions of EPA-approved methods may also be used for the measurement of mercury. Methods approved under Part 136, such as 245.1 and 245.2, may be modified to achieve lower quantitation levels than can be achieved by the method as written.³ Modifications to an EPA-approved method for mercury that meet the method

² Many states have adopted mercury water quality criteria of 12 ppt for protection of aquatic life and 50 ppt for the protection of human health, and for discharges to the Great Lakes Basin, the applicable water quality criteria for mercury are 1.3 ppt for the protection of wildlife and 1.8 ppt for the protection of human health. In 2001, EPA issued new recommended water quality criteria guidance for the protection of human health. This new guidance recommends adoption of a methylmercury water quality criterion of 0.3 milligrams of methylmercury per kilogram (mg/kg) in fish tissue. EPA is currently developing implementation guidance to assist states in implementing the criterion, and *Draft Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion* (EPA-823-B-04-001) was released for public comment in August 2006.

³ Examples of such modification may include changes in the sample preparation digestion procedures such as the use of reagents similar in properties to ones used in the approved method, changes in the equipment operating parameters such as the use of an alternate more sensitive wavelength, adjusting the sample volume to optimize method performance, and changes in the calibration ranges (provided that the modified range covers any relevant regulatory limit).

performance requirements of Part 136.6 are considered to be approved methods and require no further EPA approval. See 72 FR 11239-40 (March 12, 2007). For analytical method modifications that do not fall within the flexibility of Part 136.6, the modified methods may be approved under the alternate test procedure program as defined by Parts 136.4 and 136.5.

ACTIONS RESULTING FROM THE MARCH 12, 2007, RULEMAKING

To implement the March 12, 2007, rule, the Office of Wastewater Management (OWM) provides the following guidance:

Monitoring Data Submitted as Part of NPDES Permit Applications

As noted, most states have adopted water quality criteria for the protection of aquatic life and human health that fall in the range of 1 to 50 ppt, and Methods 245.1 and 245.2, as written, do not detect or quantify mercury in this range. A “did not detect” result using Method 245.1 or Method 245.2 would show only that mercury levels are below 200 ppt but would not establish that they are at or below the applicable water quality criterion. Therefore, when a permit writer receives a permit application reporting mercury data analyzed with Method 245.1 or Method 245.2 as “did not detect” results, the permit writer in reality may lack the information needed to make a “reasonable potential” determination. In contrast, Method 1631E is able to detect and quantify mercury concentrations at these low levels.

EPA therefore expects, in general, that all facilities with the potential to discharge mercury will provide with their NPDES permit applications monitoring data for mercury using Method 1631E or another sufficiently sensitive EPA-approved method. For purposes of permit applications, a method for mercury is “sufficiently sensitive” when (1) its method quantitation level is at or below the level of the applicable water quality criterion for mercury or (2) its method quantitation level is above the applicable water quality criterion, but the amount of mercury in a facility’s discharge is high enough that the method detects and quantifies the level of mercury in the discharge.⁴ Accordingly, EPA strongly recommends that the permitting authority determine that a permit application that lacks effluent data analyzed with a sufficiently sensitive EPA-approved method such as Method 1631E is incomplete unless and until the facility supplements the original application with data analyzed with such a method. See 40 CFR 122.21(e) (a permit application is determined to be complete at the discretion of the permitting authority) and 40 CFR 122.21(g)(13) (the applicant shall provide to the Director, upon request, such other information as the Director may reasonably require to assess the discharge). Such data would allow the permitting authority to characterize the effluent to determine whether the discharge causes, has the reasonable potential to cause, or contributes to an excursion of state water quality standards for mercury and would consequently allow the permitting authority to determine whether a water quality-based effluent limit for mercury is necessary in the permit.

⁴ To illustrate the latter, if the water quality criterion for mercury in a particular state is 2.0 ppt, Method 245.7 (with a quantitation level of 5.0 ppt) would be sufficiently sensitive where it reveals that the level of mercury in a facility’s discharge is 5.0 ppt or greater. In contrast, Method 245.7 would not be sufficiently sensitive if it resulted in a level of non-detect for that discharge because it could not be known whether mercury existed in the discharge at a level between 2.0 and 5.0 (less than the quantitation level but exceeding the water quality criterion).

Monitoring Requirements in Permits

Where a permit authority establishes a permit limit for mercury, it also needs to consider specifying an analytical method that the permittee must use to monitor for mercury during the term of the permit. Methods 245.1 and 245.2, as written, are not likely to be sensitive enough to detect or quantify the concentration of mercury in the discharge at a level that matches the limitation for mercury in the permit. EPA therefore expects the permitting authority to require the use of a sufficiently sensitive EPA-approved method for monitoring under the permit in order to ensure that the sampling and measurements required are “representative of the monitored activity” (as required by 40 CFR 122.41(j)(1)). For purposes of monitoring under a permit, a method for mercury is “sufficiently sensitive” when (1) its method quantitation level is at or below the level of the mercury limit established in the permit or (2) its method quantitation level is above the mercury limit in the permit, but the amount of mercury in a facility’s discharge is high enough that the method detects and quantifies the level of mercury in the discharge.⁵

EPA Permit Review and Objection to State Issued Permits

For NPDES-authorized states, EPA regions are expected to review state permits and should strongly consider objecting to permits that are issued based on analytical data collected and analyzed using an EPA-approved method that is not sufficiently sensitive or that do not require use of a sufficiently sensitive EPA-approved method for monitoring when the permit includes a limit for mercury. OWM is expecting to undertake a permit quality review of a small representative number of permits with respect to mercury limitations and other conditions.

If you have questions concerning the content of this memorandum, please contact Linda Boornazian, Director of the Water Permits Division, at 202-564-0221 or have your staff contact Marcus Zobrist of the State and Regional Branch at 202-564-8311 or zobrist.marcus@epa.gov.

cc: NPDES Branch Chiefs Regions 1 – 10

⁵ See footnote 4.