

Mercury concentrations in produced gas, condensate, rock and water from the Montney Formation

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Summary

Elemental mercury is a common trace contaminant in many petroleum reservoirs globally. Mercury has been shown to increase corrosion and contamination of well, pipeline and facility infrastructure, as well presents a significant potential risk to health, safety and environment. This study on the Montney Formation was carried out to measure mercury concentrations in produced gas, condensate and water, plus nearby core samples, to assess the total content and partitioning behavior of mercury. The intent of this paper is 1) to increase awareness of trace metals in petroleum fluids and rocks, and 2) to discuss potential mercury sources and modes of transport in petroleum reservoirs.

Theory / Method / Workflow

Produced gas samples from 16 wellheads were collected, along with co-produced condensate and water at 11 comingled group separators. Samples were obtained from Shell Canada well sites in both British Columbia and Alberta. The sites were selected to compare the different Montney reservoir conditions including present day temperature, rock and fluid thermal maturity, water saturation and especially hydrogen sulfide content.

Due to the generally very low concentrations observed in petroleum reservoirs, mercury testing requires specialized analytical methods performed using laboratory duplicates, blanks and standardized spiked samples. Shell operation staff and Agat Laboratories collected the gas samples in aluminum cylinders, condensate samples in both amber glass and HDPE plastic, and water samples in HDPE plastic bottles. Agat also coordinated the analysis of each sample type that included work at Agat Laboratories, Flett Research Ltd and Ohio Lumex. Trace sulfur in gas and condensate was performed using sulfur chemoluminescence detection at Agat laboratories. Total mercury in gas and condensate samples was performed using a pyrolysis mercury analyzer. Utilization of gold sorbent traps allowed for sufficient gas volume to be sampled to achieve excellent lower detection limits of 1 ng/m³ (~ 0.001 ppb). Total mercury concentrations were measured in water by using oxidation, purge and trap method along with cold vapour atomic fluorescence spectrometry (CVAFS). Methyl mercury in water was measured by distillation, aqueous ethylation, purge and trap, and CVAFS. To build a mercury profile in a nearby vertical type well, 12 core samples from upper, middle and lower Montney lithologies were collected and analyzed for mercury concentrations using whole rock acid digestate and ICP-MS.

Results, Observations, Conclusions

Overall, the concentrations of mercury analyzed in produced gas, condensate and water samples from the Montney Formation are relatively low compared to other produced petroleum reservoir fluids. For example, produced Montney gas sample mercury concentrations ranged from 5 to 45 ng/m³ (0.006 to 0.055 ppbw), which are lower than reported produced gases from other petroleum reservoirs globally that can range several orders of magnitude up to 450,000 ng/m³ (~500 ppbw assuming gas density 0.8 kg/m³) in on shore reservoirs in China (Yan et al., 2017). The Gorgon gas field in Northern Carnarvon Basin, Australia reported gas sample mercury concentrations up to 1,000,000 ng/m³ (Bourdet et al., 2020).

Measured mercury concentrations for 6 of 7 produced Montney condensate samples were below the 1 ppbw detection limit, but one condensate sample measured elevated mercury at 4.6 ppbw. The mercury concentration in this one well sample is relatively low compared to other light crude oils refined in Canada that range from 0.4 to 45 ppbw, with heavy oils up to 275 ppbw (Hollebone and Yang, 2007). The one produced Montney condensate sample mercury concentration also appears to be relatively low compared to other produced crude oil samples from the Alberta Basin that range from 2 to 399 ppb (Hitchon & Filby, 1983, 1984).

Produced Montney water sample total mercury concentrations ranged from 6 to 93 ng/l (0.006 to 0.90 ppbw assuming water density 1040 kg/m³). These concentrations are orders of magnitude lower than 500 to 12,200 ng/l mercury concentrations (0.480 to 11.731 ppbw) reported for produced waters from a gas field in Japan (Yamada et al., 2017). Methylmercury was also measured in Montney produced water samples that ranged from 0.7 to 12.1 ng/l. Methylmercury was highest in Alberta Montney waters that also have high C₁ to C₄ methyl-mercaptans concentrations ranging from 33 to 107 ppm in coproduced gas and condensate.

The measured Montney core whole rock acid digestate mercury concentrations range from 20 to 195 ppbw. These concentrations are similar to core samples from the northwest shelf offshore Australia that range from 20 to 390 ppbw. This whole rock sample digestate mercury measurements from a related study was performed at the same time, lab and method so are directly comparable.

Novel/Additive Information

One surprising result of this study is that the measured Montney core and northwest shelf offshore Australia core samples have a similar amount of total mercury content in rock, but the produced gases from these reservoirs have vastly different mercury concentrations from 5 to 1,000,000 ng/m³. This indicates that other mechanisms control mercury mobility in the fluid phases, such as reservoir temperature and pressure, redox conditions and fluid compositions, sulfur content and/or mineral associations of mercury sources.

One contributing factor for the low mercury concentrations in the BC and Alberta Montney well produced fluids is the relatively low Montney reservoir temperature that ranges from 80 to 90 °C, compared to the northwest shelf offshore Australia reservoirs that have high mercury in produced fluids and are over 120 to 130 °C.

The role of sulfur rich fluids to transport mercury in the subsurface was examined by selecting wells with large variation of H₂S and mercaptan concentrations. For example, 3 of 17 wells sampled had high coproduced H₂S gas concentrations ranging from 3.3 to 5.3 mol%, and the other 14 of 17 wells had only 0 to 15 ppm H₂S gas. Despite the large difference in H₂S and mercaptans in gas and condensate, the measured mercury concentrations remain consistently low for all produced Montney gas samples (Figure 1). There is a slightly higher mercury in the Alberta versus BC Montney gas samples but is not statistically significant. More data would be useful to further corroborate these potential trends between reservoir temperature, H₂S, mercaptans and mercury transport.

In the Alberta Montney wells, the H₂S concentrations are several mole percent, which is out of thermodynamic equilibrium with present day siliciclastic reservoir conditions (Bryndzia and Inan Villegas, 2020). In the Montney wells sampled, the reservoir temperatures are below the onset of thermochemical sulfate reduction (TSR) to produce H₂S ~120 °C. The H₂S in the Alberta Montney is interpreted to be derived from late stage gas migration, plus maybe some in situ TSR generation in places, since max burial 45 Ma and several kilometers of uplift. This Alberta Montney reservoir case with high H₂S and low mercury suggests that high H₂S concentrations alone may not lead to mercury transport. The Alberta Montney produced fluids case could also reflect a low availability of mercury from the mineral and organic phases present, despite the whole rock mercury data. Or, perhaps the source of the high H₂S gas in the Montney came from low mercury sources that include TSR in the underlying Devonian carbonate reefs. Additional produced fluid samples from more thermally mature, sour parts of the basin could further test sulfur related mercury transport in the Montney petroleum system.

Another interesting aspect of the study is the fact that methylmercury was shown to be the primary species of aqueous mercury species versus total mercury in the Alberta Montney produced waters (Figure 2). In contrast, the BC Montney waters are different with very low methylmercury concentrations versus total mercury. Similar speciation trends including small proportion of methylmercury have been reported including alkyl mercury compounds, plus ionic and elemental mercury in crude oil samples (Bloom, 1999), plus in gas condensates and formation brines from Germany (Zettlitzer et al., 1997). Zettlitzer et al., 1997 reported relatively low aqueous phase alkylmercury compounds ranging from 5 to 1,000 µg/l, compared to condensate phase total mercury concentrations ranging from 3,000 to 6,000 µg/l in produced fluid samples. These results may suggest that H₂S mediated mechanisms involving alkylated mercury compounds and dimethylmercury sulfide solid (Craig and Bartlett, 1970, Jonsson et al., 2016) are involved in mercury transport between fluid phases in both subsurface and surface environments.

These Alberta Montney water samples with notable concentrations of methylmercury also have high alkyl mercaptans concentrations in coproduced gas and condensate samples. Perhaps the presence of alkyl mercaptans and alkylmercaptan-mercury organic complexes in the petroleum phase (e.g. Wilhelm and Bloom, 2000) facilitate the mobility of mercury by enabling mercury to move between the aqueous, gas and condensate phases in the subsurface. Downhole samples would be ideal to better assess in reservoir phase partitioning with alkyl mercury compounds. Despite the interesting methylmercury in the Alberta Montney produced water sampled, most of the mercury is partitioned into the gas phase versus the aqueous phase by 3 to 10 times (at surface separator conditions 50 °C, 3000 KPa).

One additional consideration is the overprint of aqueous and mineral phase reactions that also may impart controls on mercury mobility in the subsurface and wells infrastructure. Pore waters of Montney reservoirs across the basin commonly have abundant barium, calcium and sulfate ions as determined by core salt extracts (separate study) and public produced water composition data. These salt extract and water compositions result in higher barite and calcite mineral saturations that may lead to more oxidized, and less mobile forms of mercury in petroleum reservoirs. Mercury is known coprecipitate with barite minerals which may further exhaust the aqueous partitioned phase of mobile mercury. Further reactive transport modeling could be helpful to understand these mineral controls on inorganic speciation.

In summary, the relatively low reservoir temperature appears to be the main controlling mechanism of low mercury mobility in the BC and Alberta Montney produced fluids compared to other reservoirs globally. Despite the low mercury concentrations in high sulfur fluids in the Alberta Montney, this study may also hint at a role of sulfur related mercury transport via H_2S and mercaptan organic mercury complexes providing increased solubility in fluid phases. For example, since nearly all the aqueous phase mercury was present as methyl mercury in the Gold Creek produced water samples, then this suggests that alkyl mercury compounds play a role of mercury transport in multiple phases under different reservoir conditions. Furthermore, since H_2S is commonly transported in the aqueous phase, then it seems possible that mercury transport from source (e.g. coals, volcanos, etc) to sink (petroleum reservoir) can occur naturally in the subsurface aqueous phase via ionic and alkyl mercury organic compound complexes. In addition to understanding mercury mobility in the subsurface, monitoring for alkylmercury compounds is also important for health, safety and environment due to the very high toxicity and mobility of alkylmercury in the air and water phases on surface.

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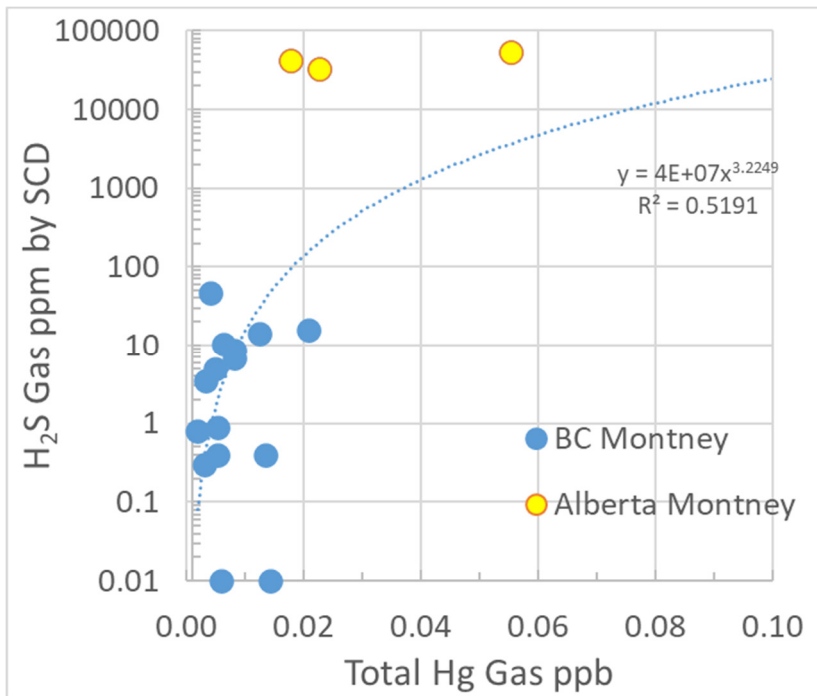


Figure 1 - Mercury versus H₂S concentration in produced Montney gas samples.

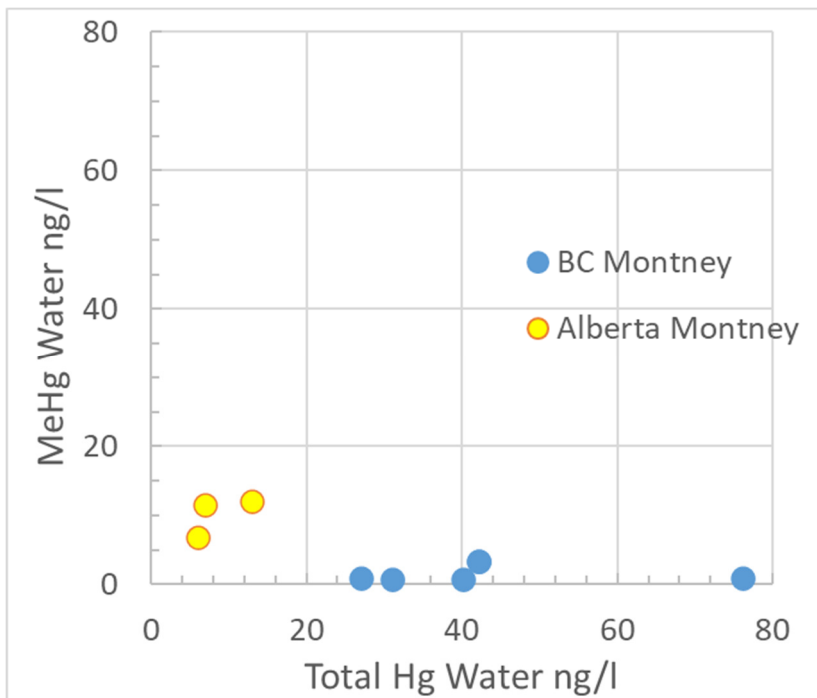


Figure 2 – Total mercury versus methylmercury concentrations in produced Montney water samples.

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