

Mercury management in petroleum refining

An IPIECA Good Practice Guide

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Executive summary

This Guide provides an overview of mercury management in petroleum refining, describing good practices and strategies related to environmental controls, worker health and safety, process safety, product safety and waste management.

Mercury occurs naturally in soil and rock and is also released into the environment by volcanic eruptions. For the past 150 years, increased human industrial activity has also generated significant environmental releases of mercury. A recognized toxin, exposure to mercury can result in adverse human health effects ranging from acute to chronic. Mercury has a range of forms with varying levels of toxicity.

In 2009, the United Nations Environment Programme (UNEP) promoted a global initiative to limit and mitigate anthropogenic mercury emissions in order to protect human health and the environment, which in 2013 culminated in the Minamata Convention.

As part of the UNEP initiative, the oil and gas sector assisted in the generation of data on mercury releases from its activities. In 2012, IPIECA published the largest publicly available dataset on mercury levels covering 446 crude oils and condensates. IPIECA data indicates the refining sector's contribution to global mercury emissions is 0.07% of the total global mercury releases to air, and less than 0.01% to water. Although mercury releases from refining are small, they should be managed appropriately and in accordance with local laws and regulations.

This Guide provides a brief review of the varying forms of mercury and the chemical reactions that can cause them to interchange, with particular reference to mercury in the refining process. It reviews studies into the fate of mercury once it enters a refinery as well as it examines the human exposure to mercury and the potential health impacts, providing examples of exposure limits and exploring potential specific exposure routes in refineries. Exposure control measures;



personal protective equipment; a general approach to the health impacts of mercury; exposure monitoring and sampling; hazard communication and worker training; and safe work practices are briefly described.

Any workplaces handling mercury should implement appropriate procedures for waste measurement, analysis, treatment and disposal, which should be incorporated into a specific Mercury Waste Management Procedure or included in existing waste management plans or procedures. If mercury-containing waste is to be transferred to a third party for handling and disposal, the refinery should confirm that the third party is appropriately qualified for these tasks.

Refineries sell many products, and this Guide emphasizes the importance of stewardship across the supply chain. In assessing product-related risks, each refinery should consider the stewardship issues for both their finished products and the intermediates sold to other manufacturers. For intermediates, refinery product safety becomes process safety in another plant.

There is currently only one proven technology to remove mercury from crude oil and condensates, and accordingly most mercury removal occurs in refinery processes or in treating refinery products and effluents. The Guide offers a brief discussion of treatment options, with an added focus on mercury removal from wastewater.



Introduction and background

Introduction

This IPIECA Guide describes good practices and strategies used to manage mercury in the petroleum refining industry. The Guide addresses practices concerning environmental controls, worker health and safety, process safety, product safety and waste management.

Although mercury concentrations are less than 2 parts per billion (ppb) in most crudes, mercury has the potential to accumulate and cause operational issues in refining facilities. The industry has developed a range of technologies and solutions to manage this challenge effectively.

In this report, IPIECA recommends good practices such as:

- knowing the mercury content of the crude oil entering refining facilities;
- monitoring to assure a safe workplace for workers;
- taking appropriate precautions during operations and maintenance work;
- the use of mercury removal units (MRUs), when appropriate; and
- following proper waste management procedures.

These good practices are a collection of operational, equipment and procedural actions related to mercury management in petroleum refining. Since each refinery is uniquely configured, some of these practices may or may not be applicable at each specific refinery.

Background

Mercury is a natural component of the Earth. The average concentration of mercury in the Earth's crust is approximately 0.05 mg/kg (50 wt ppb), but there are significant local variations (UNEP, 2002).

Mercury sulphide, HgS, is the most common form of mercury in nature (USGS, 2003). Mercury sulphide is among the least mobile and most stable forms of mercury. However, it decomposes at high temperatures, releasing elemental mercury. It is also converted biologically under anaerobic conditions into organic mercury species.

Once mercury enters the biosphere, it becomes part of a mercury cycle, as illustrated in Figure 1. Mercury, in its various forms, can cycle between the atmosphere, water bodies and sediments. It can be carried over long distances from its source, mainly via air and/or water.

Figure 1 Mercury cycle in the biosphere

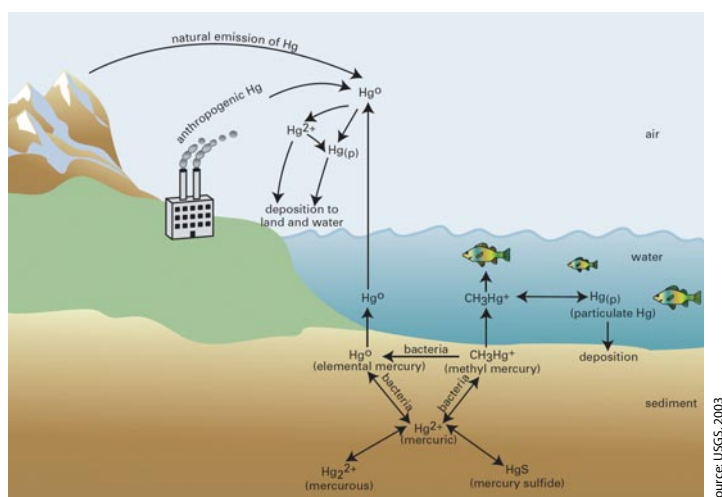
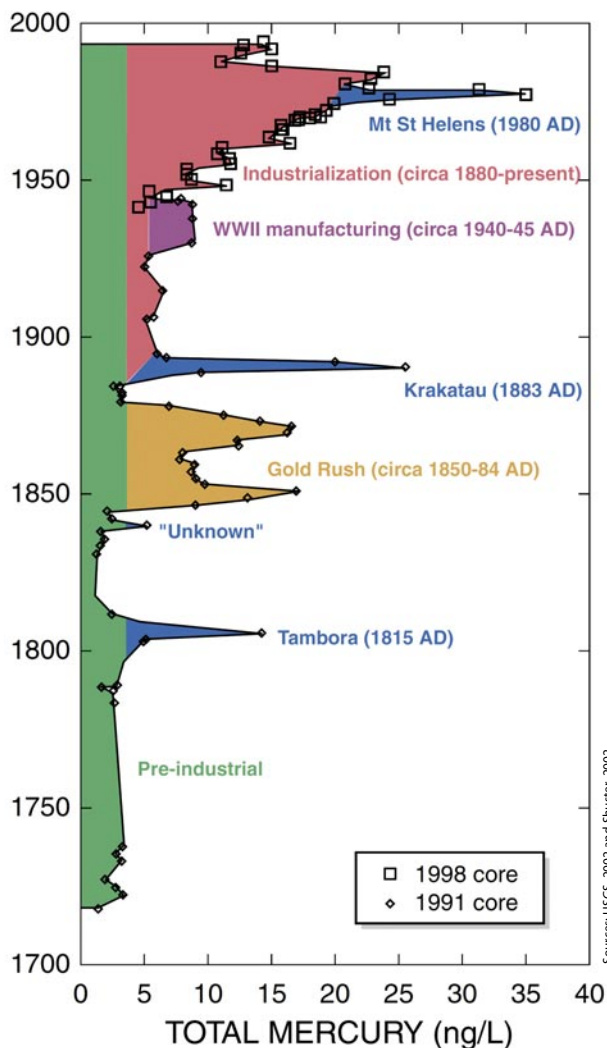


Figure 2 Mercury data from glacier samples



The variation of mercury in the biosphere over time has been discussed in multiple literature studies. One specific study is highlighted here in Figure 2, from the U.S. Geological Survey (USGS). This graph illustrates the variation in mercury concentrations within a glacier in the western USA, which is indicative of the variation of mercury in the local atmosphere.

In Figure 2, time is shown on the y-axis, while mercury levels within the glacier core are expressed on the x-axis. The units of measure are nanograms per litre, which is equivalent to parts per trillion by weight for a liquid with a specific gravity of 1.

As illustrated, mercury levels in the biosphere undergo significant changes from year to year. For example, there are three spikes due to volcanic activity, which are shown in blue. There were two distant Indonesian eruptions in the 1800s (Tambora and Krakatau) plus a smaller eruption in 1980 (Mt. St. Helens). This illustrates the important point that volcanic activity is a key source of mercury in the biosphere.

Also of interest is the period highlighted in the gold colour, which represents the gold rush in the western USA. Mercury was widely used during the gold rush because of its ability to react with trace quantities of gold, and to release the gold when heated. The USGS has cited estimates that more than 10,000,000 pounds of mercury were released to the environment in California during the gold rush (USGS, 2005). Artisanal gold mining in some countries has been unregulated and is a major focus of the UN mercury treaty signed in October 2013.

The red portion in Figure 2 is attributed to general releases of mercury due to industrialization. The impact of industrialization is a key driver behind the current focus on human activities related to mercury.

The growth of industrialization since the 1900s is a key driver behind the current focus on anthropogenic mercury emissions.

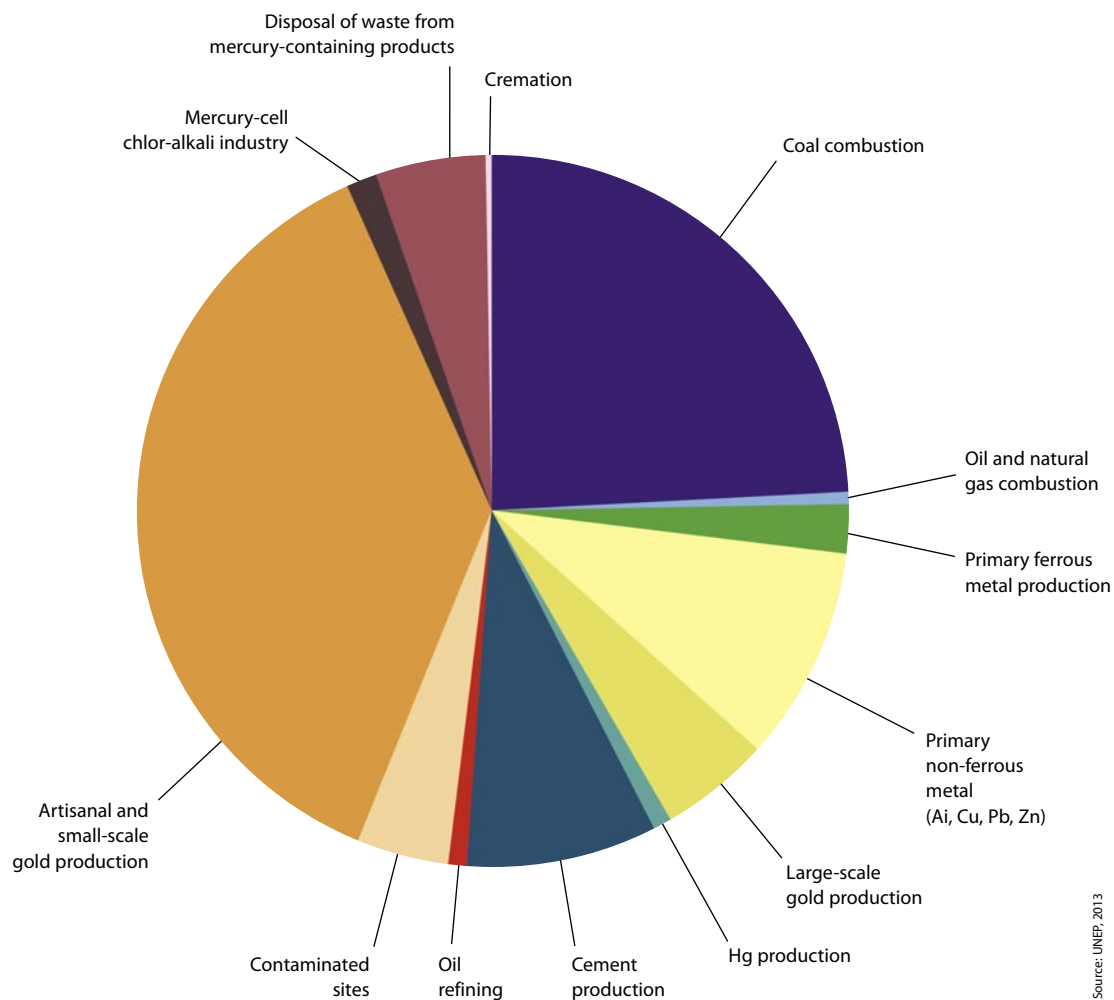


The United Nations Environmental Programme (UNEP) recently updated its estimates of contributions from human activities to annual global emissions to air (see Figure 3). The figure shows that artisanal and small-scale gold mining represents the largest contributor to mercury emissions. The burning of coal represents the second largest contributor.

UNEP’s estimates include two emissions related to oil and gas: direct combustion of oil and natural gas, and oil refining. Each represents less than 1% of total anthropogenic emissions.



Figure 3 Relative contributions to estimated emissions to air from anthropogenic sources in 2010



UNEP’s estimates of emissions to air from human activities show that artisanal and small-scale gold mining is the largest single contributor to mercury emissions, while oil and gas industry emissions from refining and the combustion of oil and natural gas constitute less than 1% of total anthropogenic emissions.

Source: UNEP, 2013

Forms of mercury

Mercury occurs naturally in soil and rock throughout the earth's crust, including the formations that comprise oil and gas reservoirs. Mercury occurs at varying concentrations, and in various forms. A brief review of the forms of mercury, as well as the reactions of each form, is given below. These reactions are important because of the potential for mercury to change forms during the refining process.

Elemental mercury (Hg⁰)

Elemental mercury is the shiny silver-coloured liquid that most people think of when they hear the word 'mercury' (Figure 4). However, it is not the most common form of mercury, and is unstable in the presence of sulphur and some sulphur compounds. When exposed to these compounds, elemental mercury will form mercury sulphide.

Elemental mercury has some properties that are unusual for a heavy metal. For example, it is liquid at room temperature. Another unusual property of elemental mercury is its vapour pressure: unlike most heavy metals, mercury has a measurable vapour pressure at room temperature (Table 1).

Table 1 Vapour pressure of elemental mercury

Temperature		Vapour pressure	
°C	°F	Pa	psi
0°	32°	0.027	0.00004
20°	68°	0.17	0.0002
40°	104°	0.86	0.001
60°	140°	3.5	0.005

Source: U.S. NIST (Huber, 2006)

Although mercury's vapour pressure is high relative to other heavy metals, it is actually lower than most liquids. For example, elemental mercury has a much lower vapour pressure than liquid water; laboratory studies have shown that droplets of mercury do not evaporate quickly into air (Winter, 2003). This is an important factor when responding to mercury spills. In general, droplets should be left undisturbed until they can be dealt with by appropriately trained personnel using appropriate procedures and equipment.

Elemental mercury exhibits different behaviour when it is mixed with hydrocarbons. This is discussed later.

Mercury sulphide (HgS)

Mercury sulphide is the predominant form of mercury in nature. This is due to the strong affinity of mercury and sulphur.

At room temperature, mercury sulphide is a solid. It has very low solubility in either water or hydrocarbon. The solubility has been estimated to be less than one part per quadrillion. The affinity of mercury for sulphur is so high, and the solubility of mercury sulphide in water is so low, that samples of pure mercury sulphide created by simple mixing of mercury with sulphur have passed EPA leachability tests (Lopez, 2010). This strong affinity may be important in determining mercury's behaviour in the sulphur-rich environment that exists within many refinery processes.

Figure 4 A droplet of elemental mercury



Source: UNEP, 2002

However, when heated with a torch, such as during hot work¹, mercury sulphide will begin to decompose, liberating elemental mercury.

Mercury sulphide has lower toxicity than most other forms of mercury. Due to its low solubility in water, exposures are very low. In fact mercury sulphide was often used to make jewellery and ornamental plates.

As described later in this report, mercury sulphide may be the predominant form of mercury leaving most refineries.

Mercury sulphate (HgSO₄)

Mercury sulphate is considered to be an important part of the mercury cycle in the biosphere. In open water bodies such as lakes and rivers, sulphate-reducing bacteria may play a role in the creation of organic mercury species.

However, the chemistry of refining does not typically involve the oxidation conditions that would lead to sulphate formation. For example, many key processes within refineries are carried out in the presence of hydrogen, and convert sulphur-containing molecules to sulphides. Sulphates are not stable in these refinery processes. There are no available data to indicate that mercury sulphates exist in refineries. Sulphates are not discussed further in this report.

Mercury mercaptides (RS–Hg–SR)

Mercury mercaptides are formed when mercaptans² (thiols) react with mercury. The most commonly cited way to make mercury mercaptides is the reaction of ionic mercury (Hg²⁺) with light mercaptans. For example, a

1961 paper discusses an analytical method for determining mercaptan concentrations by titrating with an aqueous solution containing Hg²⁺ (Fritz and Palmer, 1961).

The prevalence of mercaptans, plus the relative instability of mercury mercaptides, may influence the behaviour of mercury within a refinery. However, mercury mercaptides are much less stable than mercury sulphide. When the mercaptides decompose, the end products may be elemental mercury and disulphides. Mercury mercaptides may be too unstable to be present in refinery products or waste streams.

Organic mercury (R–Hg–R or R–Hg–X)³

Light organic mercury species, such as dimethyl mercury, are liquids that are somewhat soluble in both water and oil. In the environment, methyl mercury appears to be the most common form, as dimethyl mercury is relatively unstable. Methyl mercury is an ion, soluble in water.

Light organic mercury species are believed to be among the most toxic forms of mercury. Literature papers suggest that the toxicity of these forms of mercury is due to their ability to dissolve in, and ultimately pass through, cell membranes and tissue.

Species such as methyl mercury and dimethyl mercury are the result of organic processes, such as those that exist within the tissue of algae and fish. The tendency of biological processes to methylate mercury is one key reason why regulators want to limit total mercury in the biosphere. There are limits on the organic mercury concentrations in fish and seafood intended for human consumption. These limits

¹ Hot work is any activity that creates heat, flame, sparks or smoke.

² Mercaptan: from the Latin mercurium captans, meaning 'seize mercury' (CDC.gov)

³ X is indicative of non-organic matter, e.g. Cl⁻ (chloride) and R indicative of organic matter, e.g. CH₃.

are typically on the order of 0.5 to 1 part per million (500 to 1000 ppb).

IPIECA members have never observed light organic mercury species being a product of refining processes. In fact, the nature of refinery processes would tend to destroy, rather than create, light organic mercury species. However, good waste management practices are directed towards avoiding biologic conversion in the environment.

Mercury chloride (Cl–Hg–Cl)

Mercury can also exist in the form of mercury chloride, HgCl_2 . Pure mercury chloride is a white crystalline material.

Mercury chloride and mercury sulphide are both examples of inorganic mercury. Some literature studies lump them together under the label of inorganic mercury, but this may overlook the substantial differences between the properties of the chloride vs. the sulphide.

Mercury chloride is quite soluble in water (more than 1% by weight), and can form a number of species depending on the other ions present. It is also somewhat soluble in hydrocarbon, and somewhat volatile.

Analytical methods and challenges

As described in the previous section, mercury can exist in several forms, such as elemental mercury or mercury sulphide.

Analytical techniques for detecting mercury have improved in recent years, but it is important to note that the most common analytical tests report the total concentration of mercury, not the concentration of individual species. This is particularly true for the trace mercury concentrations that exist within the hydrocarbon streams in a refinery.

It is not clear how much mercury chloride could persist within a refinery. Mercury chloride is very reactive with sulphur, including mercaptans and H_2S , which are common components in many intermediate refinery streams.

The instability of mercury chloride was demonstrated, for example, by a hygienist in Quebec (Pare, 1966). IPIECA is not aware of any data showing that mercury chloride is common in refineries.

Summary of mercury types

This section has presented a brief summary of some of the types of mercury that may exist in nature or within a refinery. The discussion included brief mention of some of the chemical reactions that can cause mercury types to interchange.

The two species of mercury that are believed to be prevalent in refineries are elemental mercury and mercury sulphide.

This will serve as background for the good practices discussed later.

For example, one common test method can be described as a four-step process: (1) converting all forms of mercury to elemental mercury; (2) capturing the elemental mercury via a reaction with a gold film; (3) releasing the mercury from the gold film via heating; and (4) measuring the total mercury that is emitted. This method is useful but does not provide information about which species of mercury may have existed in the original sample. This is one of the drivers behind ongoing research on improved analytical methods.

Mercury concentrations in crude oils and condensates

In 2009, UNEP’s Governing Council agreed to begin negotiations on a legally binding instrument on mercury. The Council asked its Executive Director to convene an intergovernmental negotiating committee (INC) with the mandate to prepare that instrument. The INC process included five sessions (INC 1 through INC 5) over the time period from June 2010 to January 2013.

At the INC 2 session in January, 2011, the INC requested that the UNEP Secretariat prepare a document on the releases of mercury from the oil and gas sector. After preparing a draft report, the UNEP Secretariat invited IPIECA and others to comment. IPIECA provided comments and data to the UNEP Secretariat, and IPIECA representatives were invited to present comments and data at the Technical Briefing Session of the INC 3 meeting in Nairobi, Kenya, in October 2011.

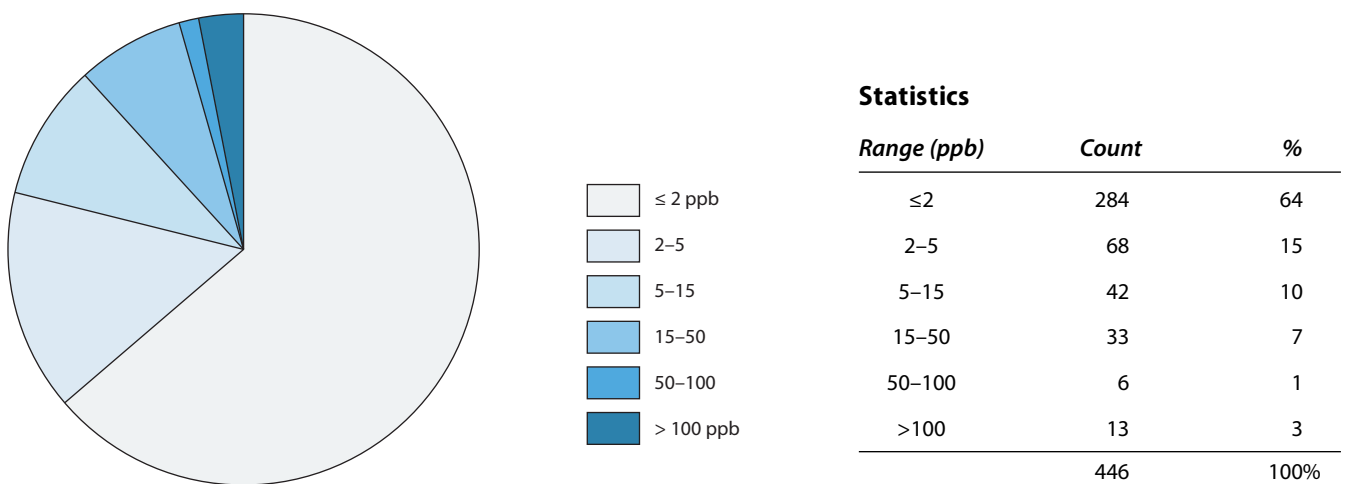
In support of the INC process, IPIECA requested that its members provide data on the mercury

levels in crude oil. The purpose in assembling this data was to document the amount of mercury in crudes, and to help resolve uncertainties around the mercury levels in crude oils and condensates.

The IPIECA data set, which included a total of 446 crude oils and condensates, is summarized below. For each crude oil, the mercury measurement in the IPIECA database is the best assessment of the typical mercury content, according to the IPIECA member who provided the value for that crude. The majority of the IPIECA data were generated during the 2007–2011 timeframe. The analytical methods used in generating the data were deemed comparable to an older UOP⁴ method, UOP 938-00 (UOP, 2000), or a newer ASTM⁵ standard method, D7623-10 (ASTM, 2010).

More details about the data can be found on the IPIECA website and in Doll *et al.*, 2012. The overall distribution of mercury in crude oil from the IPIECA data set is summarized in Figure 5.

Figure 5 Range of mercury levels in global crude grades (summarized from the IPIECA dataset, which includes 446 crude assays)



⁴ Formerly known as Universal Oil Products Ilp, UOP is a leading international supplier and licensor for the oil and gas industry.

⁵ ASTM International (formerly known as the American Society for Testing and Materials) is a globally recognized leader in the development and delivery of international voluntary consensus standards.

This chart and the corresponding statistics have not been adjusted for the production volumes of the various crudes. For example, many of the crudes that are below 2 ppb of mercury are high-volume crudes from large fields in the Middle East, while some of the crudes above 100 ppb are from small fields in other parts of the world. Considering the production volumes, IPIECA data suggests that the 13 crudes that contain more than 100 ppb of mercury make up less than 1% of the global volume of crude oil production.

There are regional differences in the range of mercury concentrations within the IPIECA data set, as illustrated in Table 2.

The Middle East shows the lowest mercury levels, with 79% of crudes from this region showing less than or equal to 2 ppb of mercury. No Middle East crude in this dataset is above 15 ppb of mercury.

Countries in the Pacific and Indian Ocean region represent the highest mercury levels, with 30% above 15 ppb, and 8% above 100 ppb.

In order to estimate the global average mercury concentration in crude, IPIECA has updated a calculation that was first done by Mark Wilhelm and co-authors (Wilhelm *et. al.*, 2007).

The study by Wilhelm estimated the total mercury in crude oil refined within the United States. This was done by first calculating the simple arithmetic mean mercury level of known crudes from individual countries. This was multiplied by the volume of crude imported into the USA from that country. The sum of these values was calculated, and divided by the total estimated refinery input.

For example, the numeric average mercury level in crudes coming from Saudi Arabia was estimated by Wilhelm to be 0.9 parts per billion, and the volume of crudes imported to the USA from Saudi Arabia was estimated to be 547,000,000 barrels in 2004. Wilhelm did this calculation for each country, but limited his scope to the crudes and crude volumes imported into the USA. Using this methodology, Wilhelm estimated that crude oils refined in the USA had a mean mercury concentration of 3.5 wt ppb.

IPIECA has extended Wilhelm's methodology in order to calculate a global estimate. This involved using the more extensive IPIECA data set for mercury concentrations in crude oil (Doll *et al.*, 2012), and the total production of crude oil by country (as assembled by the Petroleum Association of Japan) as opposed to Wilhelm's focus on only the crude imported into the United States.

Table 2 Regional breakdown of mercury in crude

Crude region	Count	Median Hg level (ppb)	Percentage of crudes and condensates containing specific ranges of mercury (ppb of mercury)					
			≤2 ppb	2–5 ppb	5–15 ppb	15–50 ppb	50–100 ppb	>100 ppb
Africa	90	1.0	72%	15%	9%	3%	1%	-
Eurasia	95	1.2	74%	10%	6%	4%	1%	5%
Middle East	34	1.0	79%	18%	3%	-	-	-
North America	95	1.2	64%	21%	9%	6%	-	-
Pacific and Indian Ocean	93	3.0	41%	13%	16%	18%	4%	8%
South America	39	1.4	69%	12%	8%	8%	-	3%

The IPIECA calculation was:

$$GWA = \sum_{Countries} Mass^C \overline{Hg}^C$$

where *GWA* is the global weighted average mercury concentration, *Mass^C* is the mass of crude produced by an individual country 'C', and *Hg^C* is the simple arithmetic mean of the mercury concentration in crudes produced in a given country.

According to this methodology, the weighted average mercury content of the global crude supply is 7.5 wt ppb. This is higher than the 3.5 ppb value estimated by Wilhelm *et al.* for crudes processed in the USA. The difference is largely driven by the fact that refineries in the United States process large quantities of crudes from the USA, Canada, Mexico and the Middle East, where average mercury levels are low. The global refining industry processes additional crudes that are higher in mercury content.

The IPIECA estimate for global crudes, 7.5 wt ppb, is much lower than the 55 ppb originally estimated by UNEP as part of their 2011 'Mercury Toolkit' methodology.

It is important to note that, in the above analysis, both crude oil and 'condensate' are included. The 'condensate' label is used here in the same way that it is used in the commercial crude oil market. Different crude suppliers may have different criteria for labeling their product as a



'condensate' as opposed to calling it a 'crude'. In some cases materials called 'condensates' may not fit the typical engineering definition of the word, which involves something that has condensed from the vapour phase to form a liquid. Because of the inconsistent use of the word 'condensate', caution must be used in assuming that 'condensates' share any particular trait, such as containing specific levels of mercury.

In the IPIECA data set, self-identified 'condensates' show only slightly elevated levels of mercury compared to non-'condensates'. For example, 52% of the 'condensates' are above 2 ppb of mercury, compared to 35% of the non-'condensates'. However, even for 'condensates', the majority are below 5 ppb of mercury (Table 3).

Table 3 Mercury in 'condensate' vs. non-'condensates'

	Count	Median Hg level (ppb)	Percentage of crudes and condensates containing specific ranges of mercury (ppb of mercury)					
			≤2 ppb	2–5 ppb	5–15 ppb	15–50 ppb	50–100 ppb	>100 ppb
'Condensates'	51	2.4	48%	14%	14%	12%	8%	4%
Non-'condensates'	395	1.3	65%	15%	9%	7%	1%	3%

Mercury fate in refining

A number of studies have been published which examine the fate of mercury once it enters a refinery. One example is the Western States Petroleum Association (WSPA) study of mercury in five refineries in the San Francisco, USA region (WSPA, 2009).

In the WSPA study, multiple samples of the feed to each of seven refinery crude units were analysed. The mercury levels in the feeds were found to range from 1.5 ppb to 19 ppb. The study attempted to determine the mercury mass balances at the five San Francisco refineries. The results are shown in Figure 6 which indicates that the majority of the mercury left the refineries in waste streams. Small amounts of mercury were found in refined products or were emitted to the air, and smaller amounts were found in petroleum coke and waste water.

The WSPA study relied in part on literature data. Several literature studies are available, including:

- 'Ft. McHenry Tunnel Study: Source profiles and mercury emissions from diesel and gasoline powered vehicles' (Landis, 2007);
- 'Estimate of mercury emission from gasoline and diesel fuel consumption, San Francisco Bay area, California' (Conaway, 2005); and
- 'Mercury emissions from automobiles using gasoline, diesel, and LPG' (Won, 2007).

The studies agree that only trace levels of mercury, typically less than 1 ppb, are found in gasoline and diesel fuel.

While the WSPA study is useful, it might not apply to all refineries, and further study may be justified. Any future study should consider not only the amount of mercury entering a refinery, but also the amount of sulphur.

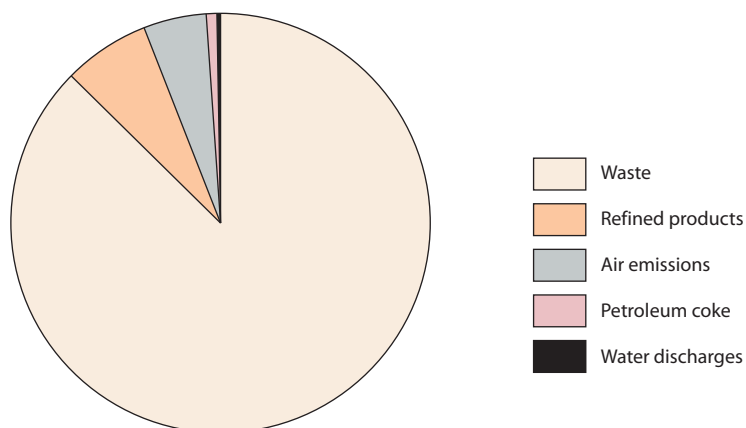
Some refineries process crudes that contain very little sulphur. As already described, several forms of sulphur have a strong affinity for mercury. Low-sulphur refineries may have a tendency to accumulate deposits of elemental mercury. On the other hand, refineries that process high-sulphur crudes may have a tendency to accumulate mercury sulphide, which has low volatility and solubility.

Some refineries process crudes which contain higher levels of mercury (for example 50 wt ppb or more). IPIECA members have noted that such refineries may see increased levels of elemental mercury, as opposed to mercury sulphide. When mixed with hydrocarbons, elemental mercury behaves very differently from how it does in air. In particular, elemental mercury tends to show an apparent vapour pressure similar to that of light hydrocarbons such as propane and butane. Hence, crudes that are high in elemental mercury may cause elevated levels of mercury in the overheads of crude distillation units, and in light streams such as LPG.

Mercury's behaviour is affected when refineries run mixtures of crudes and at least some of the crudes are high in sulphur (for example, >1 wt % sulphur). This sulphur has at times caused mercury to appear in streams such as atmospheric residuum, as well as the light ends.

In these cases, secondary conversion units like cokers or other resid crackers might re-convert the mercury to more volatile species. Such volatile species would again tend to migrate

Figure 6 Example of a mercury mass balance for five refineries in the San Francisco region



Source: WSPA, 2009

2. Performing additional, periodic measurements on crudes known to contain mercury, or that are relevant for confirming that the refinery is within its operating envelope. These measurements might be done on a scheduled basis, such as multiple times per year.
3. Performing frequent measurements on any crude known to contain an elevated level of mercury, for example if the crude is known to contain more than 100 ppb of mercury. (IPIECA member experience shows that such crudes can show significant variation from cargo to cargo.)

The specific method used by a refinery must be fit for purpose, and should be based on that refinery’s specific circumstances.

Potential accumulation of mercury in process equipment

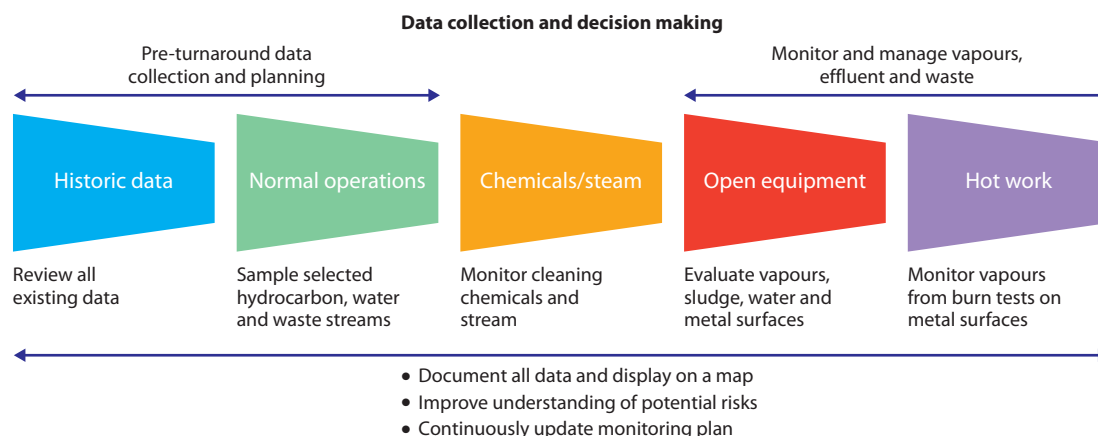
It is important to note that mercury can accumulate in refining equipment even when good operating practices and feed stock controls are implemented. Table 4, illustrates the potential accumulation of liquid mercury in a ‘small’ or ‘large’ refinery. Figure 8 is an example of the logic that could be used to monitor and mitigate the potential for accumulation.

Table 4 Comparison of annual mercury accumulation for range of concentrations in a ‘small’ and ‘large’ refinery⁶

Mercury in crude, µg/kg (ppb)	Potential annual accumulation		
	1 µg/kg	10 µg/kg	200 µg/kg
50,000 bbls/day — ‘small’ refinery	0.5 kg/year	5 kg/year	90 kg/year
250,000 bbls/day — ‘large’ refinery	2.5 kg/year	25 kg/year	450 kg/year

⁶ Total accumulations may be higher assuming the average time between turnarounds is between 3–4 years. Typical crudes are 1–10 µg/kg mercury; API gravity assumed was 32°. Crudes with elevated mercury tend to be lighter; API gravity assumed was 45°. Accumulation estimate is based on the assumption that 20% of the mercury in the incoming crude accumulates in the process equipment or associated wastes. In addition, plants need to consider that units have been in place for many years, and may have pre-existing accumulation of mercury, including equipment downstream of MRUs.

Figure 8 Logic for selecting focus areas during turnarounds



Worker health and safety

Potential health effects on humans

The different forms of mercury are toxic, to varying extents. Exposure to humans can happen via inhalation, via contact with skin and eyes, or via ingestion. Depending on the duration of the exposure, different toxic effects are distinguished, ranging from acute to chronic. The toxic effects have been described in detail by the World Health Organization (WHO, 2007), among others.

High short-term exposures to metallic mercury may cause lung damage, nausea, vomiting, diarrhoea, increases in blood pressure or heart rate, skin rashes and eye irritation. While frequent repeated exposures to low concentrations mostly target the nervous system affecting the brain, this type of exposure may also affect the kidneys and developing fetus. In

general, it should be noted that mercury's half-life in adults is long, i.e. months, thus even low exposures repeated monthly could result in the accumulation of mercury in the body at potentially toxic levels.

Examples of occupational exposure limits for mercury

Due to the toxic effect of mercury, some countries and authoritative bodies have established occupational exposure limit values. These values vary by country and agency, as illustrated by the examples in Table 5. Companies generally adopt appropriate standards for their medical surveillance programmes. Additionally, companies comply with national, regional or local regulatory requirements, whichever is more stringent.

Table 5 Examples of occupational exposure limits for mercury

UK WEL (Workplace Exposure Limits)	DFG MAK (German Research Foundation)	The Netherlands	US ACGIH (American Conference of Governmental Industrial Hygienists)	US OSHA (Occupational Safety and Health Administration)
Elemental and inorganic mercury 0.02 mg/m ³ (8 hours)	Elemental and inorganic mercury 0.02 mg/m ³ (8 hours)	Elemental and inorganic mercury 0.02 mg/m ³ (8 hours)	Elemental and inorganic mercury 0.025 mg/m ³ (8 hours)	Elemental and inorganic mercury 0.1 mg/m ³ (8 hours)
		Alkyl mercury 1.1 mg/m ³ (8 hours) 1.2 mg/m ³ (15 minutes)	Alkyl mercury 0.01 mg/m ³ (8 hours) 0.03 mg/m ³ (15 minutes)	Alkyl mercury 0.01 mg/m ³ (8 hours) 0.04 mg/m ³ (Ceiling)
		Methyl mercury 0.01 mg/m ³ (8 hours) 0.1 mg/m ³ (15 minutes)	Aryl Mercury 0.1 mg/m ³ (8 hours)	Aryl Mercury 0.1 mg/m ³ (8 hours)
		Organic mercury forms 0.01 mg/m ³ (8 hours) 0.03 mg/m ³ (15 minutes)		

Potential exposure routes in refineries

The most probable exposure risk for refinery workers will be via inhalation of elemental mercury vapour. Because of the low vapour pressure of mercury compounds, airborne exposures will most likely be highest during confined space entry or when the contaminated equipment is heated, for example during welding.

Moreover, workers could have skin contact with elemental mercury and mercury salts during opening or entry of equipment or handling contaminated parts. Potentially, workers in mercury adsorption process units could have an elevated risk of skin exposures during adsorber change-out, draining equipment in preparation for opening, draining low points in vessels or piping, and other tasks involving opening. In all cases, it is unlikely that workers will absorb toxicologically significant quantities of mercury salts via intact skin as these workers should be wearing suitable personal protective equipment (PPE—see below under *Exposure control measures*) to prevent not only contact with mercury but also with other substances such as hydrocarbons, caustics or acids.

As activities that involve potential exposure to mercury are typically related to process unit shutdowns and openings, the ordinary worker exposures are typically infrequent. Most refinery operators and craftworkers working in non-mercury units will have infrequent, i.e. annual, exposures associated with unit shutdown and maintenance. It is therefore unlikely that non-mercury unit workers would suffer the diseases associated with chronic, low-concentration exposures. Nevertheless, it is prudent to ensure that workers in plants with mercury in the process fluids are not exposed to chronic (or acute) concentrations, by providing medical surveillance examinations (see page 18).

IPIECA member experience shows a number of areas where mercury might be detected within a refinery. Examples include:

- desalter sludge/desalter tank bottoms;
- crude units, crude distiller, crude unit gas stabilizer, crude unit overhead gas splitters, crude oil tank bottoms;
- bundle cleaning sludge;
- petroleum coke burning, petroleum coke;
- waste polymerization catalyst;
- waste adsorbent;
- heavier residue fractions associated with asphaltenes and mercuric sulphides;
- lighter product streams such as gases, LPG or naphtha;
- amine and sulphur systems;
- filters;
- waste water treatment plant sludges and sediments; and
- decommissioned process equipment and pipelines.

In addition to these specific areas where mercury might be found, there are also specific activities that could liberate mercury. Some examples of refinery activities that can create mercury vapours are provided in a paper published by the National Petrochemical & Refiners Association (Grice and Alvarez, 2011). One specific example, related to hot work, is shown in Box 1.

There can also be other sources of mercury within a refinery, where the mercury does not originate in the feedstock. Examples include:

- instrumentation containing mercury, including flow meters and barometers;
- fluorescent lamps and high-intensity discharge lamps;
- electrical devices, including switches, relays, batteries and thermostats; and
- medical devices, including thermometers and blood pressure gauges.

Box 1 *Example of specific activities that can generate mercury vapours*

Hot work, grinding and blasting on mercury impacted metals requires special attention:

- Initial surface reading with vapour monitor may be zero—but once heated, the vapour level may exceed $>50 \mu\text{g}/\text{m}^3$.
- Adjacent impacted metals may be the exposure source on a larger piece of equipment.
- Engineering controls such as a simple fan can help to control open air exposures—other techniques such as local exhaust ventilation, underwater welding, wet grinding/blasting and wet cutting may offer other control options.
- Air emissions may be a factor on downwind work areas.

Source: Grice and Alvarez, 2011



Exposure control measures

As shown in Table 5 (page 15), various occupational exposure limits exist which are designed to protect workers from exposure to mercury. Mercury hazard control programmes typically apply a hierarchy of controls to prevent, reduce and maintain mercury and other contaminant exposure at or below the applicable exposure limit. Examples include:

- **Acceptance criteria for crude oil intake:** refineries can apply acceptance criteria for the crude oil to limit the intake of mercury into their processes and subsequently reduce potential exposure of their workers to mercury.
- **Design and engineering controls:** for example preventing bends in equipment and avoiding temperature drops; implementing flushing facilities for cleaning the internal components of installations; utilizing exhaust systems or ventilation to capture or disperse mercury vapour.
- **Procedural control:** identification of suspected locations of mercury; designating safe work areas; application of the permit-to-work (PTW) system; flushing; monitoring and

sampling to detect mercury and measure its concentration; employee training and hazard communication; shift work.

- **Worker protection:** if the above measures are considered insufficient, PPE and medical surveillance examinations can be provided to maintain exposures below the exposure limit and to monitor potential actual exposures, respectively.
- **Decontamination** of equipment in case of exposure.

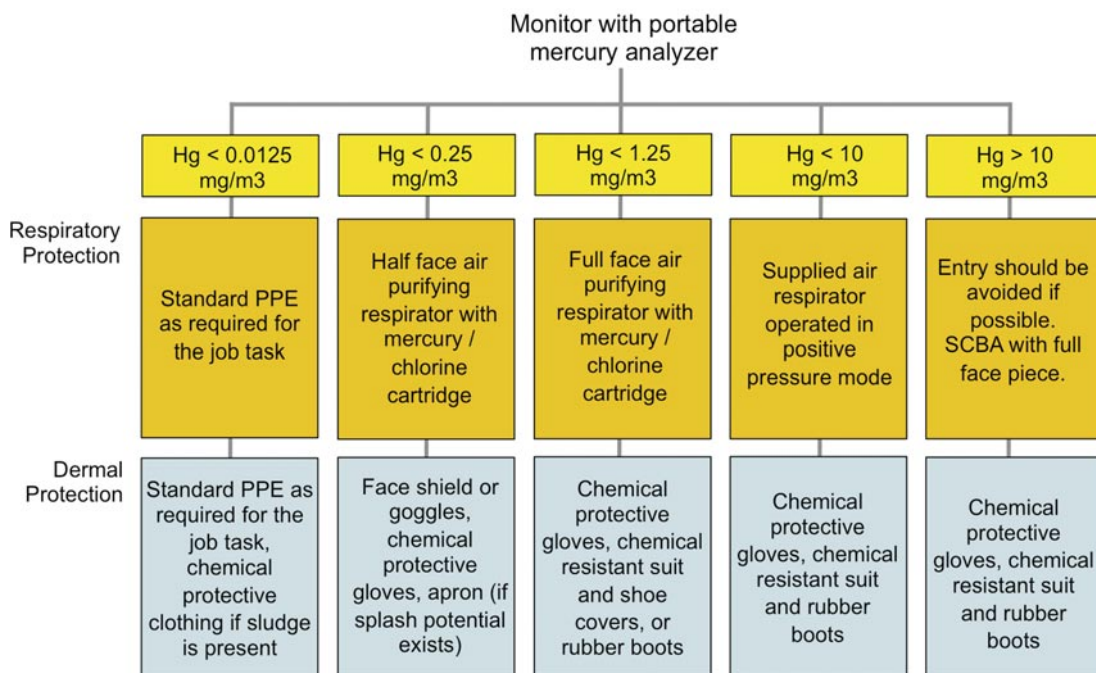
A general approach is described below, together with more information on some of the available control measures.

Personal protective equipment

The potential for mercury exposure, and the varying exposure limits, result in the need for a tiered approach to the use of PPE. An example is shown in Figure 9 (overleaf). This example was developed by the Oil Companies International Marine Forum (OCIMF) and applies to the shipboard handling of crude oil; however, it can

This action-level matrix for PPE was developed by OCIMF for the shipboard handling of crude oil, but can also be used as a guide for protection against mercury exposure in refineries.

Figure 9 Example of an action-level matrix for PPE



Source: OCIMF, 2011

also be used as a guide for protection against mercury exposure in refineries.

The OCIMF matrix involves, as a first step, the monitoring of mercury levels using a direct reading instrument. OCIMF provides examples of such devices, which include the 'EMP 1-A Mercury Gas Monitor' (Nippon Instruments Corporation) and the 'Jerome® J405 Mercury Vapor Analyzer' (Arizona Instrument LLC). Other analysers may also be suitable.

OCIMF's recommendations for PPE depend on the readings obtained from the analyser, and state the following:

'Personal protective equipment:

The following respiratory protection and Personal Protective Equipment (PPE) action levels are provided as an example of how risks of workforce exposure may be controlled when work is being undertaken in close proximity to

mercury vapour or when handling mercury-containing materials. It is recommended that companies develop their own procedures to protect personnel against exposure.'

Medical surveillance examinations

Medical surveillance examinations may cover the following aspects:

- **Programme participation:** pre-placement, periodic, and end-of-duty examinations.
- **Biological monitoring considerations:** urine and/or blood sampling, timing, exposure history information, diet history, frequency of testing, entrance and exit criteria.
- **Medical removal provisions:** handling of background/dietary mercury, handling hourly/daily variation in results, repeat/follow-up testing, including physical examination including signs/symptoms information.
- **Emergency exposure provisions.**

Personnel contaminated with mercury metal or other mercury compounds should seek medical attention. Medical personnel might recommend steps such as washing the eyes (if they were affected), removing contaminated clothing (if clothing was affected), and appropriate testing to quantify the exposure (blood tests, urine tests, etc.).

General approach to the health impacts of mercury

A general approach to dealing with the potential impacts of mercury is given in the report entitled, *Guidelines on Mercury Management in the Oil and Gas Industry*, published in 2011 by the Department of Occupational Safety and Health (DOSH), Ministry of Human Resources, Malaysia.

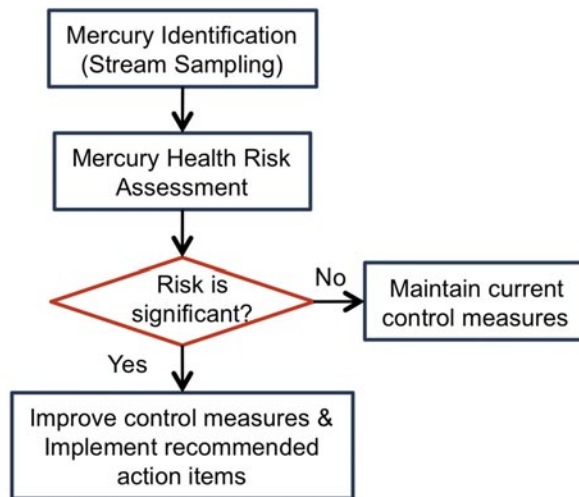
The DOSH approach begins with a high-level risk assessment, as shown in Figure 10.

The risk assessments for mercury should consider the locations where mercury might be detected in a refinery. Once the risks have been identified, and PPE strategies have been established, a health monitoring programme may also be put into place. The DOSH recommendations for a risk-based monitoring approach is illustrated in Figure 11.

Exposure monitoring and sampling

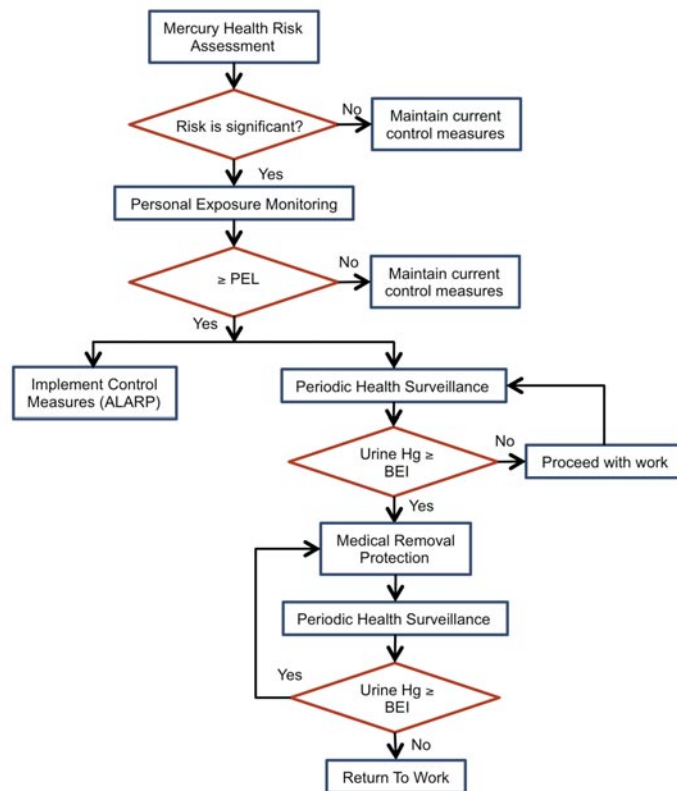
Instantaneous elemental mercury readings in $\mu\text{g}/\text{m}^3$ concentrations may be measured with instruments such as the Lumex RA-915+, NICEMP 1A or Jerome® 431. Other analysers may also be suitable. Time-weighted average personnel exposures may be collected using adsorbent tubes, diffusion badges or filters (inorganic mercury) followed by laboratory

Figure 10 Example of a risk-based approach to dealing with mercury



Source: DOSH, 2011

Figure 11 Example of a risk-based monitoring approach ⁷



Source: DOSH, 2011

⁷ Acronyms are defined as follows: PEL = Permissible Exposure Limit; BEI = Biological Exposure Indices (the 'BEI' acronym is copyright ACGIH®); ALARP = As Low As Reasonably Practicable.

analysis methods. Surface wipe sampling can be done to assess contamination.

Precautions for identifying and testing for potential contamination typically include sampling at selected locations such as gas compressors, the distillation column and overhead coolers/exchangers.

Hazard communication and worker training

Any workers who might potentially be exposed to mercury should receive appropriate instructions and training. This should be part of their workplace hazard training, and should be structured to enable them to prevent workplace exposure and to respond appropriately to circumstances within the specific refinery.

Examples of topics that might be covered during training sessions include:

- Material Safety Data Sheets (MSDS) for mercury or mercury-containing materials, to provide an understanding of the physical properties of mercury and the potential health effects, such as the symptoms of mercury exposure;
- exposure guidelines/limits;
- locations where exposure to mercury may occur in the workplace;
- how to identify mercury contamination;
- origin and consequence of mercury in plant feeds;
- measures used to control and/or monitor potential mercury exposures;
- description of mercury vapour monitoring techniques;
- signs used to identify areas where there is a potential for exposure to mercury or its associated compounds, and the appropriate use of warning labels;
- proper PPE selection and use;
- basic chemistry of mercury;

- proper personal hygiene procedures (e.g. proper hand washing/decontamination before eating, etc.);
- special precautions to minimize exposure, techniques for spill prevention, proper procedures for spill clean-up; and
- toxicity of mercury exposures.

Safe work practices

During refinery maintenance activities and other operations, situations may arise where the presence of mercury is anticipated, or is indicated by measurement or visual inspection. During such events, specific areas should be designated for the application of dedicated controls. A designated area might be as small as the walkway near a specific manway, and placed under appropriate controls until such time that direct measurements show the manway to be free of mercury vapours. At the other extreme, the designated area might be large, for example before opening a low point drain that is suspected to contain elemental mercury.

It is advisable to be prepared with written procedures, training and appropriate equipment, including procedures and capabilities to:

- restrict and control access to a designated area;
- implement spill prevention and containment procedures;
- provide awareness training to personnel;
- assure the availability of appropriate instruments, tools and protective equipment;
- implement decontamination procedures for personnel and tools to prevent migration of mercury out of the designated area; and
- implement spill clean-up procedures, if needed.

Process safety

In addition to personnel safety, there are also process safety aspects related to mercury.

A phenomenon known as liquid metal embrittlement (LME) can occur when some equipment is exposed to liquid elemental mercury. Equipment made of aluminium is especially susceptible to LME.

LME has been the cause of multiple equipment failures within the oil and gas industry. One example took place at the Moomba gas plant in Australia, where a piece of cryogenic aluminium equipment was unknowingly exposed to liquid mercury, leading to a metallurgical failure; a significant rupture occurred (Figure 12) which led to a loss of containment resulting in a fire.

The following are examples of questions to be considered when dealing with potential equipment issues:

- How much mercury is (or was) present in the feed to the plant?
- What is (or was) the concentration of mercury in the streams entering the aluminium equipment?
- Is there an upstream dehydration system and does it perform to specification?
- Is there an upstream MRU and does it perform to specification?
- Is the pressure drop across the equipment constant or increasing?
- Can mercury condense to a liquid or solid phase due to cooling, for example in a heat exchanger?

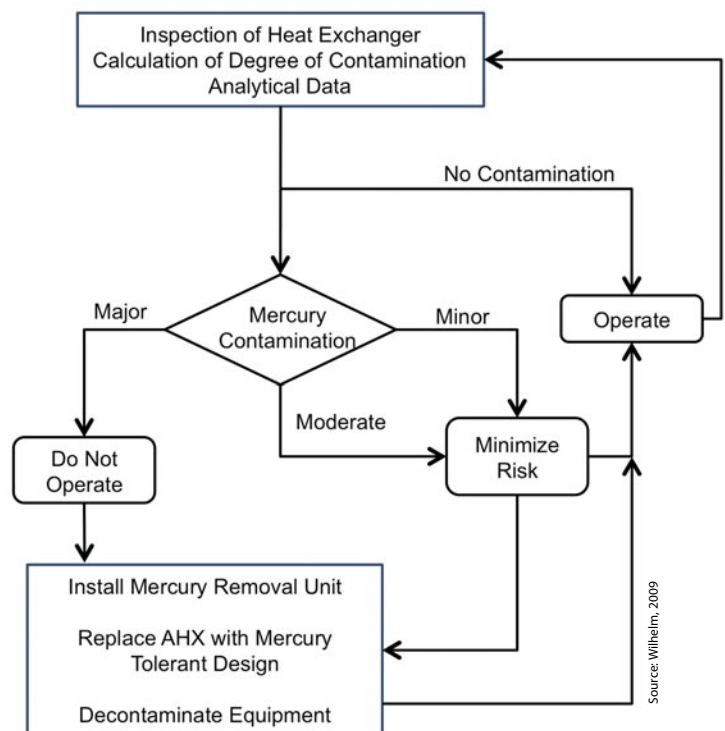
Figure 12 Metallurgical failure caused by liquid mercury



The potential for LME has led to a risk-based process to minimize the risk to equipment, as described in Wilhelm, 2009. Figure 13 shows an example of this process.

Other metals besides aluminium are, to varying extents, also susceptible to LME. These include brass and copper alloys, which can often be found in water-cooled heat exchangers in crude unit overhead systems.

Figure 13 Example of a decision tree for equipment risk minimization



- Are mercury deposits known to be present in the heat exchanger?
- What is the amount and distribution of the contamination?
- Do welds have backing rings?
- Is liquid mercury in contact with aluminium welds having a susceptible metallurgical microstructure?
- At the locations of mercury deposits, are stresses present that have sufficient magnitude to allow LME?
- What is the frequency of strain events (trips, shutdowns, upsets)? Are strains dynamic?
- How old is the equipment? Who made it and what are the construction details?
- What unusual operating procedures are employed, for example methanol injection, derime (defrost) procedures, particulate intrusion, upstream chemical usage, etc.?



Environmental considerations

Mercury is released into the environment by natural processes such as volcanic activity. It is also released from human activities such as mining and coal combustion.

Mercury is also released into the environment during the refining process, and from the combustion of refinery products such as gasoline and diesel fuel. Direct contributions from refining activities are small. IPIECA's dataset indicates that the refining sector's contribution to global mercury emissions is 0.07% of the total global mercury releases to air, and less than 0.01% to water. These estimates of mercury emissions are lower than the estimates contained in the 2013 UNEP global mercury assessment. There are two reasons for this:

1. The amount of mercury entering refineries is lower than assumed by UNEP. The IPIECA dataset shows that the global average mercury concentration in crude oil is 7.5 ppb. (The IPIECA calculations are discussed on page 10.) This is substantially lower than the 55 ppb assumed in the earlier UNEP work.
2. The amount of mercury leaving refineries via air and water is lower than assumed by UNEP. This was demonstrated by the WSPA study discussed on page 12 (WSPA, 2009).

Additional details can be found in the IPIECA fact sheet, *Mercury in crude oil and contribution to global mercury emissions*, which is reproduced on pages 28–29 of this Guide.

Although mercury releases from refining are small, it is still important to ensure that mercury releases are properly monitored and controlled. Some of these considerations are discussed below.

Waste water treatment

Refinery water effluents typically show very low mercury concentrations, as long as the solids have already been removed from the water.

Most of the mercury entering a refinery waste water treatment facility will end up in the solid fraction (i.e. waste water treatment sludge). This is due to the chemistry and behaviour of mercury. Most mercury in refinery water tends to associate with particles rather than remaining in solution in the water. One IPIECA member has tested the particulates in waste water, and reports that the mercury was in the form of mercury sulphide particulates.



The primary variable affecting mercury in effluent water appears to be the amount of suspended solids. High levels of suspended solids in water streams can lead to an apparent high level of mercury in those same streams. This can be resolved by removing the solids.

The wastewater from a specific US refinery is the subject of a detailed study by the Argonne National Laboratory. Initial results have been published in Negri *et al.*, 2011.

Solid waste

The following are some general principles that apply to all refinery solid wastes:

- Solid wastes from refineries need to be identified, properly labelled, stored in appropriate waste containers, and disposed of in an appropriate manner.
- If a particular waste stream has unique properties and disposal issues, it should be segregated from other waste streams.
- If third parties are involved in handling and disposing of waste, they must be appropriately qualified.

Mercurial solid waste originates from process units dedicated to mercury removal, such as spent catalysts, rags and contaminated PPE. In a refinery running elevated-mercury crudes, other wastes may also contain mercury. Mercurial wastes should be classified, disposed of and managed according to country regulations, e.g. in accordance with EU Directives (EU member countries classify mercury as a hazardous waste, which is to be disposed of and managed responsibly in specific plant facilities).

The potential presence of mercury is another variable in a refinery's waste management system, but also fits within these general principles.

Waste streams should be analysed to determine whether they contain mercury. If the waste does contain mercury, the waste stream might require classification as mercury-contaminated waste, and hence might need to be collected and disposed of appropriately. For example, some third parties might use incineration as a means to destroy refinery waste; this may not be appropriate for certain mercury-contaminated waste if the third-party facility doesn't control mercury in its waste gases.

Workplaces handling mercury waste should develop a Mercury Waste Management Procedure or integrate mercury waste into their existing Waste Management Procedure. Some examples of essential considerations can be found in DOSH, 2011.

In few cases, the 'waste' may be a piece of equipment, such as a length of pipe. Three ways to sample and determine whether material is contaminated with mercury are:

- non-destructive, in-situ, online measuring using handheld X-ray fluorescence analysis (XRF, HXRF) that provides measuring results immediately;
- 'conventional' sampling and sample analysis in a laboratory—a technique that is generally destructive (e.g. it involves drilling a hole) and cannot be executed while equipment is still in operation; and
- non-destructive assays for determining mercury per area (quantity per area unity), for example by using cotton swabs or via mercury check surface sampling.

If mercury-containing waste is to be transferred to a third party for handling and disposal, the refinery should confirm that the third party is appropriately qualified for such tasks.

Product stewardship



Refineries sell many products. Some products, such as gasoline, are sold directly to consumers. Other products are sold to other manufacturers, for example when propane is sold to a chemical company as an intermediate product for use in the manufacture of propylene and polypropylene.

The amount of mercury that might be found in these products varies, as does the species of mercury. In the case of lighter products such as propane, the mercury might be in the form of elemental mercury. In the case of heavy products such as petroleum coke, the mercury may be in the form of mercury sulphide.

It is important to emphasize that when a refinery product is sold to be processed in another manufacturing process, the product safety issue becomes a process safety issue in another plant. See page 21 for a discussion on process safety and the potential effect of liquid mercury on some equipment.

The mercury limits on feeds to some chemical plants may be as low as 1–5 parts per billion. This is because some chemical plants contain cryogenic aluminium equipment which could be affected by liquid elemental mercury. For

example, olefin plants that generate propylene from propane often contain 'cold boxes' with large amounts of aluminium equipment. Some olefin plants have MRUs. However, some have aluminium equipment but lack MRUs, and could therefore be subject to process safety issues.

Thus, in assessing product-related risks, each refinery should consider not only the finished products, but also the intermediates that are sold to other manufacturers. In some cases these intermediates will be subject to stringent constraints on mercury levels. A good practice is to have fit-for-purpose, agreed-upon constraints on mercury in these intermediate streams.

Mercury removal technologies

Mercury removal technologies can be applied in refineries. However, they are most applicable to refinery products and effluents; there is only one proven technology for the removal of mercury directly from crude oil and condensates. This technology is in use by one IPIECA member in southern Argentina.

Mercury removal from hydrocarbon products typically consists of a mercury removal unit, or MRU. MRU technology is available from several vendors; an example is shown in the photograph below.

MRUs typically consist of beds that are filled with an adsorbent. The words 'adsorbent' and 'absorbent' are sometimes used loosely. In the case of MRUs, there may be either a surface adsorption, or a chemical reaction, involving mercury in the feed and sulphur in the adsorbent.

In some cases the beds might be arranged in a lead-lag configuration, where the lead bed is the one that is actively removing mercury, while the

lagging bed is on standby, ready to be utilized for when the lead bed is spent.

Once a bed becomes spent (i.e. once it has exhausted its capacity to remove mercury), the bed is taken out of service, and the adsorbent material is removed and disposed of appropriately. Some companies (e.g. Johnson Matthey) offer a cradle-to-grave service, and will both supply the material and handle the disposal.

Mercury removal from waste water

Mercury removal from waste water is discussed briefly in the section on *Environmental considerations* on page 23. The primary issue when treating waste water is the removal of any solids from the water, because the mercury will typically be associated with those solids. In general, conventional waste water treatment systems used by refineries have demonstrated an excellent capacity to remove solids and therefore also remove the associated mercury.

Vendors offer water treating additives to assist in the process of controlling mercury levels in waste water. For example, Nalco offers a product called NalMet™, and G. E. Betz offers a product called MetClear™. In each case the vendor states that small amounts of the additive will help to ensure that the mercury will be bound to solids, which can then be removed via settling or filtration.

Solids from waste water treatment typically contain a variety of contaminants, as well as trace levels of mercury. These solids should be managed appropriately and in accordance with local laws and regulations.

Example of a mercury removal unit (MRU)



Source: Johnson Matthey, 2008

Conclusion

Mercury is present in trace levels in crude oil and condensates. IPIECA data show that the majority of the world's crudes are low in mercury. For example, 64% of the crudes in the IPIECA database show mercury levels of 2 wt ppb or less, although a small fraction of crudes (3%) contain over 100 wt ppb of mercury. On a global basis, IPIECA estimates that the weighted average mercury content of the global crude supply is 7.5 wt ppb of mercury.

Mercury exists in several forms in nature, but the two species of mercury that are believed to be prevalent in refineries are elemental mercury and mercury sulphide.

This Guide has highlighted some important good practices for managing mercury in the refining industry. Examples include tracking mercury in refinery input, assuring worker protection via proper training and appropriate use of personal protective equipment, having fit-for-purpose constraints on mercury in products and intermediates, and assuring process safety via awareness of mercury's potential impact on equipment.



IPIECA fact sheet on mercury

Prepared for UNEP's INC-5, Geneva, January 2013

Mercury in crude oil and contribution to global mercury emissions

Mercury has become a focus of global scrutiny with the United Nations leading the negotiations to develop a legally binding global treaty on the control of mercury releases. In 2012 IPIECA published the largest publicly available dataset on mercury levels covering 446 Crude Oils and Condensates.

UNEP has estimated global mercury emissions from many sources. As illustrated in the pie chart¹, UNEP currently estimates the petroleum refining sector is responsible for 0.8% of the total anthropogenic emissions to air (this was revised downward from their earlier estimate of 2.4%)-this data does not incorporate IPIECA dataset.

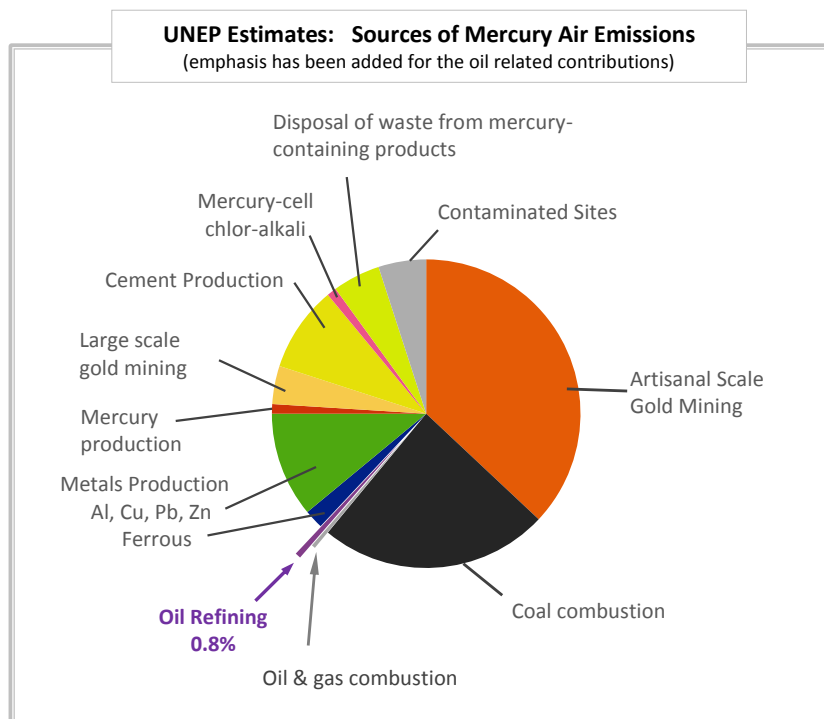


Figure 1: 'Relative contributions to estimated emissions to air from anthropogenic sources in 2010', UNEP Draft Global Mercury Report 2012

IPIECA's dataset indicates that Mercury concentrations in crude oil are lower than determined by UNEP. The refining sector's contribution is 0.07% of the total global mercury releases to air (12 times lower than UNEP's estimate) and less than 0.01% to water (37 times lower than UNEP's estimate).

In a study of a number of refineries in California, U.S, the data showed that most of the mercury that enters petroleum refineries is removed as solid waste (87%). This proportion is representative of most refinery operations. The waste is then disposed of in accordance with local regulations.

(See next page for calculations and additional references.)

IPIECA is the global oil and gas industry association for environmental and social issues. It develops shares and promotes good practices and knowledge to help industry improve its environmental and social performance; and is the industry's principal channel of communication with the United Nations. For information, please visit www.ipieca.org

1 UNEP, 'Global Mercury Report 2013, DRAFT', 3. Anthropogenic Emissions to Atmosphere, 13 November 2012

UNEP 2011 & 2012 and IPIECA 2012 data

- UNEP's 2011 Toolkit Methodology for total mercury **input** to the petroleum refining sector was as follows:

Assumed average mercury content of crude oil	55 parts per billion (by weight) ²
Multiply by total crude production	<u>x 3.6 billion tonnes / year of crude</u>
Total mercury input to petroleum refining sector	= 200 tonnes / year of mercury (UNEP, 2011)

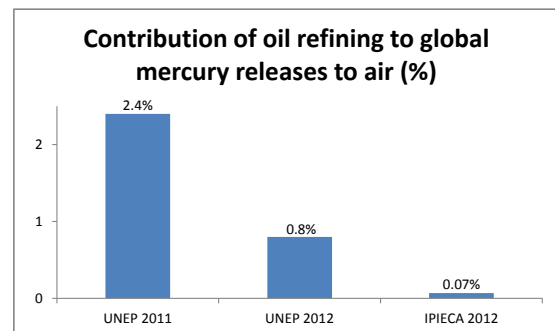
- IPIECA data and calculation of total mercury **input** to the petroleum refining sector shows **a much lower number**:

IPIECA average mercury content of crude oil	7.5 parts per billion (by weight) ³
Multiply by total crude production	<u>x 3.6 billion tonnes / year of crude</u>
Total mercury input to petroleum refining sector	= 27 tonnes / year of mercury (IPIECA, 2012)

- For mercury emissions to **air**:

- UNEP estimated that the refining sector contributed 0.8% (16 t/y)¹ of total global air emissions (revised downward from their previous estimate of 2.4%).
- The corresponding IPIECA calculation indicates that emission levels are 12 times lower (0.07% of the total air emissions):

$(27 \text{ tonnes total mercury input}^3) \times (5\% \text{ emission to air}^4) = 1.35 \text{ tonnes / year to air (IPIECA)}$



- For mercury emissions to **water**:

- UNEP estimated the refining sector contributed 0.1% (2t/yr)¹:
(200 tonnes total input) x (1% to water) = 2 tonnes / year to water (UNEP)
- IPIECA estimated the refining sector contributed less than 0.01% which is 37 times less than the UNEP estimate:

$(27 \text{ tonnes total input}^3) \times (0.2\% \text{ emission to water}^4) = 0.054 \text{ tonnes / year to water (IPIECA)}$

- For **waste**:

- Most of the mercury that enters the refinery ends up as solid waste (87.4%)⁴. This waste is being disposed of and managed according to country regulations (e.g. EU Directive, EU member countries classify mercury as hazardous waste, which is disposed of and managed responsibly in specific plant facilities). This will be discussed as part of an IPIECA good practice guide on waste management to be released in mid-2013.
- The mercury that is not contained in waste (12.6% of the total) is accounted for in refined products (6.7%), refinery air emissions (4.9%), water discharges (0.2%) and petroleum coke (0.8%)⁴.

2 UNEP, 'Toolkit for Identification and Quantification of Mercury Releases, Reference Report-Revised Inventory Level 2 Report', Table 5-14, 2011.

3 Weighted average based on SPE/APPEA International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Perth, Australia, 'Industry Input to the UN Global Mercury Treaty Negotiations Focus on Oil and Gas', IPIECA Dataset for Mercury in Crudes and Condensates, 2012.

4 Western States Petroleum Association (WSPA), 'Bay Area Petroleum Refinery Mercury Air Emissions, Deposition and Fate', Environmental Resource Management, 2009.

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