Mercury in Crude Oils

2013 MCA Spring Seminar Series

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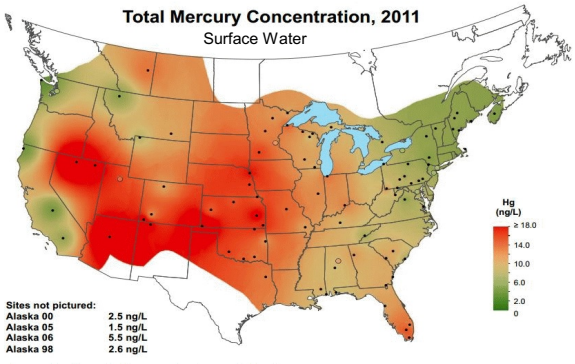
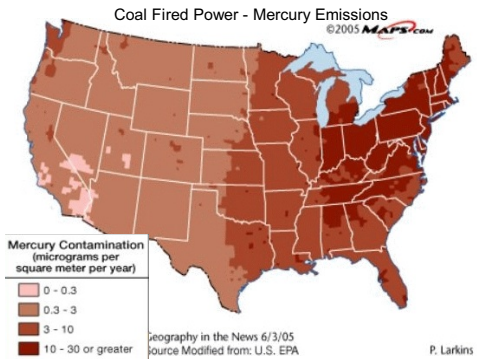
Overview

Mercury is a persistent bio-accumulative toxin found in atmospheric in amounts of 1-2 ng/m³ (billionth of a gram). It can persist for extended periods by cycling back and forth between the air and soil surface, all the while changing chemical forms. The atmospheric half life of elemental mercury is estimated to be six months, as methyl-mercury in soils for decades, and as inorganic forms, much longer.





The diagrams above seem to contradict each other, but point out a conundrum in the literature. Mercury exists in multiple chemical forms, both soluble and insoluble. Soluble compounds are easily stripped from the atmosphere and soil surface by rainfall. By this mechanism, arid areas will likely have a greater surface water mercury content than areas with more abundant precipitation. Conversely, coal-fired power plants are considered to be the largest mercury generators, but only a portion of the discharge will be a soluble form of mercury. The understated caveat - how you sample and what you test will affect your results.

As solubility plays a role in environmental dispersion, by the same mechanism, it is also correlated with toxicity. Solubility is just one aspect. There are multiple mercuric compounds, each with different properties. The biologically active cation, methyl-mercury (H_3C-Hg)+, has a completely different life style than its parent dimethyl-mercury.

Coal, which has an average content of about 89 µg/k Hg (ppb w/w), has held the most concern in environment mercury release. Until the late 1990's, petroleum products were seldom mentioned in the research involving mercury emissions. However, crude oil averages about 4 µg/k Hg, about 5% of coal's content. As noted in the following chart, the U.S. processed nearly six billion barrels of crude annually. That works out to be a mercury release of about 11 tons.

Origins of Mercury in Fossil Fuels

Mercury is a fairly rare element in the earth's crust, usually found in concentrations of mercury sulfide (cinnabar). While most of the mercury in the atmosphere is elemental, most of the environmental mercury in water, soil, sediments, or plants and animals is in the form of inorganic mercury salts and organometallics (mostly methyl-mercury).

Mercury is metabolized by bacteria (bio-methylation), absorbed by plants, incorporated within the food chain, and can be detected in most any biomass. As an example, biosolids (sewage sludge) have customarily been monitored by detection of its mercury in the 1-5 ppm range. Fossil fuels, the remains of ancient biomass, will still contain a trace mercury component. This includes natural gas, gas condensate, crude oil, coal, tar sands, and other bitumens.

Mercury also appears to be incorporated in crude oil and gas through a secondary geological process. Geological mercury is often associated with the boundaries of tectonic plates. Significant deposits are located in regions where plate subduction has occurred in combination with a degree of volcanic activity or hot springs. The highest contents of mercury in crude oils and natural gas are usually associated with these areas.

Mercury Levels in Crude Oil

Mercury levels in crude and gas can be widely variable, both between and within reservoirs and geographical areas. Unfortunately, the same can be said for historical laboratory data, due to the variety of Hg compounds and test methods. Detectable mercury components of crude oils would include elemental mercury, mercuric chloride, mercuric sulfide, mercuric selenide, dimethylmercury, diethylmercury, and asphaltenes (tars). These can exist in soluble, insoluble, gaseous, solid and liquid states. That variation significantly influences sampling and test methods.

Mercury Levels in US Crude Oil Annual Supply, Crude Oil Quality Group, Feb 2007

Source	Volume in Barrels	% US Supply	Hg µg/kg (ppb w/w)
Africa	705,714,000	11.75	2.7
Asia	50,333,000	0.84	220.1
Canada	591,489,000	9.845	2.1
Europe	198,389,000	3.30	8.7
Mexico	585,023,000	9.74	1.3
Middle East	883,946,000	14.71	0.8
South America	677,169,000	11.27	5.3
United States	2,315,760,000	38.55	4.3
Annual US Total 6,007,823,000		**Weighted Average 3.5 µg/kg ± 0.6**	

To put average crude oil mercury content of 3.5 µg/kg in perspective, the concentration in people is about the same. Most of the population will have a similar mercury body burden. Determining our personal mercury levels is complicated due to different tissues having different affinities for the various forms of organic and inorganic mercury. As an example, in human autopsy tissue evaluations, total mercury level in the occipital cortex of the brain was twice that of the blood. Toenails have been shown to have approximately 59 times total mercury as blood levels, and hair will have close to a ratio of 250. Different ratios have been reported in the literature, but it does point out that hair seems a lot easier to sample than brain tissue.

In 2001, the EPA established a whole blood reference dose (RfD) of 5.8 µg/L methyl-mercury, below which adverse health effects would not be expected. One published study found that 8% of women of childbearing age exceeded the blood level RfD. Another study suggested that 25% of the adult population in the New York area likely exceeded this level. These higher mercury levels are generally correlated with seafood, the most common mercury source. Beware, that convenience store sushi could contain close to 1 ppm Hg.

The Problem with Crude

The low mercury levels found in crude oil do not seem to represent a significant personal toxic exposure or environmental hazard. Refining those six billion barrels per year, does. It is a volume issue. The refining process tends to concentrate and collect the mercury components and direct the emissions to air release, petroleum product, waste-water and waste-solids. In 2001, the EPA's estimated that US petroleum refineries were responsible for approximately 11 tons of mercury release annually.

Mercury poses several issues for refineries. The easy ones to recognize are the environmental release and health issues. Mercury is detrimental to the refining process through amalgamation with other metals, poisoning of catalysts, and liquid metal embrittlement (cracking) with metals such as aluminum. Of particular concern are LNG & LPG cryogenic heat exchangers made of aluminum alloy. For the same reason, liquid metallic mercury is not permitted in nuclear facilities, subs, or aluminum aircraft.

Elemental Mercury

Due to its high density and tendency to agglomerate and bead, elemental mercury can be concentrated in drains and other low points of process plants. Upon breaching any mercury contaminated tank, pipework or equipment, there is a likelihood of worker airborne exposure, though there are few published studies in the oil industry. If hot work is involved, the 0.1 mg/m^3 PEL and 0.025 mg/m^3 TLV can be readily exceeded. To add insult to injury, mercury contaminated components may require classification as hazardous waste and may not be treatable as ordinary scrap iron.

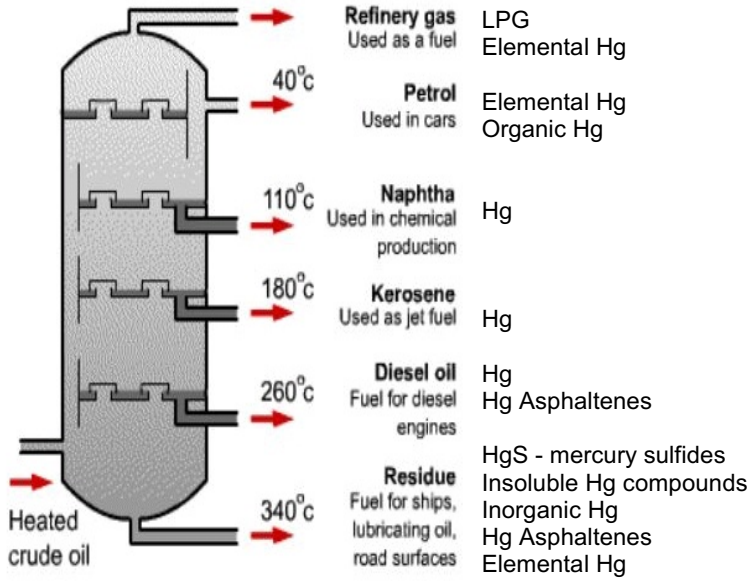
At 20°C, elemental mercury has a vapor pressure of 1.2 µm Hg, which provides a surprising degree of volatility in the ppm range. Since a vapor pressure exists, it can be found in natural gas and distilled petroleum products. With this phase change, mercury concentration can also be modified. Just as any liquid evaporates, the partial pressure of mercury vapor in natural gas could make its concentration higher than that of the reservoir oil from which it came.

During refinery distillation, that segment of elemental mercury vapor is predominantly distributed in liquefied petroleum gas (LPG) and light distillate streams. But due to its weight, it can also be found in the residual fraction, which also contains the majority of the insoluble and inorganic mercury salts. Little work has been carried out to assess the health impact arising from the mercury that is contained in fuels such as LPG and light distillates, and used by consumers (cooking or transportation). Research is growing in these areas with reports confirming existing mercury emissions from common fuels. Need a thesis, here you go.

Published Examples of Mercury Levels in Petroleum Products, multiple sources

Type	Range ppb	Hg Average ppb
Natural Gas (Indonesia)	200 - 300	
(Germany/Netherlands)	70 - 3500	
(Algeria)	50 - 200	
(South America)	0.01 - 120	
(Middle East)	1 - 9	
(North America)	0.001 - 0.05	
Gasoline	0.22 – 1.43	0.7
Gasoline	0.72 – 3.2	1.5
Gasoline	0.4	0.4
Diesel	2.97	2.97
Kerosene	0.04	0.04
Heating Oil	0.59	0.59
Light distillates		1.32
Utility fuel oil		0.67
Asphalt		0.27
Naphtha	3 - 40	15
Naphtha	8 - 60	40
#6 Residual Fuel Oil	60-120	90
Petroleum Coke	0 - 250	50

Distribution of Mercury Components in Distillation



Refinery Waste Water

Most of the mercury in refinery waste water is derived from crude oil. In de-salter applications,

water is mixed with the crude to scrub soluble chlorides. If chlorides were not removed, hydrogen chloride could be formed downstream and lead to corrosion. Other contaminates removed by the water are soluble mercury compounds, inorganic salts, elemental mercury and other heavy metals.

Mercury Recovery
Additional mercury recovery in the crude oil processing can be accomplished by mercury sorbents (elemental sulfur, metal sulfides, halide impregnated carbon particles, ion exchange resins, and molecular sieves). This and the wash water account for the majority of liquid and solid mercury waste generated by refineries.

Shipboard Mercury
Practically all information on mercury in crude oil is related to the refinery industry. That process will produce a concentrating effect, but the physics could produce similar conditions aboard marine vessels and storage tanks. Wash water could be expected to strip out a soluble mercury component. Elemental and inorganic mercury could be expected to be greater in tank bottoms and sludge. Since crude oil tanks are seldom coated, elemental mercury could form an amalgamation with the steel. The partial vapor pressure of mercury could result in a greater concentration in a saturated atmosphere than in its source.

From the data presented here, it might be noted that No. 6 Fuel Oil may likely have a mercury content 25 times that of crude oil averages, and sludge in CHT tanks could be another order of magnitude greater. We need not restrict our concern to crude oil.

Summary
Mercury is a trace contaminant in crude oil and petroleum products in the part per billion level. It can be encountered in a variety of forms and vary from one source to another. Over a period of time, possibilities include settling, amalgamations or other forms of concentration.

Crude oil is common in our industry. Though known to have the potential to contain mercury, these concentrations are generally considered too low to produce any observable effect. There are no readily available studies or experiences to confirm or deny adverse mercury exposure in the maritime and shipyard industries. Our dilemma, there is one way to find out.