



California Regional Water Quality Control Board

San Francisco Bay Region



Linda Adams
Agency Secretary

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Arnold Schwarzenegger
Governor

**TO: Chevron Products Company
Conoco Phillips
Shell Opus Refining Company
Tesoro Corporation
Valero Refining Company**

DATE: April 12, 2007

REQUIREMENT UNDER CALIFORNIA WATER CODE SECTION 13267 FOR SUBMITTAL OF TECHNICAL REPORTS ON MERCURY IN CRUDE OIL AND ASSOCIATED PRODUCT AND WASTE STREAMS IN BAY AREA PETROLEUM REFINERIES RELATING TO POTENTIAL DISCHARGES OF MERCURY INTO SAN FRANCISCO BAY

Pursuant to California Water Code (CWC) Section 13267, as a petroleum refinery discharging mercury into San Francisco Bay (the Bay), you are hereby required to submit the technical reports listed in the Schedule of Deliverables (Table 1) and described below regarding the amount and fate of mercury in crude oil processed in your refinery. The reports shall be submitted in accordance with the schedule in Table 1 for Executive Officer concurrence. We prefer that you collaborate with the above named recipients to produce a single study. However, if you choose not to participate with the other refineries, you will be required to submit identical studies that contain the required elements for your facility according to the schedule in Table 1.

The Water Board initially sent you a similar Section 13267 requirement letter on February 17, 2005. In response to the February 2005 letter, the refineries were required to submit information on the fate of mercury in air emissions from Bay Area refineries, with a final report on mercury air emissions and fate due May 31, 2007. As an attachment to the February 21, 2007, letter by the Western States Petroleum Association, on behalf of the five Bay Area refineries, Environmental Resources Management described the work done to date towards completing this final report, including completion of a pilot study at one refinery aimed at determining an appropriate mercury sampling method that could be used to sample the emissions from all of the refineries. That attachment proposed an updated schedule for undertaking sampling work and completing the final report. We recognize the challenges inherent both in developing the sample method and conducting the sampling for a period of one year. However, while we concur with the proposal to initiate sampling at all refineries by June 2007, we do not agree that the final report submittal should be delayed to February 28, 2009.

In addition to the delay in submitting the final report required in the February 2005 letter, since issuing that letter there has been slow progress in securing additional information from the refineries on the fate and content of mercury in crude oil necessary for the Water Board to assess the completeness and quality of the results of the air emissions study. Since 2005, Water Board

staff has also gathered additional information about petroleum refinery processes that suggest important modifications (described below) to the original study requirements. Thus, there are additional requirements in this current letter that were not contained in the February 2005 letter. As such, the petroleum refineries must make modifications to the sampling and analysis plan submitted in accordance with the original February 2005 letter, and the schedule of submittals must be changed to accommodate these modifications. This letter, therefore, replaces and supersedes the February 2005 letter and its Schedule of Deliverables.

There are many possible pathways by which petroleum refinery mercury could enter the Bay. The purpose of this letter is to develop an estimate of the amount of mercury entering petroleum refineries in crude oil and the amount of mercury leaving the refineries in non-wastewater streams, especially the amount of mercury emitted from the refineries directly to the atmosphere, which could then enter the Bay via direct deposition to the Bay surface or deposition to the Bay's watershed and subsequent transport to the Bay via tributaries or urban runoff.

The required analysis and submitted reports shown in Table 1 shall accomplish the following:

- Report mercury concentrations of crude oil processed in Bay Area petroleum refineries during the time when conducting air sampling as well as total amounts processed (volume and/or mass) of each sampled crude type during the study period;
- Report mercury concentration and amount of all processed crude oil originating from the San Joaquin Valley, an area known to yield high mercury concentrations in crude oil;
- Estimate mass of mercury contained in crude oil processed in Bay Area petroleum refineries using a laboratory analysis technique that achieves a method detection limit no higher than 0.5 µg/kg. Water Board staff recommend using the combustion atomic fluorescence method (Liang et al. 2000) developed at Cebam Analytical in Seattle, Washington, a lab which has vast experience and excellent precision in measuring mercury in crude oil. For crude stocks processed during the study period but not sampled for mercury, report barrels used and report an estimated mercury concentration based on mercury measurements of crude oil of similar origin;
- Report amounts and mercury concentrations of all waste (except wastewater) and product streams. For waste stream data submitted to the Toxics Release Inventory (TRI), report the raw TRI data regarding mass of mercury in off-site transfers for the years 2000-2006, and summarize these data by year;
- Report dates of turnarounds at each facility for the years 2000 through the end of the study period required by this letter;
- Conduct air sampling at least once per month at each facility for a period of one year;
- Conduct sufficient sampling events at each petroleum facility to characterize air emissions during facility turnarounds;
- Measure mercury emissions both in fuel gas and from flare systems at each facility, including during turnaround sampling;
- Provide a thorough discussion of calculation methodology, uncertainties in the estimate, and assumptions used in the calculation;



- Estimate the total mass of mercury emitted per year directly to the atmosphere from all Bay Area refineries combined; and
- Provide a discussion of the fate of this mercury emitted to the air and an estimate of how much of this mercury would be discharged to the Bay via direct or indirect deposition along with a discussion of the basis for this estimate.

The Water Board requires the foregoing information in order to better assess the significance of petroleum refineries as a source of mercury discharges into San Francisco Bay, as well as more accurately to calibrate implementation actions for petroleum refineries commensurate with their mercury loads to the Bay as specified in the San Francisco Bay mercury TMDL and its implementation plan. The Mercury TMDL Staff Report identifies this information need as a major source of uncertainty that needs to be resolved for successful TMDL implementation (Water Board 2004, pages 77, 90).

Report	Due Date	Comments
Revised Draft Sampling, Analysis, and Calculation Methodology Plan for Bay Area Petroleum Refinery Mercury Mass Balance, Air Emissions and Fate.	May 31, 2007	Water Board staff will review the draft to confirm that the plan is suitable to address information needs.
Final Sampling, Analysis, and Calculation Methodology Plan for Bay Area Petroleum Refinery Mercury Mass Balance, Air Emissions and Fate.	July 31, 2007	The Executive Officer will approve or disapprove the Final Plan, subject to any conditions.
Interim Report of monitoring data plus TRI and waste stream analysis.	May 31, 2007	
Draft Report on Bay Area Petroleum Refinery Mercury Mass Balance, Air Emissions and Fate.	August 31, 2008	Water Board staff will review the Draft Report to confirm that the report addresses the intent of the information request.
Final Report on Bay Area Petroleum Refinery Mercury Mass Balance, Air Emissions and Fate.	October 31, 2008	The Executive Officer will approve or disapprove the Final Report, subject to any conditions.

Technical Background Relevant to Information Requirement

As explained in the Mercury TMDL Staff Report (Water Board 2004), the fate of mercury originally contained in crude oil is not well understood. This mercury may be emitted directly to the air from the refinery, transferred to a variety of refinery products, discharged in wastewater, or contained in solid waste and conveyed off-site for disposal or other processing. The amount of mercury in refinery crude oil processed in the Bay Area was estimated to be about 380 kg/yr (Water Board 2003(b)). This estimate assumed that all crude oil processed in Bay Area refineries contains

10 ppb mercury. A subsequent staff estimate suggests that the amount of mercury could be much (more than four times) higher, as discussed below.

Wilhelm (2001) estimates that the mean concentration of mercury processed in the United States is about 10 ppb, but crude oil from California ranged from 80 to 30,000 ppb mercury. The crude oil known as Cymric was the highest in mercury content, and this oil comes from the San Joaquin Valley. There are joint efforts underway through the American Petroleum Institute (API) and the U.S. Environmental Protection Agency (EPA) to improve the overall estimate and range of mercury concentrations in crude oil processed in the United States, but the results are not available yet. Water Board staff have worked with local petroleum refineries to gain access to information about mercury concentrations in locally processed crude oil, but have not been successful. Based on communications with one of the co-authors of the study from EPA, it appears that Bay Area petroleum refineries did not submit crude oil samples for analysis as part of the API-EPA study.

Assuming that Bay Area petroleum refineries process 781,000 barrels (California Energy Commission website, March 2006) of crude oil per day and that 60% of the crude comes from non-California sources and contains 10 ppb mercury, and the remaining 40% comes from California sources and contains 100 ppb mercury, then the amount of mercury entering Bay Area petroleum refineries would be more than 1700 kg/yr. This is a mass of mercury greater than all estimated mercury loads to the Bay according to the TMDL analysis. It is important to have an accurate estimate of the amount of mercury contained in crude oil processed in Bay Area petroleum refineries for two related reasons. First, this input mercury mass represents the upper bound on the mercury processed through petroleum refineries that could be released to the environment in product and waste streams. Second, this mass bounds the estimates for the mercury mass in output streams so that the quality of the mass balance may be assessed. In other words, knowing how much mercury enters these facilities is the only way to know if there has been an adequate accounting of how much mercury is leaving these facilities through the various pathways. The effort and expense in achieving this mass balance is justified because the input mercury mass appears to be very large compared to the mass of mercury entering the Bay from all other sources.

Based on refinery wastewater monitoring data, a very small amount of this mercury (less than 1 kg/yr) is discharged in wastewater effluent (Water Board 2003(a)). Based on monitoring information, only about 5 kg per year of mercury ends up in automobile fuels (Conaway et al. 2005). Information reported to the TRI database regarding off-site transfers of solid waste from the petroleum refineries suggests that, on average, at least 460 kg/yr of mercury was transferred off-site in various forms of solid waste during the years 2000 through 2005. This fact alone suggests that the previous staff estimate of mercury in crude oil (380 kg/yr) was too low. A large amount of this mercury appears to be associated with equipment cleanout residues, and these are generated in large quantities during plant turnarounds. Plant turnarounds are described by the American Petroleum Institute in the website: (<http://www.api.org/aboutoilgas/sectors/refining/refinery-turnaround.cfm>). During such maintenance periods, equipment is steamed out and material is burned off in flares, catalysts are regenerated and fuel sources are changed. Turnarounds, therefore, are of interest because they likely



generate elevated mercury emissions to the atmosphere, and they appear to be a process generating large amounts of mercury-rich solid waste for offsite transfer as well. Therefore, special emphasis will be placed on gathering and submitting data on air emissions during turnarounds. With currently available information, we can only account for approximately 460 kg/yr of mercury when 1700 kg/yr or more may enter these petroleum refineries in crude oil. Some of this mercury is likely being discharged (directly or indirectly) to the Bay through atmospheric deposition or other pathways.

More information is available in the Water Board's administrative record for the Water Board's Basin Plan Amendment for the San Francisco Bay mercury TMDL. The purpose of this information request is to determine the extent to which mercury entering petroleum refineries reaches the Bay via one of the potential pathways (direct emission to the air and subsequent direct and indirect deposition). Because it is possible that a very large amount of mercury is entering Bay Area petroleum refineries, but that only a fraction of it can be accounted for in automobile fuels, wastewater, and solid waste, the Water Board requires additional information both on the amount of mercury entering and leaving the petroleum refineries. This is known as a mass balance. The reason that a mass balance approach is important is that there will be uncertainty associated with the estimates for inputs and outputs. The mercury enters the petroleum refineries only in one stream, as crude oil, so it is possible to account for the amount of mercury in this one stream. By contrast, mercury can leave the facilities through a variety of pathways. In order to be sure that the mercury mass in these pathways has been adequately accounted for, it is important to know the mass of mercury input as a check on the validity of the mass accounting.

Please be aware that failure to comply with the requirements of this CWC Section 13267 Order may subject you to civil liability of a maximum amount of \$1,000 per day of violation. Examples of non-compliance include, but are not limited to, failure to timely submit a required plan or report or failure to submit an adequate plan or report. Any request to amend the requirements of this Order must be set forth in writing. Any approval of such a request will be made by the Executive Officer in writing.

The Fact Sheet attached below provides basic information about Section 13267 requirement letter. If you have any additional questions, please contact Richard Looker at (510) 622-2451, or via e-mail at rlooker@waterboards.ca.gov.

Sincerely,

Bruce H. Wolfe
Executive Officer



References

Conaway, Christopher H. et al. 2005. *“Estimate of mercury emissions from gasoline and diesel fuel consumption, San Francisco Bay area, California.”* *Atmospheric Environment* 39 no.1.

Liang, L., Lazoff, S., Horvat, M., Swain, E., and Gilkeson, J., *“Determination of mercury in crude oil by in-situ thermal decomposition using a simple lab built system”*, *Fresenius’ J. Anal. Chem.*, 367, 8, (2000) 8.

San Francisco Bay Regional Water Quality Control Board (Water Board). 2003(a). *Revised Statistical Analysis of Mercury Data from Bay Area Refineries*. Prepared by R. Schlipf. February 18.

San Francisco Bay Regional Water Quality Control Board (Water Board). 2003(b). *“Estimated Mercury Mass in Bay Area Automobile Emissions and Crude Oil Processed By Bay Area Refineries.”* Prepared by R. Looker, April 1.

San Francisco Bay Regional Water Quality Control Board (Water Board). 2004. *Mercury in San Francisco Bay: Total Maximum Daily Load (TMDL). Proposed Basin Plan Amendment and Staff Report*. September 2.

Wilhelm, Mark 2001. *Estimate of Mercury Emissions to the Atmosphere from Petroleum*. *Environmental Science and Technology* Vol. 35 no. 24.

Attachment: Fact Sheet on Section 13267

Cc (w/o): Kevin Buchan, Western States Petroleum Association



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Fact Sheet – Requirements For Submitting Technical Reports Under Section 13267 of the California Water Code

What does it mean when the regional water board requires a technical report?

Section 13267¹ of the California Water Code provides that "...the regional board may require that any person who has discharged, discharges, or who is suspected of having discharged or discharging, or who proposes to discharge waste...that could affect the quality of waters...shall furnish, under penalty of perjury, technical or monitoring program reports which the regional board requires."

This requirement for a technical report seems to mean that I am guilty of something, or at least responsible for cleaning something up. What if that is not so?

The requirement for a technical report is a tool the regional water board uses to investigate water quality issues or problems. The information provided can be used by the regional water board to clarify whether a given party has responsibility.

Are there limits to what the regional water board can ask for?

Yes. The information required must relate to an actual or suspected or proposed discharge of waste (including discharges of waste where the initial discharge occurred many years ago), and the burden of compliance must bear a reasonable relationship to the need for the report and the benefits obtained. The regional water board is required to explain the reasons for its request.

What if I can provide the information, but not by the date specified?

A time extension may be given for good cause. Your request should be promptly submitted in writing, giving reasons.

Are there penalties if I don't comply?

Depending on the situation, the regional water board can impose a fine of up to \$5,000 per day, and a court can impose fines of up to \$25,000 per day as well as criminal penalties. A person who submits false information or fails to comply with a requirement to submit a technical report may be found guilty of a misdemeanor. For some reports, submission of false information may be a felony.

Do I have to use a consultant or attorney to comply?

There is no legal requirement for this, but as a practical matter, in most cases the specialized nature of the information required makes use of a consultant and/or attorney advisable.

What if I disagree with the 13267 requirements and the regional water board staff will not change the requirement and/or date to comply?

You may ask that the regional water board reconsider the requirement, and/or submit a petition to the State Water Resources Control Board. See California Water Code sections 13320 and 13321 for details. A request for reconsideration to the regional water board does not affect the 30-day deadline within which to file a petition to the State Water Resources Control Board

If I have more questions, whom do I ask?

Requirements for technical reports indicate the name, telephone number, and email address of the regional water board staff contact.

Revised August 2005

¹ All code sections referenced herein can be found by going to www.leginfo.ca.gov.

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