

## Mercury in Crude Oil Processed in the United States (2004)

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The mean and range of concentrations of mercury in crude oil processed by U.S. refineries in 2004 were determined using two analytical methods. One hundred seventy separate crude oil streams were sampled repetitively to obtain 328 individual samples. Samples were retrieved immediately upstream of refinery tank farms. Losses of mercury during production, separation, and transportation were not examined. The arithmetic mean and median of 170 oil streams were 7.3 and 1.5  $\mu\text{g}/\text{kg}$  in total mercury, respectively. The total mercury concentration of oil processed in the United States in year 2004, including all species and both dissolved and suspended forms, expressed as a volume-weighted mean was calculated to be  $3.5 \pm 0.6 \mu\text{g}/\text{kg}$ . The range of measured concentrations extended from below the analytical detection limit (0.5  $\mu\text{g}/\text{kg}$ ) to approximately 600  $\mu\text{g}/\text{kg}$ . Good agreement was found with other recent and independent studies of mercury in crude oil refined in North America. The total amount of mercury in crude oil processed in the U.S. annually is less than five percent of the amount contained in U.S. coal produced annually.

### Introduction

The major sources of anthropogenic mercury emissions in the United States are fossil fuel and waste combustion. Mercury in coal has been studied extensively and it contributes the largest amount of atmospheric emissions of any fuel source (1, 2). An obvious analogy exists between mercury in coal and mercury in petroleum; however, the amount of mercury in crude oil, and thus potentially liberated by liquid fuel combustion or other pathways, has remained uncertain because of a paucity of accurate mercury concentration data across the huge range of crude oils entering U.S. refineries.

Studies of mercury in crude oil published before the year 2000 reveal a range of concentrations of total mercury (THg) in crude oil between approximately 0.1 and 20 000  $\mu\text{g}/\text{kg}$  (3). The breadth of the range reflects the wide variability of natural geological conditions. Calculations of a mean concentration from measured concentration data published before year 2000 were biased high because of poor analytical detection

limits and because analysts tended to select oils with higher concentrations for investigations (3). A consistent and broadly focused study of mercury in crude oil has not been available to allow comparison to coal and other fuels.

In 2003, the United States Environmental Protection Agency's Office of Research and Development initiated a study directed to determining the mean and range of concentrations of mercury in crude oil processed in the U.S. for the point in time accessible. The research program was organized into three parts, all now complete. Part 1 examined analytical procedures (4). Part 2 examined sampling and species effects (5, 6). In Part 3 and reported here, total mercury concentrations were measured for a wide variety of crudes made available to the study by the U.S. oil refining industry.

**Mercury in Crude Oil.** A number of mercury species have been identified in crude oil (7–9). The list includes elemental mercury (typically the major component) and dialkylmercury (typically a trace component), both volatile and reactive and mercuric sulfide and asphaltene mercury (major component in some oils), both nonvolatile and relatively nonreactive. Complexed ionic mercury species are also present in some oils as a minor component.

In measuring total mercury concentration (THg) in crude oil matrix, samples must reflect the homogeneous amounts of all mercury species that are present in the stream being sampled and analytical methods must avoid losses of volatile species in aliquot removal procedures. Because some mercury compounds are associated with oil sediment, some loss of mercury is expected in stagnant tanks that allow settling or stratification of suspended material. Elemental and organic mercury are volatile and losses are also expected when volatile components escape heated tanks or in transportation. Elemental mercury also reacts with steel surfaces irreversibly and some losses likely occur in pipelines. In the present study, such possible losses were not investigated. The focus of the study was not the wellhead concentration of mercury but rather the “as delivered” concentration in crude entering the refining process.

**Crude Oil Processed in the United States.** A wide variety of materials are processed by U.S. refineries to make liquid fuels and other products derived from crude oil (asphalt, coke, wax, lubricants). The raw material categories include condensates, crude oil, heavy crude oil, and synthetic crudes. Samples in all crude oil categories were donated and analyzed in the project. Oils having trade names are blends of oils that come from several or many individual wells and are typically consistent in composition and characteristics. The conscious desire to maintain consistency of oil properties likely constrains the range of mercury concentration in trade-named oils as well. The variation of measured mercury concentrations of trade-named crude oil streams over time is not well studied, but it was postulated that the range of concentrations exhibited by a single trade-named oil was much less than the range of mercury concentrations found in crude oils generally.

This study relied on industry volunteers to donate samples of crude to the project for analysis. Considerable efforts were made to ensure that the sample ensemble reflected both domestic production and imports in proportion to what is actually processed. No major crude sources are known that were left out of the group of oils analyzed, but certainly not all of the oil streams processed in U.S. refineries were included.

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**TABLE 1. Laboratory Performance Parameters**

|                        | reagent blank  | control CRM recovery                           | average RPD (THg>0.5) | average RPD (all) | RPD > 20% (THg>0.5) | average spike recovery                      |
|------------------------|--|--|-----------------------|-------------------|---------------------|---|
| CAF                    | 88.5% <0.1 μg/kg<br>6.2% 0.1 μg/kg<br>5.3% 0.2 μg/kg | mean = 98.1%<br>σ = 3.9%<br>range: 87.4–107.7% | 7.8%                  | 8.4%              | 2.1%                | mean: 96.0%<br>σ = 8.5%<br>range: 75.1–117% |
| number of measurements | 113  | 56   | 289                   | 335               | 289                 | 136   |
| DAF                    | mean = 0.07 μg/kg<br>σ = 0.181 μg/kg                 | mean = 85.0%<br>σ = 6.8<br>range 78.9–102.3%   | 6.8%                  | 41.4%             | 0                   | mean = 98.8<br>σ = 7.6<br>range 85.2–116.2% |
| number of measurements | 24   | 10   | 26                    | 43                | 26                  | 24  |

**Experimental Section**

**Analytical Methods.** Analytical methods targeted the total concentration of mercury (THg) in crude oil. Because several mercury species exist in oil, the analytical methods needed to be robust so that the chemically inert species (HgS and asphaltene-Hg) can be retrieved quantitatively while at the same time avoiding losses of the volatile mercury species. Techniques to retrieve and retain volatile species were investigated early on in the project and incorporated into the analytical methods and procedures (5). Because mercury is associated with material suspended in oil, sampling procedures and homogenization of samples were deemed important and were optimized to retrieve suspended mercury components.

Two independent laboratories, each using a different method, were selected to analyze crude oil samples. Methods were selected based on literature pedigree, performance comparison, and measured method detection limit (MDL). MDLs for the two methods that were selected were less than 0.5 μg/kg. The methods and procedures employed to analyze mercury in oil have been described previously, but a brief summary is offered here. Table 1 summarizes each laboratory’s performance relative to data quality objectives.

Laboratory A (Cebam Analytical, Seattle, Washington) used a combustion method developed and constructed in-house (10, 11). The combustion system consisted of a quartz temperature-controlled combustion column, a gas filter, and gas flow apparatus. The combustion column was divided into two independently controlled heating zones. The initial segment vaporized the hydrocarbon and mercury compounds and the second segment combusted the hydrocarbon. Liquid aliquots were drawn from the sample vial by penetrating the septum using a needle preconditioned microsyringe without opening the vial. Aliquots were then injected directly into the vaporization section of the instrument. Purified air, from which mercury was removed by passing through a gold-coated sand trap, was used as the carrier and combustion gas. Mercury vapor in combustion product gas exiting the combustion chamber was filtered to remove partially combusted hydrocarbons and then collected by amalgamation on a gold trap (single amalgamation). The mercury on the gold trap was released by heating in flowing argon that passed to the atomic fluorescence (AF) detector (Brooks Rand). This method is referred to as “Combustion–AF” or “CAF”.

Laboratory B (Frontier Geosciences, Seattle Washington) used a digestion – atomic fluorescence method in which homogenized oil aliquots were placed in quartz vials containing concentrated nitric acid. The vials were capped with quartz lids and heated to 300 °C under approximately 130 bar pressure in an autoclave (Anton-Paar high-pressure asher) until the sample dissolved. After cooling and removal from the autoclave, the samples were diluted with reagent water, and aliquots of sample digests were transferred by

pipet into a bubbler to which a stannous chloride (SnCl<sub>2</sub>) solution was then added. Argon was passed sequentially through the bubbler, through soda-lime traps, and finally through a gold sand amalgam trap. The first gold trap containing the collected mercury was heated in flowing argon to transfer the collected mercury to a second gold amalgam trap. Mercury collected on the second trap was likewise desorbed by heating in flowing argon and passed into an atomic fluorescence (AF) detector (Tekran 2500). The detector response was recorded and integrated. This method is referred to as “Digestion–AF or DAF”.

For the CAF method, detector calibrations were accomplished using dilutions of constructed standards. A 1000 mg/L stock solution was prepared by dissolving CH<sub>3</sub>HgCl (99%, Johnson Matthey, U.S.) into isopropanol. Working standard solutions (10, 20, and 50 ng/mL) were prepared by serial dilution of the stock solution with toluene. The stock standard was traced to NIST standards using the EPA1631 method (12). The working standards in glass vials were found to be stable at 20 °C for at least a month, but were prepared twice monthly. The CAF method used calibration factors (CFs) for calculation of concentrations. A CF was calculated as the standard value in pg divided by the difference of the standard peak area (PA) and the mean PA of method blanks (unit pg/PA). At least four nonzero CF points were analyzed daily. Samples were processed only when RSD of CFs was less than 15%. 80% of RSDs were within 5–10% during the project. The verification of a daily calibration was performed by analyzing a lab control sample (LCS) in duplicate following the standard curve. Two LCSs, no. 5-01 heavy oil and a Conostan (Ponca City, Oklahoma) oil standard (100 ppm as Hg), were used. The no. 5-01 heavy oil was certified as 288.0 ng/g for THg as Hg by three independent labs using three independent techniques. The sample was found to be stable for past years since it was certified in 2001. The two LCSs were serially diluted to 10.0 ng/mL with toluene prior to use. Diluted standards were prepared monthly. Analyses of matrix spikes and spike duplicates (MS/MSD) for the CAF method were performed by injecting a spiked oil sample aliquot using the sample syringe. Spikes were methylmercury in toluene working standards. The criteria for MS/MSD recovery was 75–125%.

For the DAF method, certified reference materials (CRMs) were purchased (high purity standards, 1000 ± 3 μg/mL and absolute standards, 100.4 ± 0.378 μg/mL). A working calibration standard (10 ng/mL) was constructed by dilution using reagent water containing 2% BrCl and used for 3 months. Daily calibrations of the Hg analyzer were performed using a 5-point (0.05, 0.10, 0.50, 2.00, 4.00 ng) standard calibration curve. Linearity was better than 0.999 for all calibrations. Calibration was verified using BrCl water blanks (mean = 0.06 μg/kg, n = 38, σ = 0.055 μg/kg) and separately constructed aqueous verification standards (mean > 99.1% recovery, n = 38, σ = 6.3%). Mercury in oil certified reference

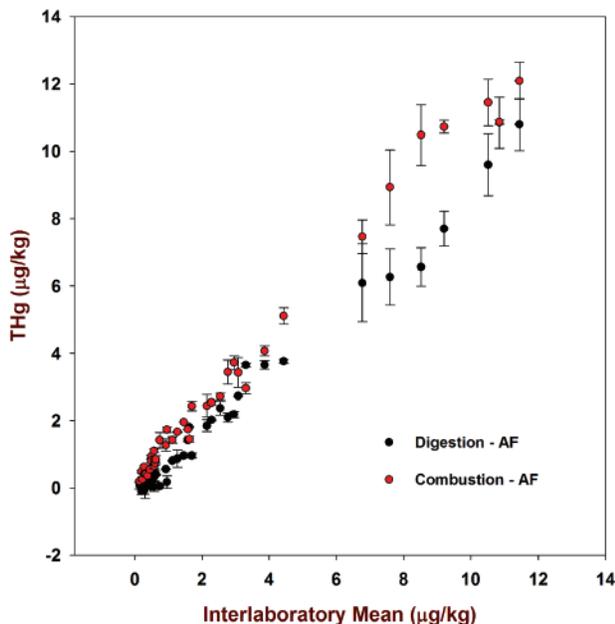


FIGURE 1. Laboratory and method comparison (CAF and DAF).

material (5000 µg/kg THg; Spex Certiprep Inc.) was used as a control (each sample batch) to verify method performance. A 1000× dilution of the 100 µg/mL CRM (100 ng/mL Hg) was used for matrix spikes.

Method detection limits were calculated according to procedures set forth in EPA Method 40 CFR 136 (Appendix B) and found to be 0.11 and 0.47 µg/kg for CAF and DAF, respectively.

**Crude Oil Sampling.** Crude oil samples were retrieved at the entry point to refineries prior to crude oil tanks. For oils that arrived by pipeline, the sample point typically was that used for refinery quality assurance sampling. For oil tankers, the sampling point was typically the discharge and metering point. Refineries used their normal sampling procedure, modified as needed to accommodate sample containers for mercury analysis. Techniques for sampling crude oils were investigated early in the project and details have been discussed previously (5).

**Sample Reproducibility.** An oil “sample” consisted of four vials filled simultaneously with vials labeled “A, B, C, D”. Sample vials were homogenized prior to removal of aliquots for analysis by ultrasonication (CAF) or manual shaking (DAF). In the normal procedure, one vial (usually B) was analyzed in duplicate (two aliquots from one vial) by the CAF laboratory. Fifteen percent of samples were analyzed more than twice to check vial-to-vial homogeneity and sample age variation. Reproducibility of measurements was judged by calculation of relative percent difference (RPD = average of the sum of differences expressed as a percentage of the mean). Reproducibility of aliquots of a single sample is a measure of laboratory and method performance, as opposed to oil mercury concentration variability, assuming homogeneous samples (all vials the same) and uniform aliquots were obtained from vials. As shown in Table 1, RPD for the CAF and DAF laboratories averaged 8 and 7%, respectively.

**Interlaboratory Comparison.** Laboratory/method bias was assessed by examination of the differences of duplicate means as a percentage of the interlaboratory mean. Laboratories analyzed the same sample but different vials. Forty-three samples, selected at random, were analyzed in parallel using CAF and DAF methods. The data are shown graphically in Figure 1. The error bars shown are simply the range of

duplicate measurements. In the graph, two points at interlaboratory means of 77 (RPD = 18.8) and 80 µg/kg (RPD = 10.4) are not shown so as to expand the scale of the plot. Interlaboratory reproducibility above MDL met data quality objectives for the project. Systematic bias averaged 24% (range = 0.1–94%) for samples where the interlaboratory mean was greater than 0.5 µg/kg. The bias was not investigated but is thought to derive from minor losses of volatile mercury in the DAF procedure. Oil aliquots are exposed to the atmosphere and have opportunity for slight evaporation prior to digestion in the DAF procedure. As shown in Table 1, the DAF method also demonstrated slightly poorer CRM recovery.

## Results and Discussion

An “oil stream” was defined as a trade-named oil received by an individual refinery. For each oil stream, THg was measured in one or more discreet sampling events. An independent sampling event retrieved four 40 mL vials of oil, either from a tanker discharge or from a pipeline. Samples were independent if taken days or weeks apart from pipelines or from different tankers. Obtaining three independent samples was the goal but numerous exceptions occurred because of supply dynamics. The mean concentration of an oil stream ( $\bar{C}^{OS}$ ) was calculated as the average of  $n$  individual sample measurements with each sample result ( $c_i$ ) the mean of two or more replicates.

$$\bar{C}^{OS} = \frac{1}{n} \sum_{i=1}^n c_i \quad (1)$$

The number of samples ( $n$ ) averaged to obtain stream concentrations was between 1 and 9. The standard deviation ( $s^{OS}$ ) of oil stream sample concentrations was calculated according to eq 2.

$$s_{n>2}^{OS} = \sqrt{\frac{\sum_{i=1}^n (c_i - \bar{C}^{OS})^2}{(n-1)}} \quad (2)$$

The mean mercury concentration of 170 oil streams treated independently was calculated to be 7.3 µg/kg (median = 1.5 µg/kg, SD = 46.1 µg/kg, range = 593 µg/kg). Fifty-seven percent of streams in the range of 1–10 µg/kg and 93% were less than 10 µg/kg. A very few oils were measured with concentrations over 50 µg/kg. All of these oils (THg > 50 µg/kg) came from Asia, however, which is known in the industry to be a “mercury prone” region. Few Asian oils reach the U.S. refineries because of transportation costs and Asian market demands. Asian imports represented less than 1% of oil processed in the U.S. in 2004, but this percentage may increase in the future.

Inadvertent volume weighting affects the calculation of the simple mean. Because several participating refineries may have received the same trade-named oil, some trade-named oils are represented in the “oil stream” ensemble (170 oil streams) more than once. Popular oils that are desired due to characteristics and high volume oils are represented by several donated oil streams and thus contribute to the calculated mean in proportion to the replication of their donation.

**Volume Weighting.** To obtain a mean concentration of mercury in oil processed in the 50 United States, concentrations of market-named oils were weighted by the volume of U.S. refined oil they represented in 2004. This was accomplished in the following manner. Statistics are not kept, nor therefore available, of the amount of oil refined according to individual trade names. Statistics on production volume

**TABLE 2. Mercury in Oil by Country (Imports) and by State (Production)**

| country       | country volume (1000 barrels) | % U.S. supply | country average (μg/kg) | Σn        | N         | s <sup>CS</sup> (μg/kg) | country            | country volume (1000 barrels) | % U.S. supply | country average (μg/kg) | Σn         | N          | s <sup>CS</sup> (μg/kg) |
|---------------|-------------------------------|---------------|-------------------------|-----------|-----------|-------------------------|--------------------|-------------------------------|---------------|-------------------------|------------|------------|-------------------------|
| Algeria       | 78 719                        | 1.31          | 13.3                    | 2         | 2         | 4.4                     | Qatar              | 1 383                         | 0.02          |                         |            |            |                         |
| Angola        | 112 018                       | 1.86          | 1.6                     | 2         | 2         | 0.6                     | UAE                | 1 885                         | 0.03          |                         |            |            |                         |
| Cameroon      | 6 756                         | 0.11          |                         |           |           |                         | Oman               | 3 570                         | 0.06          |                         |            |            |                         |
| Chad          | 20 805                        | 0.35          | 1.2                     | 3         | 2         | 0.5                     | Syria              | 501                           | 0.01          |                         |            |            |                         |
| Congo         | 8 019                         | 0.13          |                         |           |           |                         | Yemen              | 1 365                         | 0.02          |                         |            |            |                         |
| Gabon         | 52 061                        | 0.87          | 0.5                     | 2         | 1         | 0.2                     | Saudi Arabia       | 547 125                       | 9.11          | 0.9                     | 28         | 14         | 0.1                     |
| Guinea        | 24 212                        | 0.40          | 0.3                     | 1         | 1         | 0.1                     | <b>Middle East</b> | <b>883 946</b>                | <b>14.71</b>  | <b>0.8</b>              | <b>45</b>  | <b>24</b>  |                         |
| Ivory Coast   | 1 840                         | 0.03          | 0.3                     | 1         | 1         | 0.2                     | Argentina          | 21 499                        | 0.36          | 16.1                    | 1          | 1          | 7.1                     |
| Libya         | 6 724                         | 0.11          |                         |           |           |                         | Brazil             | 18 733                        | 0.31          | 1.1                     | 2          | 2          | 0.2                     |
| Nigeria       | 394 560                       | 6.57          | 1.8                     | 20        | 12        | 0.1                     | Columbia           | 52 049                        | 0.87          | 3.4                     | 10         | 7          | 0.6                     |
| <b>Africa</b> | <b>705 714</b>                | <b>11.75</b>  | <b>2.7</b>              | <b>31</b> | <b>21</b> |                         | Ecuador            | 84 937                        | 1.41          | 1.8                     | 11         | 6          | 0.3                     |
| China         | 5 273                         | 0.09          |                         |           |           |                         | Bolivia            | 311                           | 0.01          |                         |            |            |                         |
| Indonesia     | 12 360                        | 0.21          |                         |           |           |                         | Guatemala          | 6 699                         | 0.11          |                         |            |            |                         |
| Kazakhstan    | 3 228                         | 0.05          |                         |           |           |                         | Peru               | 383                           | 0.01          |                         |            |            |                         |
| Australia     | 7 855                         | 0.13          | 0.8                     | 1         | 1         | 0.3                     | Trinidad           | 18 027                        | 0.30          |                         |            |            |                         |
| Brunei        | 5 616                         | 0.09          |                         |           |           |                         | Venezuela          | 474 531                       | 7.90          | 4.2                     | 18         | 12         | 13                      |
| Malaysia      | 6 551                         | 0.11          |                         |           |           |                         | <b>S. America</b>  | <b>677 169</b>                | <b>11.27</b>  | <b>5.3</b>              | <b>42</b>  | <b>28</b>  | <b>0.0</b>              |
| Thailand      | 194                           | 0.003         | 593.1                   | 2         | 1         | 184                     | AK                 | 332 464                       | 5.53          | 3.7                     | 16         | 6          | 0.5                     |
| Viet Nam      | 9 256                         | 0.15          | 66.5                    | 5         | 2         | 4.9                     | CA                 | 240 206                       | 4.00          | 11.3                    | 6          | 3          | 3.6                     |
| <b>Asia</b>   | <b>50 333</b>                 | <b>0.84</b>   | <b>220.1</b>            | <b>7</b>  | <b>4</b>  |                         | GOM                | 531 900                       | 8.85          | 2.1                     | 19         | 7          | 0.2                     |
| <b>Canada</b> | <b>591 489</b>                | <b>9.845</b>  | <b>2.1</b>              | <b>72</b> | <b>32</b> | <b>0.2</b>              | LA                 | 72 824                        | 1.21          | 9.9                     | 7          | 7          | 2.6                     |
| Denmark       | 821                           | 0.01          |                         |           |           |                         | MT                 | 24 724                        | 0.41          | 3.1                     | 2          | 2          | 1.0                     |
| Norway        | 52 365                        | 0.87          | 19.5                    | 3         | 2         | 8.2                     | OK                 | 62 502                        | 1.04          | 1.4                     | 4          | 2          | 0.4                     |
| Russia        | 58 010                        | 0.97          | 3.1                     | 5         | 4         | 0.2                     | TX                 | 392 865                       | 6.54          | 3.4                     | 6          | 3          | 22                      |
| UK            | 87 193                        | 1.45          | 3.6                     | 10        | 3         | 1.0                     | UT                 | 14 628                        | 0.24          | 2.2                     | 1          | 1          | 0.9                     |
| <b>Europe</b> | <b>198 389</b>                | <b>3.30</b>   | <b>8.7</b>              | <b>18</b> | <b>9</b>  |                         | WY                 | 51 621                        | 0.86          | 2.7                     | 15         | 8          | 0.4                     |
| <b>Mexico</b> | <b>585 023</b>                | <b>9.74</b>   | <b>1.3</b>              | <b>25</b> | <b>9</b>  | <b>0.1</b>              | X                  | 592 026                       | 9.85          | 3.1                     | 12         | 3          | 0.6                     |
| Iraq          | 239 758                       | 3.99          | 0.7                     | 10        | 6         | 0.1                     | <b>U.S.</b>        | <b>2 315 760</b>              | <b>38.55</b>  | <b>4.3</b>              | <b>88</b>  | <b>42</b>  |                         |
| Kuwait        | 88 359                        | 1.47          | 0.8                     | 7         | 4         | 0.2                     | <b>total</b>       | <b>6 007 823</b>              |               |                         | <b>328</b> | <b>170</b> |                         |

are available but typically only for some major oil streams. Records are compiled of oil produced in each U.S. state and, for imports, by country of origin. Imported oil cargoes have trade names that identify the country of origin, hence attaching country import volumes to oil concentrations is straightforward. Likewise oil produced and traded in the U.S. is identified by origin such that state volumes can be associated with most streams. Many of the smaller U.S. refineries tap local production and, in some cases, the identity and volume of local domestic sources are elusive to any association. Import, production and processing statistics were obtained from the Energy Information Agency (U.S. Department of Energy) website (13). Year 2004 oil volumes were chosen for the statistical base. Samples were acquired in years 2004, 2005, and 2006, but the majority of samples were gathered in 2004.

In Table 2, country and state THg averages are compiled along and attached to volumes of oil processed in U.S. refineries from countries and volumes of oil produced within states. The country or state average was calculated as the arithmetic mean of *N* oil stream concentrations ( $\bar{C}^{OS}$ , eq 1) obtained from that country or state.

$$\bar{C}^{CS} = \frac{1}{N} \sum_{j=1}^N \bar{C}_j^{OS} \quad (3)$$

As with the calculation of the simple mean, inadvertent weighting occurred in this procedure also. Oil streams (eq 3) were treated independently within countries and states. More than one oil stream may have derived from a single trade-named oil. Larger streams contributed a stream average from each refinery that received the oil and donated samples. Larger volume streams were, therefore, more likely to contribute more streams in calculating country/state averages because they were processed by more refineries during the time samples were collected. In Table 2, “Σn” is the total number of samples from a state or country and “N” is the number of oil streams from that country or state.

The weighted mean was calculated from country and state averages weighted by their associated fraction of oil contributed using the following formula:

$$\bar{C}^{US} = \sum_{CS} \left[ \bar{C}^{CS} \frac{V^{CS}}{0.9V^{US}} \right] \quad (4)$$

where  $\bar{C}^{US}$  is the mean total mercury concentration of U.S. processed oil;  $\bar{C}_{CS}$  is the average concentration in a country or state obtained from oil streams and  $V^{CS}/0.9V^{US}$  is the ratio of country/state volume to total U.S. oil volume. The sum was taken over all countries and states that contribute to the U.S. total processed oil volume and for which concentrations of THg were measured. The factor of 0.9 comes from the fact that only 90% of U.S. oil volume was accessed in the set of samples obtained in the program. In weighting, state and country average oil density was assumed to be approximately equal to the U.S. average oil density. The calculation yields a value of  $\bar{C}^{US} = 3.5 \mu\text{g}/\text{kg}$  for the mean concentration of mercury in oil refined in the U.S.

**Uncertainty.** Ten percent of oil processed in the U.S. was not accessed in the project. The 10% number derives from states and countries, known to contribute to U.S. totals, but for which no oil mercury concentrations were measured, and thus no concentrations were available to be associated to the volumes known to be imported (countries) or produced (states). Within individual countries and states, some oil streams likely to contribute to U.S. totals also were not accessed, but it was not possible to know exactly how many, or the corresponding volume excluded, because import and production volumes are not compiled for all individual trade-named oils. It is thought that the greatest uncertainty in the calculated mean concentration of mercury refined in the U.S. lies with calculated country mean concentrations due to inaccessibility, not with analytical uncertainty. Analytical uncertainty, estimated as the average difference from the mean of duplicates, was about 8% overall for measured values above 0.5 μg/kg. It was hypothesized that individual oil

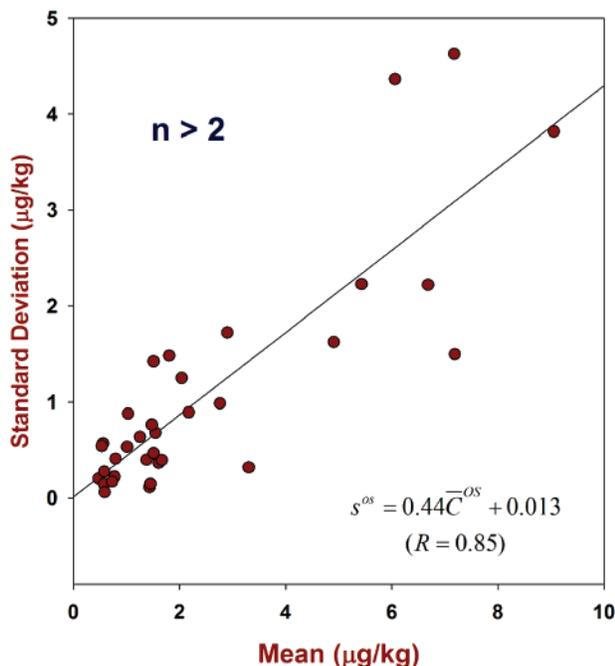


FIGURE 2. Oil stream standard deviation versus mean mercury concentration.

streams exhibited normal distributions of mercury content but the number of samples obtained from many streams was not sufficient to judge.

Oil stream estimated standard deviation ( $s^{os}$ ) was found to depend on the mean (eqs 1 and 2) in the manner shown in Figure 2 for oil streams with more than two samples.

The U.S. average mercury in oil concentration was calculated according to eq 4 where country/state averages of  $N$  oil streams have the following estimated variance:

$$(s^{cs})^2 \approx \frac{1}{N^2} \sum_{j=1}^N [(s_j^{os})^2/n_j] \quad (5)$$

where  $(s_j^{os})^2$  is the variance of each of the  $n_j$  samples of the  $j$ th oil stream in a country or state. To calculate country/state variances, oil stream variances at sample numbers  $n = 1$  and  $n = 2$  used the proportionality shown in Figure 2. The volume weighted variance in the U.S. mean ( $S_{US}^2$ ) was estimated in the same manner as the volume weighted mean:

$$S_{US}^2 \approx \sum_{CS} \left\{ \left( \frac{V^{CS}}{0.9V^{US}} \right)^2 (s^{cs})^2 \right\} \quad (6)$$

The estimated uncertainty in the U.S. mean mercury concentration was therefore estimated to be

$$\bar{C}^{US} \pm 1.96S_{US} \quad (7)$$

Using the stated methods and approximations, the estimated uncertainty in the volume (2004) weighted mean mercury concentration is  $3.5 \pm 0.6 \mu\text{g}/\text{kg}$ . While more sophisticated ANOVA methods might improve the accuracy of the estimate of uncertainty, the calculated variance likely suffices for practical purposes.

**Comparison to Recent Studies.** Long and Kelly (14) reported concentrations of mercury in crude oil obtained using an isotope dilution method. The sample ensemble

derived from oils delivered to the strategic petroleum reserve (SPR). The average concentration measured for the limited set of samples obtained from SPR deliveries was less than  $2 \mu\text{g}/\text{kg}$ .

Magaw et al. (15) reported data on 26 crude oils that were regionally identified and described as purchased by U.S. refineries. Magaw's data span the major U.S. west coast crude streams and include concentrations for both domestically produced and imported crudes. Magaw reported total mercury concentrations below  $10 \mu\text{g}/\text{kg}$  (the detection limit of the CVAA instrument) for all oils except one. Magaw reported one California crude oil (Cymric) as having  $1.5 \text{ mg}/\text{kg}$  THg, which is the single exception to all of the 25 other crude oils that tested below the instrumental detection limit.

The New Jersey Department of Environmental Protection reported concentrations of total mercury in oil delivered to U.S. East Coast refineries (16). The methods of analysis were similar to those employed in this study, i.e., combustion and digestion with CVAF detection. Approximately 25 oil streams were analyzed with replication. The oils originated in the Middle East, South America, Africa, North Sea, Canada, and Mexico. The range of THg was  $0.1\text{--}12.3 \mu\text{g}/\text{kg}$ . The mean and median were reported as  $3.5$  and  $2.7 \mu\text{g}/\text{kg}$ , respectively.

In parallel to the study reported here, Environment Canada investigated mercury in crude oils refined in Canada (17). In the Canadian study, samples of crude oil were collected from refineries for crude types covering approximately 70% of the total crude volume processed in Canada in 2002. The sampling procedures and methods of analysis in the Canadian study were similar (combustion, atomic fluorescence and atomic absorption detection) to those employed in this investigation. The volume weighted average for Canadian refined oils is reported preliminarily as less than  $4 \mu\text{g}/\text{kg}$  (95% <  $10 \mu\text{g}/\text{kg}$ ).

Nothing is obvious in the literature to suggest that analytical methods other than those employed in this study and used to measure total mercury concentrations in crude oil provide consistently higher THg values. One can make a case for low method bias in some literature studies when precautions against loss of volatile mercury or procedures to homogenize samples were not incorporated into the method procedures. No ensemble bias was obvious or suspected. It should be noted, however, that the calculated mean is sensitive to even a few high mercury oil streams that may arrive to U.S. refineries now or in the future. If refineries processed an additional 30 million barrels per year (0.5% of the U.S. total) having an average  $1000 \mu\text{g}/\text{kg}$  total mercury concentration, the calculated U.S. volume weighted average would more than double.

**Significance.** The mass of coal burned in the U.S. annually ( $\sim 10^{12} \text{ kg}/\text{y}$ ) is approximately the same as the mass of oil refined in the U.S. annually (13). The concentration of mercury in all U.S. coal (coal rank volume corrected) is approximately  $100 \mu\text{g}/\text{kg}$  (1, 2). From the measured mean concentration for total mercury in oil and total annual volume (2004), oil that passes through U.S. refineries contains approximately 3 metric tons of mercury. The maximum amount of mercury released to the ecosphere from oil processed in the U.S. is, therefore, approximately less than 5% of that which may be derived from burning coal in any given year.

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