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# MERCURY RELEASES FROM CRUDE OIL AND OTHER FUELS

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## ***Project Description***

This project focuses on gathering relevant information from a broad range of possible fuel sources and evaluating the information for accuracy, validity, and completeness. The focus to date has been on collecting data on mercury in oil. Crude oil samples have been selected from several oil fields and analyzed for mercury. An additional effort has been initiated to assess the potential release of mercury from other alternative fuels such as biomass, oil and tar sands, oil shale, etc. This effort will involve identification of other fuel sources of mercury through review of literature and sample acquisition and analysis.

## ***Goal***

The goal of the work is to determine the amount of mercury released from crude oil and alternative fuels into the environment. The specific objectives are in the “Approach” section below.

## ***Rationale***

The U.S. Environmental Protection Agency (EPA) *Mercury Study Report to Congress* [1] listed U.S. mercury emissions from coal at 72 tons/yr compared to a rough estimate of 11 tons/yr from oil. However, sources at EPA state that there is very little basis for the estimate for oil.

The United States consumes 19.6 MM barrels/day of oil, or about 26% the total world demand of 76 MM barrels/day. However, the United States produces only 9 MM barrels/day. The 19.6 MM barrels/day corresponds to approximately 1 billion tons/yr of oil, which is equivalent on a tonnage basis to current U.S. coal consumption. Reported concentrations of mercury in crude oil vary by many orders of magnitude, and overall emissions from oil could be either higher or lower than emission from coal. If the average mercury level in crude oil were similar to that in coal, at about 0.08 ppm, the potential emissions from oil would be equivalent to that from coal and would be considered a major source. Based on limited information, mercury appears to occur in relatively high concentrations in crude oils from particular producing areas, which suggests that certain oil imports to the United States may cause hot spots of mercury emissions where these sources are refined and utilized.

Information is lacking on the amount of mercury contained in most of the fuel alternatives that are under consideration for supplementing or reducing use of traditional fossil fuels. While most of these fuels can be expected to be low in mercury concentration on a mass basis, because of lower heating values, the quantities of mercury could be significant on a heating value basis. Considerably more information is needed in order to estimate the contribution of alternative fuel sources to overall mercury emissions.

## *Approach*

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 available information to answer basic questions:

- 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?

Possible sources of information on the mercury levels in U.S. and imported crude oils include the American Petroleum Institute, the U.S. Geological Survey, the International Energy Agency, individual oil companies, and state agencies. Along with a review of literature, 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. A similar effort has been initiated to evaluate the range of mercury concentration that can be found in other fuel sources.

## *Progress*

### **Mercury in Oil**

Recent published data on mercury in crude oil and its refined products suggest that certain crude oils may be high in mercury and that their refined products are extremely low [2–5]. Highly accurate determinations of mercury concentration in coal and oil standard reference materials indicate that mercury concentrations in on-road diesel fuel and residual fuel oil are very low [4].

Knowledge of the mercury concentrations in crude oil is much less certain. Bloom gives a mean of 1.505 ppm (1 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 [5]. However, in a report on mercury in Massachusetts, the range in crude oil was given as 0.007 to 30 ppm [6]. Unfortunately, there exists no representative database for the weighted mean values of mercury in crude oil, fuel oil, or motor fuels.

Through the literature survey, it has been found that a majority of the research on mercury has been done in the United States. However, different authors also have analyzed the mercury concentration for imported oils. The information collected so far could be summarized as follows.

### ***Estimate of Mercury in Crude Oil***

The mean values of mercury concentration in crude oil differ in various studies for the reasons mentioned above. Various investigators performed their analysis using different sampling and analytical techniques. The results of these studies are summarized in Table 1, which suggests that a very wide range of values can be expected for mercury concentrations in various crude oils.

Again, note that representative concentrations of mercury may be lower than the mean values presented in Table 1 because of sampling and analytical limitations and a skewed evaluation of high-mercury oils. Crude oil contains both dissolved (i.e., elemental mercury [Hg<sup>0</sup>], dialkyl mercury, dimethyl mercury and

monomethyl mercury halides) and suspended mercury compounds (i.e., mercuric sulfide and selenide). There could be considerable differences in mercury concentration for samples taken from upstream or downstream of holding tanks or separators [7].

The majority of the mean mercury concentrations in Table 1 fall below 20 ppb, however there are several exceptionally high values reported by Bloom and Wilhelm et al. [5, 7]. The highest mean values reflect very high mercury concentrations, some in samples taken from California (in the range of 24,000 ppb). The high mean values reported by Bloom [5] were for samples provided by clients who were faced with problems relating to high mercury contents in their crude oil. The available data are, therefore, not a true representation of the sources. A valid statistical evaluation will require representative sampling of many different sources and application of verified analytical methods.

### ***Mercury in Refined Products***

The mercury in crude oil enters the environment by different avenues that can include emission during refining into wastewater, solid waste streams, and refined products. Solid waste disposal and incineration processes may contribute significantly to atmospheric mercury emissions from petroleum [8]. However, no reliable data verify the contribution of oil and oil products to mercury in solid wastes and wastewaters.

Various recent studies show that mercury concentrations in refined products are relatively low (0.7–50 ppb) (see Table 2). Liang et al. [3] reported mercury concentrations in gasoline, diesel fuel, kerosene, and heating oil in the range of 0.04 to 2.97 ppb. Bloom [5] reported mean values of 1.32 and 0.27 ppb for light distillate and asphalt, respectively. Higher mean values up to 50 ppb were reported for petroleum coke and naphtha, as shown in Table 2.

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 ppb, and the mean concentration of three replicate samples of a California crude oil was 0.9 ppb. 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 10 times lower in mercury than some U.S. coals and is, therefore, not alarming, but high enough to be of concern as a source of mercury if it is indicative of other crude oil samples.

Based on the limited information available, mercury concentrations in crude oil from a number of locations appear to be high enough to be of concern. This implies there may be 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 important 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 approximate fate of the mercury present in raw crude.

### ***Sampling and Analytical Techniques for Mercury in Oil***

Most researchers agree that much of the reported results for Hg in petroleum products are unreliable because of insufficient quality assurance/quality control documentation associated with sampling and analytical techniques [7, 9]. 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<sup>0</sup> to the headspace of sample containers, and failure to account for mercury adsorbed to sample containers [7]. 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

**Table 1.** Mercury Concentration in Crude Oil from Different Origins (references cited in this table are found in Wilhelm and Bigham [7])

Reference	No. of Samples	Range, ppb	Mean THg, ppb	Source	Analytical Techniques
Shah et al., 1970	NR <sup>a</sup>	23–30000	3200	Mixed <sup>b</sup>	NAA <sup>c</sup>
Filby and Shah, 1975	NR <sup>a</sup>	<4–23100	5803	Mixed <sup>d</sup>	NAA
Hitchon and Felby, 1983	86	<2–400	21.9	Alberta	NAA
Musa et al., 1995	7	0.1–12	3	Libyan	NAA
Liang et al., 2000	11	1–7	4	NR <sup>a</sup>	TD-CVAF <sup>e</sup>
Bloom, 2000	76	NR <sup>a</sup>	1505	NR <sup>a</sup>	E-CVAF <sup>f</sup>
Bloom, 2000	39	NR <sup>a</sup>	1.2	NR <sup>a</sup>	E-CVAF
Bloom, 2000	37	NR <sup>a</sup>	3009	NR <sup>a</sup>	E-CVAF
Tao et al., 1998	1	0.1–12	<1	Asia	ICP-AE <sup>g</sup>
Magaw et al., 1999	2	NR <sup>a</sup>	<10	Middle East	CVAA <sup>h</sup>
Magaw et al., 1999	4	NR <sup>a</sup>	<10	Africa	CVAA
Magaw et al., 1999	11	ND <sup>i</sup> –1560	146	North America	CVAA
Magaw et al., 1999	4	NR <sup>a</sup>	<10	Asia	CVAA
Magaw et al., 1999	4	NR <sup>a</sup>	<10	South America	CVAA
Magaw et al., 1999	1	NR <sup>a</sup>	<10	North Sea	CVAA
Morris, R., 2000	7	1.0–3.2	1.7	Africa	E/TD-CVAF <sup>j</sup>
Morris, R., 2000	2	2.4–5.7	4.3	Middle East	E/TD-CVAF
Morris, R., 2000	1	1.9	1.9	Canada	E/TD-CVAF
Morris, R., 2000	4	2.5–9.3	5	North Sea	E/TD-CVAF
Morris, R., 2000	2	0.1–2.7	1.4	Mexico	E/TD-CVAF
Morris, R., 2000	6	0.8–12.3	5.2	South America	E/TD-CVAF
Morris, R., 2000	1	3.1	3.1	Mixed	
Environment Canada, 2000	11	NR <sup>a</sup>	<15	U.S.	ICP-AE
Environment Canada, 2000	2	NR <sup>a</sup>	<15	Canada	ICP-AE
Environment Canada, 2000	2	NR <sup>a</sup>	<15	Mexico	ICP-AE
Environment Canada, 2000	3	NR <sup>a</sup>	<15	South America	ICP-AE
Environment Canada, 2000	2	NR <sup>a</sup>	<15	North Sea	ICP-AE
Duo et al., 2000	8	<2–9	1.6	Canadian refineries	CVAA

<sup>a</sup> Not reported.

<sup>b</sup> [California – 5, Libya – 3, Louisiana – 1, Wyoming – 1]

<sup>c</sup> Neural activation analysis.

<sup>d</sup> [California – 1, Venezuela – 1, Alberta – 1, Libya – 1].

<sup>e</sup> Thermal digestion–cold-vapor atomic fluorescence.

<sup>f</sup> Extraction–cold-vapor atomic fluorescence.

<sup>g</sup> Inductively coupled plasma–atomic emission.

<sup>h</sup> Cold-vapor atomic absorption.

<sup>i</sup> Not detected.

<sup>j</sup> Extraction/thermal digestion–cold-vapor atomic fluorescence.

**Table 2.** Mercury Concentration in Refined Products (references cited in this table are found in Wilhelm and Bigham [7])

Reference	Type	No. of Samples	Range, ppb	Mean	THg, ppb	SD	Origin
Liang et al., 1996	Gasoline	5	0.22–1.43	0.7	0.7	NR <sup>a</sup>	U.S.
Liang et al., 1996	Gasoline	4	0.72–3.2	1.5	1.5	NR	Foreign
Liang et al., 1996	Diesel	1	0.4	0.4	0.4	NR	U.S.
Liang et al., 1996	Diesel	1	2.97	2.97	2.97	NR	Foreign
Liang et al., 1996	Kerosene	1	0.04	0.04	0.04	NR	U.S.
Liang et al., 1996	Heating oil	1	0.59	0.59	0.59	NR	U.S.
Bloom, 2000	Light distillates	14	NR <sup>a</sup>	1.32	1.32	2.81	U.S.
Olsen et al., 1987	Utility fuel oil	32	NR	0.67	0.67	0.96	U.S.
Bloom, 2000	Asphalt	10	NR	0.27	0.27	0.32	U.S.
Olson et al., 1997	Naphtha	4	3–40	15	15	NR	Asian
Olson et al., 1997	Naphtha	3	8–60	40	40	NR	U.S.
EPA, 2000	Petroleum coke	1000	0–250	50	50	0.05	U.S.

<sup>a</sup> Not recorded.

level [2]. From the available literature there are researchers who have analyzed a variety of petroleum products for mercury. Table 3 lists the capabilities of some of the currently available analytical techniques.

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 obtaining better quality data.

### Mercury in Other Fuels

An initial review of literature was performed to assess the potential of other alternative fuel sources (e.g., oil/tar sand, oil shale, coalbed methane, and biomass) as significant contributors to mercury emissions. One study (Anuela-Tapola et al. [10]) found that oil shale-fired power plants emit significant amounts of heavy metals (e.g., Hg, Cd, As, and Pb) in the form of either vaporous metal species or metals condensed on very small particles in the flue gases. However, the exact amount is uncertain, and detailed analysis is necessary to determine the emissions of mercury due to oil shale combustion. Wilkerson [13] quantified the abundance of metals including As, Co, Fe, Hg, Mo, Ni, Sb, Se, V, and Zn in oil shale samples (in Green River shale oil) and also analyzed the possible chemical nature of several metals. Crude shale oils from surface and underground retorting processes were characterized for 26 trace element constituents. The shale oils were associated with moderately high levels of Fe (33–63 ppm) and As (9.3–29 ppm) and lower levels of other trace elements including mercury.

In general, biomass fuel sources are expected to emit less mercury than is typical for traditional fossil fuels. However, more data are required to characterize the potential for mercury emissions from biomass utilization. Among biomass fuels, leaf and tree needle litter contain some of the highest concentrations (up to 71 ppb on dry weight) of mercury [14]. According to Friedli et al. [14], mercury is emitted primarily as Hg<sup>0</sup> (more than 95%) in most of the cases, with particulate mercury accounting for the remainder. From some of the laboratory experiments, it is expected that mercury emitted from forest fires is significant. Hence, measurements on wildfires are needed to verify and quantify balances as inputs for its regional and global environment. In this context, it is important to evaluate mercury emissions from biomass in different technologies, including biomass gasification and biomass cofired power plants.

**Table 3.** 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 <sup>a</sup>	1.5–6.5	0.2	Eleven crude oils were analyzed and compared to NAA <sup>b</sup> [11]
Gasoline	Total Hg	E-CVAF <sup>c</sup>	0.22–3.3	0.04	Nine samples from various geographic areas. BrCl Extraction [3]
Crude Oil	Total Hg	NAA	0.10–12.2	0.05	Seven samples from Libya [12]
Crude Oil, Condensate, Fuel Oil	Total Hg, Hg <sup>0</sup> , particulate Hg, Hg(II), and methyl-Hg	ES-CVAF <sup>d</sup>	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 methyl-Hg [5]

<sup>a</sup> Thermal decomposition–cold vapor atomic fluorescence.

<sup>b</sup> Neutron activation analysis.

<sup>c</sup> Extraction–cold-vapor atomic fluorescence.

<sup>d</sup> Extraction and separation–cold-vapor atomic fluorescence.

The review and evaluation of mercury from other fuels will continue, and fuel samples will be analyzed to add to the information obtained to date. The results will provide a better understanding of the levels of mercury that can be potentially released from these current and future fuel sources.

### **Status**

Several additional papers have been added to the open literature and will be reviewed for incorporation into this study in the next several months. Additional oil samples have also been obtained and will be analyzed for inclusion in the project summary report. Work is progressing into the area of mercury in alternative fuel sources. During the next year, samples will be obtained for numerous fuel sources under consideration for continued and expanded use in the U.S. energy supply. Examples that will be considered include oil shale, oil sands, tar sands, and biomass (e.g., crops, trees, etc). In addition, new information on mercury in oil will be incorporated as it becomes available.

### **Potential Users/Technology Transfer**

This work has significant implications in determining if crude oil is a major source of mercury emissions to the atmosphere and whether it should be regulated. EPA may require oil companies to report 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.

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