The impact of H₂S on Hg accumulation on non-corroded pipelines and the implications for assessing risks of offshore decommissioning

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ABSTRACT

In the event of decommissioned oil and gas infrastructure being left in place the operators will have to guarantee that contaminant concentrations are as low as reasonably practicable. To achieve this for a persistent contaminant like mercury (Hg), there are several aspects which must be well understood. Including concentrations of Hg present on infrastructure like pipelines, the species present, how to assess the risk associated with each compound and which analytical methods are available to achieve these knowledge targets. The work displayed in this article aims to shed light on the first two points, specifically, when pipelines have been kept free of corrosion and when exposed to hydrogen sulphide (H₂S) over a long term. Here, it was identified that the kinetics of Hg uptake onto carbon steel resulted in high Hg accumulation on the timescale of months and years with total Hg levels being as high as 0.8 g Hg•m^{-2} after 36 months of exposure to elemental mercury (Hg^0). Across a 5-month period the impact of H₂S on Hg species was investigated finding that the presence of H₂S reduced the fraction of labile Hg species which were most likely to enter the marine environment. Nevertheless, even after co-exposure of Hg^0 and H₂S, 15 % of Hg was mobilised with seawater and was, therefore, potentially bioavailable. This study holds critical information for future risk assessments, particularly of dry gas pipelines, by showing that Hg will accumulate on polished steel surfaces and that a significant fraction of the total may be available to local marine environments.

Introduction

Hydrocarbon fuel sources like oil, natural gas and coal are all known to contain trace levels of contaminants such as mercury (Hg) which has been established as one of the most prominent contaminants in oil and gas (O&G) processing [1,2]. Giving the established toxicity and bioaccumulation risks associated with Hg it is essential to manage any contamination which is present [3,4]. As a response to the presence of Hg, O&G operators have invested in research and infrastructure to model the mobility of Hg throughout their infrastructure [5–8] and, in some cases, remove the Hg entirely via mercury removal units [9,10]. However, these actions are primarily focused on the point Hg reaches onshore processing facilities and much less is known about Hg which does not make its way onshore [11].

It is known that Hg concentrations measured offshore, near reservoirs, and onshore often differ which can be attributed to Hg accumulating along the internal walls of pipelines [11,12]. This has tremendous implications for offshore O&G decommissioning activities which are

expected to increase significantly over the coming decades across the world. Decommissioning activities are expected to cost tens of billions of dollars in Australia where much of the decommissioning focus has been in recent years [13–18]. It is critical that marine environments are preserved and protected to the greatest degree possible throughout this period. With this requirement comes a great deal of debate on what to do with the extensive network of infrastructure presently occupying a portion of the seabed. One option is to have all of the infrastructure, like pipelines, extracted, brought onshore and cleaned. Naturally, this is a costly measure. Alternatively, it may be possible to leave infrastructure in place and this is supported from an environmental perspective as the extraction of pipelines could greatly disturb ecosystems which have developed along the kilometres of pipeline since their installation. However, given the nature of the contents which flow through pipelines, particularly the presence of contaminants such as Hg, it is essential that once these pipelines degrade there is not subsequent contamination of the local environments which could have consequences on marine food webs. In the case of Hg, it is known to bioaccumulate and biomagnify

especially in the marine food web [19,20]. An increase in sea concentrations must be taken seriously as it is possible that a small change to Hg levels in some marine communities could have consequences further up the food chain. In Australia, where progress on decommissioning regulation is a major focus, the regulators (NOPSEMA) require that O&G operators apply "best environmental practices" in line with the Minamata Convention on Mercury [21]. However, as there is limited data on total Hg and speciation it is difficult to assess what should qualify as suitable to be left in place in a marine environment. To accurately risk assess this leave-in-place strategy it is necessary to know what concentrations of Hg may be expected in decommissioned pipelines, which species are present and how they may interact in a marine environment and if they are likely to contribute to bioaccumulation.

There is a significant knowledge gap in the literature with limited knowledge on expected Hg concentrations and what impacts this most [22]. It has been shown that Hg can accumulate to levels exceeding 1 g Hg•m^{-2} in pipelines [11]. Furthermore, laboratory studies have shown that this accumulation is likely benefited by the presence of corrosion [12] and could result in the release of environmentally mobile Hg species [23]. O&G operators often introduce strategies such as internal pipeline coatings or corrosion-inhibitors to prevent corrosion build up and inadvertently this may suggest that Hg accumulation would be limited. This should be similarly true in dry gas pipelines where an absence of moisture should inhibit corrosion formation. Therefore, based on the available information on what affects Hg accumulation and how O&G operators treat their pipelines it may be expected that pipelines with low corrosion levels will have low Hg concentrations.

The aim of this article is to investigate these scenarios where Hg is passing through a pipeline which has not corroded. Here, the concentrations one may expect from longitudinal exposure to Hg are evaluated and secondly the presence of several species are inferred based on chemical fractionation. Finally, the influence which trace levels of hydrogen sulphide (H$_2$S) has on total Hg accumulation and speciation is detailed. This is critical as H$_2$S is commonly found in natural gas and given the strong bonding affinity between Hg and S there is a potential for H$_2$S to promote the formation of sulphides like HgS which will have different associated risks compared to other Hg compounds like HgCl$_2$ or Hg^0.

Methods and materials

Chemicals

Hg^{2+} standard solution, 1000 ± 2 mg•L^{-1} was purchased from Merck (Vienna, Austria) and Hg^0 (99.99+ %) was purchased from Acros Organics. Hydrochloric acid 37 % (for analysis, Honeywell, Hg $\leq$ 0.0000005 %), 70 % nitric acid (analytical grade) and tin (II) chloride (anhydrous, 98 %) were purchased from Fischer Scientific (Vienna, Austria). Ultrapure water (MilliQ, 18.2 MΩ•cm, Millipore) was produced in house. Sample preparation was completed using borosilicate glass vials from Fischer Scientific (Vienna, Austria).

Hg exposure

Samples of non-corroded carbon steel were exposed to either Hg^0 vapour or both Hg^0 and H$_2$S vapour. Two, airtight, desiccators were used to keep these exposure conditions separate. Both desiccators contained an open vessel of Hg$^0_{(l)}$ but only one also contained a beaker which was used to generate H$_2$S$_{(g)}$ at a final concentration in the desiccator of 80 µg•L^{-1} which represents a concentration which could readily be found in gas streams with some natural gas having percent concentrations of H$_2$S. The H$_2$S$_{(g)}$ was produced by reaction of 4 mg of FeS and 100 µL of concentrated HCl [23]. The desiccators were sealed resulting in both being saturated with the respective gas mixtures. The steel was never in direct contact with Hg^0 or the FeS/HCl mixture as each chemical source was stored in the desiccators in separate glass beakers. Hg exposures ran

for between 1 and 36 months, at the end of this period there was no apparent corrosion on the non-corroded steel. H$_2$S exposed samples were not investigated after 36 months as the experiments had to be set up with significant foresight and H$_2$S was not a focus of the research at the beginning of the experiment.

Total Hg analysis by CV-AFS

Sample preparation has been elucidated in detail in two previous publications [12,23]. To summarise, Hg is removed from steel surfaces by 40 % *aqua regia* (*v/v*) solution which has been shown to be effective in removing at least 99 % of the total Hg [12]. Hg analysis was then done using a cold vapour atomic fluorescence spectrometer (CV-AFS, PS Analytical, UK). The strong oxidising power of *aqua regia* ensured that all Hg present in the sample was Hg^{2+}. The Hg^{2+}-containing solution was introduced to the CV-AFS alongside 2.5 % Sn^{2+}Cl$_2$ reductant solution which was prepared in 10 % HCl (37 %, *v/v*). Sample introduction occurred at a 2:1 ratio of sample to reductant. The Hg^{2+} in the sample is reduced by the excess of Sn^{2+} resulting in Hg^0 (and Sn^{4+}) being produced. Newly formed Hg^0 is then introduced to a gas/liquid separator where it is sparged from the liquid matrix by Ar gas and transported through dryer tubes and finally to the detector where it is detected by fluorescence.

The instrument was calibrated using Hg^{2+} (TraceCERT, Merck) standards in a calibration range from 25–1000 ng Hg•L^{-1}. The standards and the samples were always matrix matched meaning that standards were prepared in either 5 % HCl (*v/v*, from 37 % HCl) or 5 % HCl spiked with a 1:10 solution of 40 % *aqua regia* solution (i.e., 4 % *aqua regia*). A limit of detection was typically calculated to be 2.9 ng Hg•L^{-1} based on the average of the blank level + 3.3•standard deviation of the blank signal. A representative calibration is shown in **Figure S1**.

Hg fractionation

To elucidate chemical species information a fractionation approach was employed based on a strategy used previously on the same sample types [23]. The strategy employed here is illustrated in Fig. 1. The concept aimed to do two things, the first was to allow for some interpretation of Hg species by separating ionic (seawater) from insoluble (aqua regia). Methanol and hexane would indicate if there were polar (methanol), or non-polar (hexane) compounds present on the surface which are insoluble or poorly soluble in seawater. Methanol and hexane were utilised as methanol is often injected directly into natural gas pipelines to inhibit gas hydrate formation [24] and hexane is a
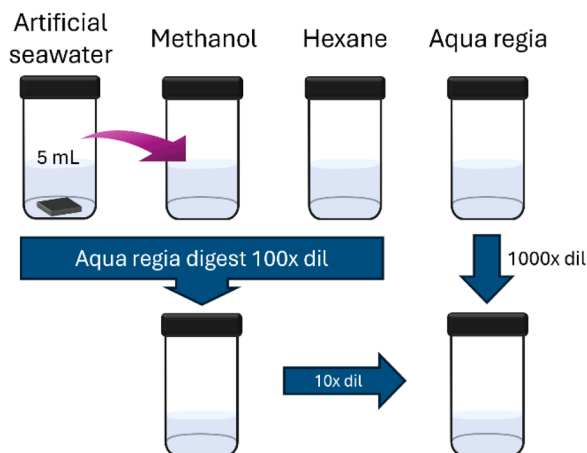

Fig. 1. Illustration of the chemical fractionation approach used, showing a Hg-contaminated steel coupon being sequentially washed in several solvents before being digested in aqua regia. In each case an aqua regia digest was performed to ensure all species were oxidised before analysis by CV-AFS.

commonly available non-polar solvent. Overall, this method gives a picture of how complex the sample is. If everything is removed in one fraction, then diversity of species is likely lower than if every step has Hg present. Secondly, this method uses seawater to promote data relevant to risk assessment in a decommissioning context. This fraction helps to elucidate if mobile Hg species (soluble or nanoparticulate) [23,25] are present and in what concentration, this is critical as these species would be among those which could be considered higher risk for bio-accumulation given their lability.

The method involved taking a contaminated steel section, placing it in one solution and after 10 min it is transferred to the second solution (first it is dabbed dry to prevent transfer between samples). Each sample is then diluted in 5 % HCl and analysed by CV-AFS as described previously. Total Hg is achieved by the summation of Hg in each fraction.

Results and discussion

Long term exposure of non-corroded steel to Hg^0

In an earlier publication it was identified that corrosion-free carbon steel accumulated low levels of Hg (0.00001 g Hg•m^{-2}). In comparison, corroded carbon steels which accumulated over 0.1 g Hg•m^{-2} of steel in the same timeframe. It is true that corroded steels appear to accumulate more Hg than non-corroded steels; however, initial investigations looked at these accumulation rates across 1 week of exposure. Naturally, pipelines have Hg-containing hydrocarbons flowing through them for years and to understand Hg accumulation a longer study was necessary. Here, Hg accumulation was considered at 4-time points; 1 3, 5, and 36 months. At each time point Hg was removed from contaminated steel sections by *aqua regia* and the subsequent concentrations were determined by CV-AFS. These results are displayed in Fig. 2. It was found that total Hg accumulation on non-corroded steel reached levels as high as 0.01 g Hg·m^{-2} of steel by the 5-month time point (Fig. 2, Left). This is 1000 times higher than what was previously shown after 1-week of Hg exposure [12]. Total Hg accumulation on steel was then seen to increase again when looking at steel samples which had been exposed to Hg for 36 months. Following this period of exposure total Hg on steel was found to reach 0.8 ± 0.2 g Hg·m^{-2} ($n = 4$). This is in the same order of magnitude as the concentrations found on corroded steel following one week of Hg exposure and is comparable to the estimations published by Wilhelm and Nelson from their analysis of an offshore pipe segment [11, 12].

For the 1, 3, and 5-month Hg exposures a concurrent experimental design was used to investigate the impact of H$_2$S on total Hg accumulation and Hg speciation on the surface on the steel coupons. The plot shown in Fig. 2 (left) captures the concentrations of Hg which accumulated on non-corroded steel samples when exposed to either Hg^0 vapour or a gaseous mixture of Hg^0 and H$_2$S, which were determined by CV-AFS analysis. The results from these exposures showed that total Hg concentrations on the steel were comparable between H$_2$S exposed steels and those which had no H$_2$S in the incubation atmosphere. After 5 months, the co-exposed samples were found to have twice the total Hg on the steel surface. Samples which had been held in a Hg^0 environment had 0.005 ± 0.002 g Hg•m^{-2} while the samples which were co-exposed to both Hg^0 and H$_2$S were 0.01 ± 0.001 g Hg•m^{-2}. Data is not available for Hg^0 + H$_2$S after 36 months to identify if this trend is maintained.

These findings are critical for O&G operators, as it is a strong indication that significant levels of Hg uptake onto steel is feasible even in corrosion free environments, although on a different time scale to corroded pipeline sections. Therefore, over the years that a pipeline is active the current data available in the literature suggests that Hg will have accumulated on any carbon steel infrastructure which it was exposed to regardless of corrosion. There are clear differences between Hg accumulation in corroded and corrosion-free environments. The most apparent and well-established difference between the two systems being Hg uptake kinetics with corroded steel accruing high Hg concentrations within days. However, the absence of corrosion could impact Hg speciation in pipelines with iron oxide phases not being readily available to the oncoming Hg^0 vapour. Speciation will have a substantial impact on the risk associated with Hg-contaminated pipelines being left in place following decommissioning with questions such as lability and bioavailability in the environment being directly dictated by the Hg species present. To investigate this potential for speciation to change, the Hg concentrations determined after 5-months were generated from sequentially washing the steel pieces with seawater, methanol, hexane and finally aqua regia. Total Hg was determined for each solution and summed to give g Hg·m^{-2} and the percentage of the total found in each wash solution is presented in Fig. 2 (right).

Two separate environments were used for steel exposure with one having a Hg^0 enriched environment and the other with Hg^0 and H$_2$S being present in the incubation atmosphere. This difference is important, as Hg has a well-established chemistry associated with sulphides with compounds such as meta-cinnabar (HgS) being frequently found in O&G processing [11,26]. It is expected that HgS will have a lower inherent risk associated relative to other Hg species which are labile in marine environments. Although, the long-term stability of HgS has not been studied in a deep-sea environment and it is evident that this stability is dependent on particle size and chemical environments.
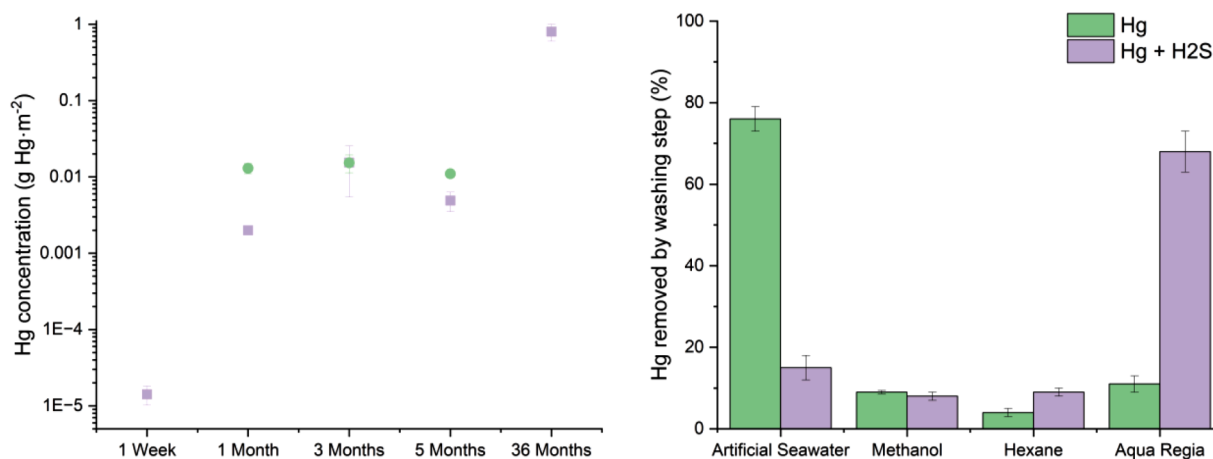

Fig. 2. Left) Total Hg on carbon steel (API 5L-X65) coupons following 1 week [12] and 1 ($n = 2$), 3, 5, and 36 months (this study) of exposure to an atmosphere of Hg^0 (green) and a mixture of Hg^0 and H$_2$S (purple) at a concentration of 80 μg•L^{-1}. Right) Fractionation data for the 5-month data point from the figure on the left-hand side. Showing how H$_2$S co-exposure alters the Hg speciation and ultimately the % available to each solution, resulting in a majority of the Hg being insoluble in the chosen solvents. Error bars are representative of the standard deviation from a method triplicate (i.e., $n = 3$ steel samples).

Similarly, the methylation and bioavailability of HgS, particularly when in nanoparticulate form, has not yet been well established and is an aspect of risk which should be investigated [27–29]. In some gas streams, H_2S concentrations can be as high as percent level. Fig. 2 (right) clearly shows that when H_2S is present in concentrations as low as 80 $\mu g \bullet L^{-1}$ a clear change in Hg speciation is still visible. In the absence of H_2S, 75 % $\pm$ 3 % ($n = 3$) of the Hg accumulated on carbon steel was removed from the steel surface into artificial seawater. Conversely, when H_2S was present in the experimental design this seawater fraction dropped to 15 % $\pm$ 3 % of the total with a majority being removed by *aqua regia* digestion. This is a significant difference and makes it clear that differences in pipeline (i.e., dry gas vs mixed phase) and their risk assessments will likely vary on a case-by-case basis as the local geology and the fuel being transported changes from site to site. An increase in relevant data is desperately needed from offshore sites from around the globe and with those the development of standard methods and analytical approaches, which overcome the challenges of Hg sample preparation and analysis, to accurately determine Hg levels and speciation.

Conclusions

Risk assessment of decommissioning practises will be reliant of a comprehensive understanding of Hg contamination throughout deep sea infrastructure. This article adds to a growing body of knowledge on this subject by investigating the extent to which Hg can accumulate on corrosion-free carbon steel. It was found that when the steel is exposed to a Hg containing environment for a time frame on the order of 1–5 months, Hg accumulation can consistently reach concentrations greater than 0.001 g $Hg \bullet m^{-2}$ and after 36 months Hg concentrations can exceed 0.8 g $Hg \bullet m^{-2}$. It was possible to identify that Hg accumulation on steel was not limited by the presence of H_2S with total Hg concentrations being comparable between the samples exposed to H_2S and those which were not. However, H_2S co-exposure with Hg^0 impacted the chemical speciation of Hg on the steel surfaces. A chemical fractionation approach indicated that the percentage of the total Hg which would become rapidly solubilised in seawater dropped from 70 % to 15 % of the total Hg when 80 $\mu g \bullet L^{-1}$ of H_2S was present in the exposure atmosphere. This article is adding to a growing body of literature which is indicating that Hg can accumulate in high concentrations on steel pipeline surfaces and that it is likely that the speciation will change depending on the chemical composition of the fuel flowing through the pipeline. The published data available makes it clear that any seawater which passes through a pipeline is likely to be contaminated with Hg and should be treated as such. It is evident that more work is required in this field to understand the short and long-term consequences of leaving these pipelines in place which must consider apparent complex Hg speciation which exists and the ultimate interaction between the Hg species and the local environments. This should consider species-specific bioavailability, bioaccumulation and toxicity.

CRediT authorship contribution statement

Lhiam Paton: Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Data curation, Conceptualization. **Sandra Kiesel:** Writing – review & editing, Formal analysis, Data curation. **Jörg Feldmann:** Writing – review & editing, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Lhiam Paton reports financial support was provided by Austrian Science Fund. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jfueco.2025.100149.

Data availability

Data will be made available on request.

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