MERCURY RELEASE FROM CRUDE OIL

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Project Description

There is much uncertainty over the amount of mercury released into the environment from the extraction, transport, refining, and consumption of crude oil and its products. This project evaluates the information available to answer basic questions, such as:

- What are typical mercury concentrations in crude oil from the major producing areas in the world?
- During crude oil refining, is mercury released into the environment or concentrated in specific refinery products?
- If mercury concentrates in specific products, how is that mercury eventually released into the environment?
- Compared to other sources, is mercury from crude oil usage a significant source of emissions to the atmosphere?
- If mercury emissions from crude oil usage are significant, what strategy could be implemented to reduce these emissions?

The project focused on gathering relevant information from a broad range of possible sources and evaluating the information for accuracy, validity, and completeness. Second, based on the information obtained and availability of samples, crude oil samples were selected from several oil fields and analyzed for mercury.

Goals

The goal of the work is to determine the amount of mercury released from crude oil into the environment. Specific goals include:

- Obtain data from available sources on the range of mercury concentration in crude oil from major producing areas in the world.
- Evaluate the refining process (utilizing any available mercury measurements at refineries) to predict likely pathways for mobilization of mercury in crude oil and release into the environment.
- Select, obtain, and analyze crude oil from several different oil-producing regions.

- Based on available information, determine relative impact of mercury emissions from crude oil utilization compared to other sources.

Rationale

The U.S. Environmental Protection Agency (EPA) *Mercury Study Report to Congress* listed U.S. mercury emissions at 72 tons/yr from coal compared to an estimate of 11 tons/yr from oil. However, sources at EPA state that there is very little basis for the estimate from oil.

The United States consumes 18.6 MM barrels/day of the total world production of 66 MM barrels/day (about 28%) of oil, but it produces only 6.3 MM barrels/day. The 18.6 MM barrels/day corresponds to approximately 1 billion tons/yr of oil, which is equivalent to the current U.S. coal consumption rate. If the mercury in crude oil averaged only 1 ppm, mercury emissions from oil could be over 10 times the amount from coal. Even if average mercury levels in crude oil were only 0.1 ppm, the amount would be equivalent to coal and be considered a major source. The United States imports large amounts of oil from North America, South America, Africa, Europe, and Asia. Some oil production areas could be hot spots of mercury, but reliable available information on this question appears to be lacking.

Approach

Possible sources of information on the mercury levels in U.S. and imported crude oil include the American Petroleum Institute, the U.S. Geological Survey, International Energy Agency, individual oil companies, and state agencies. Along with a brief literature review, contacts were made with these sources to obtain current information on mercury in crude oil. This information was supplemented with mercury analysis of raw crude oil samples obtained from different oil fields.

Progress

Recently, concentration data on mercury in crude oil and its refined products have been published that indicate that crude oil on average may be high in mercury and, conversely, its refined products may be extremely low [1–4]. Recent high-accuracy determinations of mercury in coal and oil standard reference materials indicate that on-road diesel fuel (<500 ppm sulfur) and residual fuel oil are very low in mercury [3].

Knowledge of the mercury concentrations in crude oil is much less certain. Bloom gives a mean of 1.505 ppm (l s = 3.3 ppm) for 76 crude oils, but cautions that this mean may have a positive bias since clients may have sent him samples for analysis when a high mercury value was suspected [4]. However, in a report on mercury in Massachusetts, the range in crude oil is given as 0.007 to 30 ppm [5]. Unfortunately, there exists no representative database for the weighted mean values of mercury in crude oil, fuel oil, or motor fuels.

Two U.S. crude oil samples were analyzed at the EERC. The mean concentration for five replicate analyses of a North Dakota crude oil sample was 4.4 ng/g, and the mean concentration of three replicate samples of a California crude oil was 0.9 ng/g. These values are far below the mean concentration reported by Bloom. However, they are single samples and should not be considered representative of other U.S. or world samples. The North Dakota sample is about 30 times lower in mercury than typical U.S. coals on a concentration basis and is, therefore, not alarming, but high enough to be of concern as a source of mercury if it is indicative of the lower range of mercury concentrations for oils.

Based on the limited information available, crude oil from a number of locations can be high enough in mercury to be of major concern. This implies that there are hot spots of mercury from some oil fields worldwide. Since the United States imports approximately two-thirds of its oil from around the world, there is potential for significant mercury emissions in the United States from petroleum usage, even if U.S. crude oils are relatively low in mercury. It appears that a significant effort to document the actual mercury concentration in raw crude oil from domestic or imported sources is warranted. Since mercury may escape during extraction or transport, it is imperative that samples be collected as near to the source as possible or at the point of import to the United States to facilitate an understanding of the eventual fate of the mercury present in raw crude.

Accurate determination of Hg in petroleum hydrocarbons is critical due both to its toxicity as an environmental pollutant and its adverse affect on equipment at processing facilities. In addition to the potential bias in the data from more frequent measurement of samples that are high in mercury, there is also uncertainty associated with sampling and measurement techniques. Most researchers agree that much of the reported results for Hg in petroleum products are unreliable due to insufficient quality assurance/quality control documentation associated with sampling and analytical techniques [6, 7]. Inconsistent sampling and handling procedures can lead to large differences in Hg concentrations reported for the same crude oil. Sampling and handling issues can be associated with the large variety of mercury forms present as well as difficulties in obtaining homogeneous samples that are representative of the actual suspended fraction, loss of volatile Hg^0 to the headspace of sample containers, and failure to account for mercury adsorbed to sample containers [6]. Sampling procedures aside, analytical methods for the determination of Hg in hydrocarbons have improved dramatically in recent years and have allowed for the detection of total mercury and speciated mercury down to the ppt level [1]. From the available literature, there are researchers who have analyzed a variety of petroleum products for mercury. Table 1 lists details for some of the more current analytical techniques available.

Table 1. Analytical Methods for the Determination of Hg in Petroleum Products

Media	Speciation	Analytical Method*	Range, ppb	Detection Limit, ppb	Comments
Crude Oil	Total Hg	TD–CVAF	1.5–6.5	0.2	Eleven crude oils were analyzed and compared to NAA [8]
Gasoline	Total Hg	E–CVAF	0.22–3.3	0.04	Nine samples from various geographic areas. BrCl extraction [2]
Crude Oil	Total Hg	NAA	0.10–12.2	0.05	Seven samples from Libya [9]
Crude Oil, Condensate, Fuel Oil	Total Hg, Hg^0, particulate Hg, Hg(II) and methylmercury	ES–CVAF	0.50–50,000	0.1	76 crude oil samples and 18 condensates. Most of the total Hg was present as particulate Hg, the least was methylmercury [4]

* E–CVAF = extraction–cold-vapor atomic fluorescence; ES–CVAF = extraction and separation–cold-vapor atomic fluorescence; NAA = neutron activation analysis; TD–CVAF = thermal decomposition–cold-vapor atomic fluorescence.

Although the Hg present in petroleum hydrocarbon has been an issue for the petroleum industry for several decades, only recently has there been an increased effort on producing better-quality data.

Status

Work continues on this project in order to summarize findings from recently available papers. During the next year, additional sources of information will be explored to expand on the limited information that was previously available.

Potential Users/Technology Transfer

The mercury concentrations from crude oil sources is an area that has raised questions. Current estimates are under question because of sampling procedures, uncertainties in analyses, and biases in the measured population. This work has significant implications because if crude oil is shown to be a major source of mercury emissions to the atmosphere, it will likely eventually be regulated. Initially, EPA may require oil companies to report on mercury levels for crude oils in an information collection request (ICR) similar to the ICR that was required for coal. Assuming concentrations are high enough to be of concern, the development of mitigation strategies to reduce mercury emissions from oil would then follow.

References

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