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UNEP Global Mercury Partnership Advisory Group Thirteenth meeting 9 and 10 November 2022, Paris (France) and online

#### Study report on mercury from oil and gas for consideration by the Global Mercury Partnership Advisory Group at its thirteenth meeting

#### Note by the secretariat

1. The Partnership Advisory Group (PAG) decided at its tenth meeting (Geneva, 23 November 2019) to initiate work on mercury from oil and gas.

In follow up to expert consultations which gathered interested partners and stakeholders in 2. April 2020, Partnership Area leads agreed to guide a process for developing a study report with the aim, amongst others, to better understand potential releases of mercury from the sector, as well as possibly how wastes are treated and accounted for and may be entering the market for other uses. As per the leads guidance, the report could also distinguish the key differences between oil and natural gas related information, and therefore address them separately and identify the differences in the presence and management of mercury in the respective sectors. 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; and finally initial ideas for further research and cooperation.

3. The development of the study report benefitted from a consultative process, involving experts from governments, intergovernmental organizations, civil society, academia and the private sector, members of the Partnership as well as from other relevant organizations. Further background on the development of the report may be found on the website of the Partnership.<sup>1</sup>.

4. The final version of the study report is attached to the present note for consideration by the PAG at its thirteenth meeting and discussion on possible next steps.

<sup>1 /</sup>www.unep.org/globalmercurypartnership/

## UNEP GLOBAL MERCURY PARTNERSHIP



# NERCURY FROM OLD GAS

# UNEP GLOBAL MERCURY PARTNERSHIP STUDY REPORT **MERCURY FROM OIL AND GAS**



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The present study report has been developed in the context of the United Nations Environment Programme (UNEP) Global Mercury Partnership (hereinafter referred to as "the Partnership"). Established in 2005, the Partnership aims to protect human health and the environment from the release of mercury and its compounds to air, water and land. With over 200 partners to date from governments, intergovernmental and non-governmental organizations, industry and academia, the Partnership focuses its work on supporting the implementation of the Minamata Convention on Mercury, providing state-of-the-art knowledge and science and raising awareness towards global action on mercury.<sup>1</sup>

The Partnership Advisory Group (PAG) decided at its tenth meeting, held in Geneva on 23 November 2019, to begin work on the subject of mercury from oil and gas, which it had identified as cross-cutting between different Partnership areas. In follow-up to expert consultations in April 2020, Partnership area leads agreed to oversee a process for developing a study report, with a view to better understanding how mercury can be released, in addition to how waste is treated and accounted for and how it may enter the market for other uses. As per the leads' guidance, the report could also identify the key differences between oil- and natural gas-related information, and thereby address the issues separately in order to determine the differences in the presence and management of mercury in the respective sectors.

The guidance provided also indicated that the report could include: a review of existing knowledge and gaps in understanding of mercury content, emissions and releases; relative geographic mercury concentrations; waste flow and treatment during each stage of the oil and gas processes, including the decommissioning of infrastructure on both onshore and offshore sites; available information on the ways in which mercury from the sector may potentially enter the market for other uses; if available, information on the quantities of mercury that may be entering the market; information on the presence of mercury when using new extraction techniques for non-conventional gas, such as shale gas through fracking; a review of the different methods used, highlighting best practices for reducing the frequency of mercury releases, for waste treatment (including treatment at dismantling yards for the decommissioned infrastructure that may contain mercury) and for detecting and monitoring mercury releases; and ideas of avenues to be explored for further research and cooperation.

The International Society of Doctors for the Environment (ISDE) was commissioned to draft the report, under the overall coordination of Lilian Corra (ISDE). The study report benefitted from the input of partners of the Partnership as well as experts and stakeholders from various organizations and backgrounds; the drafting process was a consultative one involving experts from governments, the private sector, civil society, academia and intergovernmental organizations, members of the Partnership and other relevant organizations. Experts provided input into the preparation of the study report. They gave feedback on the draft and the annotated outline of the report, invited comments and held an expert consultation in May 2021. UNEP would like to acknowledge the financial contribution from the Government of Sweden which allowed this work to be carried out.

<sup>&</sup>lt;sup>1</sup> For more information, please visit: <u>www.unep.org/globalmercurypartnership</u>



The UNEP Global Mercury Partnership wishes to thank all individuals and organizations that have contributed their expertise, time and energy to this work, in particular the International Society of Doctors for the Environment (ISDE), commissioned to draft the report, under the overall coordination of Lilian Corra (ISDE), with the support of Carlos M. López-Alled (Tragsatec, Ministry for the Ecological Transition and the Demographic Challenge of Spain) and Gaspar Corra (Argentine Society of Doctors for the Environment - AAMMA). Special thanks are also extended to Ana García (Ministry for the Ecological Transition and the Demographic Challenge of Spain) and Judith Torres (Ministry of Housing, Territorial Planning and Environment of Uruguay), co-leads of the Partnership Area on Supply and Storage, for taking into consideration the concerns generated by the issue of "mercury in the oil and gas sector" and highlighting to the Partnership Advisory Group the need to fully understand the reality and consequences of the mercury mobilized and released from this sector.

The Partnership also wishes to thank the co-chairs of the Partnership Advisory Group, Rodges Ankrah (Environmental Protection Agency of the United States) and Teeraporn Wiriwutikorn (Ministry of Natural Resources and Environment of Thailand) as well as the co-leads of the Partnership Areas on Mercury Air Transport and Fate Research, Celia Chen (Dartmouth Toxic Metals Superfund Research Program, Dartmouth College), Nicola Pirrone (Institute of Atmospheric Pollution Research, National Research Council of Italy), David Evers (Biodiversity Research Institute), and on Mercury Waste Management, the Ministry of the Environment of Japan and Misuzu Asari (Graduate School of Global Environmental Studies, Kyoto University) for their guidance and support.

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# Executive summary – Key highlights

The present study report has been developed in the context of the United Nations Environment Programme (UNEP) Global Mercury Partnership (hereinafter referred to as "the Partnership"). Established in 2005, the Partnership aims to protect human health and the environment from the release of mercury and its compounds to air, water and land. Mercury is an extremely harmful pollutant which, owing to its toxicity, long-range mobility, and persistence, poses a global threat to human health and to the environment. Not only can mercury cause localized harm, to which children and pregnant women are especially vulnerable, through airborne emissions or soil and water contamination, but it can also travel long distances through the air and be widely dispersed across the globe. Mercury is a trace element in the Earth's crust, often found as cinnabar (mercuric sulphide), which may be found in all fossil fuels, including oil and natural gas, at varying concentrations. Mercury contained in oil and gas may enter the environment through various pathways and at different stages of various processes, including the decommissioning of oil and gas infrastructure. A fraction of the mercury released may be captured, for operational, health and environmental reasons, among others, and subsequently treated as waste. However, practices around the world vary and a comprehensive overview of the extent of uncontrolled releases into the environment is still lacking.

This report, aims to present a compilation of available knowledge on the life cycle of mercury in crude oil and natural gas, to better understand the behaviour and emission and release pathways of mercury, particularly during the extraction, processing, management and waste disposal stages, and to illustrate various technologies for controlling the releases. It has been compiled from expert consultations and open access sources of information in order to present a critical review of existing knowledge and information gaps concerning mercury from oil and gas, to showcase the different reduction methods, and to provide relevant suggestions for further work including research and cooperation. It is intended for stakeholders from governments, intergovernmental and non-governmental institutions, industry, academia and any other interested parties.

## Key highlights

Crude oil and natural gas are composed of hydrocarbons and contain various elements, including mercury, which may be emitted or released at various stages of oil and gas processing and use. In the absence of adequate control measures, mercury may not only impact processing systems (for example by damaging equipment and contaminating chemical processes and wastewater), but also pose serious health risks to operators exposed to elemental mercury vapour or organic mercury in the workplace.

Mercury can be emitted and/or released at various stages of the life cycle of crude oil. Release of mercury into the environment during extraction arises mainly through discharge of wastewater that may contain mercury. In 2016, the International Petroleum Industry Environmental Conservation Association (IPIECA) estimated that 13.5 tons of mercury were released per year into the environment from extraction water. Mercury can also accumulate with sludge in crude oil storage tanks. During processing, the fate of mercury varies depending on, among other factors, the type of facility, the composition of the crude oil and the processing methodology adopted. Mercury concentrations in crude oil and natural gas also vary according to the timeline of the analysis: an on-site analysis carried out after gas removal would show a much higher mercury concentration than a sample taken after transporting the oil to an onshore laboratory, owing to evaporation or precipitation of some of the mercury.

According to the 2018 UNEP Global Mercury Assessment, 0.1% (or 0.56 tons) of the total mercury released into aquatic ecosystems and 0.65% (14.4 tons) of the mercury emitted into the atmosphere comes from crude oil refining, while domestic inputs account for 0.12%, industrial combustion for 0.06% (1.4 tons) and combustion in power plants for 0.11% (2.45 tons). The report highlighted, however, that the process of oil and gas extraction, as is the case for other sources of mercury emissions, is one that is currently difficult to quantify on a global scale. This is largely due to the lack of comprehensive activity data and emission factors for the wide variety

of processing technologies. The report further indicated a general lack of knowledge on mercury content, removal efficiency and the risk of releases into the environment.

There is a significant risk of mercury release into the environment during the extraction of natural gas owing to the injection of low-pH water resulting in the dissolution of heavy metal salts. The water that is then extracted has been identified as rich in heavy metals, including mercury. Mercury can also be released during the transport of natural gas, or it can form mercury sulphide on the inner surface of the pipeline. This accumulation of mercury during transport is a source of contamination not only for the equipment, but also for the workers responsible for the pipeline and the waste produced. During processing, elemental mercury may also be emitted into the atmosphere or dissolved in the wastewater produced. Use of the finished product may also result in mercury emission and/or release.

Mercury distribution, emissions and releases at various stages of oil and gas refining depend on several physical-chemical conditions such as temperature, pressure and reactivity in the presence of other chemicals. Accumulation of mercury and/or its amalgams, formed with other metals, on the inner surfaces of processing equipment may reduce process efficiency through corrosion and embrittlement of the equipment. Used equipment therefore becomes mercury-contaminated waste that requires appropriate management.

Based on current knowledge, the following recommendations were formulated:

- Progress still needs to be made regarding mercury removal from crude oil. According to IPIECA, good
  practices include the removal of mercury before the refining stage for concentrations below 100 parts
  per billion (ppb) and during refining for concentrations exceeding 100 ppb. In the case of natural gas, this
  removal could be carried out before the cryogenic distillation stage to avoid the accumulation of mercury
  in the cryogenic equipment. Existing technologies for mercury removal in crude oil include mercury
  removal units (MRUs) on condensates, filtration, chemical addition and filtration through MERCAWAY
  technology, as well as decomposition and adsorption.
- Reduction in mercury emissions and releases from crude oil and natural gas processing would require a strengthening of facilities, human and technical capacities to ensure sound processing, as well as appropriate management and disposal of mercury-containing waste.
- Steps for maintenance and inspection should be carefully planned in order to limit the emission and release of any mercury accumulated in separators and heat exchangers.

A number of priority areas would benefit from further research in order to better understand the fate of mercury in crude oil and natural gas. These priority areas include (i) the monitoring of mercury in life cycles of both crude oil and natural gas; (ii) a greater attention to the mass balance; (iii) the identification and promotion of best available approaches for taking samples and determining mercury concentrations; (iv) gathering additional information on the production and fate of mercury waste and mercury-containing waste flows in regions where concentrations are estimated to be higher in crude oil and natural gas and (v) enhanced access to information on mercury-containing waste resulting from the processing of crude oil and natural gas.

According to the report, the oil and gas sector is responsible for a significant portion of anthropogenic mercury emissions. The information available allowed for a detailed study of the sector. However, the industry and countries alike are encouraged to make available additional information in order to study in greater depth the complete life cycle of mercury in this sector.



## 1. Introduction

"Mercury is a chemical of global concern owing to its long-range atmospheric transport, its persistence in the environment once anthropogenically introduced, its availability to bioaccumulate in ecosystems and its significant negative effects on human health and the environment", as stated in the first preamble of the Minamata Convention on Mercury.

Established in 2005 by a decision of the Governing Council of the United Nations Environment Programme (UNEP), 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, eliminating global, anthropogenic mercury releases. The goals of the Partnership are consistent with Article 1 of the Minamata Convention, which states that its objective is "to protect the human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds". With over 200 partners to date from governments, intergovernmental and non-governmental organizations, industry and academia, the Partnership focuses on supporting the timely and effective implementation of the Minamata Convention, providing state-of-the-art knowledge and science and raising awareness towards global action on mercury.

### Report development process

At its ninth meeting, held in Geneva on 18 November 2018, the Global Mercury Partnership Advisory Group (PAG) agreed to examine issues of potential interest, to carry out an analysis of the level of concern, available data and potential for input by the Partnership and to initiate work on mercury emissions resulting from the oil and gas sector.

At its tenth meeting, held in Geneva on 23 November 2019, the PAG requested that the Secretariat of the Partnership convene targeted discussions with interested partners and stakeholders on the issue of mercury from oil and gas. It had identified this issue as a cross-cutting one, for which the need for further information was recognized; the collaboration of the Partnership across various areas of work would facilitate the development of the necessary information, interventions and projects.

In response to this request, expert consultations were launched in April 2020, with the overall objective being to identify the potential for useful input by the Partnership, within the context of its mission and its existing areas of work. The meeting was attended by approximately 65 participants<sup>2</sup>, both partners and non-partners, and included representatives from governments, intergovernmental and non-governmental organizations, academia, the scientific community and the private sector.

#### Experts explored the following three aspects in their discussions:

- (1) Needs and challenges associated with the management of mercury in oil and gas production, distribution and infrastructure decommissioning,
- (2) Relevant existing work and guidance on best practices, and
- (3) Potential for input by the Partnership to support the promotion of best practices and make progress on the issue.

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 potential avenues of input for the Partnership were suggested, including an enhanced overview of mercury throughout each of the different stages of the oil and gas value chains, including the fate and transport of mercury, measurement techniques and the different species of mercury found. Another suggestion was that the Partnership could facilitate information and experience-sharing on mercury from oil and gas and best practices for its environmentally sound management.

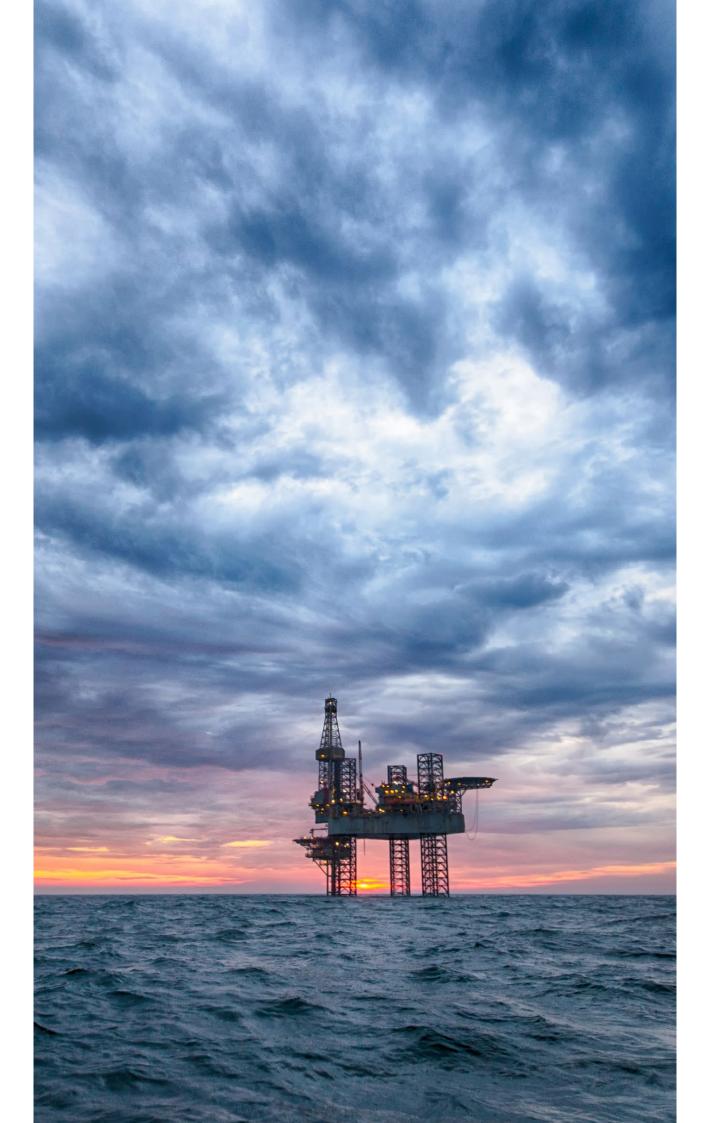
<sup>&</sup>lt;sup>2</sup> Approximately 57% of meeting attendees were men and 43% were women.

Interested Partnership area leads subsequently agreed to oversee a process for developing a study report on the topic of mercury in oil and gas.

## **Objective of the report**

The objective of this report is to analyse the life cycle of mercury in the oil and natural gas value chains and understand how this heavy metal, which is naturally present in oil and natural gas, may be released into the environment at different stages of the process, including the decommissioning of oil and gas infrastructure, and increase mercury concentrations in the environment, thereby presenting risks to human health and to ecosystems.

It also aims to assess waste management in the sector by identifying and analysing the quantities produced, the potential mercury emissions from the treatment phase, waste disposal and, where applicable, the impacts of mercury recovery and reuse in the market.



## 2. Mercury in oil and natural gas

### Current knowledge

The potential emissions and releases of mercury into the environment from crude oil and natural gas processing and use were discussed during the preparatory process of the Minamata Convention.<sup>3</sup>

The available information on the potential releases and emissions of mercury from different methods of processing and using crude oil and natural gas is limited, in terms of comprehensiveness or accessibility in the public domain. This may be impeding a good understanding of:

- emissions and releases into the environment during the extraction, production and decommissioning phases;
- mercury or mercury-containing waste from extraction or processing;
- occupational exposure;
- human exposure (even low-level chronic exposure may be particularly dangerous in early stages of human development).<sup>4</sup>

Emissions and releases of mercury can be harmful to human health and the environment. Owing to the persistence of mercury, it remains in the environment and the environmental pool of mercury grows over time.

Once present in the different environmental media – in air, water or soil – mercury can be carried long distances and can enter the food chain, becoming part of all living things and affecting the health and quality of life of humans, plants and animals.

Mercury is considered by the World Health Organization (WHO)<sup>5</sup> as one of the top ten chemicals or groups of chemicals of major public health concern.

It is well known that heavy metals are present in crude oil and natural gas at varying concentrations depending on the geological formation of the producing reservoir.<sup>6</sup>

The presence of mercury in crude oil and natural gas can cause problems for industry operators and can potentially have detrimental effects on processing operations, the environment and human health.

Although it is widely recognized that mercury may impact processing operations and affect the health of workers in the absence of adequate control measures,<sup>7</sup> few publications or investigations address the question in depth. The number of such publications and investigations is, however, increasing.

The main aim of most crude oil processing is to maximize gasoline output, while that of natural gas is to separate methane from other components. The outcome of both types of processing depends on the composition of the hydrocarbon mix and the market objectives.

The ability of mercury to form amalgams with other metals, to poison catalysts and to accumulate in processing equipment makes it likely to cause problems during the processing of oil and gas.<sup>8</sup>

The management of mercury-containing waste from petroleum processing can be a complex process, particularly in terms of separation, storage and disposal.<sup>9</sup>

It is important to take into consideration the difficulties of treating sludge deposits containing hazardous substances, contaminated liquids and mercury-containing sludge from water treatment systems, and mercury-

<sup>&</sup>lt;sup>3</sup> UNEP (DTIE)/Hg/INC.3/5.

<sup>&</sup>lt;sup>4</sup> <u>https://www.who.int/news-room/fact-sheets/detail/mercury-and-health</u>

⁵ ibid.

<sup>&</sup>lt;sup>6</sup> ibid.

<sup>&</sup>lt;sup>7</sup> Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.

<sup>&</sup>lt;sup>8</sup> <u>https://www.thermofisher.com/blog/metals/xrf-and-the-impact-of-mercury-in-the-oil-and-gas-industry/</u>

<sup>&</sup>lt;sup>9</sup> Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.

sorbent materials. There are also challenges associated with storing and processing for disposal. It is reported that storage or burial of such mercury-containing waste material is common in many remote locations, although these solutions are not recognized best practices and have major environmental impacts.<sup>10</sup>

In order to contextualize the issue of mercury in oil and gas, we must consider the magnitude and importance of the oil and gas industry. Over 85% of the world's energy comes from hydrocarbon resources, which include coal, crude oil and natural gas, the energy produced from the latter two accounting for approximately 55% of global energy consumption. Production reached an all-time high in 2019, with around 95.2 million barrels of oil being produced daily. This quantity includes crude oil, shale oil, oil sands and natural gas liquids (NGLs – the liquid recovered in the processing of natural gas), but not liquid fuels from biomass and coal derivatives.<sup>11</sup>

### Mercury affecting the oil and gas processing systems

The share of the oil and gas sector in global mercury emissions was previously considered to be very limited.<sup>12</sup> However, mercury has been receiving growing attention, and the optimization of the efficiency of oil and gas plants in addition to the tightening of environmental and health laws, have made mercury an important factor for many oil and gas process engineers.<sup>13</sup> In its 2014 Good Practice Guide entitled 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".<sup>14</sup>

Crude oil and natural gas are composed primarily of hydrocarbons. They also contain a wide range of elements such as mercury, arsenic and vanadium in varying concentrations depending on the reservoir, the stage of processing and how they are used.

Mercury can be found in three different chemical forms: elemental mercury, organic mercury and inorganic mercury, which can be found dissolved or suspended in or adsorbed on particulate material. Mercury, in its chemical forms, is present in crude oil and natural gas in low concentrations, between 0.1 and 20,000 ppb in crude oil and between 0.05 and 5,000  $\mu$ g per Nm<sup>3</sup> in natural gas, according to Lang (2012).<sup>15</sup>

As a natural constituent of crude oil and natural gas, mercury is detrimental to petroleum processing systems and, in certain circumstances, may expose workers to mercury concentrations that are dangerous to health.

In gas processing, mercury may contaminate and damage equipment such as cryogenic heat exchangers. In chemical manufacturing and refining, it may poison certain catalysts, contaminate process chemicals (such as triethylene glycol (TEG), which can be reused in gas processes) and also enter wastewater.

Technical difficulties caused by mercury in refineries are now well known and include equipment degradation, toxic waste generation and poisoning of catalysts. These difficulties are linked to the unequal distribution of mercury in vapour, oil, condensate and aqueous phases, depending on the pressure and temperature.<sup>16</sup>

### Occupational exposure

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

According to Qa<sup>3</sup>, "The biggest potential risk to workers arises during plant shutdowns or during service/ maintenance work when mercury that has accumulated on the internal surface of processing equipment via adsorption can be released into the atmosphere after depressurization of the system. This process is

<sup>&</sup>lt;sup>10</sup> Chalkidis, A. et al. (2019). 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.

<sup>&</sup>lt;sup>11</sup> Garside, M. (30 September 2020). Oil - global production 1998-2019. <u>https://www.statista.com/statistics/265203/global-oil-production-since-in-barrels-per-day/</u>

<sup>&</sup>lt;sup>12</sup> IPIECA Annual Review 2013-2014.

<sup>&</sup>lt;sup>13</sup> Subirachs Sanchez, G. (2013). Mercury in extraction and refining process of crude oil and natural gas, University of Aberdeen.

<sup>&</sup>lt;sup>14</sup> Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.

<sup>&</sup>lt;sup>15</sup> Lang, D. et al. (2012). Mercury arising from oil and gas production in the United Kingdom and UK continental shelf. IMKIP Oxford.

<sup>&</sup>lt;sup>16</sup> Lombardi, F. G. (2018). AXION ENERGY SA, Procesamiento de crudos con mercurio, Petrotecnia.5.

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 be above the occupational exposure limit (OEL). The OEL for mercury varies from region to region but is typically in the range 20-50 µg/m<sup>3.<sup>717</sup></sup>

When processing hydrocarbons containing mercury (with the total mercury concentration being above a few ppb<sup>18</sup>), cleaning and inspections must be carefully planned in order to handle the accumulation of mercury deposits in equipment such as separators and heat exchangers.

Mercury concentrations in vapour can be much higher in vessels than in the process stream owing to accumulation mechanisms including adsorption on equipment surfaces and dissolution in sludge.

Chemical exposure during maintenance could be several times higher than that of normal work routines. During comprehensive turnaround (TA), workers could have significant exposure.<sup>19</sup>

Other potential sources of exposure are decontaminated units, when measuring concentrations of toxic chemicals, and wastewater drained in the water treatment system.<sup>20</sup> 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.<sup>21</sup>

Based on the existing literature review, the above-mentioned situations are not isolated cases, but are rather representative of concerns about occupational exposures.

Organic mercury, while not originally present in oil and gas, can be created by bacterial conversion when released into the environment. It is estimated to be many times more toxic than elemental mercury on an equivalent weight basis. Dermal absorption efficiencies for elemental mercury in vapour are typically lower than 3% of the absorbed dose but must nonetheless be strictly avoided.<sup>22</sup>

In working areas, mercury presence in vapour shows considerable variation depending on the temperature and convection, highlighting the importance of monitoring as part of an overall surveillance programme to understand the source and concentration of chemicals of concern.<sup>23</sup>

The combination of dietary, environmental and occupational mercury can cause total exposure to exceed the threshold of chronic damage. 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. Therapies are mostly palliative.

Prevention is therefore critical, along with raising awareness 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).

<sup>&</sup>lt;sup>17</sup> Qa<sup>3</sup>. Unconsidered Mercury Emissions from the Oil and Gas Industry. ANNUAL BUYERS GUIDE 2016.

 <sup>&</sup>lt;sup>18</sup> Muadchim, M. *et al.* (2018). Case study of occupational mercury exposure during decontamination of turnaround in refinery plant.
 <sup>19</sup> ibid.

i ibid.

<sup>&</sup>lt;sup>20</sup> 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.

<sup>&</sup>lt;sup>21</sup> Muadchim, M. et al. (2018). Case study of occupational mercury exposure during decontamination of turnaround in refinery plant.

<sup>&</sup>lt;sup>22</sup> WHO (2003). Elemental mercury and inorganic mercury compounds: Human health aspects. Geneva. <u>https://apps.who.int/iris/handle/10665/42607</u>

<sup>&</sup>lt;sup>23</sup> Gasmet, Emissions Monitoring Handbook.

#### Case study 1: "Escalante crude", Argentina<sup>24</sup>

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

Petroleum crudes have been identified in the Fueguina basin as containing mercury in high concentrations, up to 80 ppb.

Since 2009, the Campana refinery in Argentina has been receiving warnings, through external alerts and following crude assays performed on crude oil,<sup>25</sup> about the possible presence of mercury in the crude oil. High levels of mercury were detected in "Escalante" crude (the leading exported crude from Argentina).

This refinery installed low-concentration-mercury-detection equipment in order to monitor mercury levels during the process and in commercial products.

According to the monitoring outcomes, the average mercury concentration, with predominantly Escalante crude being monitored, increased up to 25 ppb.

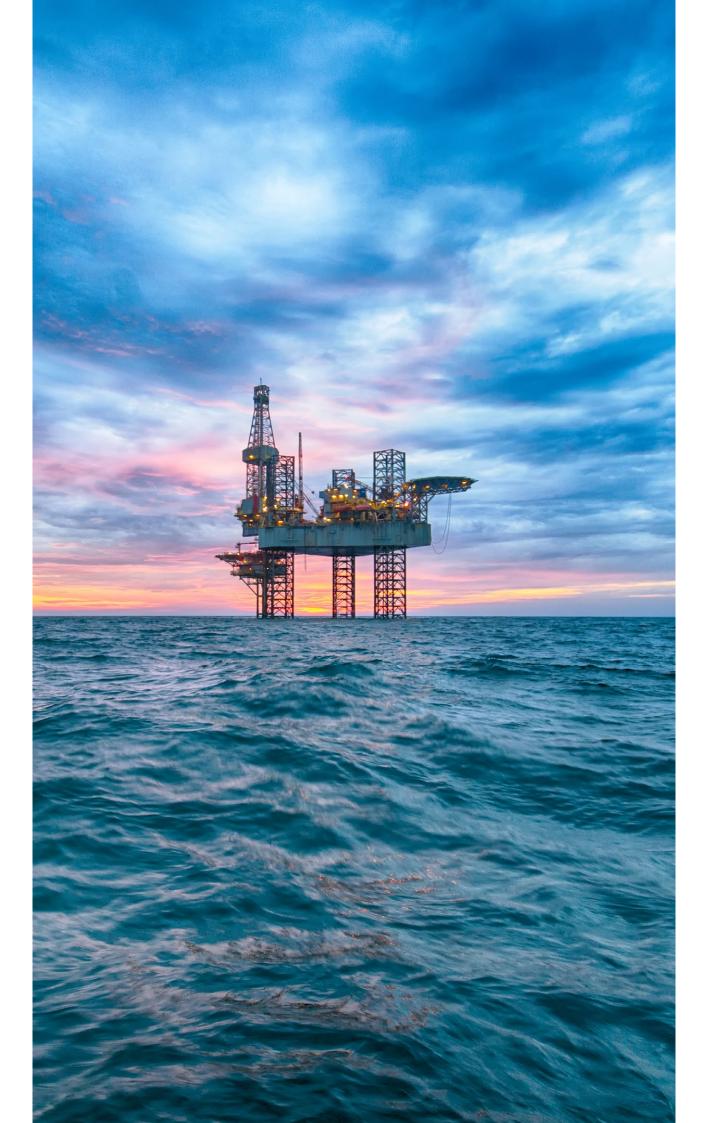
According to the publication consulted, trace mercury in to-be-refined crude oil must be investigated, with a special emphasis placed on the crudes of Argentina as the mercury concentration in local crudes has increased over time.

The article also highlights that mercury tends to be present in all the cuts, with a high occurrence in lighter ones (like liquefied petroleum gas (LPG) and naphtha). It goes on to strongly recommend studying mercury levels in order to prevent occupational and environmental exposure, to ensure the quality of the products and to protect the equipment.

Finally, the article highlights some yet-unanswered questions: Is mercury accumulating? Where? In which cuts? How can we predict the effects? What actions must be taken?

<sup>24</sup> Lombardi, F. G. (2018). Axion Energy SA, Procesamiento de crudos con mercurio, Petrotecnia.5.

25 ibid.



## 3. Mercury content in oil and gas deposits

Mercury occurs naturally in oil and gas deposits, likely as the product of both primary and secondary geological processes releasing mercury into reservoirs. Comprehensive, wide-ranging research on the origin of this metal has not, however, been published.

Standards for the determination of mercury in crude oils were first developed by the American Society for Testing and Materials (ASTM International) in 2010, providing the means to quantitatively determine the amount of mercury in crude oils.<sup>26</sup>

### Different forms of mercury in deposits (chemical speciation)

In natural gas, mercury is present mostly 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 (such as HgS, HgK2, HgK, HgSe and other salts), but also organic compounds (mainly Hg thiols), all of them with different chemical and physical properties.<sup>27</sup>

These forms of mercury may be dissolved or suspended in or adsorbed on inert particles of substances such as sand or wax.

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

It is important to clarify that both gas condensates and crude oil are referred to in the bibliography mainly under the general denomination of "oil", "crude" or "crude oil".

Mercury levels in crude oil can vary significantly depending on the origin of the oil and on geological factors, such as regional tectonic position, structural features of the deposit and seismic activity. Levels can also depend on the operation conditions.<sup>28</sup> Consequently, under the influence of these factors, mercury concentrations can show great variation within a short period of time.

According to the IPIECA 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 existing literature: although the IPIECA database does not register levels over 1,000 ppb, other texts, such as a 2001 publication by the United States Environmental Protection Agency (EPA),<sup>29</sup> mentions 20,000 ppb. IPIECA attributes this difference to old and non-comparable analytical techniques.<sup>30</sup>

It is important to highlight that global multicentre harmonized studies using comparable analytical techniques and data analysis have not been carried out. In addition, owing to potential variations in concentration, it is advisable to keep the concentration mapping updated.

A simple mass balance for the mercury content of crude oil and natural gas and of mercury waste or mercurycontaining waste is difficult to obtain. This is due to the lack of information on the origin of the mercury in the deposits and the significant variation in mercury concentration in crude oil and natural gas in basins and deposits.

### Methodologies for estimating the concentration of mercury in crude oil

In general, as a first approach to calculating the amount of mercury present in crude oil, the average concentration per region is presented. The source of the crude oil can be a good indicator for evaluating releases and emissions.

<sup>&</sup>lt;sup>26</sup> Determination of Mercury in Crude Oil Is Covered in New ASTM Petroleum Standards

<sup>&</sup>lt;sup>27</sup> Wilhelm, S.M. et al. (2004). Mercury in crude oil processed in the United States.

<sup>&</sup>lt;sup>28</sup> Subirachs Sanchez, G. (2013). Mercury in extraction and refining process of crude oil and natural gas, University of Aberdeen.

<sup>&</sup>lt;sup>29</sup> Office of Air Quality Planning and Standards, EPA (2001). Research and Development. Mercury in petroleum and natural gas: estimation of emissions from production, processing and combustion.

<sup>&</sup>lt;sup>30</sup> Mercury management in petroleum refining An IPIECA Good Practice Guide, 2014.

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

## 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<sup>31</sup>

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 the regional average is to take the median of the total mercury present in different deposits. This method was used by IPIECA to obtain the results presented in table 2 below.

Higher levels of mercury (over 100 ppb) are considered unusual. This methodology can be a more robust means of estimating a global average, but the results tend to show lower averages for regional levels as shown in the table below.

## TABLE 2: TOTAL MERCURY BY REGION CALCULATED AS THE MEDIAN OF THE RESULTS BY COUNTRY<sup>32</sup> COUNTRY<sup>32</sup>

Region	<b>Hg concentration</b> (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 in the tables above are not directly comparable as they cover different regions, in which different analytical techniques and data processing were used. It can nonetheless be seen in both tables that results are similar for the zones with the lowest mercury concentration and with the least data dispersion in the IPIECA report. For example, in the Middle East, both tables show similar results as no figure exceeds 15 ppb of mercury in the mentioned report.

Yet, for regions with higher and wider data dispersion for mercury concentration in deposits – meaning a combination of very low and very high concentrations in one region –, the results can differ significantly between different methods of calculating estimates.

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

<sup>&</sup>lt;sup>31</sup> Wilhelm, S. M. *et al.* (2004). Mercury in crude oil processed in the United States.

<sup>&</sup>lt;sup>32</sup> Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.

Even when using a data analysis method similar to that used by Wilhelm *et al.*, the simple unweighted average of mercury levels in the IPIECA dataset<sup>33</sup> gives 51 ppb for the "Pacific and Indian Ocean" region. This result is still far from the 220.1 ppb presented in the publication by Wilhelm *et al.*. This difference may be due to the number of samples studied, their origin or the analytical techniques used.

In addition, the time frame of the analysis of the crude oil will significantly influence the result. A crude oil analysed on site immediately following gas extraction will, in most cases, contain more mercury than the same crude when analysed after transport onshore or to a laboratory. Volatile mercury can be lost from the oil or mercury can precipitate from the oil and then may not get included in the analysis. This process can occur in pipelines, storage tanks and sampling bottles.<sup>34</sup> 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

As is the case for crude oil, natural gas deposits can show a significant variation in mercury concentration, ranging from 0.05 to 9,000  $\mu$ g per Nm<sup>3</sup>, depending on the source.<sup>35 36</sup>

Almost all mercury present in natural gas is elemental mercury, and only a small fraction, in low and difficultto-measure concentrations, is in a more bioavailable form like dialkylmercury.<sup>37</sup>

The regions that have higher mercury concentrations in oil tend also to have higher mercury concentrations in natural gas, because in most cases crude oil and natural gas come from the same deposits.

The available information published on wellhead mercury levels in natural gas in different areas and countries shows that the Middle East and North America have the lowest average values, whereas Indonesia and South America, where the lowest measured levels are 200 µg per Nm<sup>3</sup> and 69 µg per Nm<sup>3</sup>, have high average values:

Region/country	<b>Mercury concentration</b> (µg per Nm³)	
Algeria	50 - 80	
Eastern Europe	1-2,000	
Far East	0.02 - 193	
Germany (Northern)	15 - 450	
Germany (Southern)	<0.1 - 0.3	
Indonesia (Sumatra)	200 - 300	
Middle East	1 - 9	
North America	0.005 - 40	
South America	69 - 119	

#### TABLE 3: WELLHEAD LEVELS OF MERCURY IN GAS IN DIFFERENT AREAS<sup>38</sup>

Although the highest wellhead levels were found in Eastern Europe, this does not imply that the region has a high average concentration (the lowest levels were  $1 \mu g$  per Nm<sup>3</sup>), but simply indicates the presence of deposits with high mercury concentrations.

<sup>&</sup>lt;sup>33</sup> Doll, B. et al. (IPIECA) (2012). Industry Input to the UN Global Mercury Treaty Negotiations Focus on Oil and Gas. SPE/APPEA International Conference on health, Safety and Environment.

<sup>&</sup>lt;sup>34</sup> Qa<sup>3</sup> during document consultation. May 2021.

<sup>&</sup>lt;sup>35</sup> Lang, D. et al. (2012). Mercury arising from oil and gas production in the United Kingdom and UK continental shelf. IMKIP Oxford.

<sup>&</sup>lt;sup>36</sup> Information provided by Qa<sup>3</sup> during first draft consultation, November 2020.

<sup>&</sup>lt;sup>37</sup> Office of Air Quality Planning and Standards, EPA (2001). Research and Development. Mercury in petroleum and natural gas: estimation of emissions from production, processing and combustion.

<sup>&</sup>lt;sup>38</sup> Lang, D. et al. (2012). Mercury arising from oil and gas production in the United Kingdom and UK continental shelf. IMKIP Oxford.

Natural gas (also referred to in the publications as "non-condensates") notably shows a slightly lower concentration of mercury overall compared with crude oil. This difference is shown in Table 4, which compares the median mercury level measured in crude oil and natural gas.

	Median Hg level (ppb)	Pe	ercentage of		<b>condensates</b> of <b>mercury</b> (ppb	containing spec	:ific
		<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%

#### TABLE 4: MERCURY IN OIL VERSUS GAS (IPIECA)<sup>39</sup>

Other publications and consulted experts<sup>40</sup> also highlighted that estimating mercury concentrations in gas at the wellhead is potentially as difficult as it is for crude oil. The following table shows some examples of mercury concentrations in oil and gas from the same source. In most cases, the mercury levels are in the same order of magnitude in both crude oil and natural gas, while in a few others mercury levels in natural gas are considerably higher than in crude oil.

## TABLE 5: EXAMPLES OF CONCENTRATIONS MEASURED BY QA<sup>3</sup> IN OIL AND GAS FROM THE SAME SOURCE (INFORMATION PROVIDED BY QA<sup>3</sup> DURING FIRST DRAFT CONSULTATION, NOVEMBER 2020)

Country	<b>Hg in oil</b> (ppb)	<b>Hg in natural gas</b> (ppb)		
Thailand	~80	~9,000		
United Kingdom	~80	~110		
Norway	~12	~12		
Viet Nam	~90	~560		
Algeria	< 1	~14		
Azerbaijan	< 1	~9		
Australia	~2	~25		
Oman	~20	~130		
Tunisia	~38	~30		

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

If a precise analysis has not been carried out, regional averages of mercury concentration are necessary in order to understand mercury emissions and releases into the environment in a region or country where crude oil and natural gas are going to be processed or used and where the origin of the crude oil is known.

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

Owing to the great difference between the maximum and minimum mercury content of different deposits, regional averages are not good indicators for understanding and making decisions on the impact of mercury during the extraction process at the local level.

For example, even the highest level ever found in crude oil worldwide – higher than 10,000 ppb<sup>41</sup> – belongs to a deposit located in California. North American crude oil is considered to have the second-lowest regional average level of mercury after the Middle East, as shown in figure 1, where there are hotspots in regions with low averages.

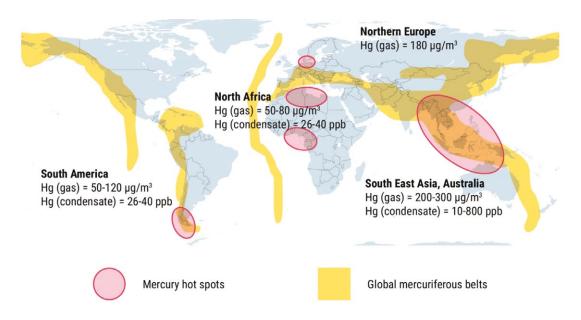
<sup>&</sup>lt;sup>39</sup> Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.

<sup>&</sup>lt;sup>40</sup> Qa<sup>3</sup> and Morelli, G. (PhD Environmental Geochemistry Researcher. Consiglio Nazionale delle Ricerche-CNR. Instituto di Geoscienze e Georisorse-IGG) consultation, November 2020.

<sup>&</sup>lt;sup>41</sup> Wilhelm, S.M. and Bloom, N. (2000). Mercury in petroleum. Fuel Processing Technology 63.

In the case of natural gas, rather than considering regional averages, it appears more relevant to focus on mercury concentrations in the pipelines and deposits of origin, since natural gas is mostly commercialized in or between neighbouring regions. This situation is, however, currently changing.





<sup>&</sup>lt;sup>42</sup> Adapted from Chalkidis, A. et al. (2019). 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.



## 4. Mass of mercury potentially released from crude oil

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

#### **Extraction**

Crude oil production or 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.<sup>43</sup> Most of the production systems separate the produced water in situ from the crude oil, which will be transported to processing facilities.<sup>44</sup>

The wastewater produced 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 wastewater, some of which may generate hazardous sludge or solid waste with high concentrations of mercury (mercury-containing waste).<sup>45</sup> According to a preliminary assessment in 2016 by IPIECA, 13.5 tons of mercury are released, per year, into the environment worldwide from produced water, with about 90% of these releases occurring offshore.<sup>46</sup>

Flaring operations are very common during exploration for and production of hydrocarbons. These operations may be carried out in several situations:<sup>47</sup>

- Initial exploration and well testing: during these activities, all of the produced oil and gas is sent to flare. This can last anywhere from a few hours to several weeks.
- During production: when it is not economically viable to export the gas.
- Operation interruptions: when gas cannot be sent to sales pipelines or into a national grid-based network. This may occur when there is no infrastructure in the region to accept the gas, or when infrastructure is under maintenance.
- Low pressure flares: during production, off-gases are regularly sent to flare, requiring a flare to be kept continuously running.

In most cases, mercury is not removed from gas before flaring, meaning that all mercury present in the gas is released into the air. Regional or global estimates of mercury emissions from gas flaring have not yet been published. However, these emissions can be significant and should not be overlooked.

#### **Transport**

There is a risk of accumulation of sludge with high mercury concentrations 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 high mercury concentrations 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, especially if this activity is taking place in countries that do not have the required installations for sound management of such hazardous wastes.

In addition, should a spillage accident occur, this sludge can present a significant risk of acute toxic exposure at a local level owing to the subsequent emissions of mercury.<sup>48</sup>

<sup>&</sup>lt;sup>43</sup> Produce water, definition: naturally occurring water that comes out of the ground along with oil and gas.

<sup>&</sup>lt;sup>44</sup> Garside, M. (30 September 2020). Oil - global production 1998-2019. <u>https://www.statista.com/statistics/265203/global-oil-production-since-in-barrels-per-day/</u>

<sup>&</sup>lt;sup>45</sup> OSPAR Commission (2013). Background Document concerning Techniques for the Management of Produced Water from Offshore Installations.

<sup>&</sup>lt;sup>46</sup> AMAP/UNEP (2019). Technical Background Report for the Global Mercury Assessment 2018.

<sup>&</sup>lt;sup>47</sup> Qa<sup>3</sup> (2021). Unconsidered Mercury Emissions from the Oil and Gas Industry.

<sup>&</sup>lt;sup>48</sup> Pandey, S. K., Kim, K. H., Yim, U.H., Jung, M.C. and Kang, CH. (2009). Journal of Hazardous Materials. Vol. 164, pp. 380–384.

#### 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 already mentioned, crude oil may contain mercury. It is therefore relevant to know the fate of this mercury once it enters the refining process. Mercury fate varies depending on the design of the facility, the nature of the input crude oil, the methodology followed by the operators, the commercial needs and the environmental regulations of the country, among other factors.

However, we can identify a number of common ways in which mercury can be released, as illustrated in figure 2 below.



FIGURE 2: MERCURY IN REFINERIES MASS BALANCE

All output from 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, steam stripping and alkylation. A typical refinery generates approximately 40 to 60 litres of wastewater for every barrel of oil produced.<sup>49</sup>

The desalting process takes place before distillation. During this process, the crude oil and condensates are washed with water to remove undesired constituents, in particular 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, in addition to mercury in suspension.

The United States EPA analysed the total mercury present in desalter sludge from wastewater processed at four refineries in the United States of America (1996). The results showed concentrations of 0.01 ppm, 4 ppm, 39 ppm and 41 ppm.<sup>50</sup>

In 2019, a study calculated the mass balance of mercury in two oil refineries of the Republic of Korea that did not have mercury removal systems installed. It found that 4.5% and 33.2% of the mercury that entered the two refineries ended up in sludge, whilst 3.1% and 5.6% left the facilities in wastewater.<sup>51</sup>

According to the 2018 UNEP Global Mercury Assessment, 0.1%, or 0.56 tons, of the total mercury released into aquatic systems came from crude oil refining.<sup>52</sup>

<sup>&</sup>lt;sup>49</sup> Wilhelm S. M. *et al.* (2004). Mercury in crude oil processed in the United States.

<sup>50</sup> ibid.

<sup>&</sup>lt;sup>51</sup> Mojammal, A.H.M., Back, S.K., Seo, Y.C., and Kim, J.H. (2019). Atmospheric Pollution Research. Vol. 10 (1), pp. 145-151.

<sup>&</sup>lt;sup>52</sup> AMAP/UNEP (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 it is not carried out by many companies. Where it is carried out, 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 sulphide (solid), centrifugation/filtration alone may be an option for reducing the mercury content. This process generates mercury-containing solid waste.<sup>53</sup>

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 or filter cake with elevated mercury concentrations also generate hazardous solid waste that contains high mercury concentrations.<sup>54</sup>

#### Mercury in air emissions

There is evidence of higher concentrations of atmospheric mercury in oil refineries and their surroundings.<sup>55</sup>

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 into the atmosphere.<sup>56</sup>

In 2001, the EPA estimated emissions to the environment from the production, processing and combustion of crude oil and gas in the United States alone was 13 tons per year, but stated that the estimates were uncertain due to lack of statistical data.<sup>57</sup>

According to the 2018 UNEP Global Mercury Assessment, crude oil refining represented, in 2015, 0.65% (14.4 tons) of the total emissions of mercury into the atmosphere.<sup>58</sup>

#### Mercury in petroleum products

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

However, inorganic mercury (that has not been removed during desalting or transformed into volatile mercury species during distillation) 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. It should be remarked that these refineries did not have MRUs installed.

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

<sup>&</sup>lt;sup>53</sup> Qa<sup>3</sup> (2001). Unconsidered Mercury Emissions from the Oil and Gas Industry.

<sup>&</sup>lt;sup>54</sup> Wilhelm S. M. *et al.* (2004). Mercury in crude oil processed in the United States.

<sup>&</sup>lt;sup>55</sup> Lan, X., Talbot, R., Laine, P., Torres, A., Lefer, B. and Flynn, J. (2015) Environ. Sci. Technol. Vo. 49, 10692–10700

<sup>&</sup>lt;sup>56</sup> Mojammal, A.H.M., Back, S.K., Seo, Y.C., and Kim, J.H. (2019). Atmospheric Pollution Research.

<sup>&</sup>lt;sup>57</sup> Office of Air Quality Planning and Standards, EPA (2001). Research and Development. Mercury in petroleum and natural gas: estimation of emissions from production, processing and combustion.

<sup>&</sup>lt;sup>58</sup> AMAP/UNEP (2019). Technical Background Report for the Global Mercury Assessment 2018.

A study performed in South Korea, in 2007, suggests that mercury present in gasoline and diesel is emitted into the air by motor vehicles.<sup>59</sup>

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 into air in 2015, while industrial combustion represented 0.06% (1.4 tons) and the combustion in power plants 0.11% (2.45 tons).<sup>60</sup>

Reference	Туре	Number of samples	<b>Range</b> (ppb)	<b>Mean</b> (ppb)	SD
Liang <i>et al.</i> (1996)	Gasoline	5	0.22-1.43	0.7	NR
Liang <i>et al.</i> (1996)	Gasoline	4	0.72-3.2	1.5	NR
Liang <i>et al.</i> (1996)	Diesel	1	0.4	0.4	NR
Liang <i>et al.</i> (1996)	Diesel	1	2.97	2.97	NR
Liang <i>et al.</i> (1996)	Kerosene	1	0.04	0.04	NR
Liang <i>et al.</i> (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 <i>et al.</i> (1997)	Naphtha	4	3-40	15	NR
Tao <i>et al.</i> (1998)	Naphtha	3	8-60	40	NR
US EPA (2000)	Coke	1000	0-250	50	NR

TABLE 6: SUMMARY OF TOTAL MERCURY IN REFINING PRODUCTS, EXPRESSED IN MASS PPB<sup>61</sup>

#### • Mercury mass balance in crude oil distilleries

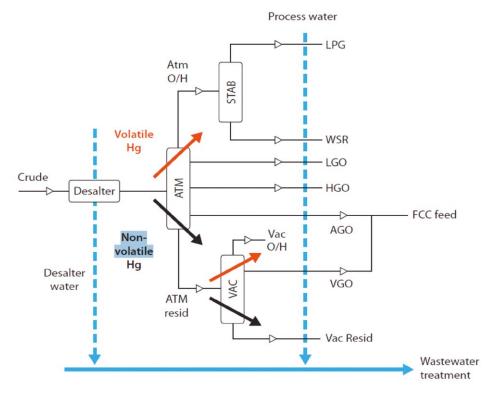
The following figure 3, from a 2014 IPIECA report, provides a simplified example of where diverse forms of mercury may distribute or accumulate in a crude refinery.

<sup>&</sup>lt;sup>59</sup> Won, J. H., Park, J. Y., Lee, T. G. (2007). Atmospheric Environment, Vol. 41, 7547–7552.

<sup>&</sup>lt;sup>60</sup> AMAP/UNEP (2019). Technical Background Report for the Global Mercury Assessment 2018.

<sup>&</sup>lt;sup>61</sup> Wilhelm S. M. et al. (2004). Mercury in crude oil processed in the United States.

#### FIGURE 3: THE MOST COMMON MERCURY DISTRIBUTION PATHS IN HYDROCARBONS AND WATER (IPIECA)<sup>62</sup>



The mass balance of mercury provides information on 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.

Owing to the chemical properties of mercury present in crude oil, such as its volatile nature and tendency to damage aluminum-based equipment and form amalgams, some refineries have reported troubles<sup>63</sup> 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.<sup>64</sup> Other reasons for a poor mass balance can include different designs of sample points across the refinery, some of which may not afford representative samples and multiple sample points cannot usually be sampled simultaneously; thus, mass balance evaluations across a refinery usually take place over several days, during which the crude feeding the refinery may change, which can directly affect the mercury measured.<sup>65</sup>

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.

<sup>&</sup>lt;sup>62</sup> Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.

<sup>&</sup>lt;sup>63</sup> Lombardi, F. G. (2018). Axion Energy S.A., Procesamiento de crudos con mercurio, Petrotecnia.5.

<sup>64</sup> ibid.

<sup>&</sup>lt;sup>65</sup> Qa<sup>3</sup> during document consultation. May 2021.

#### TABLE 7: COMPARISON OF ANNUAL MERCURY ACCUMULATION FOR EACH RANGE OF CONCENTRATION<sup>66</sup>

Potential annual accumulation			
Mercury in crude (ppb)	1	10	200
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

According to the IPIECA publication, the 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, so they may have pre-existing accumulation of mercury.

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 the metal into smaller manageable sections or smelting the steel back into a recycled reusable form, could inadvertently release mercury into the environment.<sup>67</sup>

<sup>&</sup>lt;sup>66</sup> Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.

<sup>&</sup>lt;sup>67</sup> Qa<sup>3</sup> (2016). Unconsidered Mercury Emissions from the Oil and Gas Industry. ANNUAL BUYERS GUIDE 2016.



# 5. Mass of mercury potentially released from natural gas

### **Extraction**

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.<sup>68</sup> There is evidence in the literature that flowback water is rich in heavy metals and, in some cases, mercury, <sup>69 70 71 72</sup> which may be released into the surrounding environment.

Flowback water storage tanks may not incorporate sufficient safeguards to ensure that this water cannot come into contact with surface water. Although there are not many publications about mercury levels in the surroundings (surface water, soil and biota) of production sites, one study that analysed samples from Pennsylvania found higher concentrations of mercury in water and biota close to extraction sites by fracking and suggests they could be related to the natural gas extraction.<sup>73</sup>

### **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 can adsorb on to the steel surface structure and react with iron sulphide to form a mercury-rich layer of mercury sulphide on the internal surfaces of pipelines.<sup>74</sup>

This effect increases with natural gas humidity and also with the presence of  $H_2S$  that reacts to form an iron sulphide layer.

When natural gas is transported long distances, an appreciable decrease in mercury concentration can be observed. The 2001 EPA 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 of a mercury-rich scale during transport contaminates the equipment and may represent a risk for workers during maintenance and decommissioning activities. These activities can produce significant amounts of mercury waste and mercury-containing waste that must be managed in an environmentally sound manner.

<sup>68</sup> Grant, C. J., Lutz, A. K., Kulig A D. and Stanton, M. R. (2016). Ecotoxicology, Vol. 25, 1739–1750.

<sup>&</sup>lt;sup>69</sup> Maguire-Boylea S. J. and Barron, A. R. (2014). Environ. Sci.: Processes Impacts, Vol. 16, 2237–2248

<sup>&</sup>lt;sup>70</sup> 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.

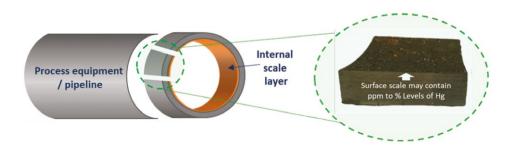
<sup>&</sup>lt;sup>71</sup> Leff, E. (2011). Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program, Well Permit Issuance for Horizontal Drilling and High-Volume, Hydraulic Fracturing to Develop the Marcellus Shale and Other Low-Permeability Gas Reservoirs. New York State Department of Environmental Conservation: New York, NY.

<sup>&</sup>lt;sup>72</sup> Abualfaraj, N., Gurian, P. L. and Olson, M. S. (2014). Environmental Engineering Science, Vol. 31 (9).

<sup>&</sup>lt;sup>73</sup> Grant, C. J., Weimer, A. B. Marks, N. K., Perow, E. S., Oster, J. M., Brubaker, K. M., Trexler, R. V., Solomo C. M. and Lamendella, R. (2015). Journal of Environmental Science and Health, Part A. 50, 482–500.

<sup>&</sup>lt;sup>74</sup> Wilhelm S. M. et al. (2004). Mercury in crude oil processed in the United States.

#### FIGURE 4: EXAMPLE OF MERCURY RICH SCALE OFTEN FOUND ON THE INTERNAL SURFACE OF PROCESS EQUIPMENT AND PIPELINES. IMAGE PROVIDED BY QA<sup>3</sup>



### **Processing**

Natural gas processing is typically not as complex as crude oil refining 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 such as water, carbon dioxide, hydrogen sulphide and metals.

When it is needed,  $H_2S$  and  $CO_2$  removal are carried out with an amine absorption process, which can capture some mercury present in the gas.

The gas is then dehydrated, passing through an adsorbent material, usually dry triethylene glycol, that captures the water. Following this, 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 may be emitted into the atmosphere if the flue gas is not treated or re-dissolved in the wastewater of the facility.

Other cleaning processes, such as  $CO_2$  (when membrane technologies are used) or  $N_2$  removals, can also retain mercury in membranes and columns that can eventually be liberated into the atmosphere<sup>75</sup> (case study 2). If necessary, to protect the equipment, an MRU is used before implementing these processes.

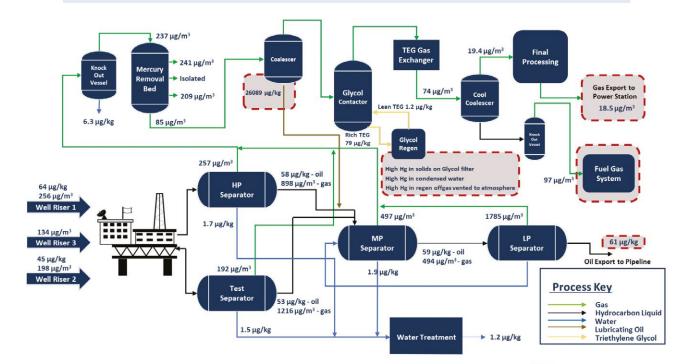
<sup>&</sup>lt;sup>75</sup> Qa<sup>3</sup> Unconsidered Mercury Emissions from the Oil and Gas Industry. ANNUAL BUYERS GUIDE 2016.

#### Case study 2 by Qa<sup>3 76</sup>

Region: South-East Asia.

Type of facility: Offshore production of oil and gas where an MRU is used upstream in the process.

**Mercury issues**: Although this facility uses a mercury removal unit upstream in the process, the mercury removal bed has become saturated, allowing mercury to pass. This results in mercury contamination throughout the entire process, leading to emissions from flaring, combustion of fuel and produced gas.



The separation process for natural gas liquids typically takes place using cryogenic techniques, which have an inherent risk of condensing elemental mercury in the systems if the concentration of mercury is sufficiently high.<sup>77</sup>

Such condensation occurs in gas separation plants that have a content of mercury in feeds higher than  $10-20 \ \mu g \ per \ m^3$ .

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 may encounter problems associated with mercury condensation and reduce mercury attack of aluminum, both of which may cause serious accidents (see figure 5).<sup>78</sup>

They then use removal techniques, described in chapter 7.

The out-stream gas that leaves the MRUs usually has a mercury content of less than  $1 \mu g$  per m<sup>3</sup>.<sup>79</sup> The saturated adsorbent material of the MRUs is a source of solid waste with a high mercury concentration, which must be disposed of correctly.

<sup>&</sup>lt;sup>76</sup> Qa<sup>3</sup>, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15.

<sup>&</sup>lt;sup>77</sup> Qa<sup>3</sup> (2021). Unconsidered Mercury Emissions from the Oil and Gas Industry.

<sup>&</sup>lt;sup>78</sup> Wilhelm S. M. et al. (2004). Mercury in crude oil processed in the United States.

<sup>&</sup>lt;sup>79</sup> Society of Petroleum Engineers (SPE) International (2007). Mercury monitoring and removal at gas processing facilities.

#### FIGURE 5: METALLURGICAL FAILURE CAUSED BY MERCURY IN A GAS PROCESSING FACILITY (IPIECA)<sup>80</sup>



The risk of atmospheric emissions during gas processing is also present. 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 per Sm<sup>3</sup> in the condensate tank area.<sup>81</sup>

#### **Products**

Mercury can be present in the final products derived from natural gas, as shown in 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, while industry represented 0.01% (0.16 tons) and power plants 0.02% (0.33 tons).<sup>82</sup>

The report, however, highlighted that mercury emissions from oil and gas extraction, along with other sources, are currently difficult to quantify on a global scale, largely owing to the lack of comprehensive activity data, as well as the lack of emission factors for highly variable process technologies. The report further indicates a general lack of knowledge on mercury content, removal efficiency and risk of releases into the environment.

<sup>&</sup>lt;sup>80</sup> Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.

<sup>&</sup>lt;sup>81</sup> El-Fekya, A.A., El-Azaba, W., Ebiada, M.A., Masoda, M. B. and Faramawya, S. (2018). Journal of Natural Gas Science and Engineering. 54. 189–201

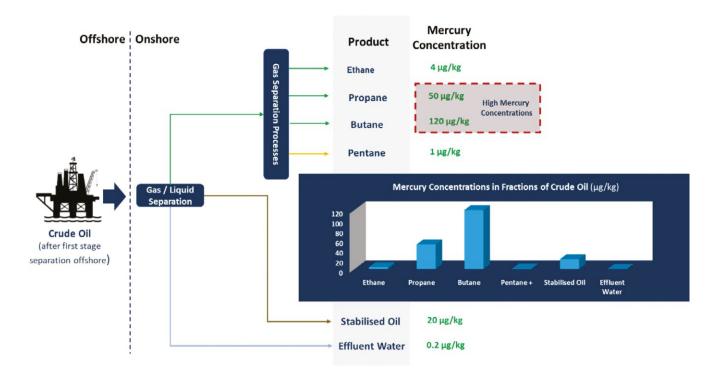
<sup>&</sup>lt;sup>82</sup> UNEP (2019). Global Mercury Assessment 2018. <u>https://www.unenvironment.org/resources/publication/global-mercury-assessment-2018</u>

### Case study 3 by Qa<sup>3 83</sup>

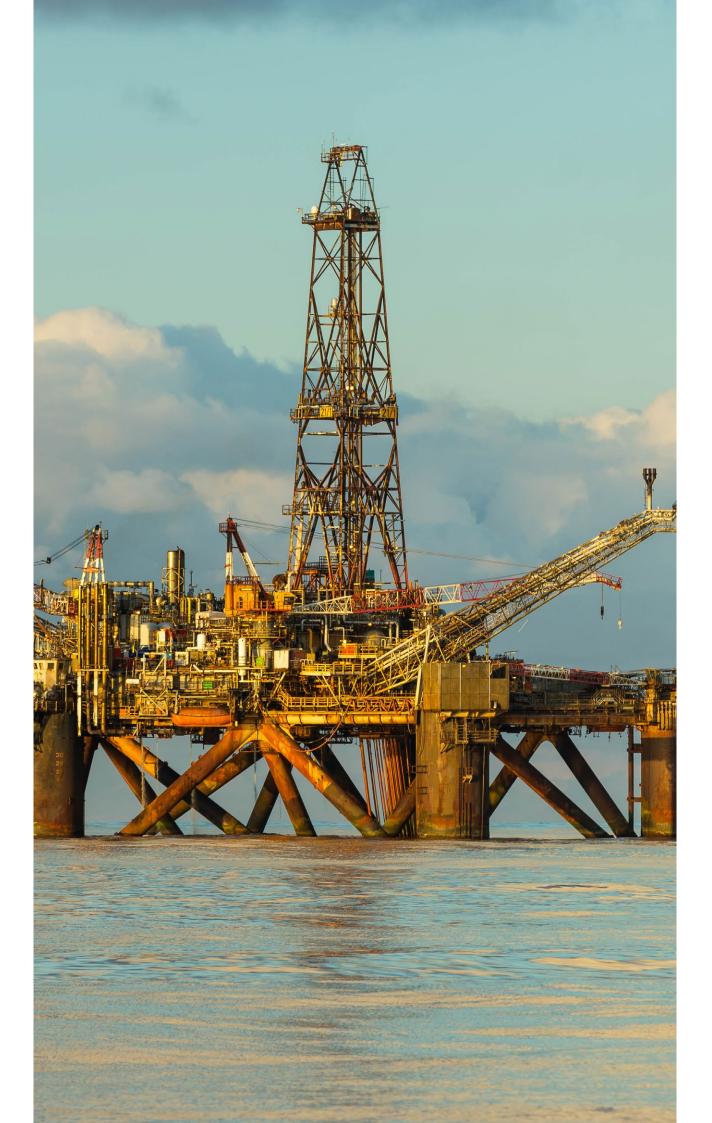
### Region: Europe

**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 and pentane).

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



<sup>&</sup>lt;sup>83</sup> Qa<sup>3</sup>, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15



# 6. 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, owing to its reactivity and ability to form amalgams with some other metals, it may accumulate in process equipment (especially on internal metal surfaces).

The accumulation may cause catalyst poisoning (reducing the efficiency of some processes), corrosion and embrittlement of equipment. The latter of these 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.<sup>84</sup>

Owing 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 compounds in hydrocarbon, such as asphaltenes, and can appear in heavier refinery cuts or fractions.

The process of producing and refining oil and gas subjects the fluids to many varying conditions, including temperature, pressure and contact with other chemicals. This results in a distribution of the mercury, according to the reaction and partitioning properties of the mercury species present, into the final products and waste streams produced.

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

### 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 refinery plants. An example of a general rule, following IPIECA's Good Practice Guide:<sup>85</sup>

"The mercury content of incoming crudes to refinery X will be less than 10 ppb, on a month-average basis, and no individual crude should exceed 100 ppb" otherwise it is treated when it enters the refinery.

These good practice levels are significantly 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 or blending down with crudes containing lower levels of mercury.

In accordance with IPIECA, 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.<sup>86</sup>

Removing mercury from crude oil is not an easy process and there are very few facilities operating this technology. During the refining process, mercury partitions into the light fractions (predominantly the LPG) and in some refineries, the mercury in the LPG is removed from the crude oil entering a refinery plant with gas phase mercury removal units (MRUs, described in the next section).

<sup>&</sup>lt;sup>84</sup> Qa<sup>3</sup>. Unconsidered Mercury Emissions from the Oil and Gas Industry. Published online 2021.

<sup>&</sup>lt;sup>85</sup> Mercury management in petroleum refining, An IPIECA Good Practice Guide, 2014.

<sup>&</sup>lt;sup>86</sup> ibid.

# Mercury removal from natural gas and LPG

As mentioned in chapter 5, processes for natural gas production are often simpler than for crude oil as they only involve a separation of the raw material into commercial products: gas and natural gas liquids (NGLs). The product 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 gas plant, the gas is treated to remove water, by using triethyleneglycol (TEG) or adsorbents.
- (2) The gas is cleaned through acid gas scrubbers (before water removal, when H<sub>2</sub>S is captured with amines, or after, when CO<sub>2</sub> is captured with membranes).
- (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 an 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 into the environment during amine regeneration and end up in the carbon dioxide vent stream, where applicable, in the recovered sulphur or in solids captured by filters.

The mercury removal process must be deployed upstream of the cryogenic distillation because mercury may deposit in the cryogenic equipment, causing embrittment of aluminum heat exchangers. This may increase the risk of a catastrophic failure.

This process is carried out by a mercury removal unit (MRU), that consists of beds typically filled with adsorbents. The most commonly used adsorbents used to remove mercury from natural gas and LPG are based on metal sulphides or sulphur-impregnated carbon.

Once these adsorbents are exhausted (saturated with mercury) or contain high concentrations of mercury they must be removed, transported, treated and disposed of as hazardous wastes by a specialized and authorized company.

Adsorbents may need to be replaced in advance in cases where:<sup>87</sup>

- there is a mercury breakthrough;
- pressure drop is increased by liquid carryover or hydrocarbon condensation inside the beds;
- the adsorbent is fouled by free water and causes either a loss of adsorption capacity or plugging of the column making their replacement necessary before the full adsorption capacity can be achieved;
- the adsorbent material is replaced during a vessel inspection.

When  $CO_2$  removal is required, a membrane technology may be employed. This technology also removes mercury from the gas. This mercury may be emitted into the atmosphere as part of a continuous removal process and also when the membrane material is changed and replaced during maintenance.

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, such as  $CO_2$  and/or  $H_2$ .

<sup>&</sup>lt;sup>87</sup> Information provided by BATREC and IPIECA during consultation.

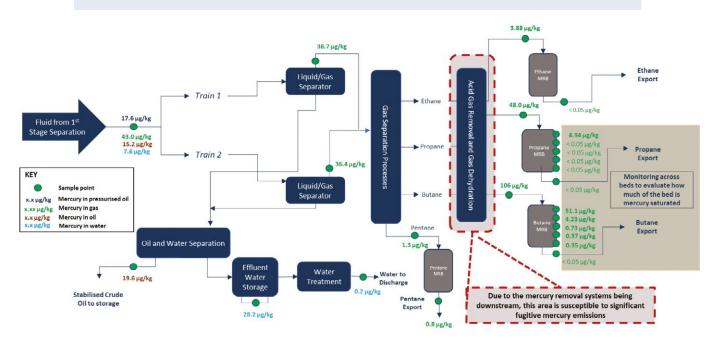
More recently, with the development of mercury removal media that is more tolerant to the presence of water, many companies are choosing to place mercury removal beds upstream in the process ahead of acid gas removal and dehydration.<sup>88</sup> This could prevent generation of mercury-containing waste streams during moisture and acid gas removal (case study 4).

### Case study 4 by Qa<sup>3 89</sup>

### Region: Europe.

**Type of facility:** Gas separation and fractionation plant (methane already removed through upstream processing, remaining gas removed from oil and separated into individual products; ethane, propane, butane and pentane).

**Mercury issues:** This case study shows a process with downstream MRBs and highlights the area in the process where there are often unconsidered emissions.



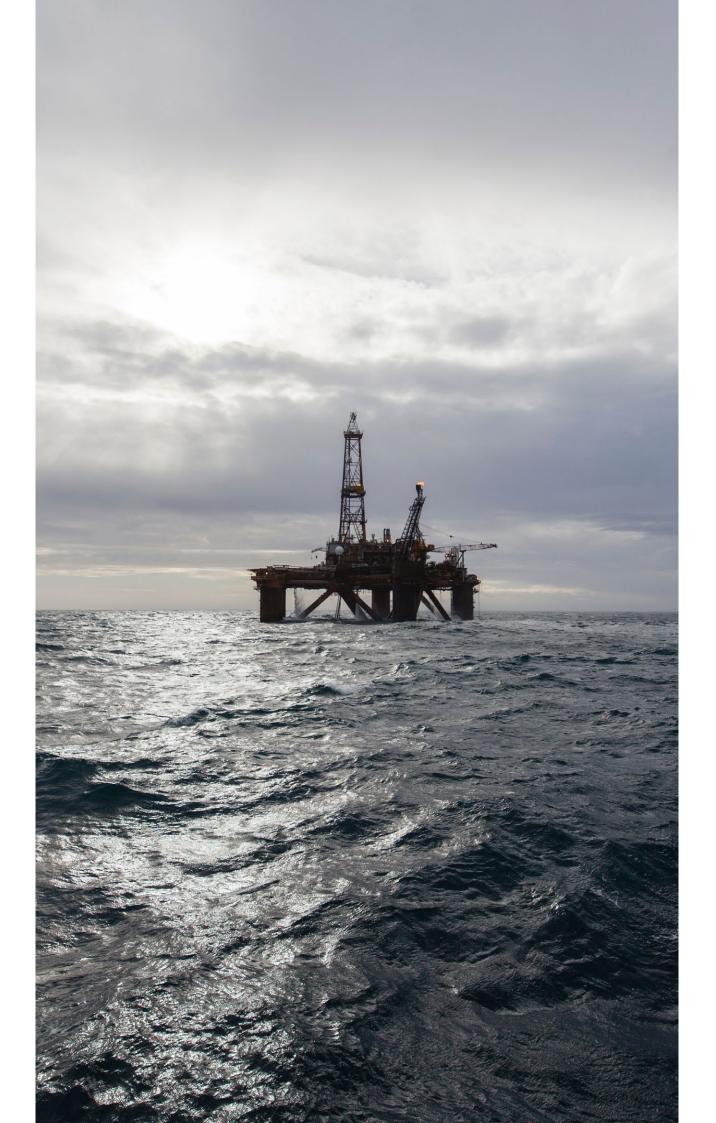
The disposal of the mercury collected by a mercury removal system (mercury waste) varies depending on the type of system used. As previously mentioned, the most commonly used MRU media are based on metal sulphides on inert support material (e.g., alumina), or sulphur-impregnated carbon, these can be regarded as "non-regenerative sorbents". The spent adsorbent, depending on local regulations, may be classified as hazardous waste, which must be treated in an environmentally sound manner.

Lang, in his publication "Mercury arising from oil and gas production in the United Kingdom 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"*.

Regenerative mercury adsorbents that utilize the high affinity of mercury for precious metals such as gold and silver are less used. The unit is 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 concentrated in the regeneration stream. This stream requires the mercury to be removed, which is typically achieved with a smaller non-regenerative MRU that may then need an appropriate treatment of the adsorbent.

<sup>&</sup>lt;sup>88</sup> Qa<sup>3</sup> (2021). Unconsidered Mercury Emissions from the Oil and Gas Industry.

<sup>&</sup>lt;sup>89</sup> Qa<sup>3</sup>, Mercury in the Oil and Gas Industry. Document for the UNEP Global Mercury Partnership, Sheet Reference: INF15.



# 7. 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 on Mercury, 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.

Based on in-house data generated from a number of studies and the total mass of mercury in natural gas and LPG for each region (BP - Statistical Review of World Energy 2020, 69<sup>th</sup> edition), Qa<sup>3</sup> has estimated that approximately 300 tons of mercury were produced as a by-product by the oil and gas sector in 2020.<sup>90</sup>

For instance, under Article 3 of the Minamata Convention, 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 into 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 releases into water and soil from the relevant point sources not addressed in other provisions of the Convention.

Article 11 of the Convention, which addresses "Mercury wastes", calls for collaboration with the Basel Convention. In paragraph 2 on the definition of relevant thresholds and in paragraph 3 on measures to be adopted for the environmentally sound management of mercury wastes, considering the guidelines developed under the Basel Convention<sup>91</sup> (last guidelines adopted in 2015 and currently under review).

### 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. Refineries that run elevated mercury crudes may generate solid waste with a high mercury concentration that requires sound disposal.<sup>92</sup> Reinjection is a common disposal option for oil and gas liquid waste streams and some solid waste streams (including sludge) in several regions.

A review published in 2019 provides an overview of methods used in the treatment and disposal of petroleum sludge from wastewater treatment, amongst which incineration, stabilization/solidification, oxidation and biological treatment are included.<sup>93</sup> None of the techniques mentioned in this publication addresses the presence of mercury in the sludge nor the prevention of its release into the environment. The practices mentioned in the document are not the best available techniques for the treatment of mercury-containing waste.

<sup>&</sup>lt;sup>90</sup> Qa<sup>3</sup> (2020), Unconsidered Mercury Emissions from the Oil and Gas Industry. <u>https://www.qa3.co.uk/images/pdfs/Unconsidered\_Mercury\_Emissions\_from\_the\_Oil\_and\_Gas\_Industry\_July\_2021.pdf</u>

<sup>&</sup>lt;sup>91</sup> 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 to update at its fourteenth meeting (Decision BC-14/8)

<sup>&</sup>lt;sup>92</sup> IPIECA (2015). Mercury management in petroleum refining. An IPIECA Good Practice Guide.

<sup>&</sup>lt;sup>93</sup> Johnson, O. A. and Affam, A. C. (2019). Environ. Eng. Res., Vol. 24(2), 191-201.

### 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 adsorbent material contains 1–15% mercury by weight at the time it is replaced. 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 requires environmentally sound treatment and disposal.<sup>94</sup>

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

These hazardous wastes should be managed by specialized and certified operators as indicated by IPIECA in its Good Practice Guide, "Mercury management in petroleum refining". Providers of MRUs and adsorbent materials may also offer a service which includes the sound disposal of the adsorbent materials at the end of their useful life as hazardous wastes.<sup>95</sup>

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 the waste management operators that treat waste from the oil and gas sector and are members of the Partnership.<sup>96</sup>

The Swiss company BATREC (interviewed during the development of this report) indicated that in its facility, 1,000 to 2,000 tons per year of material can be treated per furnace (three 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.<sup>97</sup> 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. As discussed previously, a large fraction of the mercury mobilized is captured by MRUs and other techniques generating mercury-containing solid waste. Unfortunately, it is not possible to provide an accurate estimate for the quantities of mercury captured by the oil and gas sector. Consequently, it is difficult to assess how much of this mercury may be entering the market after being captured, if any, as facilities that treat waste from oil and gas also treat mercury waste from other sources.

According to BATREC, only a fraction of mercury-containing solid waste is treated in specialized facilities. In addition, the complexity of the process and the required (expensive) equipment makes it difficult to address such waste locally. However, the German company Econ Industries reported their experience with an on-site mercury waste treatment technology in Australia.

## 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 into the atmosphere as elemental mercury after its combustion in vehicles and heaters.

<sup>&</sup>lt;sup>94</sup> 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

<sup>&</sup>lt;sup>95</sup> Matthey (2017). Handling mercury in gas processing plants.

<sup>&</sup>lt;sup>96</sup> https://wedocs.unep.org/bitstream/handle/20.500.11822/27819/WMA\_catalog.pdf?sequence=1&isAllowed=y

<sup>&</sup>lt;sup>97</sup> 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.

The fact that automobiles emit mercury at ground level, where people get direct exposure, should be considered as an important factor.<sup>98</sup> <sup>99</sup> In 1997, the United States Environmental Protection Agency (EPA) estimated the amount of mercury that was emitted into the atmosphere from combustion of distillate fuel oil (DFO) and residual fuel oil (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.<sup>100</sup>

Boiler	<b>Btu/year</b> (10 <sup>17</sup> )	Fuel type	<b>Fuel Oil Amount</b> (10 <sup>10</sup> L/year)	<b>Emission Factor</b> (kg/10 <sup>13</sup> Btu)	<b>Hg</b> (kg/year)	<b>THg in fuel</b> (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	

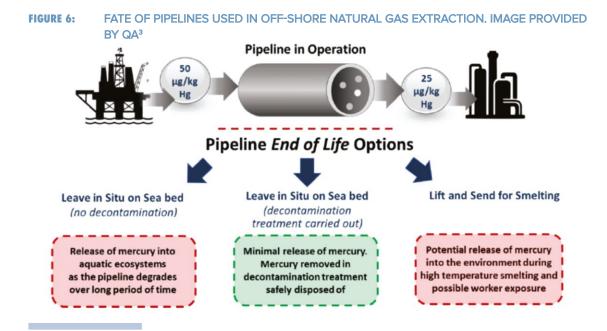
#### TABLE 8: ESTIMATION OF MERCURY EMISSIONS FROM COMBUSTION OF FUEL<sup>101</sup>

### Other sources of mercury: Decommissioning of facilities and pipelines

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 into the environment. It is estimated that 20% of mercury present in oil and gas is accumulated in the processing facilities.<sup>102</sup>

Some mercury can be removed from pipelines and equipment by cleaning them (chemically, scrubbing and scrapping) on site at the facility. This process generates sludge with a high mercury content that must be treated by specialized companies.

According to Qa<sup>3</sup>, there are three end-of-life options for pipelines used in off-shore natural gas extraction: leaving them in situ on the seabed, leaving them in situ on the seabed after cleaning, or sending them for smelting and recycling.<sup>103</sup>



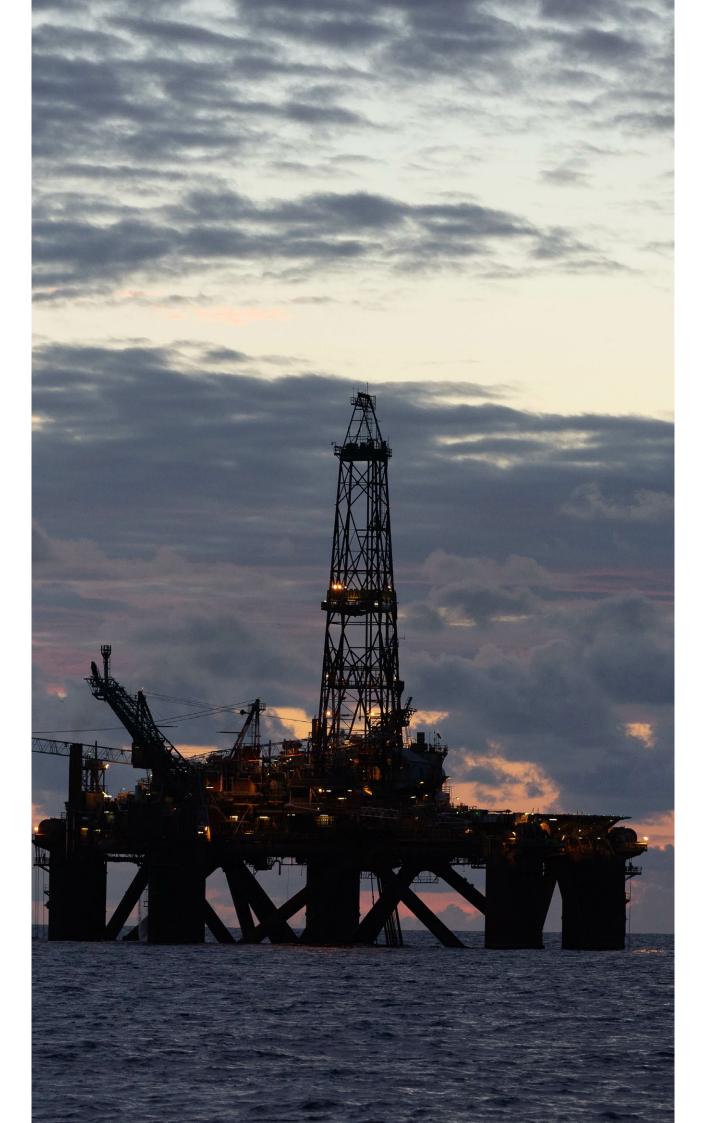
<sup>&</sup>lt;sup>98</sup> Won, J. H., J. Y. Park, J. H., Lee, T. G. (2007). Atmospheric Environment, Vol. 41, 7547–7552.

 <sup>&</sup>lt;sup>99</sup> Landis, M. S., Lewis, C. W., Stevens, R. K., Keeler, G. J., Dvonch, J. T. and Tremblay, R. T. (2007). Atmospheric Environment.. 41. 8711–8724.
 <sup>100</sup> United States EPA (1997). Mercury Study Report to Congress, EPA/452/R-97/003 (NTIS PB98-124738), Office of Air Quality Planning and Standards.

<sup>&</sup>lt;sup>101</sup> Office of Air Quality Planning and Standards, EPA (2001). Research and Development. Mercury in petroleum and natural gas: estimation of emissions from production, processing and combustion.

<sup>&</sup>lt;sup>102</sup> Qa<sup>3</sup> (2021). Unconsidered Mercury Emissions from the Oil and Gas Industry.

<sup>103</sup> ibid.



# 8. Initial ideas for further research and cooperation

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

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

- Monitor the whole process, from production to refined products, in a systematic, standardized, comparable and multicentric way.
- Complete mercury mass balances of every oil and gas process in the most accurate way.
- Promote information exchange on mercury determination and sampling methods where mercury is known to be emitted and released into 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 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 oil and gas sector:

- Identify, monitor and assess mercury waste and mercury-containing waste volumes generated by the sector.
- Understand and track the fate of such waste.
- Disseminate information on best available practices as well as best environmental technologies.<sup>104</sup>
- Improve the capacities of the concerned facilities to process mercury and mercury-containing waste and safely dispose of it. 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 dissemination of guidelines to support the implementation of best available techniques (BAT) and best environmental practices (BEP) for the removal of mercury from oil and gas at the different stages of the process.

In relation to workers' 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, the above remains 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 to supporting an enhanced overview of mercury along the different stages of the oil and gas value chains, including mercury fate and transport, measurement techniques and the species of mercury found, as well as facilitating information and experience sharing on the subject of mercury from oil and gas, and best practices for its environmentally sound management.

According to the report, the oil and gas sector is responsible for a significant portion of anthropogenic mercury emissions. The information available allowed for a detailed study of the sector. However, the industry and countries alike are encouraged to make available additional information in order to study in greater depth the complete life cycle of mercury in this sector.

<sup>&</sup>lt;sup>104</sup> Guidance on Best Available Techniques and Best Environmental Practices, Secretariat of the Minamata Convention on Mercury. September 2017. <u>https://wedocs.unep.org/bitstream/handle/20.500.11822/33122/BAT\_BEP.pdf?sequence=1&isAllowed=y</u>





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### For more information, contact:

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Secretariat of the UNEP Global Mercury Partnership Chemicals and Health Branch Economy Division <u>United Nations Environment Programme</u>

Palais des Nations 8-14 avenue de la Paix CH-1211 Geneva 10, Switzerland E-mail: metals@un.org

www.unep.org/globalmercurypartnership