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

OFFICE OF
WATER

MEMORANDUM

SUBJECT: Interim Petroleum Refinery Dioxin Discharges Activities and Guidance Update

FROM: James R. Elder, Director
Office of Water Enforcement and Permits

Martha G. Prothro, Director
Office of Water Regulations and Standards

TO: Water Management Division Directors, Regions I - X

The purpose of this memorandum is to provide an interim report on the available information regarding the potential presence of dioxins and furans in wastewater discharged from petroleum refineries and to provide the Regions with recommendations concerning notification of petroleum refineries about the detection of dioxins and furans in certain refinery wastestreams. This interim report contains information on the most recent developments in the preliminary field sampling for analytical methods evaluation and the National Bioaccumulation Study. An additional update along with permit guidance recommendations will be forthcoming upon completion of the analyses for measuring dioxins and furans in the refinery wastewater and sludge samples taken during the preliminary field sampling work.

BACKGROUND:

On December 5, 1988 Environment Canada released monitoring data detecting dioxins and furans for two of the three petroleum refineries tested. From this data, it appears that dioxins and furans are generated during some types of catalytic reformer regeneration processes. The Canadian data found, for final combined effluents, that the concentrations for total dioxins including 2,3,7,8-TCDD (and for all furans except one) were determined to be below the detection limit due to dilution and possibly some treatment. The internal wastestream analyses found total dioxins including 2,3,7,8-TCDD at concentrations between 1.8 and 22.2 parts per billion (ppb) and total furans at

concentrations between 4.4 and 27.2 ppb. Total dioxin and furans were also found in the refinery's biological sludge at maximum concentrations of 75.4 ppb and 125 ppb respectively.

It is not known at this time how much of the dioxins and furans remain in the gasoline product or in air emissions from the process. Attempts to measure dioxins and furans in the product stream from a reformer were unsuccessful due to analytical methods problems. Any future work on the product stream will necessitate an analytical methods development project.

The American Petroleum Institute (API) stated that the catalytic reforming process is used in most U.S. refineries and is essential for the production of high octane gasoline. API has provided the attached list of refineries identifying location and types of catalytic reforming processes.

There are three general types of catalytic reformer regeneration processes: semi-regenerative, cyclic or fully regenerative, and continuous. The cyclic and continuous regeneration processes, reviewed for several refineries to-date, do not generate a wastewater stream. This is accomplished by maintaining the regeneration temperatures at a high enough level to prevent condensation of the water present in the vapor phase. In some of these instances, the gas phase emissions are scrubbed and a scrubber wastewater discharge occurs.

The semi-regenerative process has a number of variations, and all of them reviewed to date have a wastewater discharge associated with them. The water used to wash the catalyst bed or formed during the high temperature burning of the bed (decoking phase) is passed through a heat exchanger and condensed. This discharge is neutralized with caustic prior to discharge. Also, during the regeneration, chlorine is added to reactivate the catalyst. Variations in the decoking temperature, type of chloride added, and the times of chloride addition have been identified in the semi-regenerative process to-date. Based on the limited number of refineries reviewed to-date it is not known whether only refineries using a selected regeneration process would discharge dioxins and furans or whether the catalytic reforming process is the only refinery process resulting in the formation of dioxins and furans.

EPA ACTIVITIES:

EPA has completed sampling at three petroleum refineries. One of the refineries which was sampled on March 14, 1989 uses a cyclic catalytic regeneration process. Samples were collected from internal waste streams generated after the reforming process step, discharges after biological treatment, biological sludge and product stream after discharge from the reformer. In this case no scrubber or catalyst bed wash wastewater was generated directly from the reformer.

Two additional refineries were sampled on May 26-28 and June 26-28, 1989. Both of these refineries use a semi-regenerative process during the regeneration of the catalyst. The last refinery also has a continuous regeneration reforming process which does not have a wastewater discharge. The preliminary results from the last two refineries sampled are being evaluated. A summary report on all of the data will be prepared and should be completed by the end of November 1989.

The primary objective of the preliminary sampling work is to evaluate the analytical methods for measuring dioxins and furans in the petroleum refinery wastewater matrices. The analytical method being used in these evaluations includes high resolution GC/MS similar to methods used to detect dioxins and furans in pulp and paper discharges and sludges. A copy of method 1613 is attached and has been revised to incorporate the experience from analyzing refinery samples.

In addition, EPA Headquarters, with support from the Regional offices, has reviewed sampling site information from the National Bioaccumulation Study and determined that 38 ambient fish tissue monitoring sites were located near petroleum refineries using the reforming processes. The presence of chlorinated dioxins and/or furans in fish tissues from these sites has been identified, including 2,3,7,8-TCDD which has been detected in fish at 32 of the 38 sites near the refineries. Data showed 2,3,7,8-TCDD levels in whole fish ranging up to 18 parts per trillion. The current sampling site information does not identify whether other known sources of dioxin are in the vicinity of the sampling locations. An inventory of sources of contamination for each sampling location is in progress. These site specific characterizations are expected to be completed soon.

NPDES PERMITS

Since the above mentioned efforts are not yet completed, EPA Regions will need to address dioxin in permits that are expired or will expire before this new information is available. The permitting strategies developed for dioxin/furans for pulp and paper mills are generally not useful for permitting petroleum refineries because inadequate data exists to either characterize discharges from the reforming process or the refinery or to link dioxin levels in the environment to refinery discharges. Headquarters recommends that refineries be notified that dioxins/furans have been detected in certain refinery waste streams and that the refineries may be required to provide additional information on their production process and treatment facility to assess dioxin/furan generation potentials at their facility. An example of an appropriate notification letter is attached.

Refineries that submit NPDES Application Form 2C for permit reissuance should not be allowed to check "believed to be absent" for the pollutant dioxin. Rather, refineries which produce gasoline and have a wastewater discharge from their catalytic reformer regeneration step should indicate that dioxins and furans are "believed to be present" and include sufficient information to characterize these pollutants at their facility (dependent on acceptable analytical protocols).

Since sufficient dioxin/furan information may not be available to determine the need for effluent limitations for most NPDES permits issued in the near future to refineries with the catalytic reforming processes, these permits should require monitoring and a specific reopener. In instances where final effluent monitoring is unlikely to provide useful data, sampling points may be established for individual process discharges or other appropriate in-plant locations. In addition to effluent and in plant monitoring, the permits may require ambient monitoring of the water column, sediments and fish in the vicinity of discharge(s). The Agency is aware of less than ten laboratories capable of performing the analytical measurements of dioxins/furans in the above mediums. Therefore, monitoring frequencies and schedules for obtaining analytical methods will be determined by available laboratory capacities.

As an alternative to monitoring requirements for dioxins/furans and a reopener in NPDES permits, it may be appropriate to require Best Management Practices (BMPs) for segregation, storage or separate disposal of the regeneration wastewater stream prior to discharge to receiving waters. If segregation, storage or separate disposal of wastewaters containing dioxins/furans is necessary, the potential for cross media contamination by dioxin/furan contamination should be considered (e.g. sludge, air emissions).

The permit should also contain a specific reopener to provide for modification of the permit to reflect any additional guidance or data, including information on the feasibility of process changes or new treatability data.

Please feel free to call us: Jim Elder (FTS: 202-475-8488) if you have any questions on NPDES permitting or the industrial notification letter, or Martha Prothro (FTS: 202-382-5400) with questions on water quality standards, catalytic reformer regeneration process and/or analytical methods evaluation or the results from the National Bioaccumulation Study.

Attachments

ATTACHMENT

DRAFT NOTIFICATION LETTER TO PETROLEUM REFINERIES

[name and address of refinery]

Dear Sir or Madam:

As your company is probably aware, petroleum refineries using certain types of regeneration for their catalytic reforming process during the production of gasoline have been found to have wastewaters and/or produce sludges that are contaminated with chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans (CDDs and CDFs). Preliminary indications are that these toxic pollutants originate during the regeneration of the catalytic reforming units. Data were first presented in a press release by Canada's Ministry of the Environment (see enclosure). The extraordinary persistence and toxicity of these chemicals, combined with their tendency to bioaccumulate in edible fish, has prompted the Environmental Protection Agency (EPA) to initiate an investigation.

Preliminary sampling has been conducted at three refineries covering the three general types of regeneration processes associated with catalytic reforming operations. Results of this work will be used in evaluating the analytical methods for measuring CDD's and CDF's in petroleum refinery wastewaters and sludges and to give the Agency some preliminary information on the potential for generating CDD's and CDF's. As a next step to gaining a more complete understanding of which types of refineries may exhibit the problem of CDD/CDF contamination and which processes or operations may be the sources, EPA may choose a limited number of facilities from which to sample product and waste materials to analyze for CDDs and CDFs. The factors which may be used to select additional refineries for sampling include type of catalytic reforming process used, catalytic reforming capacity, use of chlorinated hydrocarbons, and CDD/CDF contamination of fish collected from the water body receiving the wastewater discharge.

In order to enable us to accomplish the next step in the screening process, EPA may notify selected refineries and request that they provide certain existing and new information on their facilities: (1) descriptive data on portions of the facility and selected operations, including any existing monitoring results for CDDs or CDFs; and (2) results of new monitoring for CDDs and CDFs to be undertaken in accordance with an approved study plan.

NPDES Permit Application:

Finally, please be advised that on your next application for a permit to discharge wastewater under the National Pollutant Discharge Elimination System (NPDES) you must indicate that dioxins and furans are "believed to be present" and include all analytical procedures and information used to characterize these pollutants at your facility in accordance with the applicable state and federal rules and regulations as administered by the permitting authority. If an application has already been filed, but the permit has not yet been issued, you may be required to amend your application to address CDDs and CDFs.

If you have any questions on this matter, please contact [name] of my staff at [phone number].

Sincerely yours,

(NAME)
Chief, Permits Branch

Enclosure [Canadian refinery press release/monitoring data]

cc: State Water Program Director
State NPDES Permit Program Director