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

AUG 23 2007

OFFICE OF
WATER

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 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

[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.

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 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.

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[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).

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.