



California Regional Water Quality Control Board

San Francisco Bay Region



Linda S. Adams
Secretary for
Environmental Protection

1515 Clay Street, Suite 1400, Oakland, California 94612
(510) 622-2300 • Fax (510) 622-2460
<http://www.waterboards.ca.gov/sanfranciscobay>

Arnold Schwarzenegger
Governor

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

DATE: May 7, 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 To Assess 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 review and concurrence by the Water Board's Executive Officer. 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 studies that contain the required elements for your facility according to the schedule in Table 1.

The Water Board initially sent you a related Section 13267 requirement letter on February 17, 2005. In response to the February 2005 letter, you 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 Board to assess the completeness and quality of the results of the air emissions study. Since 2005, Board staff has also gathered additional information about petroleum refinery processes that suggests 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 what is required herein.

There are many possible pathways by which petroleum refinery mercury could enter the Bay. Mercury originating in crude oil that is emitted to the air or transferred to improperly managed solid waste can be transported to the Bay. Such mercury would constitute a mercury discharge to the Bay that could affect the quality of waters in the region. The ultimate purpose of this requirement letter is to develop an estimate of the amount of mercury originating from local petroleum refineries that could be discharged to the Bay. To ensure that this is accomplished, it is necessary that the refineries provide an estimate of the amount of mercury entering the refineries in crude oil as well as the amount of mercury leaving the refineries in non-wastewater streams, especially the amount of mercury emitted from the refineries directly to the atmosphere. Mercury emitted to the atmosphere could 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 reports and associated analyses shown in Table 1 shall accomplish or provide the following:

- Mercury concentrations and amounts of all crude oil types processed during the air sampling events;
 - Include the 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 the 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. 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 subsequent mercury analysis, report barrels used, and estimate mercury concentration based on mercury measurements of crude oil of similar origin;
- Amounts and mercury concentrations of all waste (except wastewater) and product streams. These data should account for mercury leaving the facility through all waste streams, including petroleum coke and material taken from sulfur removal units. 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;
- Dates of turnarounds at each facility for the years 2000 through the end of the study period required by this letter;
- The total mass of mercury emitted per year directly to the atmosphere from all Bay Area refineries combined;

- Conduct air sampling at least once per month at each facility for a period of one continuous year;
- Conduct air sampling in such a way as to account for emissions from all combustion sources such as boilers, heaters, and co-generation facilities;
- 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; and,
- 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 these estimates, including a thorough discussion of calculation methodology, uncertainties in the estimates, and assumptions used in all calculations.

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 to more accurately 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
Interim Report of available air monitoring data plus TRI and waste stream analysis.	June 15, 2007	This interim report shall include any available air monitoring data along with all mercury mass data on submitted to the Toxics Release Inventory for the years 2000 through 2006 for each refinery, a refinery-specific summary of those TRI data, and an interpretive report explaining the categories reported to the TRI.
Revised Draft Sampling, Analysis, and Calculation Methodology Plan for Bay Area Petroleum Refinery Mercury Mass Balance, Air Emissions and Fate.	June 15, 2007	Board staff will review the draft to confirm that the plan is suitable to address the information needs. This report shall also include a good faith estimate of the costs to implement the study.
Final Sampling, Analysis, and Calculation Methodology Plan for Bay Area Petroleum Refinery Mercury Mass Balance, Air Emissions and Fate.	July 31, 2007	The requirement for submitting the Final Plan is not satisfied until the EO concurs that the Plan adequately addresses all elements in the bullet list above.
Draft Report on Bay Area Petroleum Refinery Mercury	August 31, 2008	Board staff will review the Draft Report to confirm that the report addresses the intent of the information

Mass Balance, Air Emissions and Fate.		request.
Final Report on Bay Area Petroleum Refinery Mercury Mass Balance, Air Emissions and Fate.	October 31, 2008	The requirement for submitting the Final Report is not satisfied until the EO concurs that the Report accomplishes all elements in the bullet list above.

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. 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 local petroleum refineries did not submit crude oil samples for analysis as part of the API-EPA study.

Assuming that the five 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 these 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 the refineries because this mass bounds the estimates for the mercury contained in output streams. The quality of the mass balance may only be assessed by knowing this input mass. This is particularly important in view of the fact that the proposed air sampling methodology has never been implemented before and, thus, has not been previously tested and validated. Knowing the amount of mercury input to the refineries and the amounts exiting the refineries through other pathways is the only way in which the air sampling results can be validated. Moreover, 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 that are likely to result in discharge to San Francisco Bay.

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 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 Board 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 API 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 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 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. As you are aware, mercury is a serious problem in San Francisco Bay, and it now appears that the input of mercury into your facilities is very large compared to the mercury mass entering the Bay from all other sources, yet it is a mystery where the mercury ends up and, importantly, how much of it goes into the Bay. The information that will be generated under this letter is vital to closing this information gap. Moreover, the additional requirements herein do not appreciably add to the cost and burden of the planned air emissions monitoring.

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

Cc: Water Board members (via email)
Kevin Buchan, WSPA (via email)