Study report on "Mercury from oil and gas" under the UNEP Global Mercury Partnership First draft – 5 May 2021

About the report

1. The present report has been developed in the context of the UNEP Global Mercury Partnership. Initiated in 2005, the Partnership aims to protect human health and the environment from the releases of mercury and its compounds to air, water and land. With over 200 partners to date from governments, intergovernmental and non-governmental organizations, academia/ scientific community and industry/private sector, it focuses its work on supporting timely and effective implementation of the Minamata Convention on Mercury, providing state of the art knowledge and science and raising awareness towards global action on mercury[1].

2. The Partnership Advisory Group (PAG) decided at its tenth meeting (Geneva, 23 November 2019) to initiate work on mercury from oil and gas, which it had identified as a cross-cutting topic amongst different Partnership areas. The PAG requested the Secretariat to convene targeted discussions with interested Partnership area leads, partners as well as other relevant stakeholders[2]. Expert consultations were launched on 23 April 2020, with the overall objective to identify potential useful contributions from the Partnership, within the context of its mission and its existing areas of work[3]. Participants were invited to attend in their expert capacity, to share views and ideas, and any useful background information.

3. Interested Partnership area leads subsequently agreed to guide a process for developing a study report on the topic. As per their guidance, the report should be concise, and aim to better understand potential releases of mercury, as well as possibly how wastes are treated and accounted for and may be entering the market for other uses. The guidance further indicated that the report could distinguish the key differences between oil and natural gas related information, and therefore address them separately. The report could also identify the differences in the presence and management of mercury in the respective sectors. The guidance further indicated that the report could include:

- a review of existing knowledge and gaps in understanding mercury content, emissions and releases; relative geographic mercury concentrations; waste flows and treatment during the respective stages of the oil and gas processes, including decommissioning of their infrastructures of both offshore and onshore sites; and available information on the potential avenues through which mercury from the sector may be entering the market for other uses;
- if available, information related to quantities of mercury that are possibly entering the market;
- information related to how mercury is present in new techniques such as non-conventional gas (fracking, shale gas), and how it is extracted;
- a review of the different methods used, highlighting best practices for mercury releases reduction and waste treatment (including the treatment at dismantling yards for the decommissioned infrastructures that may contain mercury), and for detecting or monitoring mercury releases;
- initial ideas for further research and cooperation.

4. A draft annotated outline of the study report on mercury from oil and gas was developed and presented for consideration and discussion by the PAG at its eleventh meeting (document UNEP/Hg/PAG.11/4). Together with the information collected, the finalized annotated outline was used as a basis to develop the present study report.

5. In reviewing the draft report, reviewers are encouraged to provide general input as well as additional sources of information, data and best practice including on:

- workers exposure to mercury as well as specific guidelines on workers protection from mercury exposure along the different steps of the oil and gas processes.

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[1]For more information, please visit: web.unep.org/globalmercurypartnership
[2] The report of the tenth meeting of the Partnership Advisory Group (document UNEP/ Hg/PAG.10/5) is available at: https://web.unep.org/globalmercurypartnership/partnership-advisory-group-meeting-10
[3] Further information, including summary of main discussion points, may be found at: https://web.unep.org/globalmercurypartnership/expert-consultations-"mercury-oil-and-gas"

- the removal of mercury during maintenance procedures, at the end of the operational lifetime of the plants as well as of life cycle of the equipment.
- sources of mercury supply from the oil and gas sector generating stocks, as well as approximate annual volumes of such produced stock, including whether they exceed 10 metric tonnes per year.

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Study Report on "Mercury from oil and gas"
First draft – 5 May 2021

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EXECUTIVE SUMMARY

(To be developed on the basis of the revised draft report)

1. Introduction

Initiated in 2005 by a decision of the United Nations Environment Programme (UNEP) Governing Council, the UNEP Global Mercury Partnership aims to protect human health and the environment from the release of mercury and its compounds to air, water and land by minimizing and, where feasible, ultimately eliminating global, anthropogenic mercury releases. With over 200 partners to date from Governments, intergovernmental and non-governmental organizations, industry and academia, the Partnership focuses on supporting timely and effective implementation of the Minamata Convention on Mercury, providing state of the art knowledge and science and raising awareness towards global action on mercury.

The objective of the Minamata Convention is to protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds.

At its ninth meeting (Geneva, 18 November 2018), the Global Mercury Partnership Advisory Group (PAG) discussed mercury from oil and gas as an issue of potential interest to be examined, including with respect to the level of concern, available data and possible contribution of the Partnership. Recognizing the need for further information on the topic, the PAG agreed to initiate work on mercury from oil and gas production.

At its tenth meeting (Geneva, 23 November 2019), the PAG requested the Secretariat of the Partnership to convene targeted discussions with interested partners and stakeholders on the issue of mercury from oil and gas, which it had identified as cross-cutting, i.e., where the collaboration of Partnership areas of work would facilitate the development of needed information, interventions and projects.

In response to this request, expert consultations were launched on 23 April 2020, with the overall objective to identify potential useful contributions from the Partnership, within the context of its mission and its existing areas of work. The meeting was attended by approximately 65 participants, both partners and non-partners, and included representatives from governments, intergovernmental and nongovernmental organizations (academia, scientific community and private sector).

Experts explored the following three aspects in their discussions:

(1) Needs and challenges associated with the management of mercury from oil and gas production, distribution and infrastructure decommissioning,

(2) Existing relevant work and guidance on best practices and

(3) Possible contribution of the Partnership to support the promotion of best practices and support moving the issue forward.[4]

The discussions highlighted the cross-cutting nature of the topic, which could benefit from the complementarity and cooperation of several Partnership Areas, including on “mercury air transport and fate research”, “mercury supply and storage” and “mercury waste management”.

Several avenues were suggested as possible contributions of the Partnership, including an enhanced overview of mercury along the different stages of the oil and gas value chains, including its fate and transport, measurement techniques and the species of mercury found; and facilitating information and experience sharing on the topic of mercury from oil and gas and best practices for its environmentally sound management.

Interested Partnership area leads subsequently agreed to guide a process for developing a study report on the topic of Mercury in Oil and Gas.

2. Objective of the report

The objective of the present report is to analyze the life cycle of mercury in the oil and natural gas value chains and understand how this heavy metal, naturally present in oil and natural gas, may be released to the environment at different stages of the process (including the decommissioning of oil and gas infrastructure), and as a consequence increase the levels of mercury in the environment, posing a risk to human health and ecosystems.

It also aims to identify how waste from the sector is treated, accounted for and, where appropriate, whether mercury recovered from such waste may be entering the market for other uses.

3. Mercury in oil and natural gas

Current knowledge

The possible emissions and releases of mercury to the environment from crude oil and natural gas processing and uses were discussed during the preparatory process of the Minamata Convention.[5]

The limited available information (e.g. in terms of comprehensiveness or availability publicly) on the potential releases and emissions of mercury from the

[4] Summary of main discussion points is available at: https://wedocs.unep.org/bitstream/handle/20.500.11822/32793/GMPOiG.pdf?sequence=1&isAllowed=y
[5] UNEP(DTIE)/Hg/INC.3/5.

different processes and uses of crude oil and natural gas may be impeding a good understanding of:

- emissions and releases to the environment along the extraction/production and decommissioning phases;
- mercury or mercury containing waste from extraction or processing;
- occupational exposure;
- human exposure (low chronic exposure, particularly dangerous in early human development stages).

Emissions and releases of mercury are harmful to human health and the environment. Due to mercury's persistence, it remains in the environment and contributes to increasing the environmental pool of mercury.

Once present in the different media (air, water or soil) mercury can be transported long distances and penetrate the food chain, becoming part of all living things, affecting humans and biodiversity's health and quality of life.

Mercury is considered by WHO as one of the top ten chemicals or groups of chemicals of major public health concern.

It is well known that crude oil and natural gas contain heavy metals (in variable concentrations) depending on the nature of the geological formation of the basin of the extraction.

The presence of mercury in crude oil and natural gas has different impacts on the processing operations, the environment and human health, including in particular for the industry operators.

While it is widely recognized that mercury may impact the process operations and affect the health of operators[6], there are few (but an increasing number of) publications/investigations that go into the details of the question.

The processing of most crude oil is directed to maximize gasoline manufacture while for natural gas it aims to separate methane from other components. Both steps depend on the composition of the hydrocarbon mix and the market objectives.

The issue of mercury in the petrochemical industry is recognized nowadays, including in light of the technical difficulties encountered in the processing of oil and gas.

Moreover, mercury containing waste from petroleum processing is difficult to separate, store and process for disposal.[7]

It is important to take into consideration the difficulties of treating toxic sludge deposits, contaminated liquids and sludge containing mercury from water

[6] *Mercury management in petroleum refining,* An IPIECA Good Practice Guide, 2014.
[7] *Mercury management in petroleum refining,* An IPIECA Good Practice Guide, 2014.

treatment systems, and mercury sorbent materials. There are also challenges associated with storing and processing for disposal. It is reported that storage or burial of such waste material containing mercury are common practices in many remote locations even if these are not recognized best practices and have high environmental impacts.[8]

Over 85% of the world's energy comes from hydrocarbon resources which include crude oil, natural gas and coal. The level of production reached at an all-time high in 2019, with around 95.2 million barrels of oil produced daily. This quantity includes crude oil, shale oil, oil sands and NGLs (the liquid content of natural gas, where this is recovered separately), but not liquid fuels from biomass and coals derivatives.[9]

Mercury affecting the oil and gas processing systems

The contribution of the oil and gas sector to global mercury emissions was considered to be very limited. [10] However mercury has been receiving growing attention, and the optimization of the efficiency of oil and gas plants, as well as the tightening of environmental and health laws, has elevated this topic as one of the main concerns for process engineers. [11] In its 2014 Good Practice Guide "Mercury management in petroleum refining", IPIECA noted that "although mercury releases from refining are small, it is still important to ensure that mercury releases are properly monitored and controlled."[12]

Crude oil and natural gas are naturally composed by hydrocarbons as well as a wide spectrum of elements such as mercury, arsenic and vanadium in concentrations that vary in every basin and at each stage of the different processes and uses.

Mercury may be present in three different chemical forms: elemental mercury, organic mercury and inorganic salts. These are present in crude oil and natural gas in low concentrations (between 0,1 and 20.000 μg/kg in crude oil and between 0,05 and 5000 μg/Nm3 in natural gas).[13]

As a natural pollutant of crude oil and natural gas, mercury may expose operators and is universally detrimental to petroleum processing systems (for production, treatment, transport and refining plants).

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[8] A. Chalkidis et al. Mercury in natural gas streams: A review of materials and processes for abatement and remediation, Centre for Advanced Materials & Industrial Chemistry (CAMIC), School of Science, RMIT University, GPO Box 2476, Melbourne, VIC, 3001, Australia, b. CSIRO Energy, Private Bag 10, Clayton South, VIC, 3169, Australia. 2019.
[9] Oil - global production 1998-2019. Published by M. Garside, Sep 30, 2020 https://www.statista.com/statistics/265203/global-oil-production-since-in-barrels-per-day/
[10] IPIECA Annual Review 2013-2014
[11] Subirachs Sanchez, *Mercury in extraction and refining process of crude oil and natural gas*, University of Aberdeen, 2013.
[12] *Mercury management in petroleum refining,* An IPIECA Good Practice Guide, 2014.
[13] D. Lang. et al., Mercury arising from oil and gas production in the United Kingdom and UK continental shelf. IMKIP Oxford. 2012

In gas processing, mercury damages equipment and fouls cryogenic heat exchangers. In chemical manufacturing and refining, it poisons catalysts and contaminates wastewater.

Technical difficulties posed by mercury in refineries are today well known and include from equipment degradation, toxic waste generation, or poisoning of catalysts. These are linked to mercury's unequal distribution among vapor, condensate and aqueous phases, depending on the pressure and temperature.[14]

In working areas, mercury presence in vapor suffers considerable variation (depending on the temperature and convection), highlighting the importance of continuous monitoring (as well as rapid and numerous analyses) to understand the source and concentration.[15]

Occupational exposure

Workers may be exposed to mercury in particular through inhalation of mercury vapors and dermal absorption of organic mercury during maintenance work, inspection activities and decontamination during turnaround in the petroleum industry.

According to Qa[3], "The biggest potential risk to workers arises during plant shutdowns or during service/maintenance work when mercury that has accumulated onto the internal surface of processing equipment via adsorption/chemisorption can be released to the atmosphere. This process of releasing mercury is accelerated if any hot work is carried out (e.g., cutting or welding) and can be particularly problematic in confined spaces where the mercury concentration could potentially rise above the OEL (occupational exposure limit). OELs for mercury vary from region to region but are typically in the range 20 - 50 $\mu g/m^3$."[16]

When hydrocarbons processed contain mercury total above a few ppb[17], cleaning and inspections activities must be carefully planned due the mercury deposition in the equipment that usually accumulates in separators and heat exchangers.

Mercury concentrations in vapor can be much higher in the vessels than in the process stream due to the accumulation mechanisms that include adsorption on equipment surfaces and dissolution in sludge.

[14] Fabian G. Lombardi, AXION ENERGY SA, Procesamiento de crudos con mercurio, Petrotecnia.5, 2018.
[15] Gasmet , Emissions Monitoring Handbook.
[16] Qa3. Unconsidered Mercury Emissions from the Oil and Gas Industry. ANNUAL BUYERS GUIDE 2016.
[17] Maytiya Muadchim,aet al. Case study of occupational mercury exposure during decontamination of turnaround in refinery plant. Published online 2018.

Chemical exposure during maintenance could be several times higher than normal work routines and during the comprehensive turnaround (TA) workers could have significant exposure.[18]

Other potential exposure sources could be the decontaminated units (when measuring toxic chemical concentrations) and the wastewater drained in the water treatment system.[19] Publications noted cases where mercury exposure was several times higher than the threshold limit value (TLV), with the highest levels found among steam decontamination workers.[20]

Organic mercury (especially dialkylmercury) is estimated to be many times more toxic than elemental mercury on an equivalent weight dose basis. Dermal absorption efficiencies for elemental mercury in vapor are typically lower than 3% of the absorbed dose but nonetheless, must be strictly avoided.[21]

The combination of dietary, environmental and occupational mercury can cause total exposure to exceed the threshold for chronic detriment. Analysis of blood and urine are the most common diagnostic tools for the discovery and quantification of occupational exposure as conclusive symptomatic diagnosis of neuralgic impairment is usually at an advanced stage (and therapies are mostly palliatives).

Prevention is hence critical, along with awareness raising on the issue by promoting *"the development and implementation of science-based educational and preventive programmes on occupational exposure to mercury and mercury compounds;"* as called for under the Minamata Convention (article 16, paragraph 1).

***Case study: "Escalante crude", Argentina*[22]**

South America has the second highest regional mercury concentrations in crude oil after Asia, with 11% of crudes over 15ppb.

Petroleum crudes have been identified in the Fueguina basin as containing mercury in high concentrations, up to 500ppm.

The Campana refinery, in Argentina, was warned by crude assays usually performed on crude oil (as well as by external alerts)[23] about the possible

[18] Maytiya Muadchim, et al. *Case study of occupational mercury exposure during decontamination of turnaround in refinery plant.* Published online 2018

[19] Turnaround (TA) shutdown of refineries to allow for decontamination, repairs, replacements, inspections, and overhauls to increase equipment reliability to maintain production integrity and reduce the risk of catastrophic failures

[20] Maytiya Muadchim,et al. Case study of occupational mercury exposure during decontamination of turnaround in refinery plant. Published online 2018

[21] WHO. Elemental mercury and inorganic mercury compounds: Human health aspects. Geneva 2003. https://www.who.int/ipcs/publications/cicad/en/cicad50.pdf

[22] Fabian G. Lombardi, Axion Energy SA, Procesamiento de crudos con mercurio, Petrotecnia.5, 2018.

[23] Fabian G. Lombardi, Axion Energy SA, Procesamiento de crudos con mercurio, Petrotecnia.5, 2018.

presence of mercury in crude oil since 2009. High levels of mercury were detected in “Escalante” crude (the leading exported crude from Argentina).

This refining plant installed a low concentration mercury detection equipment in order to monitor mercury levels during the process and in commercial products.

According to the monitoring outcomes, mercury average concentrations (with predominance of Escalante crude) increased up to 25 ppb.

According to the publication consulted, trace mercury in the crude oil to be refined must be studied, with a special emphasis in the crudes of Argentina as the local crudes have increased their mercury concentration over time.

This article also highlights that mercury tends to be present in all the cuts, with a high occurrence in lighter ones (like LPG and naphtha). It further strongly recommends to study mercury levels in order to prevent workers and environmental exposure, ensure the quality of the products and protect the equipment.

Finally, the article points to unanswered questions: Is the mercury accumulating? Where? In which cuts? How can the effects be predicted? What actions have to be taken?

4. Mercury content in oil and gas deposits

Mercury occurs naturally in oil and gas deposits, probably as the product of primary geological processes as well as secondary ones mobilizing mercury into reservoirs. Even though not comprehensive, wide-ranging research has been published on the origin of this metal.

Different forms of mercury in deposits (chemical speciation)

In natural gas, mercury is mostly present in its elemental form.

Several forms of mercury have been described in gas condensate, the liquid steam separated from natural gas, and in crude oil: mainly elemental mercury and inorganic compounds (like HgK, HgK_2, HgS, HgSe and other salts), but also organic compounds (like dialkylmercury), all of them with different chemical and physical properties.[24]

These forms of mercury may be dissolved, suspended or adsorbed on inert particles like sand or wax.

[24] Wilhelm et al., Mercury in crude oil processed in the United States, 2004.

Geographical distribution of the presence of mercury in crude oil and natural gas

It is important to clarify that gas condensates as well as crude oil are usually referred to in the consulted bibliography under the general denomination of “oil”, “crude” or “crude oil”.

Mercury levels in crude oil can vary significantly depending on the origin and geological factors, such as: regional tectonic position, structural features of the deposit and seismic activities. Levels can also depend on the operation conditions.[1] Consequently, mercury concentrations may vary in a short period of time influenced by these processes.

According to IPIECA’s (International Petroleum Industry Environmental Conservation Association) database, mercury levels in crude oils can vary between 0.1 and 1,000 ppb. It should be noted that the documented maximum levels in crude oil also vary greatly in the existing literature: IPIECA’s database does not register levels over 1,000 ppb but other texts such as US EPA 2001 mentions 20,000 ppb. IPIECA attributes this difference to old and non-comparable analytical techniques.[25]

It is important to highlight that global multicentric harmonized studies using comparable analytical techniques and data analysis have not been implemented. Also, due to possible variations of the concentrations, it is desirable to keep the concentration mapping updated.

A simple mass balance between the mercury content in crude oil and natural gas and the mercury waste and mercury containing waste is difficult to obtain due to the uncertainties on the origin of the mercury in the deposits and the important variation in the concentration of mercury levels in crude oil and natural gas in among the basins and deposits.

Methodologies for estimating the concentration of mercury in crude oil

In general, as a first approach to calculate the amounts of mercury present in the crude oil, the information is presented as the average concentrations per region, which can be a good indicator to evaluate the releases and emissions according to the source of the crude oil.

To estimate the average concentration per region, Whilhelm *et al.* 2004 uses the average of the values obtained for total mercury in different crudes, weighted by the amount of oil produced by country.

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[25] IPIECA. Mercury management in petroleum refining An IPIECA Good Practice Guide. 2015.

Table 1: *Mercury concentration in crude oil by region, calculated as the average of total mercury in different crude oils weighted by production by country.*[26]

Region	**Hg Concentration (weight-average, wt. ppb)**
Middle East	0.8
Africa	2.7
North America	3.2
South America	5.3
Europe	8.7
Asia	220.1
Global	3.5

Another way of estimating regional average is to take the median of the results of the total mercury analysis in different deposits. This methodology has been used by IPIECA in the calculations presented in table 2 below.

When higher levels of mercury (over 100 ppb) are considered extraordinary events, this can be a more robust methodology to estimate a global level average, but the estimation tends to show lower averages in regional levels as shown in the table below.

Table 2: *Total mercury by region calculated as the median of the results by country.*[27]

Region	**Hg Concentration (median, wt. ppb)**
Middle East	1.0
Africa	1.0
North America	1.2
Eurasia	1.2
South America	1.4
Pacific and Indian Ocean	3.0
Global (average weighted by production)	7.5

The results of the tables are not directly comparable because different regions, analytical techniques and data processing were used. Although in both tables it can be observed that the results presented are similar for the zones with the lowest mercury concentration and with the least data dispersion. As an example, in the Middle East, the averages in both tables are alike, as no results are above 15 ppb of mercury.

[26] Wilhelm et al., Mercury in crude oil processed in the United States, 2004.
[27] *Mercury management in petroleum refining,* An IPIECA Good Practice Guide, 2014.

On the other hand, for regions with a wider dispersion of the data on concentration of mercury among deposits (very low and very high presence of mercury), the results differ significantly.

As an example, IPIECA reports an average of 3 ppb of mercury for the region identified as “Pacific and Indian Ocean” (table 2) while Whilhelm *et al.* reports 220.1 ppb for the region identified as “Asia” (table 1).

Even when using a data analysis similar to Whilhelm *et al.,* the unweighted simple average of mercury levels for IPIECA dataset results in 51 ppb for the “Pacific and Indian Ocean” region, still far from the 220.1 ppb mentioned by Whilhelm et al. in his publication. The difference may be due to the number of samples studied, their origin or the analytical techniques. In any case, systematic comparable methods would be useful for a better comprehension of the global situation.

Methodologies for estimating the presence of mercury in natural gas

Like crude oil, natural gas deposits can show an important variation in the concentration of mercury, ranging from 0.05 to 5,000 µg/Nm^3.[28]

Almost all the mercury present in natural gas is elemental mercury, and only a little fraction, in low and difficult to measure concentrations, can be in a more bioavailable form like dialkylmercury.[29]

The average regional tendency may be similar to the one for crude oil, because in most cases crude oil and natural gas come from the same deposits.

The available information published on well-head levels of mercury in natural gas in different areas and countries shows the lowest average values for Middle East and North America, and high values for Indonesia and South America (where the lowest measured levels are 200 µg/Nm3 and 69 µg/Nm3):

***Table 3**: Well-head levels of mercury in gas in different areas.*[30]

Region/Country	Mercury Concentration (µg/Nm3)
Algeria	50 - 80
Eastern Europe	1 - 2000
Far East	0.02 - 193
Germany (Northern)	15 - 450
Germany (Southern)	<0.1 - 0.3

[28] D. Lang. *et al.*, *Mercury arising from oil and gas production in the United Kingdom and UK continental shelf.* IMKIP Oxford. 2012

[29] Office of Air Quality Planning and Standards (EPA). *Research and Development. Mercury in petroleum and natural gas: estimation of emissions from production, processing and combustion.* 2001.

[30] D. Lang. et al., Mercury arising from oil and gas production in the United Kingdom and UK continental shelf. IMKIP Oxford. 2012

Indonesia (Sumatra)	200 - 300
Middle East	1 - 9
North America	0.005 - 40
South America	69 - 119

Although the highest well-head levels were found in Eastern Europe this does not imply that the region has a high average concentration (the lowest levels were 1 µg/Nm3) but it indicates the presence of deposits with high mercury concentrations.

While according to IPIECA, natural gas (also referred in the publications as "non-condensates") shows a slightly lower concentration of mercury compared with crude oil (table 4). In this case, the report compares the median mercury level measured in crude oil and natural gas.

Table 4: *Mercury in oil vs gas. (IPIECA)*[31]

	Median Hg level (ppb)	**Percentage of crudes and condensates containing specific ranges of mercury (ppb)**					
		<2	***2-5***	***5-15***	***15-50***	***50-100***	***>100***
Oil	2.4	48%	14%	14%	12%	8%	4%
Gas	1.3	65%	15%	9%	7%	1%	3%

Other publications and consulted experts[32] also highlighted that estimating mercury concentrations in gas at the well-head is potentially as difficult as in crude oil. The following table shows some examples of mercury concentrations in oil and gas from the same source. In most of the cases, the mercury levels are in the same order of magnitude in oil and natural gas while in a few cases, mercury levels in natural gas are considerably higher than in crude oil.

Table 5. *Examples of concentrations measured by Qa^3 in oil and gas from the same source (information provided by Qa^3 during first draft consultation, November 2020).*

Region	**Hg in oil (µg/kg)**	**Hg in natural gas (µg/kg)**
Thailand	~80	~9000
UK	~80	~110
Norway	~12	~12
Vietnam	~90	~560
Algeria	< 1	~14
Azerbaijan	< 1	~9

[31] *Mercury management in petroleum refining,* An IPIECA Good Practice Guide, 2014.
[32] Qa3 and Guia Morelli (PhD Environmental Geochemistry Researcher. Consiglio Nazionale delle Ricerche-CNR. Instituto di Geoscienze e Georisorse-IGG) consultation, November 2020.

Australia	~2	~25
Oman	~20	~130
Tunisia	~38	~30

Regional content of mercury in crude oil and natural gas as an indicator

Regional averages of mercury concentration are an interesting indicator to calculate mercury emissions and releases to the environment in a location (region or country) where crude oil is going to be processed or used and the origin of the crude oil is known.

It is important to consider that in general when crude oil is imported it may be a mixture from different sources of a certain region.

To understand and make decisions on the mercury impact during the extraction processes at the local level, the regional averages are not good indicators due to the wide differences (maximum and minimum) of mercury content between deposits.

For example, even the highest level historically globally found (higher than 10,000 ppb)[33] belongs to a deposit located in California, the North American crude oil is considered the second lowest regional average level of mercury after the Middle East, as shown in fig. 1 where there are hotspots in regions with low averages regions.

In the case of natural gas, rather than regional averages, it appears more significant to consider mercury concentrations in the pipelines or deposits of origin, since natural gas is mostly commercialized inside or between neighboring regions (although this situation is currently changing).

[33] S.M. Wilhelm, N. Bloom. Mercury in petroleum. Fuel Processing Technology 63, 2000.

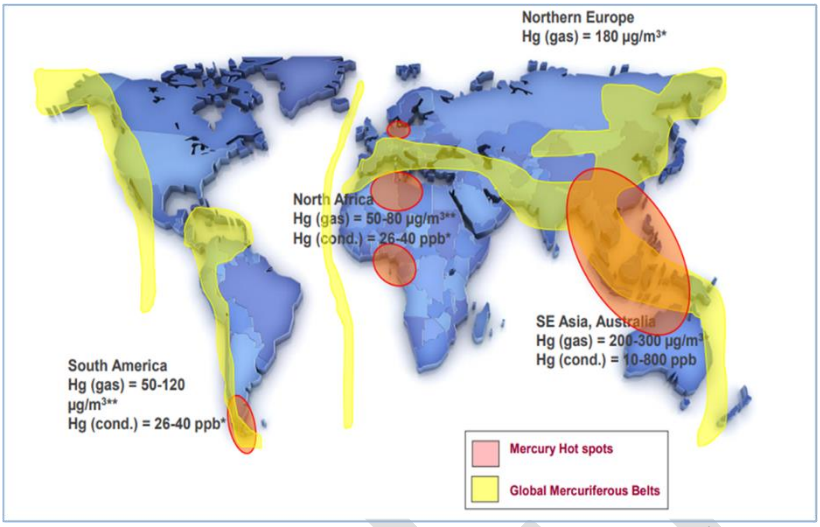

Figure 1: *Mercuriferous belts and hotspots map.*[34]

5. Mass of mercury potentially released from crude oil

Mercury may be found and released at different stages of the crude oil value chain, including extraction, transport, processing, and products.

Extraction

Crude oil production (extraction) systems provide limited opportunities for the loss of mercury from produced fluids, which are typically mixtures of hydrocarbon liquids, natural gas and produced water [35]. Most of the production systems separate the produced water *in situ* from the crude oil that will be transported to processing facilities.[36]

The produced wastewater obtained in this step may contain mercury, among other toxic substances, and must be managed, handled, transported and disposed of in an environmentally sound manner. There is a wide range of techniques designed to manage produced wastewater, some of which may generate hazardous sludge or solid waste with high concentrations of mercury (mercury containing waste).[37] According to a preliminary assessment by IPIECA in 2016, 13.5 t/y of mercury are released to the environment globally from produced water, about 90% of these occurring offshore.[38]

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1. [34] A. Chalkidis *et al. Mercury in natural gas streams: A review of materials and processes for abatement and remediation*, Centre for Advanced Materials & Industrial Chemistry (CAMIC), School of Science, RMIT University, GPO Box 2476, Melbourne, VIC, 3001, Australia, [b]. CSIRO Energy, Private Bag 10 Clayton South, VIC, 3169, Australia. 2019.

[35] Produce water, definition: naturally occurring water that comes out of the ground along with oil and gas.
[36] Oil - global production 1998-2019. Published by M. Garside, Sep 30, 2020 https://www.statista.com/statistics/265203/global-oil-production-since-in-barrels-per-day/
[37] OSPAR. Background Document concerning Techniques for the Management of Produced Water from Offshore Installations. 2013.
[38] AMAP/UN Environment, 2019. Technical Background Report

Flared gas originates from gas co-produced with oil production in situations where economics dictate that flaring is less expensive than recovery. This practice could result in the emission of mercury to the air, however the amount of mercury emitted is small and the trend downward.[39] For example, Whilhelm calculated mercury emission to the air by flaring gas in the US for the year 1996. He estimated that about 7 kg of mercury had been emitted to the air from gas flaring that year, for 7 cubic meters of gas flared, with an average content of mercury of about 1 µg/m3.

Transport

There is a risk of accumulation of sludges with high mercury concentration in crude oil storage tanks. Crude oil is most commonly transported by oil tankers. These ships may remain active for many decades, and during those years, sludge with a high mercury concentration can accumulate at the bottom of their storage tanks.

This sludge may become an important issue during the dismantling of tankers at the end of their service life, in particular if this activity is taking place in countries that do not have the required installations for the sound management of such hazardous waste.

In addition, in the case of spillages accidents these sludges can be an important risk of acute toxic exposure at local level due the massive atmospheric emissions of mercury.[40]

Processing

Once the crude oil is extracted, it is transported to processing facilities where it is distilled to obtain fractions of different hydrocarbons, or cuts. These cuts can be chemically modified or blended to obtain commercial products.

As mentioned previously, crude oil may contain mercury, so it is relevant to know the fate of this mercury once it enters the refining process. This varies according to the design of the facility, the nature of the input crude oil, the methodology followed by the operators, the commercial needs, the environmental regulations of the country and other factors.

However, a number of common mercury out streams can be identified, as illustrated in figure 2 below.

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for the Global Mercury Assessment 2018.

[39] S. Mark Wilhelm. Estimate of Mercury Emissions to the Atmosphere from Petroleum. Environmental science & technology / VOL. 35, NO. 24, 2001

[40] S. K. Pandey, K-H. Kim, U.-H. Yim, M-C. Jung, C-H. Kang. *Journal of Hazardous Materials.* 2009, **164**, 380–384

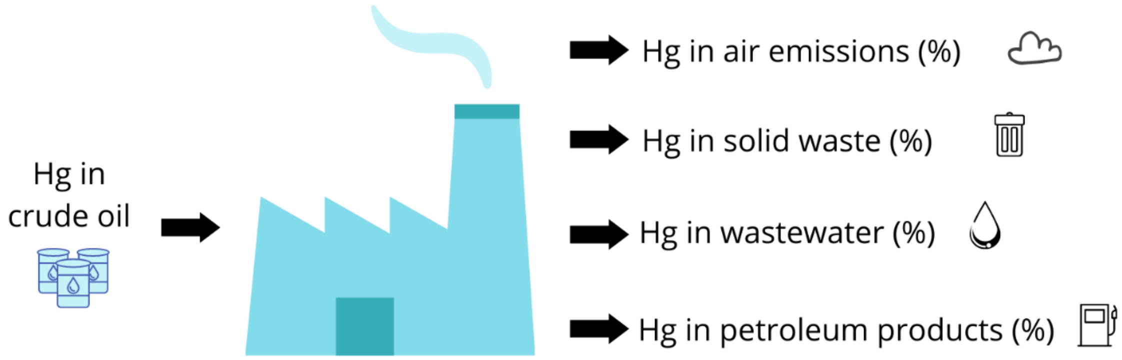

Figure 2. *Mercury in refineries mass balance.*

All the out streams of a crude oil processing facility can contain mercury in different concentrations:

- ***Mercury in wastewater***

Water is used in certain operations during the refining process, such as desalting, in stream stripping and alkylation. A typical refinery generates approximately 40–60 liters of wastewater for every barrel of oil produced. [41]

The desalination process takes place before the distillation. During this process, the crude oil and condensates are washed with water to remove contaminants, especially soluble salts. Elemental mercury and organic mercury are not soluble in water and remain dissolved in the crude oil.

However, other inorganic mercury species are soluble in water and are extracted from the crude oil, as well as mercury in suspension.

The US Environmental Protection Agency analyzed the total mercury in desalter sludge from four US refineries (1996) obtaining concentrations of 0.01, 4, 39 and 41 ppm.[42]

In 2019, a study calculated the mass balance of mercury on two Korean oil refineries, that did not have mercury removal systems installed, finding that 4.5% and 33.2% of the mercury that entered these refineries ended up in the sludge out stream, whilst 3.1% and 5.6% left the facility in the wastewater effluent out stream.[43]

According to the UNEP Global Mercury Assessment 2018, 0.1% (0.56 tons) of the total mercury released to aquatic systems came from crude oil refining.[44]

[41] Wilhelm et al., Mercury in crude oil processed in the United States, 2004.
[42] Wilhelm et al., Mercury in crude oil processed in the United States, 2004.
[43] A.H.M. Mojammal, S-K. Back, Y-C. Seo, J-H. Kim, *Atmospheric Pollution Research.* 2019, **10** (1), 145 - 151
[44] AMAP/UN Environment, 2019. Technical Background Report for the Global Mercury Assessment 2018.

- ***Mercury in solid waste***

Removal of mercury from black crude oil is a process with many technical difficulties and is not carried out by many companies. Where this is carried out (9), a chemical is added to react with elemental and/or ionic mercury and precipitate the mercury as a solid, which is then removed by centrifugation/filtration. For oils, where the predominant form of mercury is mercury sulfide (solid), centrifugation/filtration alone may be an option for reducing the mercury content. This process generates mercury-containing solid waste.[45]

Furthermore, Mercury Removal Units (MRUs) may be used in crude oil refineries to remove elemental mercury from volatile fractions. Most of these MRUs capture mercury through chemical adsorption using sulfur or other chemicals that tend to bond to mercury.

The saturated adsorbent generates solid waste with high mercury concentrations that must be disposed of correctly.

In addition, refineries may use filters or other techniques to remove mercury and other trace contaminants from water and sludge to ensure that wastewater meets environmental standards prior to discharge or disposal.

In these cases, filters saturated with mercury also generate hazardous solid waste that contains high mercury concentrations. [46]

- ***Mercury in air emissions***

There is evidence of higher concentrations of atmospheric mercury in oil refineries and their surroundings.[47]

The study published by A.H.M. Mojammal (Atmospheric Pollution Research. 2019) calculated a mass balance of mercury on two crude oil refineries and found that 4.3% and 9.8% of the mercury that entered into these refineries was emitted to the atmosphere.[38]

According to the UNEP Global Mercury Assessment (2018), crude oil refining represented, in 2015, the 0.65% (14.4 tons) of the total emissions of mercury to the atmosphere.[33]

- ***Mercury in petroleum products***

Elemental mercury is a volatile compound, so it is expected to be found in the volatile fractions of the distillation.

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https://www.unenvironment.org/resources/publication/global-mercury-assessment-2018

[45] Qa3, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15.

[46] Wilhelm et al., Mercury in crude oil processed in the United States, 2004.

[47] X. Lan, R. Talbot, P. Laine, A. Torres, B. Lefer, and J. Flynn. *Environ. Sci. Technol.* 2015, **49**, 10692−10700

However, inorganic mercury (that has not been removed during desalting) is expected to be found in the petroleum coke.

The previously mentioned study on two crude oil refineries in Korea (A.H.M. Mojamma, *Atmospheric Pollution Research.* 2019) calculated a mass balance of mercury and found that 42.6% and 39.5% of the mercury that entered into these refineries ended up in the products.[16]

A summary of mercury content in various oil products can be found in table 6.

A study performed in South Korea, in 2007, suggests that mercury present in gasoline and diesel is emitted into the air by motor vehicles.[48]

According to the 2018 UNEP Global Mercury Assessment, domestic combustion of oil (houses and transport) represented 0.12% (2.7 tons) of total emissions of mercury to air in 2015, the industrial combustion 0.06% (1.4 tons) and the combustion in power plants 0.11% (2.45 tons).[49]

Table 6. *Summary of total mercury in refining products.*[50]

Reference	Type	Number of samples	Range (ppb)	Mean (ppb)	SD
Liang *et al.* (1996)	Gasoline	5	0.22-1.43	0.7	NR
Liang *et al.* (1996)	Gasoline	4	0.72-3.2	1.5	NR
Liang *et al.* (1996)	Diesel	1	0.4	0.4	NR
Liang *et al.* (1996)	Diesel	1	2.97	2.97	NR
Liang *et al.* (1996)	Kerosene	1	0.04	0.04	NR
Liang *et al.* (1996)	Heating Oil	1	0.59	0.59	NR
Bloom (2000)	Light distillates	14	NR	1.32	2.81
Bloom (2000)	Utility fuel	32	NR	0.67	0.96
Bloom (2000)	Asphalt	10	NR	0.27	0.32
Olsen *et al.* (1997)	Naphtha	4	3-40	15	NR
Tao *et al.* (1998)	Naphtha	3	8-60	40	NR
US EPA (2000)	Coke	1000	0-250	50	NR

- ***Mercury mass balance in crude oil distilleries***

The following Figure 4, from a IPIECA 2014 report, provides a simplified example of where diverse forms of mercury may distribute or accumulate in a crude refinery.

[48] J. H. Won, J. Y. Park, T. G. Lee. *Atmospheric Environment*, 2007, **41**, 7547–7552.
[49] AMAP/UN Environment, 2019. Technical Background Report for the Global Mercury Assessment 2018. https://www.unenvironment.org/resources/publication/global-mercury-assessment-2018bn
[50] Wilhelm et al., Mercury in crude oil processed in the United States, 2004.

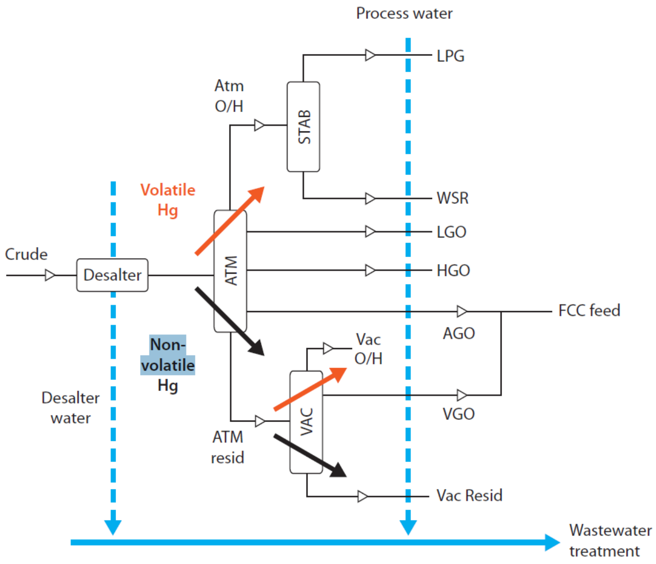


Figure 4: *The most common mercury distribution paths in hydrocarbons and water (IPIECA).* [6]

The mass balance of mercury analyses the different fates of mercury during the distillation process, considering the concentration of mercury in the crude oil entering the refining process, the presence of mercury in the final products, the mercury waste and mercury containing waste.

Due to the chemical properties of mercury present in crude oil, like its volatile nature and tendency to damage aluminum-based equipment form amalgams, some refineries have reported troubles[51] in closing a mercury mass balance, obtaining uncertainties of at least 30% (in other words, more than 30% of the mercury that entered the plant has an unknown fate).

Among others, one of the possible explanations for these high levels of uncertainty may be the accumulation in equipment and pipes due to adsorption processes or amalgam formation.[52]

In any oil refinery, the output of mercury (air, water, waste, and products) should be equal to the input. Otherwise, it is being accumulated in the systems of the installation and could cause accidents as explained in previous sections.

An estimation of the annual accumulation of mercury in refineries can be found in table 7.

[51] Fabian G. Lombardi, Axion Energy S.A., *Procesamiento de crudos con mercurio,* Petrotecnia.5, 2018.
[52] Fabian G. Lombardi, Axion Energy S.A., *Procesamiento de crudos con mercurio,* Petrotecnia.5, 2018.

Table 7. *Comparison of annual mercury accumulation for each range of concentration.*[53]

Potential annual accumulation			
Mercury in crude, µg/kg (ppb)	1	10	200
50,000 bbls/dat – “small refinery”	0.5 kg/year	5 kg/year	90 kg/year
250,000 bbls/dat – “large refinery”	2.5 kg/year	25 kg/year	450 kg/year

The internal surface of pipelines and process equipment in oil processing facilities are populated with active sites to which mercury may be adsorbed. The pipelines may accumulate mercury on their inner surface over the active lifetime of the plant. Upon decommissioning, if the presence of mercury is not taken into account, the regimens employed to discard old pipes and process equipment, such as heating and cutting of the metal into smaller manageable sections or smelting of the steel back into a recycled reusable form, could inadvertently release mercury into the environment.[54]

6. Mass of mercury potentially released from natural gas

Extraction

Similarly to crude oil, the main risk of mercury emission and release during natural gas extraction via conventional techniques is the generation of produced water, which is managed with similar techniques.

The extraction of natural gas by hydraulic fracture (fracking) presents a particular risk of mercury release into the environment due to the production of “flowback” water.

To facilitate the fracture of the shale and the release of natural gas, water with a low pH is injected into the ground. This acidic water facilitates the dissolution of salts that were previously trapped in the shale, including heavy metal salts.

During the extraction of natural gas, part of the injected water is also extracted, which is then called “flowback” water.[55] There is evidence in the literature that “flowback” water is rich in heavy metals and, in some cases, mercury, [56] [57] [58] [59] which may be released to the surrounding environment.

[53] *Mercury management in petroleum refining,* An IPIECA Good Practice Guide, 2014.
[54] *Qa3. Unconsidered Mercury Emissions from the Oil and Gas Industry. ANNUAL BUYERS GUIDE 2016.*
[55] C. J. Grant, A. K. Lutz, A D. Kulig and M. R. Stanton. *Ecotoxicology*. 2016. **25**, 1739–1750.
[56] S. J. Maguire-Boylea and A. R. Barron. *Environ. Sci.: Processes Impacts*, 2014, 16,. 2237–2248
[57] Support to the identification of potential risks for the environment and human health arising from hydrocarbons operations involving hydraulic fracturing in Europe. AEA/R/ED57281 Issue Number 11 Date 28/05/2012.
[58] Leff, E. Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program, Well Permit Issuance for Horizontal Drilling and High-Volume, Hydraulic Fracturing to Develop the Marcellus Shale and Other Low-Permeability Gas Reservoirs. New York State Department of Environmental Conservation: New York, NY, 2011.
[59] N. Abualfaraj, P. L. Gurian, and M. S. Olson. *Environmental Engineering Science*. 2014. **31** (9).

Flowback water storage tanks may not be safe enough, and this water can get in contact with surface water. One study that analyzed samples from Pennsylvania found higher concentrations of mercury in water and biota close to extraction sites by fracking.[60]

Transport

Natural gas is mostly transported by pipelines. Usually when transporting crude oil, mercury is not lost during the movement of fluid, but in the case of natural gas, elemental mercury reacts with steel and forms a mercury-rich layer on steel-pipes internal surfaces. [61]

This effect increases with natural gas humidity, and also with the presence of H_2S that acts as a catalyst in this process.

When natural gas is transported through long distances, an appreciable decrease in mercury concentration can be observed. The EPA 2001 report mentions the following example: “natural gas produced offshore that contains low mercury concentration (1-20 ppb) when measured at the wellhead, may not present any mercury at the processing facility initially”.

The accumulation during transport contaminates the equipment, and may represent a risk for workers in maintenance activities and produce mercury waste and mercury containing waste.

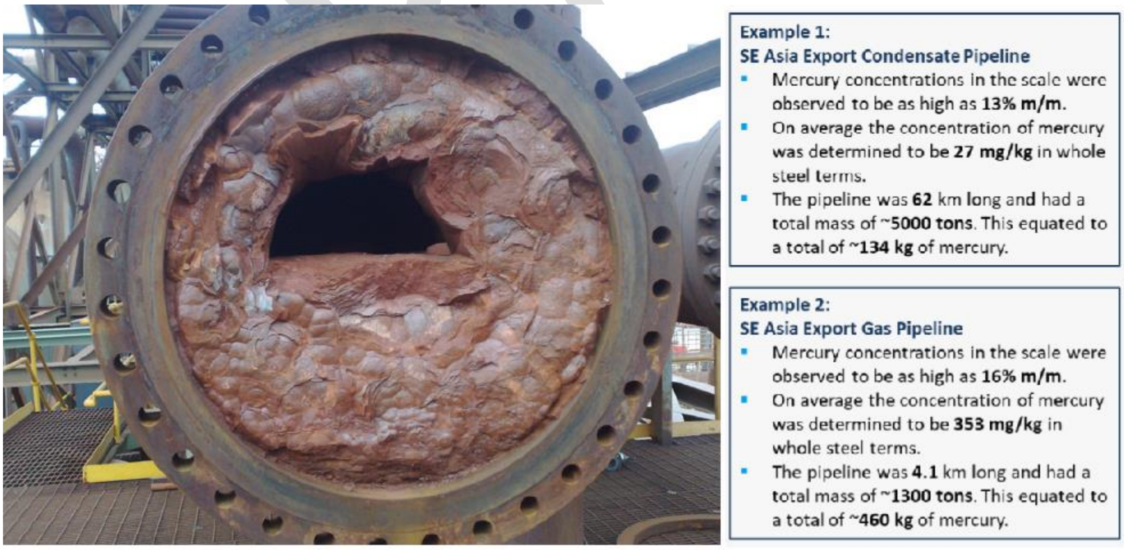


Figure 5. *Solid waste accumulated on the inner surface of a pipeline (left) and case studies (right). Data provided by Qa3.*

[60] C. J. Grant, A. B. Weimer, N. K. Marks, E. S. Perow, J. M. Oster, K. M. Brubaker, R. V. Trexler, C. M. Solomo 5 and R. Lamendella. *Journal of Environmental Science and Health, Part A.* 2015. **50**, 482–500.
[61] Wilhelm et al., Mercury in crude oil processed in the United States, 2004.

Processing

Natural gas processing is much simpler than crude oil processing and could be defined more accurately as a treatment and separation process, since chemical transformations are not expected to happen. The treatments are designed to remove unwanted impurities like water, carbon dioxide, hydrogen sulphide, and metals.

The first step of this process is the dehydration of the gas. The gas passes through an adsorbent material, usually dry triethylene glycol that captures the water. After that, the adsorbent is regenerated in a continuous process by increasing the temperature and evaporating the water.

Triethylene glycol, and other dehydration systems, can capture elemental mercury present in the natural gas, which is later evaporated during the regeneration process and emitted into the atmosphere or re-dissolved in the wastewater of the facility. Other cleaning processes like CO_2, H_2S and N_2 removal can also retain mercury in membranes and columns that will be liberated to the atmosphere eventually (case study 2).[62]

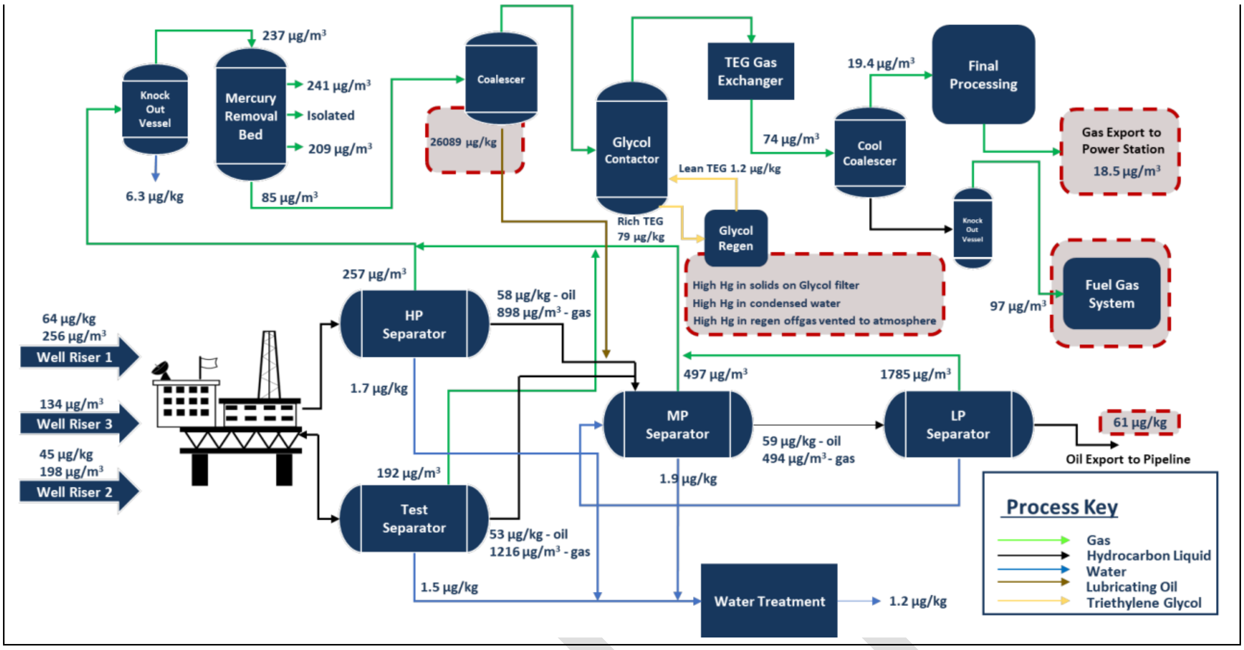
Case study 2 by Qa3[63]:

Region: South East Asia.

Type of Facility: Offshore production of oil and gas where MRB is located upstream in process.

Mercury Issues: Although this facility has the mercury removal located upstream in the process the MRB has become saturated allowing mercury to pass resulting in mercury contamination throughout the entire process leading to emissions from flaring, combustion of fuel gas and in export gas.

[62] Qa3 Unconsidered Mercury Emissions from the Oil and Gas Industry. ANNUAL BUYERS GUIDE 2016.
[63] Qa3, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15.



The separation process for natural gas products typically takes place using cryogenic techniques, which have an inherent risk of condensation of elemental mercury in the systems if the concentration of mercury is sufficiently high.[64]

Such condensation occurs in gas separation plants that have a content of mercury in feeds higher than 10–20 µg/m^3.

Mercury can also react with the aluminum (liquid metal embrittlement and amalgam corrosion) present in some heat exchanger systems, altering the properties of the material.

Liquefied natural gas (LNG) plants and many natural gas separation plants encounter problems associated with mercury condensation and reduce mercury attack of aluminum, both of which may cause severe accidents (see figure 3).[65]

They then use removal techniques, described under chapter 7.

The out-stream gas that leaves the MRUs usually has a mercury content of less than 1 µg/m^3.[66] The saturated adsorbent material of the MRUs is a source of solid waste with a high mercury concentration, which must be disposed of correctly.

[64] Qa3, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15.
[65] Wilhelm et al., Mercury in crude oil processed in the United States, 2004.
[66] SPE International. Mercury monitoring and removal at gas processing facilities. 2007.

Figure 6. *Metallurgical failure caused by mercury in a gas processing facility (IPIECA).*

The risk of atmospheric emissions during gas processing is also present, especially in the refineries and surroundings, which represents a health risk for workers. For example, a study showed that the atmospheric mercury concentration in the surroundings of a natural gas processing facility in Egypt is higher than average with a maximum value of 212 ng/Sm^3 in the condensate tank area.[67]

Products

Mercury can be present in the final products derived from natural gas, as shown in the case study 3. According to the 2018 UNEP Global Mercury Assessment, the combustion of natural gas in houses and transport represented, in 2015, 0.01% (0.16 tons) of total emissions of mercury, industry represented 0.01% (0.16 tons) and power plants 0.02% (0.33 tons).[68]

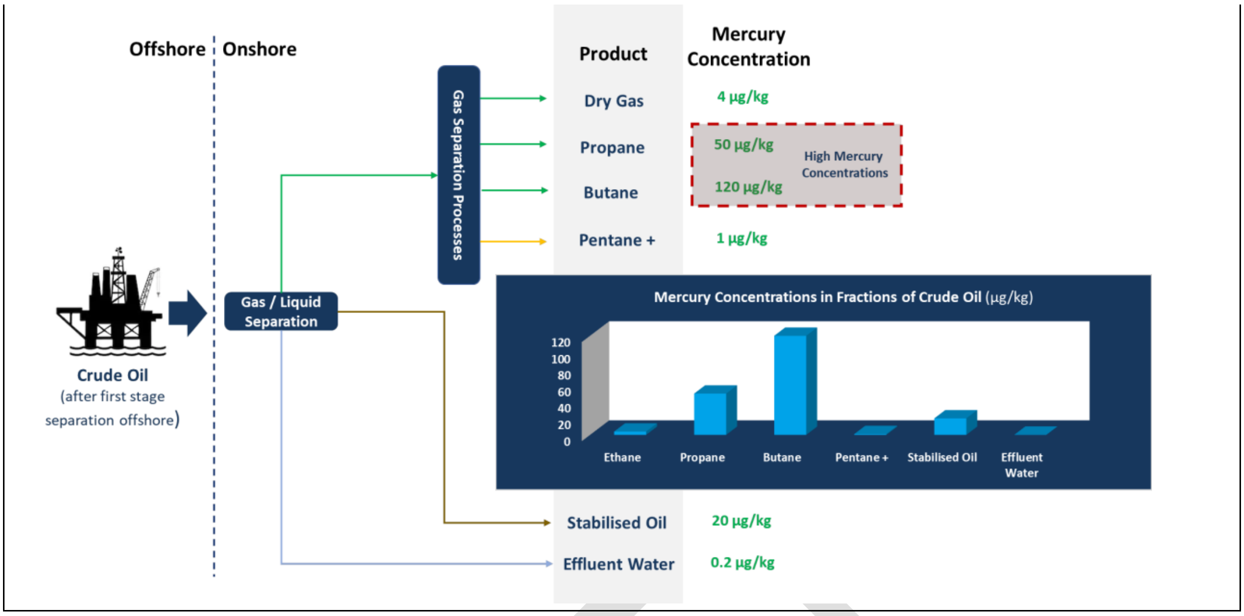
Case study 3 by Qa3[69]:

Region: Europe

Type of Facility: Gas Separations and Fractionation Plant (methane already removed by upstream processing, remaining gas removed from oil and separated into individual products; ethane, propane, butane, pentane).

Mercury Issues: This case study demonstrates the partitioning of mercury into the LPG fraction during fractionation of gas.

[67] A.A. El-Fekya, W. El-Azaba, M.A. Ebiada, M. B. Masoda, and S. Faramawya. *Journal of Natural Gas Science and Engineering. 2018.* **54**. 189–201
[68] UNEP. Global Mercury Assessment. 2018. https://www.unenvironment.org/resources/publication/global-mercury-assessment-2018
[69] Qa3, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15



7. Techniques used to remove mercury from crude oil and natural gas

Presence of mercury in crude oil and natural gas in processing plants

As mentioned above, mercury exists in varying concentrations in natural gas and crude oils extracted from different basins in all regions around the world.

Even though mercury is present in crude oil and natural gas in trace concentrations, due to its tendency to form amalgams with other metals, it may accumulate in process equipment (especially in internal metal surfaces).

The accumulation may cause catalyst poisoning (reducing the efficiency of some processes), corrosion and embrittlement of equipment. This may lead to industrial accidents. As a result of the accumulation of mercury over time, old equipment may become mercury containing waste streams that require adequate end of life treatment.[70]

Due to its volatile nature, elemental mercury tends to concentrate in light fractions like liquefied petroleum gas (LPG, see case study 4) and naphtha, but it also reacts with some hydrocarbon’s compounds, like asphaltenes and can appear in heavier refinery cuts or fractions.

The distribution and speciation of mercury in crude oil and natural gas are modified according to the different conditions of the processes. This results in a certain distribution and concentration in the by-products along the processing flux and in the final products.

[70] Qa3, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15.

The contamination of the equipment and the mercury containing remaining residues constitutes a risk for refinery workers, in particular during a plant shutdown or maintenance procedure.

Mercury removal from crude oil

Although removal of mercury from black crude oil is not straightforward and is not carried out by many companies, mercury is sometimes monitored in crude oil when entering in refineries plants. As a general rule, according to IPIECA's Good Practices Guidelines: [71]

- "The mercury content of incoming crudes to refinery will be less than 10 ppb, on a month-average basis, and no individual crude should exceed 100 ppb".

These good practice levels are way below the average and maximum levels of mercury content found in crude oil from certain regions, in particular for Asia and South America (see section 4), hence calling for mercury removal from such crude oils before refining.

There is only one proven technology for the removal of mercury directly from crude oil and condensates, known as Mercury Removal Unit or MRU, which consists of beds typically filled with adsorbents.

Once these adsorbents are exhausted (saturated with mercury) they must be removed, transported, treated and disposed of as hazardous waste by a specialized and authorized treater.

Adsorbents may need to be exchanged "earlier" in cases where:

- the unit gets saturated with sulphur long before the maximum mercury absorption capacity is reached when the material is not only used as MRU but also as sulphur guard.
- the adsorbent becomes "wet" during operation and therefore loses its adsorption capacity, making a change out necessary before the material is really spent.
- the adsorbent material is changed during a vessel inspection[72].

There are also some processes that remove mercury from crude oil and natural gas within refineries. Many refineries have removal technologies to strip out undesirable chemical components that may reduce the overall calorific value of the fuel, like CO_2 and/or N_2.

When this kind of removal is required, a membrane technology may be employed. In addition to CO2 and N_2, this technology would also remove mercury from the gas. This mercury may be emitted to the atmosphere as part of a continuous

[71] Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.
[72] Information provided by BATREC during consultation.

removal process and also when the membrane material is changed and replaced during maintenance.

Mercury removal from natural gas

As mentioned in chapter 6, processes for natural gas production are simpler than for crude oil as it only involves a separation of the raw material into commercial products: gas and natural gas liquids' (NGLs). It can be sold as gas (transported in pipelines) or liquefied (LPG) for sea shipping.

The process can be summarized in the following steps:

1. Prior to entering the refinery, the gas is treated to remove water using triethyleneglycol (TEG) or molecular adsorbents.
2. The gas is cleaned through acid gas scrubbers.
3. A mercury removal process may be included, in which case it will be deployed upstream of the cryogenic distillation stage.
4. Cryogenic distillation involves cooling the gas in an aluminum heat exchanger. The gas is then progressively heated through a number of heat exchangers, allowing the individual products to be boiled off and separated in towers.
5. The liquid product streams (condensate) are sent to petrochemical manufacturers or sold as LPG, while the gaseous product streams are sold to users as sales gas.

It was observed that solutions used for moisture and acid gas removal have affinity for mercury (see case study 2), allowing for the mercury to be removed from the gas during these processes.

There are amine-based systems usually used to remove acid gases from the gas mainstream. Mercury absorption into the amine system may occur, and this mercury can be emitted to the environment during amine regeneration and end up in the carbon dioxide vent stream where applicable.

The mercury removal process must be deployed upstream of the cryogenic distillation because mercury mostly deposits in the cryogenic equipment, cracking the aluminum heat exchangers.

More recently, with the development of mercury removal media that is more tolerant to the presence of water, many companies are choosing to place mercury removal beds upstream in the process ahead of acid gas removal and dehydration.[73] This could avoid generating mercury containing waste streams during moisture and acid gas removal (case study 4).

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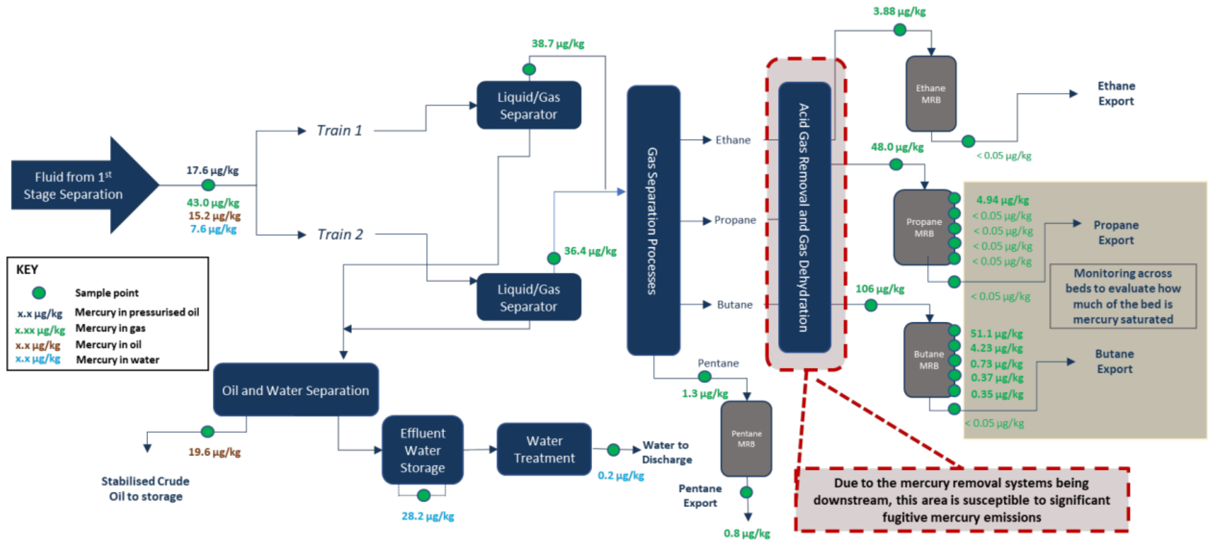
[73] Qa3, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15.

Case study 4 by Qa3[74]:

Region: Europe.

Type of Facility: Gas Separation and Fractionation Plant (methane already removed by upstream processing, remaining gas removed from oil and separated into individual products; ethane, propane, butane, pentane).

Mercury Issues: This case study shows a process with downstream MRB's and highlights the area in the process where there are often unconsidered emissions.



The disposal of the mercury collected by a mercury removal system (mercury waste) varies depending on the type of system used. Organic methods, or "non-regenerative sorbents" for removing mercury rely on the use of sulfur-impregnated activated carbon. The spent adsorbent is classified as hazardous waste, which must be treated in an environmentally sound manner.

D. Lang in his publication "Mercury arising from oil and gas production in the UK and UK continental shelf", 2012, indicates that this waste is *"stored or combusted to release the mercury.* If *the waste is combusted then mercury must be condensed, captured and disposed of".*

The inorganic methods involve regenerative mercury adsorbents, that utilize the high affinity of mercury for precious metals such as gold and silver. The unit is then regenerated by hot regeneration gas typically at temperatures around 290°C, with the cycle being repeated on a preset timeline depending on capacities. The mercury is removed from the main process stream and is

[74] Qa3, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15.

concentrated in the regeneration stream.[75] This stream may need other processes or a final disposal.

8. Fate *of mercury generated from oil and gas activities*

The oil and gas sector mobilizes, emits and releases mercury at different stages of its activity. The international policy/legal framework that deals with and establishes measures for this "anthropogenic" mercury is the Minamata Convention, which was adopted in 2013 and entered into force in 2017. The Minamata Convention contains provisions that relate to the entire life cycle of mercury and addresses issues of mercury supply, trade, uses, emissions, releases, storage and disposal, providing the framework for countries to take coordinated actions to reduce the concentration of this toxic metal in the environment. Below is a brief description of some provisions of the Minamata convention that could be of potential relevance to mercury generated from the oil and gas sector.

For instance, under Article 3 on Mercury supply sources and trade, paragraph 5, each Party shall endeavour to identify, amongst others, the sources of mercury supply that generate stocks exceeding 10 metric tons per year that are located within its territory. This provision could potentially involve the oil and gas sector. Information that may be provided by Parties in the context of this provision could contribute to further enhancing the global knowledge on mercury generated by the sector.

While article 8 on "Emissions" establishes measures to control and where feasible reduce mercury emissions to the atmosphere from the point sources falling within the source categories listed in Annex D (which does not include the oil and gas sector), Article 9 on "Releases" focuses on measures to reduce mercury emissions to water and soil from the relevant point sources not addressed in other provisions of this Convention.

Article 11 of the Minamata Convention, which addresses "Mercury waste", calls for collaboration with the Basel Convention: in its paragraph 2 on the definition of relevant thresholds and in its paragraph 3 on measures to be adopted for the environmentally sound management of mercury waste, taking into account the guidelines developed under the Basel Convention[76] (last guidelines adopted in 2015 and currently under review).

[75] Saeid Mokhatab et. al., *Handling mercury in gas processing plants*, Digital Refinfing, May 2017.

[76] The Conference of the Parties to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal adopted at its twelfth meeting the "Technical guidelines for the environmentally sound management of wastes consisting of elemental mercury and wastes containing or contaminated with mercury" (Decision BC-12/4), which it decided at its fourteenth meeting to update (Decision BC-14/8)

Mercury in aqueous waste

The mercury present in wastewater is mostly in suspension (as insoluble mercury sulphide) or associated to suspended particles.

Refineries use conventional wastewater treatments that can capture this mercury, generating solid waste with a high mercury concentration that requires sound disposal.[6]

A review published in 2019 provides an overview of methods used in the treatment and disposal of petroleum sludges, amongst which incineration, stabilization/solidification, oxidation and biological treatment.[77] None of the techniques mentioned in this publication addresses the presence of mercury in the sludge nor the prevention of its release to the environment. These practices are not the best available techniques for the treatment of mercury-containing waste.

Mercury in solid waste

Mercury Removal Units (MRUs) - used to capture mercury from natural gas or certain fractions in crude oil refineries - are based on adsorbent materials that are saturated with mercury after some months or years of use.

Some MRUs are designed to last for the whole life cycle of the processing plant, while for others there is a need to replace the adsorbent material every few months or years. The saturated adsorbent material contains 3–7% mercury by weight. Such waste contaminated with mercury, according to the Technical Guidelines on the Environmentally Sound Management of Waste Consisting of, Containing or Contaminated with Mercury or Mercury Compounds of the Basel Convention (Table 3) require environmentally sound treatment and disposal.[78]

There is very little information available in scientific databases and reports from the industry about the fate of the solid waste with a high mercury content, which comprises saturated wastewater filters, sludge from maintenance and cleaning operations and saturated adsorbent from MRUs.

This hazardous waste should be managed by specialized and certified operators as indicated by IPIECA in its guideline (Mercury management in petroleum refining). Providers of MRUs and adsorbent materials may also offer a service which includes the sound disposal of the adsorbent material at the end of their useful life as hazardous waste.[79]

[77] O. A. Johnson, and A. C. Affam. *Environ. Eng. Res.* 2019, **24**(2), 191-201.
[78] Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with mercury or mercury compounds. UNEP/CHW.12/5/Add.8/Rev.1
[79] Johnson Matthew. Handling mercury in gas processing plants. 2017

The “Catalogue of Technologies and Services on Mercury Waste Management” developed by the UNEP Global Mercury Partnership Area on Mercury Waste Management lists some of these waste management operators that treat waste from the oil and gas sector and are members of the Partnership[80].

The Swiss company BATREC indicated (interview organized during the development of this report) that in their facility, 1000 to 2000 tons/year of material can be treated per furnace (3 furnaces in operation) originating from gas processing facilities, mostly as saturated adsorbent from MRU, and that they typically receive approximately 500 tons of material per year[81]. In the process developed by the company, mercury recovered from the treatment of the solid waste is stabilized as mercury sulphide and sent to salt mines for final storage.

In order for mercury from oil and gas extraction and processing to enter the formal or informal market, it should first be extracted from solid waste. Qa3 calculated that about 420 tons of mercury were obtained each year as a by-product from natural gas and liquified petroleum gas production, mostly as part of the solid waste stream.[82] It is however difficult to assess how much of this mercury may be entering the market, including because facilities that treat waste from oil and gas also treat mercury waste from other sources. According to BATREC, a fraction of mercury containing solid waste is treated in specialized facilities. In addition, the complexity of the process and the required (expensive) equipment make it difficult to address such waste locally.

Mercury in oil and gas products

Unlike for the products used by chemical and pharmaceutical companies, there is less incentive to remove mercury from oil and gas products that will be used for combustion, as this use can tolerate higher levels of trace contaminants.

The mercury present in the different fuels will be released to the atmosphere as elemental mercury after its combustion in vehicles and heaters.

The fact that automobiles emit mercury at ground level where people get direct exposure should be considered as an important factor.[83] [84] In 1997, the US Environmental Protection Agency estimated the amount of mercury that was emitted to the atmosphere from combustion of Distillable Fuel Oil (DFO) and Residual Fuel Oil

[80] https://wedocs.unep.org/bitstream/handle/20.500.11822/27819/WMA_catalog.pdf?sequence=1&isAllowed=y

[81] The treatment consists in the roasting / thermal treatment (700 - 850 °C) of the material with the aim of vaporizing the mercury contamination and obtaining elemental mercury in a subsequent condensation step. The recovered mercury is then stabilized to form mercury sulphide, which is subsequently packed for transport and permanent storage in salt mines in Germany.

[82] Matthew Kirby et al., Unconsidered Mercury Emissions from the Oil and Gas Industry. Qa3. 2021

[83] J. H. Won, J. Y. Park, T. G. Lee. Atmospheric Environment, 2007, 41, 7547–7552.

[84] M. S. Landis, C. W. Lewis, R. K. Stevens, G. J. Keeler, J. T. Dvonch, R. T. Tremblay. *Atmospheric Environment*. 2007. **41**. 8711–8724.

(RFO) in domestic and industrial boilers in this country. It concluded that in that year, 11 tons of mercury were emitted as a result of the combustion of RFO and DFO. [85]

Table 8. *Estimation of mercury emissions by combustion of fuel*

Boiler	**Btu/year (10^{17})**	**Fuel type**	**Fuel Oil Amount (10^{10} L/year)**	**Emission Factor (kg/10^{13} Btu)**	**Hg (kg/year)**	**THg in fuel (ppb)**
Utility	840	RFO	2.4	0.24	200	10
Industrial	2,178	RFO/DFO	6.2	3.09/3.27	7,000	100
Residential	890	RFO/DFO	2.5	3.09/3.27	2,900	100
Total					**10,100**	

Other sources of mercury: Pipelines and decommissioning facilities

The replacement of pipelines that may have accumulated mercury and the decommissioning of entire facilities and tankers generate mercury-containing waste that must be correctly disposed of, otherwise this mercury will be released to the environment. It is estimated that 20 % of mercury present in Oil and Gas is accumulated in the processing facilities.[26]

Mercury can be separated from pipelines and equipment by cleaning them (scrubbing and scrapping) at the location of the facility. This process generates sludge with high content in mercury that must be treated by specialized companies. According to Qa[3], there are three end of life options for pipelines used in off-shore natural gas extraction: leaving them in situ on seabed, leaving them in situ on seabed after cleaning or sending them smelting. [86]

[85] U.S. EPA, 1997. Mercury Study Report to Congress, EPA/452/R-97/003 (NTIS PB98-124738), Office of Air Quality Planning and Standards,

[86] Qa3, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15.

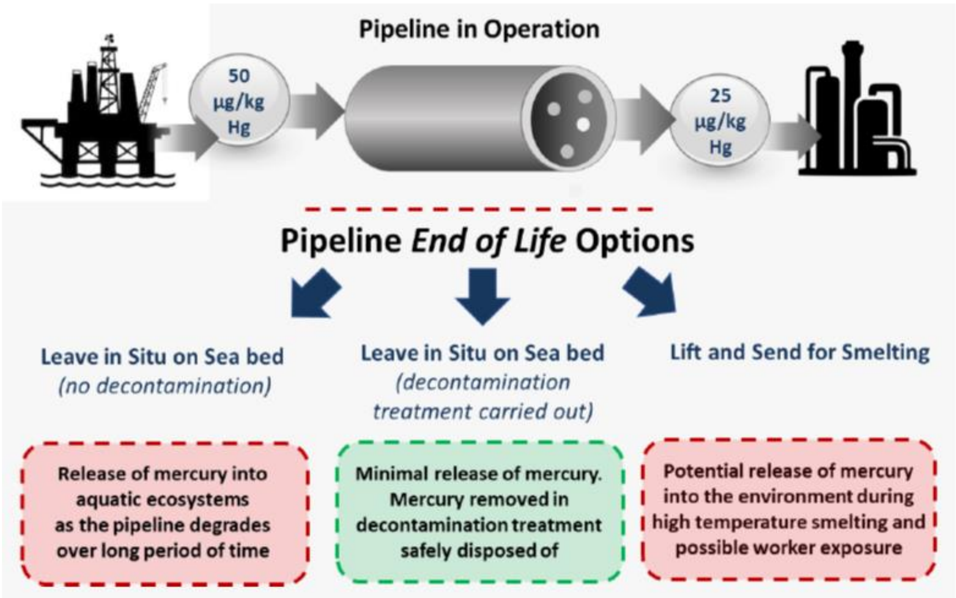


Figure 7. *Fate of pipelines used in off-shore natural gas extraction. Image provided by Qa3.*

9. Initial ideas for further research and cooperation

Standards for the determination of mercury in crude oils were first developed by the American Society for Testing and Materials (ASTM International Standards) in 2010, providing the means to quantitatively determine the amounts of mercury in crude oils.[87]

Mercury present in crude oil and natural gas, due its nature and the processes involved (during extraction, refining, transport and decommissioning of infrastructures) is released and emitted in different proportions and stages of the industrial operations.

The following would contribute to better understanding and assessing mercury emissions and releases from crude oil and natural gas:

- Monitor in a systematic, standardized, comparable and multicentric way the whole process.
- Complete the mass balance in the most accurate way.
- Promote information exchange on mercury determination and sampling methods where mercury is known to be emitted and released to the environment from gas processing plants and oil refineries.
- Facilitate the access to information on the production and fate of mercury waste and mercury containing waste flow, especially in crude oil and natural gas deposits and/or regions where mercury concentrations are known to be

[87] Determination of Mercury in Crude Oil Is Covered in New ASTM Petroleum Standards

higher (fate of the saturated adsorbent from mercury removal systems as well as from filters, pipeline pigging activities and others).

The following would support the implementation of measures to reduce or eliminate mercury emissions and releases from the sector:

- Identify, monitor and assess mercury waste and mercury containing waste volumes generated by the sector.
- Understand and track the fate of such waste.
- Spread information on best available practices as well as best environmental technologies.
- Improve the capacities of the concerned facilities to process mercury and mercury containing waste and safely dispose it off.
- Strengthen human and technical capacities, and collaboration needed to facilitate the identification and evaluation of mercury emissions and releases from oil and gas all along its value chain.

It is important to highlight that there is also a need for guidelines dissemination to support the implementation of best available technologies and best environmental practices for the removal of mercury from oil and gas at the different stages of the process.

In relation to worker's protection, while several guidelines aim to prevent chemical toxic exposure and codes of practice for the control of occupational exposure to mercury, none appear to focus specifically on workers exposure to mercury in the petrochemical industry.

From the present study, these objectives remain far from being achieved. To carry out this task in a coordinated and transparent manner, enhanced cooperation amongst relevant players would contribute to the further development and dissemination of BAT/BEP on mercury in the oil and gas industry as well as enhanced understanding of the topic.

The Global Mercury Partnership and its Partnership areas, including on “mercury air transport and fate research”, “mercury supply and storage” and “mercury waste management” may offer a multi-stakeholder and multisectoral platform for dialogue and cooperation. It may contribute supporting an enhanced overview of mercury along the different stages of the oil and gas value chains, including its fate and transport, measurement techniques and the species of mercury found; as well as facilitating information and experience sharing on the topic of mercury from oil and gas and best practices for its environmentally sound management.

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