Global warming's effect on the mercury in the terrestrial arctic

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Abstract

The global pollutant mercury has been a growing pollutant in the arctic as a result of the Anthropocene. This environmental contaminant gets onto organic food webs where it can bioaccumulate and can react to form methylmercury, which is toxic to most life. The arctic has historically been a source of storage for global mercury, causing it to have increased its mercury concentrations more than other regions after the anthropocen's increase of global mercury pollution, and while measures to decrease the anthropogenic mercury pollution has decreased the mercury contents to the arctic, the increase of global temperatures as a result of global warming now present a new anthropogenic source of change to the arctic mercury cycle, potentially causing the Arctic to become a polluter, as the mercury stored in this environment is released.

Introduction

Gaseous elemental mercury Hg(0)(GEM) is long-lived volatile pollutant and therefore has the capacity to reach the Arctic from lower altitudes *AMAP assessment 2011 : mercury in the Arctic* [1]. This heavy metal can through microbial reaction become methylated. Methylmercury is know to be a potent neurotixin to human and animal life, this is further amplifies because of its ability to biomagnify in the foodweb [24]. The unique conditions of the Arctic has made the Arctic an area of storage for the world. The mercury contents started to increasing the 1800s as a result of human activity, and while this peaked in the 1980s, the mercury has being contained in the Arctic environment because of the permafrost ability to mercury [21][23]. this makes the Arctic an important area for the global mercury cycle, as its a good place for sedimentation of mercury, but also makes the Arctic especially susceptible to changes to temperature, more so because temperature change effect the Arctic at a rate that about double that of the global temperature increase [3].

This paper attempts to address possible ramifications of global warming that change the quantity of mercury in the terrestrial arctic. And while its varying climate models leading to different changes in temperature and the effects will differ in more localised environments of the Arctic, will this paper focus on the general effects of rise in global temperatures at the Arctic as whole. This will be done by looking how temperature could cause changes to the mechanism that cause mercury deposition. In addition to how global temperature increase will cause the thawing of permafrost and the ramefications that bring in regards to mercury and lastly the ramifications of mercury released from global wildfires increase at account of global warming in conjunction with looking at potential consequences of changes global cycling of mercury from global wind patterns.

Theory

Mercury for the most part exist in the atmospheric environment in two forms. Hg(0) know as Gaseous elemental mercury (GEM), this the most substantial part of the atmosphere, contributing 98% of atmospheric mercury. The majority of the remaining mercury is Hg(II), but oxidised mercury is referred to in bulk as reactive gaseous mercury (RGM). [1]

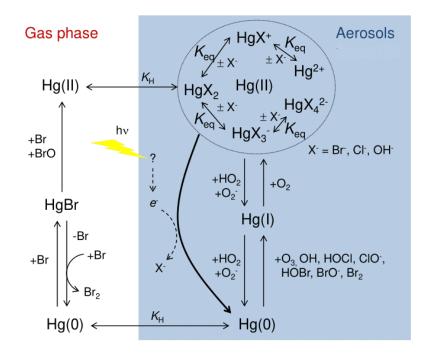
Looking at the arctic region the most important aspect is the deposition of mercury. This is usually characterised as either dry or wet deposition.

Dry deposition is Hg deposition in the absence of precipitation. RGM has higher water solubility and will therefor deposit faster during there conditions, but the primary form of mercury to be deposited this way is GEM. as the there simply is more of it [32].

Wet deposition is Hg deposition in the presence of precipitation, meaning the main aspect effecting the deposition rate is an elements solubility. This causes to GEM, being volatile, to almost not deposit from this type of deposition. this type of deposition when event lead to GEM being oxidized to RGM [32].

Deposition rates in the arctic is further accelerated by a mechanism called The arctic mercury depletion event"(AMDE) [31]. This occurs in the arctic spring as a result of the arctic sunrise. With the influx of reactive halogen coming in from the sea ice.

This influx happens at a count of the Arctic bromine explosion [31]. This event is a product of solar radiation ionizing salt ion, releasing halogens, primarily bromine, from the sea ice and into atmosphere as reactive XO_n species [25]. These halogen species can will then cause further reactions with it self, ozone and mercury, forming RGM species [15].



Figur 0.1: visual representation of the multitude of reactions occurring during AMDE [30]

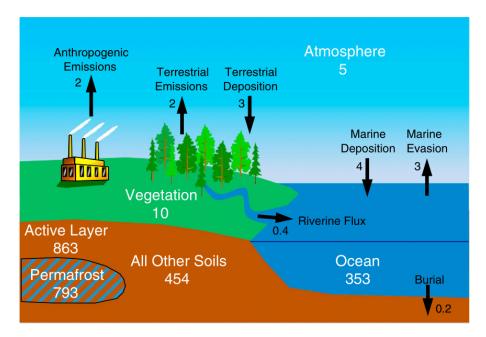
Another enhancing effect of bromine release, is the Frost flowers of the arctic, having a higher surface area and salinity then that of normal sea ice. [10]



Figur 0.2: Frost flowers on sea ice covering a lead. taken at $75^{\circ}58N$ $25^{\circ}34E$, 24 March 2003 [10].

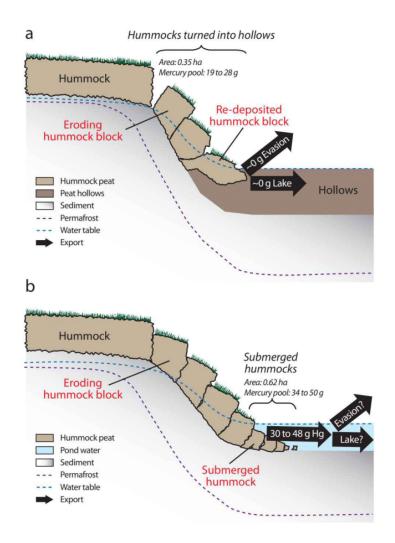
The RGM is then deposit into the snow and ice layer at significantly faster rates, through dry deposition. Following this will some of the RGM in the snow layer react through photoinduced reduction back GEM, leading to a loss of 50% to 80%* of the deposited mercury [28] [27], but the net increase of 20% to 50% is a substantial increase of mercury and will importantly increase the consecration to levels above the normal reaction equilibrium. When this snow melts, it accelerate the lost of mercury back to the air, but most of the mercury is discharged into the meltwater, allowing greater amounts of mercury to reach the arctic soil than in other regions. [6] [13]

The deposition would in most soil would disperse in time, but a majority of the arctic is permafrost witch is a soil type especially good at containing mercury. [23]



Figur 0.3: Ad schematic of the modern global Hg cycle in the northern hemisphere, with major reservoirs in white (Gg Hg) and fluxes in black (Gg Hg yr^{-1} [23]

Permafrost is ground that will remain frozen for two consecutive years. This makes it so that there is significantly less activity in the ground so movement of matter and microbial activity is so low that the ground functions as a sort of trap for elements contained in it. On top of this lies the active layer which unfreezes during summer allowing for the deposition of mercury. The soil here will over time slowly sediments down moving into the permafrost layer[23]. The mass balance is then changed allowing for new quantities of mercury to be sedimented further down. When the permafrost thaw it it also effects the local environment its in, most notable is the effect on the local peatland. This comes from the fact that during the Little Ice Age, that we are comming out of, the permafrost extended over large areas of peatland and is subsequently some of the larger areas where the permafrost is melting away. In this mercury there is bound mercury to the organic matter. As the permafrost smelts away in these peatland regions, the palsa of the peatland starts to collapse, the mercury stored in the palsa is mobilized, causing i large increase of mercury in the local environment. [21][11]

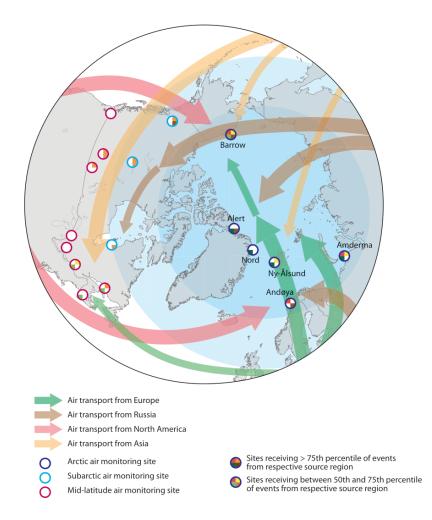


Figur 0.4: Conceptual illustration of the collapse of a hummock palsa into (a) peat hollows and (b) pond water. between 1970 and 2000 within the Stordalen palsa mire and the estimated mercury pools affected by this change. [1] [11]

Another biome is the forest biome, this is notably a biome where there is significantly more biologic matter for Hg(II) for absorb or adsorb to [26]. Mercury in plant matter over time through litterfall and throughfall [8]. organic matter in soil will in turn be consumed by micro organismic life, releasing elemental mercury into the soil [23].

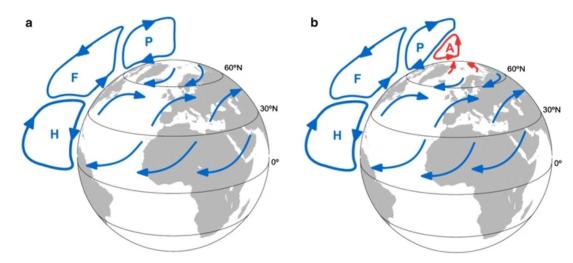
The main way the mercury of the forest biome is then released is through wildfires, which is a growing problem at the account of temperature increase. Mercury stored in vegetation that turn to ash from a wildfire, is releases to the atmosphere predominantly as GEM. The wildfire also increases the temperature of the soil allowing for further the release of GEM. [23]

While there are wildfires in arctic region the most of the mercury in the arctic from wildfires comes from sources further south, the main one being Eurasia, contributing about 55% of the mercury going to the arctic [12], compared to North America contribution about 11%. This happens due to the fact that the direction of the wind systems, favor the movement of air from the Eurasian region most of the year [20].



Figur 0.5: Dominant air transport pathways for mercury into the Arctic from major source regions, with an indication of the contribution from these source regions at specific monitoring locations [7] [1]

Wind systems are divided up into separate longitudinal cells with the arctic cell being the wind system governing air movement in the arctic and the polar cell governing air movement towards the arctic



Figur 0.6: Schematic diagrams of a three-cell model. Letters "H", "F", "P" and "A" indicate the Hadley, Ferrel, Polar and Arctic cells respectively. [7]

Discussion

With the ramifications that come with the significant loss of permafrost in the arctic region, its likely that this is the biggest contributor to change of mercury in the region. One of the changes is the growth of the active layer. This would eventually lead to a point where the active layer no longer permanently freezes during the winter. This will cause the permafrost to permanently reduce during summer and the water in it run of [9]. This presumable will cause the activity of the active layer, to open up for elemental mercury that previously would be trapped in the ice, to be released.[19] Another potential effect of the growth of the active layer, is the increased microbial activity in the active layer compared to that of permafrost. This would accelerate the breakdown of organic matter that previously bound mercury [23]. Correlation studies backs this up by finding that river running of from thawing regions with running permafrost had an increase concentration of mercury 3 to 32 times that rivers used for comparison[16].

Permafrost thawing will as stated have an a effect on the local environment of the area. One of the effects is the collapse in the local peatland. This has been found to release significant amounts of the mercury stored here into the local landscape [21]. the overall quantity om mercury that can be released has yet to be determined, but as the amount of mercury in peatland is significantly smaller than the amount in the permafrost[21], it can be surmised that the mercury released form the permafrost would have a bigger impact than its effect than the impact permafrost thawing has on peatland. but peatland collapse might have a more local impact, resulting in a bigger mercury toxification of the local fauna.

On the contrary would increasing temperatures in permafrost region cause an increase to vegetation, with has an increased capacity for storage of mercury. [9]

While its hard to give accurate estimates on the amount of mercury that would be released from thawing of permafrost. comparing the date from Schuster et al. [23] on the totality of mercury stored to be 793 ± 461 Gg frozen in permafrost, this accounts for and the reduction of permafrost in the arctic to be 13% to 28% by 2050 [1] and a projected decrease of 29% to 59% by 2200 [22]. Indicating the monumental change this terrain is going through.

Looking at Deposition of mercury. There is likely to be big changes to the arctic at account of the changes to the equilibrium in the cycle of dry and wet deposition, owing to the fact that it would effect the arctic in its entirety. But with the potential temperature increases of only a few degrees, I haven't been able to find any paper showing the impact. On the other hand there's multiple ways temperature will AMDE. Starting of by looking at bromine. There were found no temperature dependency on reaction between GEM and Br, but these studies were done around room temperature[1]. Simpson et al. [25] found an overall negative temperature dependence for Br2 release from saline ice. Toyota et al. [30] found that through simulations that bound mercury is predicted to be suppressed significantly when temperature is raised from 253 K to 268 K due to changes in the Henry's law of Hg(II)[30].

Although temperature has been found to not have a significant impact on the rate of reaction between mercury and the halogen species of the bromine explosion.[5] the amount of available bromine for the reaction could be effected. There has been found correlation temperature increase and $HgBr_2$ dissociation and a reduction[29]. This effect would tend to decrease the rate of Hg deposition associated with AMDEs. Contrarily temperature increase reduces the perennial sea ice in the region, leading to an increase of new sea ice, which is more saline than the perennial sea ice it replaces. [17], increasing the available bromine for AMDE. New sea ice has also been found to have increased quantity of frostflowers compared to that of perennial sea ice, further increasing the available bromine. increased temperatures will on the other hand lead to an less overall sea ice [1]. making the impact to mercury from the different changes to the sea ice hard to quantify.

Looking at AMDE as a whole Cole and Steffen [2] gave an estimate of 0.0086 ± 0.0014 ng $m^{-3} yr^{-1}$. This data was was based on the historical trends, so both major changes from larger increases of temperature or lower increases would make this differ. The overall change in quantity would also be difficult to quantify as temperature change will change the areas where AMDE can happen.

Lastly in the discussion of deposited mercury, there's the mercury in the snow. This would be effect by the increase of snowmelt. Here the photo chemical reactions that happen is accelerated, increasing the mercury released to the air. This was estimated by Mann, Mallory, Ziegler, Tordon and O'Driscoll [14] showing reaction rates of 0.11 to 0.60 h^1 in snow, as opposed to in 0.08 to 1.05 h^1 snowmelt. This is in addition to the fact that snowmelt, increases mercury discharge from run off water. This is especially effected by increasing temperatures, as an increase to water discharge was found to increase the mercury discharge rate two fold [1]. Dastoor et al. [4] found that export of mercury from meltwater in the arctic to be 15.5–31.0 Mg year⁻¹.

Moving on to Wildfires, there's been studies on wildfires in the Arctic and studies on the impact of wildfires wildfires mercury contribution to the arctic as a whole, there's no studies looking specifically at the potential mercury contribution as a local region. As growing temperatures leads to an increase of wildfires in the arctic [18] there's a need for the scientific community to look into this matter in order to understand the local impact. Currently wildfires were found to contribute 10% of the total mercury to the arctic, accounting for 15Mg yr^{-1} [12]

But global warming has led to a trend of weakening of the arctic cell and strengthening of the polar cell, resulting in potential reduction of distribution in the arctic but increase of air movement towards the arctic.[7] The strengthening of air movement towards the arctic would increase the amount of mercury being moved towards the arctic resulting in an increase of mercury primarily from wild fires and anthropogenic activity outside of the arctic. On the other hand would the reduction in airflow within the arctic reduce the AMDE, through reduced bromine flux within the arctic.

This comes in addition to the fact that dominant air transport pathways could change as a result of temperature increase. The effects of this for mercury is not studied, but the most important changes would possibly be to look at the potential increase from North America and subsequent decrease from Eurasia.

Conclusion

While there are still significant uncertainties into the over increase of temperature for the arctic region, an increase in temperature in the region is certain to create great changes to the current behavior of mercury. The biggest change to the mercury cycle, is likely that of mercury from the thawing of permafrost and subsequent reduction of total permafrost. This is because even though the terrain will change into terrain with its own capacity for mercury storage, looking at the sheer quantity of mercury stored in the permafrost, gives a good indication of the impact this would have if it was to be released, especially on its local environment. Deposition is similarly in a position where even small changes could bring about a significant change to the amount of mercury, just because of it's scale. Similarly is wildfire's already a big contributor and will continue to be so as the temperatures increase, but with the low amount of studies on specific development of it in the arctic, its hard to justify that it's of more importance then the previous subjects. lastly is air patters, who would undoubtedly change the arctic environment significantly if big changes were to happen, but these have been found to be hard predict and could potentially take a long time to change enough for significantly enough changes to happen.

The overall trend, seem to be that the will be more atmospheric mercury in the arctic system at account of increased temperature. As all of the of the subjects discussed in this paper show some indication of increase of mercury to the system. While there are still uncertainties that have yet to be studied enough to give a definitive answer on if it would increase of decrease the mercury pollution/deposition. The data that's been found points towards an overall increase.

Referanser

- [1] AMAP assessment 2011 : mercury in the Arctic [2011].
- [2] Cole, A. and Steffen, A. [2010], 'Trends in long-term gaseous mercury observations in the arctic and effects of temperature and other atmospheric conditions', Atmospheric Chemistry and Physics 10(10), 4661.
 URL: http://search.proquest.com/docview/856211319/
- [3] Corell, R. [2005], 'Arctic climate impact assessment', Bulletin Of The American Meteorological Society 86(6), 860–861.
- [4] Dastoor, A., Ryzhkov, A., Durnford, D., Lehnherr, I., Steffen, A. and Morrison, H. [2015], 'Atmospheric mercury in the canadian arctic. part ii: Insight from modeling', *The Science of the Total Environment* **509-510**, 16.
- [5] Dommergue, A., B. E. E. R. e. a. [2007], 'Laboratory simulation of hg0 emissions from a snowpack', Anal Bioanal Chem 388, 319–327.
 URL: https://doi.org/10.1007/s00216-007-1186-2
- [6] Dommergue, A., Ferrari, C. P., Gauchard, P., Boutron, C. F., Poissant, L., Pilote, M., Jitaru, P. and Adams, F. C. [2003], 'The fate of mercury species in a sub-arctic snowpack during snowmelt', *Geophysical Research Letters* **30**(12), n/a–n/a.
- [7] Durnford, D., Dastoor, A., Figueras-Nieto, D. and Ryjkov, A. [2010], 'Long range transport of mercury to the arctic and across canada', Atmospheric Chemistry And Physics 10(13), 6063–6086.
- [8] Grigal, D. F. [n.d.], 'Mercury sequestration in forests and peatlands', Journal of Environmental Quality 32(2), 393–405.
 URL: https://acsess.onlinelibrary.wiley.com/doi/abs/10.2134/jeq2003.3930
- [9] Huissteden, J. v. [2020], 'Thawing permafrost : permafrost carbon in a warming arctic'.
- [10] Kaleschke, L., Richter, A., Burrows, J., Afe, O., Heygster, G., Notholt, J., Rankin, A. M., Roscoe, H. K., Hollwedel, J., Wagner, T. and Jacobi, H.-W. [2004], 'Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry', *Geophysical Research Letters* **31**(16). URL: https://aqupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2004GL020655
- [11] Klaminder, J., Yoo, K., Rydberg, J. and Giesler, R. [2008], 'An explorative study of mercury export from a thawing palsa mire', *Journal of Geophysical Research: Biogeosciences* 113(G4), n/a–n/a.
- [12] Kumar, A. and Wu, S. [2019], 'Mercury pollution in the arctic from wildfires: Source attribution for the 2000s.', *Environmental science technology* 53(19), 11269–11275. URL: http://search.proquest.com/docview/2284554113/
- [13] Mann, E. A., Mallory, M. L., Ziegler, S. E., Avery, T. S., Tordon, R. and O'Driscoll, N. J. [2015], 'Photoreducible mercury loss from arctic snow is influenced by tempe-

rature and snow age', Environmental Science & Technology 49(20), 12120–12126. URL: https://doi.org/10.1021/acs.est.5b01589

- Mann, E., Mallory, M., Ziegler, S., Tordon, R. and O'Driscoll, N. [2015], 'Mercury in arctic snow: Quantifying the kinetics of photochemical oxidation and reduction', *ScienceDirect* 509-510, 115–132.
 URL: https://www.sciencedirect.com/science/article/pii/S0048969714010869bbb0425
- [15] Mao, H., Talbot, R. W., Sive, B. C., Youn Kim, S., Blake, D. R. and Weinheimer, A. J. [2010], 'Arctic mercury depletion and its quantitative link with halogens', *Journal of Atmospheric Chemistry* 65, 145–170. URL: https://search.proquest.com/docview/871783146?accountid=12870
- [16] Miller, J. [2018], 'Thousands of tons of mercury are trapped in permafrost', *Physics Today* 71(4), 14.
 URL: http://search.proquest.com/docview/2121674960/
- [17] Nghiem, S. V., Rigor, I. G., Richter, A., Burrows, J. P., Shepson, P. B., Bottenheim, J., Barber, D. G., Steffen, A., Latonas, J., Wang, F., Stern, G., Clemente-Colón, P., Martin, S., Hall, D. K., Kaleschke, L., Tackett, P., Neumann, G. and Asplin, M. G. [2012], 'Field and satellite observations of the formation and distribution of arctic atmospheric bromine above a rejuvenated sea ice cover', *Journal of Geophysical Research: Atmospheres* 117(D17).
 URL: https://aqupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2011JD016268
- [18] Pechony, O. and Shindell, D. T. [2010], 'Driving forces of global wildfires over the past millennium and the forthcoming century', *Proceedings of the National Academy of Sciences* 107(45), 19167.
 URL: http://www.pnas.org/content/107/45/19167.abstract
- [19] Potapowicz, J., Szumińska, D., Szopińska, M. and Polkowska, [2019], 'The influence of global climate change on the environmental fate of anthropogenic pollution released from the permafrost', *Science of the Total Environment* 651(Pt 1), 1534– 1548.
- [20] Qian, W., Wu, K. and Leung, J. [2017], 'Climatic anomalous patterns associated with the arctic and polar cell strength variations', *Climate Dynamics* 48(1-2), 169–189.
- [21] Rydberg, J., Klaminder, J., Rosén, P. and Bindler, R. [2010], 'Climate driven release of carbon and mercury from permafrost mires increases mercury loading to sub-arctic lakes', *Science of the Total Environment* 408(20), 4778–4783.
- [22] Schaefer, K., Zhang, T., Bruhwiler, L. and Barrett, A. P. [2011], 'Amount and timing of permafrost carbon release in response to climate warming', *Tellus B: Chemical and Physical Meteorology* 63(2), 168–180.
 URL: http://www.tandfonline.com/doi/abs/10.1111/j.1600-0889.2010.00527.x
- [23] Schuster, P. F., Schaefer, K. M., Aiken, G. R., Antweiler, R. C., Dewild, J. F., Gryziec, J. D., Gusmeroli, A., Hugelius, G., Jafarov, E., Krabbenhoft, D. P., Liu, L., Herman-Mercer, N., Mu, C., Roth, D. A., Schaefer, T., Striegl, R. G., Wickland, K. P.

and Zhang, T. [2018], 'Permafrost stores a globally significant amount of mercury', *Geophysical Research Letters* **45**(3), 1463–1471.

- [24] Shao, D., Kang, Y., Wu, S. and Wong, M. H. [2012], 'Effects of sulfate reducing bacteria and sulfate concentrations on mercury methylation in freshwater sediments', *Science of the Total Environment* 424, 331–336.
- [25] Simpson, W. R., Von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L., Frieß, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H.-W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T. and Wolff, E. [2007], 'Halogens and their role in polar boundary-layer ozone depletion', Atmospheric Chemistry and Physics Discussions 7(2), 4285–4403. URL: https://hal.archives-ouvertes.fr/hal-00302683
- [26] Smith-Downey, N. V., Sunderland, E. M. and Jacob, D. J. [2010], 'Anthropogenic impacts on global storage and emissions of mercury from terrestrial soils: Insights from a new global model', *Journal of Geophysical Research: Biogeosciences* 115(G3). URL: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2009JG001124
- [27] Steffen, A., Douglas, T., Amyot, M., Ariya, P., Aspmo, K., Berg, T., Bottenheim, J., Brooks, S., Cobbett, F., Dastoor, A., Dommergue, A., Ebinghaus, R., Ferrari, C., Gardfeldt, K., Goodsite, M., Lean, D., Poulain, A., Scherz, C., Skov, H. and Sommar, J. [2008], 'A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow', Atmospheric Chemistry And Physics 8(6), 1445–1482.
- [28] Steffen, A.; Schroeder, W. B. J. N. J. F. J. [2002], 'Atmospheric mercury concentrations: measurements and profiles near snow and ice surfaces in the canadian arctic during alert 2000', Atmos. Environ 36(15-16), 2653–2661. URL: https://doi.org/10.1016/S1352-2310(02)00112-7
- [29] Stern, G. A., Macdonald, R. W., Outridge, P. M., Wilson, S., Chételat, J., Cole, A., Hintelmann, H., Loseto, L. L., Steffen, A., Wang, F. and Zdanowicz, C. [2012], 'How does climate change influence arctic mercury?', *Science of the Total Environment* 414, 22–42.
- [30] Toyota, K., Dastoor, A. P. and Ryzhkov, A. [2014], 'Air-snowpack exchange of bromine, ozone and mercury in the springtime arctic simulated by the 1-d model phantas: Part 2: Mercury and its speciation', Atmospheric Chemistry and Physics 14, 4135–4167.
 URL: https://www.atmos-chem-phys.net/14/4135/2014/
- [31] W. H. Schroeder, K. G. Anlauf, e. a. [1998], 'Arctic springtime depletion of mercury', *Nature* 394, 331–332.
 - **URL:** https://doi.org/10.1038/28530
- [32] Zhang, X., Siddiqi, Z., Song, X., Mandiwana, K. L., Yousaf, M. and Lu, J. [2012], 'Atmospheric dry and wet deposition of mercury in toronto.(report)', **50**, 60.