

出國報告 (出國類別：國際會議)

2019 全球汞污染國際會議

服務機關：行政院環境保護署

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派赴國家：波蘭

出國時間：108 年 9 月 7 至 16 日

報告日期：108 年 12 月 5 日

摘要

第 14 屆「2019 全球汞污染國際會議(International Conference on Mercury as a Global Pollutant, ICMGP)」於波蘭克拉科(Krakow)舉行，為期 6 天，包括亞洲、歐洲、北美洲、南美洲、非洲等各地區各國家之環保部門及學術研究人員代表與會，出席人數近 800 人，希望藉由全球汞監測最新發展及區域性汞污染來源之特徵變化分析，有效管理汞排放，以減少生態系統對汞之暴露。會議內容包含：區域性大氣汞傳輸及沈降-亞太地區汞監測網(Asia-Pacific Mercury Monitoring Network, APMMN)、最新水俣公約(Minamata Convention on Mercury)現況及科學評估，運用先進技術降低汞污染排放、生態汞循環及環境中汞化合物分析技術等多項議題。

主辦單位在開幕及閉幕都特別提及我國與美國環保署國家大氣沈降計畫(National Atmospheric Deposition Program, NADP)共同組織之亞太地區汞監測網 Asia-Pacific Mercury Monitoring Network(APMMN)，也同步顯示 APMMN 全名於所有與會人員眼前，且在會場電子看板 5 天輪播，參與國家之國旗亦出現我國國旗，同時美方 NADP 的攤位也擺放 APMMN 資料，及近期發表的期刊文章數十份，被索取一空，有效將 APMMN 推向全世界。

本署於鹿林山背景測站架設大氣汞自動連續監測儀器及汞濕沈降採樣器，進行乾、濕沈降之汞監測計畫，本署「亞太地區汞監測網及環境監測技術聯合中心」計畫主持人中央大學許桂榮副教授亦發表口頭論文報告，展示鹿林山空氣品質背景測站受汞污染跨洲長程傳輸影響，比較國際與本署鹿林山測站之大氣汞監測數據趨勢，會場參與人數眾多。

本次亦召集 APMMN 之小組成員，除已加入之美國、印尼、日本、韓國、我國及斐濟，馬來西亞及俄羅斯亦表示參加合作之興趣，惟仍待確認相關可交流之細節與範疇，由參與國家共同協議。

因各國空氣污染防治政策的大力推動及污染防治設備進步，大氣汞在全球空氣中濃度趨勢持續下降，但受到全球大氣環流影響，部分地域可能受風場影響，造成大氣汞濃度持平甚至微幅提升，顯示開發及污染管制作為所造成之結果非僅國內，在大氣流動下對區域國家間仍具一定影響。研究亦顯示土壤中有機碳含量過高時，會影響甲基汞降解之速率，故封閉水域之有機碳亦應接受控管，以避免甲基汞之生物累積影響。

因汞之特性，特定產業或用途仍有相關使用者，且因汞之價格低廉，例如小規模之鍊金或加工業者，以及衛星發射時之燃料，亦有液態汞之使用。石油開採時亦可能遭遇汞之礦藏，輸油管若有汞入侵，可能會導致輸油管線遭鏽蝕而爆炸，故石油公司可能直接以較高溫度加熱石油天然氣使沸點較小之液態汞自行揮發。

故使用者端可能產生之汞污染不大，但能源生產端之汞污染仍須備受重視。

下屆全球汞污染國際會議，2021 年 7 月 11 日至 16 日將於南非開普敦舉行，預計將會有更多國家、人員參與。

我方為使不同人員增加觀摩與學習機會或因業務輪調及人事異動，故每次會議派員人員不盡相同。因本會議之議題具持續性且有待持續追蹤，未來我方或許可指定數位人員持續參與，以利窗口之延續，增加交流及互信基礎，有效推動各項事務。

目錄

一、 會議背景及目的	1
二、 會議過程及內容重點整理.....	2
三、 參加會議心得及建議.....	4
附件 1、 2019 全球汞污染國際會議議程	6
附件 2、 會議相關照片	8
附件 3、 會議討論資料.....	13

一、 會議背景及目的

第 14 屆「2019 全球汞污染國際會議(International Conference on Mercury as a Global Pollutant, ICMGP)」於波蘭克拉科(Krakow)舉行，為期 6 天，包括亞洲、歐洲、北美洲、南美洲、非洲等各地區各國家之環保部門及學術研究人員代表與會，出席人數近 800 人，希望藉由全球汞監測最新發展及區域性汞污染來源之特徵變化分析，有效管理汞排放，以減少生態系統對汞之暴露。會議內容包含：區域性大氣汞傳輸及沈降-亞太地區汞監測網(Asia-Pacific Mercury Monitoring Network, APMMN)、最新水俣公約(Minamata Convention on Mercury)現況及科學評估，運用先進技術降低汞污染排放、生態汞循環及環境中汞化合物分析技術等多項議題。

汞是在室溫唯一呈液態之金屬，容易變成汞蒸氣，以氣態形式遠距離移動，經大氣長程傳輸到達全球各地，透過大氣乾、濕沈降回地表，進入陸域及水域生態系統，再經由食物鏈累積危害人體健康，傷害腦、神經系統及腎臟，更可被微生物轉化為高毒性之甲基汞，國際癌症研究中心(The International Agency for Research on Cancer；IARC)已將甲機汞歸類為 2B 致癌物。日本最有名之集體案例即發生於熊本縣水俣市，窒素株式會社（窒素即氮，該公司於 2012 年改名為「新日本窒素肥料」）於水俣工場生產氯乙烯與醋酸乙烯，其製程中需要使用含汞的催化劑。由於該工廠任意排放廢水，這些含汞的劇毒物質流入成海，被水中生物所食用，並轉成甲基氯汞（化學式 CH_3HgCl ）與二甲汞（化學式 $(\text{CH}_3)_2\text{Hg}$ ）等有機汞化合物。汞污染對環境影響深遠，逐漸引發各國重視大氣汞污染跨境傳輸的監測課題，故聯合國於 2013 年 10 月 9 日在日本熊本市公開簽署關於汞污染防治的全球性公約：「水俣公約(Minamata Convention on Mercury)」，並於 2017 年 8 月 16 日正式生效。

我國有鑑於汞對環境會帶來嚴重影響，在 2007 年始建立鹿林山高山背景測站同時，就開始架設大氣汞自動連續監測儀器，由於臺灣位於亞洲氣流系統之下風處，高山背景測站之監測數據因而極具代表性。透過臺美環保技術合作協助，鹿林山測站目前已分別加入全球大氣汞監測網 (Atmospheric International Research Monitoring Network, AMNet) 及美國國家大氣沈降監測網(National Atmospheric Deposition Program, NADP)，監測技術與世界先進國家同步並獲得認可。2013 年我國環保署、美國環保署及 NADP 共同成立「亞太地區汞監測網 (Asia-Pacific Mercury Monitoring Network, APMMN)」，與東南亞國家共同合作，拓展區域大氣汞監測，藉以瞭解其環境濃度分布情形，強化國際共同監測機制以及監測資料交換與分享，進而訂定管制策略與控制人為排放量。

二、 會議過程及內容重點整理

本次「全球汞污染國際會議」於9月8至13日在波蘭克拉科舉行。相關議程如附件1，主要行程及內容簡如下表：

日期	行程內容
108.9.7	啟程，桃園機場起飛至荷蘭
108.9.8	抵達荷蘭轉機至波蘭克拉科，晚間出席開幕儀式。
108.9.9	探討水俣汞公約之管制成效與現況評估
108.9.10	參與環境中汞物種流佈與汞分析討論
108.9.11	探討汞污染與全球環境變遷之影響
108.9.12	探討甲基汞生物濃縮對生態及生物毒性 區域性大氣汞傳輸及沈降：亞太地區汞監測網 (APMMN)
108.9.13	出席產業與能源之汞減量、閉幕典禮
108.9.14	由波蘭前往荷蘭
108.9.15	於荷蘭阿姆斯特丹機場搭乘跨洲航線返程
108.9.16	抵達桃園國際機場

啟程(9月7日至9月8日)

因前往波蘭無直飛班機，故於桃園機場搭乘荷蘭航空 KL808 班機前往阿姆斯特丹，機型為美國波音公司之 777 長途廣體客機，KL808 之實際起訖點為菲律賓馬尼拉中停我國桃園國際機場，終點為荷蘭阿姆斯特丹，故登機時已有眾多國外旅客及轉機旅客已登機，且荷航相當重視碳足跡及減碳，於機上雜誌及視聽系統皆有相關專欄或說明影片，有關荷航之節能減碳企業責任，部分使用生質燃料及減輕飛機載重以避免增加耗油量，故每位乘客只能託運一件行李，且限重 23 公斤以內，對手提行李亦有尺寸及重量限制。

經十幾個鐘頭之飛行，抵達阿姆斯特丹，因屬申根地區，故於轉機時進行相關護照及入關查驗手續，抵達時間因遇到為數眾多之團體旅客，亦等待相當時間。荷蘭海關詳細詢問目的地及出訪原因，抽樣以放大鏡詳細查看旅客護照條碼及照片，才得以入境轉機。因本國籍航空未有飛往波蘭克拉科之班機，阿姆斯特丹至波蘭克拉科搭乘荷蘭航空班機，以利直掛託運行李，避免須領出託運行李又再次重新託運。

經數小時等待時間後，終於到轉機登機時間，因屬歐盟各國城市間之對飛班機，故使用較小型之巴西航空工業公司製造之 Embraer E-Jet 170 或 190，以接駁巴士運送旅客至停機坪。因登機時間已有延誤，且機場航班眾多須等待，且短程航線距離主跑道之滑行道距離長，故抵達波蘭較原定時間誤點。抵達克拉科機場後，搭乘波蘭之大眾運輸工具前往會場，參與本次會議開幕儀式。

第 1 天 (9 月 9 日)

於克拉科會議中心 ICE Congress center 進行汞討論會議，包括汞分析品質保證(Quality Assurance)、海水中汞化合物反應及汞生化循環、優化大氣汞量測方法及汞同位素技術應用、評估汞污染場址及生物監測等議題，並就科學角度及政策面研商改善汞污染方式；舉辦 ICMGP 開幕儀式，共有 57 國的環保部門及學術研究人員代表與會，並就 71 國已簽署水俣公約(Minamata Convention)進行廣泛討論。

搭乘公車前往市區，波蘭克拉科之歷史建築保存良好，包括昔時王國之城堡、傳統市集、大學、教堂等，亦有相當多觀光客。波蘭重要道路之車流量亦相當可觀，但景觀較為不同者，除 BRT 之多節公車、傳統之單體公車，亦有為數眾多之輕軌電車，其輕軌未必使用專用道路，而以公車、輕軌電車共用相同路廊，當電車班次不夠密或路線不夠普及時，就會有平行之公車行駛班車空檔。另軌道布設限制，部分較曲折或路寬不足之路段，則由公車行駛。雙重搭配之運輸容量較具調整彈性，但須良好之車輛交錯秩序，以及用路人遵守交通規則以避免造成交通動線打結。當乘客排隊上車時，後方車流可能暫時受影響，但當地禮讓行人之習慣也是相當良好。

第 2 天 (9 月 10 日)

進行全球汞污染影響綜合討論，包括大氣汞傳輸及沈降模式分析、環境汞化合物排放及分析、全球汞循環及汞同位素研析排放源、海洋中汞生化循環機制等事項。

因汞之特性，特定產業或用途仍有相關使用者，且因汞之價格低廉，例如小規模之鍊金或加工業者，以及衛星發射時之燃料，亦有液態汞之使用。石油開採時亦可能遭遇汞之礦藏，輸油管若有汞入侵，可能會導致輸油管線遭鏽蝕而爆炸，故石油公司可能直接以較高溫度加熱石油天然氣使沸點較小之液態汞自行揮發。故使用者端可能產生之汞污染不大，但能源生產端之汞污染仍須備受重視。

第 3 天 (9 月 11 日)

於克拉科會議中心進行汞區域性變化特徵綜合會議，討論議題包括科學方式執行水俣公約、淡水與沿海生態系統中汞來源及循環、人工淘金(Artisanal

Small-scale Gold Mining, ASGM)過程中汞排放現況及未來預測、汞處理技術無害化、氣候變遷及土地利用對汞於環境流佈影響。

另電動滑板車及腳踏車於波蘭亦相當普及，市區內有可以直接使用 app 就可租用之電動滑板車，但亦有雙載之情形，具一定風險。騎腳踏車通勤或運動之族群亦較我國多，但可能因市場定位或價格因素，我國自行車品牌之市占率似乎不高。惟波蘭之吸菸人口亦不少，室外空間不難發現抽菸身影，且男女老少皆有，公園內有時仍會有少許菸蒂存在，公車站牌附近有設置垃圾桶處，亦會有菸蒂收集處，數量不少。另克拉科之野生鴿子數量眾多，於人行道或建築物角落一段時間未打掃，可能都會發現鳥類羽毛或排泄物，清潔人員之打掃頻率不似我國，可能有時會看到遭受車輛撞擊之路殺動物遺體。因鴿子可能為腦膜炎等疾病之潛在宿主，相關衛生問題也可能值得注意。

第 4 天 (9 月 12 日)

進行汞污染場址評估綜合會議，探討汞源頭排放及土壤汞通量之相關性、評估礦場中汞含量分析、定量廢水中甲基汞濃度、活性碳去除液態汞等先進技術；，兩度提及我國對亞太地區汞監測之技術貢獻，並與本署出席人員會談監測技術合作。討論汞對生態系統影響，並就甲基汞對不同水體物種（浮游生物、魚、蛙等）之生物濃縮性研析及交換意見。

燃煤電廠在可預期的未來，仍是廉價能源的主要來源，雖目前持續更新發電機組及污染控制設備，在整體能源政策及空氣污染控制，仍須考量未來科技發展，及對環境負責，並隨科技發展，逐步達成汞排放趨近零排放之目標。

本次亦召集 APMMN 之小組成員，除已加入之美國、印尼、日本、韓國、我國及斐濟，馬來西亞及俄羅斯亦表示參加合作之興趣，惟仍待確認相關可交流之細節與範疇，由參與國家共同協議。

第 5 天 (9 月 13 日)

科學研析、政策制定與水俣公約之綜合討論，針對高濃度汞排放源彙整、銀奈米複合材及活性碳先進技術減緩汞污染影響、各國大氣汞傳輸模式及趨勢分析等項目交換意見；本署於鹿林山背景測站架設大氣汞自動連續監測儀器及汞濕沈降採樣器，進行乾、濕沈降之汞監測計畫，本署「亞太地區汞監測網及環境監測技術聯合中心」計畫主持人中央大學許桂榮副教授亦發表口頭論文報告，展示鹿林山空氣品質背景測站受汞污染跨洲長程傳輸影響，比較國際與本署鹿林山測站之大氣汞監測數據趨勢，會場參與人數眾多，並說明該測站亦加入美國大氣沈降計畫(NADP)中大氣汞監測網(AMNet)之空氣品質監測站。

主辦單位在開幕及閉幕都特別提及我國與美國環保署國家大氣沈降計畫 (National Atmospheric Deposition Program, NADP) 共同組織之亞太地區汞監測網 Asia-Pacific Mercury Monitoring Network(APMMN)，也同步顯示 APMMN 全名於所有與會人員眼前，且在會場電子看板5天輪播，參與國家之國旗亦出現我國國旗，同時美方 NADP 的攤位也擺放 APMMN 資料，及近期發表的期刊文章數十份，被索取一空，有效將 APMMN 推向全世界。下屆全球汞污染國際會議，2021 年 7 月 11 日至 16 日將於南非開普敦舉行，預計將會有更多國家、人員參與。

第 6 天 (9 月 14 日)

由波蘭搭乘荷航班機抵達阿姆斯特丹，因航班有限，登機及起飛皆相當順利。荷蘭之物價明顯高於波蘭，無論是食品、交通運輸費用及住宿房價，不過以消費金融而言，可接受之信用卡發卡機構較多，但對較大面額之歐元紙鈔似乎比較戒慎恐懼，如有需兌換歐元等貨幣時，可適度搭配不同面額之紙鈔。

另荷蘭似乎也有眾多移民，機場內之勞動力來自各國，來自東南亞國家之勞動力似乎也為數眾多。阿姆斯特丹機場之工作人員眾多，亦有直接配槍之警員巡邏，各部門分工相當明確，但若非該權責執掌，人員可能就相當冷漠，不會主動給予協助，與亞洲國家之差異較大，如有疑問可能只能尋找服務台諮詢人員，並時時刻刻注意相關告示牌及方向。因機場以放射型建置，可於較小空間容納更多空橋及班機停靠，但不同登機門之間之轉機及路程就相當遙遠。

歸程(9 月 15 日至 9 月 16 日)

於阿姆斯特丹短暫停留後，搭乘荷航 KL807 班機返國，歐盟為經濟共同體，故於離開歐盟區時才統一辦理退稅，惟於每筆消費均須事先告知店員，以開立消費明細，且均須填報為數眾多之表格，故本次未辦理相關退稅動作。以我國或日本之退稅程序，部分商店於消費當下出示護照即可現場退稅，似乎還是較為親民。班機於晚間起飛，出境速度就比入境較為迅速，安全檢查通過後就順利出關，前往登機門等待。機型同樣為波音 777，載客率似乎都相當良好，經濟艙每人只有一件可登機行李，座艙行李艙仍然近乎滿載。回程先抵達我國桃園國際機場，班機降落後才再轉往菲律賓馬尼拉。

三、參加會議心得及建議

主辦單位在開幕及閉幕都特別提及我國與美國環保署國家大氣沈降計畫 (National Atmospheric Deposition Program, NADP) 共同組織之亞太地區汞監測網 Asia-Pacific Mercury Monitoring Network (APMMN)，也同步顯示 APMMN 全名於所有與會人員眼前，且在會場電子看板 5 天輪播，參與國家之國旗亦出現我國國旗，同時美方 NADP 的攤位也擺放 APMMN 資料，及近期發表的期刊文章數十份，被索取一空，有效將 APMMN 推向全世界。

本次亦召集 APMMN 之小組成員，除已加入之美國、印尼、日本、韓國、我國及斐濟，馬來西亞及俄羅斯亦表示參加合作之興趣，惟仍待確認相關可交流之細節與範疇，由參與國家共同協議。

因各國空氣污染防治政策的大力推動及污染防治設備進步，大氣汞在全球空氣中濃度趨勢持續下降，但受到全球大氣環流影響，部分地域可能受風場影響，造成大氣汞濃度持平甚至微幅提升，顯示開發及污染管制作為所造成之結果非僅國內，在大氣流動下對區域國家間仍具一定影響。

燃煤電廠在可預期之未來，仍是重要之能源主要來源，隨燃煤廢氣所排放汞亦為大氣汞主要來源，雖然目前持續更新發電機組及污染控制設備，整體能源政策及空氣污染控制，仍須考量未來科技發展及對環境負責，並隨科技發展逐步達成汞排放趨近零排放之目標。

研究顯示土壤中有機碳含量過高時，會影響甲基汞降解之速率，故封閉水域之有機碳亦應接受控管，以避免甲基汞之生物累積影響。

因汞之特性，特定產業或用途仍有相關使用者，且因汞之價格低廉，例如小規模之鍊金或加工業者，以及衛星發射時之燃料，亦有液態汞之使用。石油開採時亦可能遭遇汞之礦藏，輸油管若有汞入侵，可能會導致輸油管線遭鏽蝕而爆炸，故石油公司可能直接以較高溫度加熱石油天然氣使沸點較小之液態汞自行揮發。故使用者端可能產生之汞污染不大，但能源生產端之汞污染仍須備受重視。

歐洲地區之輕軌電車歷史悠久，其輕軌未必使用專用道路，而以公車、輕軌電車共用相同路廊，當電車班次不夠密或路線不夠普及時，由公車行駛班車空檔及較曲折之路段，運輸容量較具調整彈性，但須良好之車輛交錯與用路人遵守交通規則以避免造成交通動線打結。

我方為使不同人員增加觀摩與學習機會或因業務輪調及人事異動，故每次會議派員人員不盡相同。因本會議之議題具持續性且有待持續追蹤，未來我方或許可指定數位人員持續參與，以利窗口之延續，增加交流及互信基礎，有效推動各項事務。

下屆全球汞污染國際會議，2021 年 7 月 11 日至 16 日將於南非開普敦舉行，預計將會有更多國家、人員參與。

附件1、2019 全球汞污染國際會議議程

	SUNDAY SEP. 8	MONDAY SEP. 9	TUESDAY SEP. 10	WEDNESDAY SEP. 11	THURSDAY SEP. 12	FRIDAY SEP. 13
08:00		Registration	Registration	Registration	Registration	Registration
08:30		Plenary 5	Plenary 1	Plenary 2	Plenary 3	Plenary 4
	Workshops					
09:00		Break	Break	Break	Break	Break
10:00		Concurrent Sessions	Concurrent Sessions	Concurrent Sessions	Concurrent Sessions	Concurrent Sessions
11:00						
12:00		Lunch Break	Lunch Break	Lunch Break	Lunch Break	Closing Ceremony & Reception
13:00				Tours & Excursions		
13:30		Poster Session	Poster Session		Poster Session	
14:00	Registration					
14:30		Concurrent Sessions	Concurrent Sessions		Concurrent Sessions	
16:00						
16:30		Poster Session	Poster Session		Poster Session	
18:00	Opening Ceremony					
19:00						

附件 2、會議相關照片

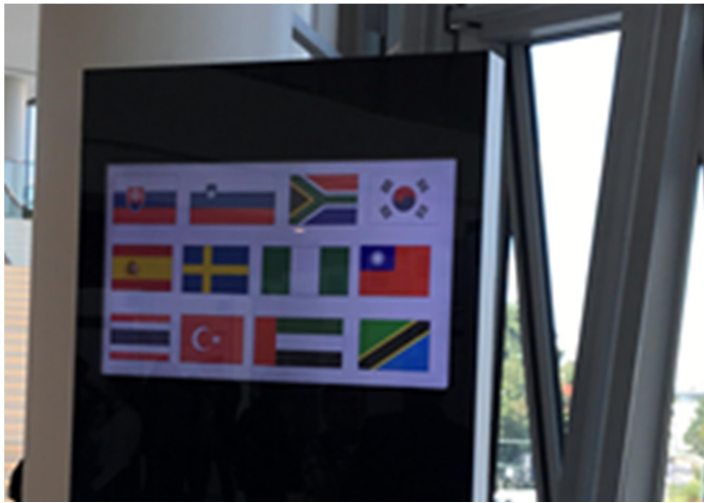


圖 1、會場電子看板展示我國國旗



圖 2、我國與美國 NADP 合作籌組之 APMMN 支持本次會議



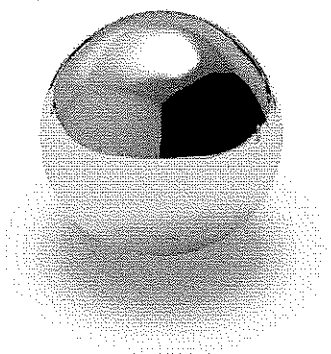
圖 3、我方、中央大學許桂榮教授與美方人員合影

附件 3、會議討論資料

**Abstract
Volume**



**September 8-13
2019, Krakow,
POLAND**



ICMGP 2019

14th International Conference on Mercury as a Global Pollutant

www.mercury2019krakow.com



PLENARY LECTURES

TUESDAY ORAL

Marine mercury cycling in a changing environment

HEIMBÜRGER-BOAVIDA, Lars-Eric¹

(1)CNRS-Mediterranean Institute of Oceanography

We are mostly exposed to mercury in the form of methylmercury, when we eat fish from our oceans. The Minamata Convention aims to protect human health from the adverse effects of mercury via the reduction of anthropogenic inorganic mercury release. To understand the efficacy and time-scales of reduced mercury emissions on fish methylmercury levels, we must precisely quantify the amount of anthropogenic Hg in the ocean and fully understand the drivers controlling methylmercury production. In this talk I will address the two aspects of environmental change likely to impact the marine mercury cycle in the future: reduced anthropogenic inorganic mercury emissions and changing climate. Mercury is one of the least concentrated elements in the ocean and measurements remain a challenge today. This makes it difficult to precisely quantify the amount of mercury in the ocean, and to estimate how much anthropogenic mercury we have added. I will briefly address the technical issues and show perspectives for marine mercury and mercury species measurements. Several lines of independent evidence speak in favor of in situ methylmercury production in oxic seawater: (1) recent large scale oceanographic expeditions find subsurface methylmercury maxima in every ocean basin; (2) incubation experiments with isotopically labeled mercury spikes show significant in situ mercury methylation in oxic seawater; (3) mercury stable isotope signatures of marine fish indicate that 60-80% of the methylmercury is produced in open ocean subsurface waters; (4) carbon stable isotopic signatures of fish methylmercury have a clear marine imprint, suggesting again in situ methylmercury production in the open ocean. A major breakthrough has been made with the discovery of key genes, that control mercury methylation in anaerobic Hg methylators. The *hgcAB* genes have been found in nearly all anaerobic environments and sea ice, yet only at very low abundances in oxic open ocean waters. The question of "who" methylates mercury in the open ocean remains to be answered. I will review the current state-of-the-art of the marine biogeochemical Hg cycling, and try to give ideas for future research.

WEDNESDAY ORAL

Terrestrial mercury cycling in a changing environment

JISKRA, Martin¹

(1)University of Basel

In this plenary talk, I will discuss recent advances in terrestrial mercury research and provide an outlook on emerging questions associated with terrestrial mercury cycling in a changing environment. Soils contain the largest pool of mercury at the Earth's surface. With the expected decline in anthropogenic mercury emission under the Minamata convention, the fate of this terrestrial mercury will play a central role in how fast freshwater and marine biota will recover from anthropogenic mercury pollution. The dual role of vegetation and soils in drawing down and storing atmospheric mercury and at the same time releasing it to aquatic ecosystems or back to the atmosphere makes it critical to understand how terrestrial ecosystems react to environmental changes. Over the last years increasing evidence, in particular from mercury isotope fingerprints, suggests that terrestrial vegetation acts as a pump for atmospheric mercury. The uptake of atmospheric mercury by vegetation appears to be a major driver of mercury storage in soils, seasonal variations in atmospheric mercury concentrations and mercury transfer to aquatic ecosystems. Climate change has a broad impact on terrestrial ecosystems, which in turn affects terrestrial mercury cycling. Plant growth increased over the last decades driven by CO₂ and nitrogen fertilization and may have led to an increase in the plant mercury pump and therefore in deposition to terrestrial surfaces. Other phenomena such as permafrost thaw, drought or deforestation however may release large amounts of mercury into aquatic ecosystems or the atmosphere and thereby counter-act efforts in curbing anthropogenic mercury emissions. Understanding the relative importance of these

processes and predicting how they will evolve in the future poses a great challenge for research and policy making.

THURSDAY ORAL

The microbiome: modulating methylation in the environment and biota

SILBERGELD, Ellen K¹

(1)Johns Hopkins University

Our concepts of mercury as a global pollutant are largely shaped by our knowledge of the complex relationships and transitions of mercury from inorganic to organic species (WHO). These transitions not only condition Environmental fate and transport is conditioned but also ecotoxicity as well as toxicity to humans is also defined in large part by mercury speciation. In addition, research on individual susceptibility has been linked to specific human genes (Basu).

Responses to mercury exposures are based on the standard toxicological model of ADME in which the critical stages are arrayed in a process beginning with external exposure, absorption of an internal dose, delivery to target organs, metabolism, excretion. This model was expanded to include external exposure and more defined stages of organ and organism response but the basic ADME model been maintained with all stages after absorption assumed to take place with the exposed organism (NRC). In 2012, we proposed that this concept requires revision to incorporate the new science of the microbiome. At that time, there was compelling evidence that microbiomes in the environmental and the human gut were capable of methylating and demethylating arsenicals based on experimental evidence in vitro and in vivo (Dietert and Silbergeld). Since that time, further work has shown that the mammalian gut microbiome can activate procarcinogens, de-activate pharmaceuticals, and alter other substances.

It has long been known that environmental microbiomes may possess bacteria that methylate and demethylate mercury. Additional evidence now indicates that as with arsenic, bacteria within the human gut microbiome possess the same metabolic pathways to methylate and demethylate mercury. The implications of these findings are important for several reasons: (1) alter risk assessments for mercury based on speciation; (2) explain population or individual differences in outcomes related to mercury based on differences in gut microbiomes in addition to human genomes (Rodriguez); (3) present opportunities for preventing toxicity through regulation of host microbiomes.

FRIDAY ORAL

Mercury reduction from power and industry – how much is possible?

SLOSS, Lesley¹

(1)International Energy Agency – Clean Coal Centre

Coal combustion is a major source of mercury emissions to the atmosphere globally and this sector is specifically targeted under the Minamata Convention. Unlike sources such as small-scale gold mining, stationary coal combustion sources are easy to identify and quantify. Also, it is theoretically relatively simple to reduce emissions of mercury from coal combustion. Technologies are commercially available which can reduce emissions by, in some cases, over 90%. However, some sources can be challenging. Further, smaller combustion sources and industry often slip under the radar for emission control whilst still being responsible for a significant quantity of emissions globally.

The challenge of mercury reduction is often more economic or political than technical. Whilst many western economies are starting to turn their back on coal, emerging economies may prioritize energy security over sustainability and see coal as an affordable option for decades to come. It is possible for these regions to minimize emissions of pollutants, including mercury, whilst transitioning to cleaner energy options. For this to happen, countries must work together to share experiences and expertise. Funding will have to be mobilized in regions with financial limitations.



ORAL ABSTRACTS

Monday 9th September 2019

1.1A Atmospheric mercury cycling and transformations: Insights from measurements and models

M.O.1.1A-1

SUBSTANCE FLOW ANALYSIS FOR MERCURY IN POLAND FOR YEAR 2016

PANASIUK, Damian¹

(1)Cardinal Stefan Wyszyński University in Warsaw, Poland

Summary: Substance flow analysis (SFA) is a useful tool for providing environmental policy. It shows main pollutant emissions to air, water and soil, as well as flows between environmental compartments. Due to official national inventory for 2016 coal and lignite combustion in the energy sector is a main source of mercury emission to the atmosphere in Poland (5.1 Mg/year) before other industrial sectors (4.2 Mg) and residential sector and commercial plants (0.9 Mg). Another sources of emission to air was estimated by author: from use of mercury-containing products based on model for distribution and emission (0.8 Mg) and from dental practice and bodies cremation (0.3 Mg). From mercury load 11.5 Mg emitted to air, part (7.8 Mg) is deposited to soil inside Poland. Due to E-PRTR data for 2016, reported mercury releases and transfers to water in Poland was 0.97 Mg, mainly from large and medium industrial facilities (0.91 Mg) and also from urban waste water treatment plants (0.06 Mg). Lack of amalgam separators was important source of mercury in urban waste waters. Sewage sludge from urban WWTPs is later source of mercury emission to soil in agriculture (0.31 Mg). Mercury discharges to water and soil from dental amalgam in buried bodies was estimated on level 0.16 Mg. Significant flow of mercury to municipal wastes is associated with use of mercury-containing products (6.6 Mg mercury in batteries, light sources and other electrical and electronic equipment launched to the market in year). Load of 1.7 Mg of mercury is transferred to municipal landfills, next 3.7 Mg is re-collected and stored safely. Another significant mercury flow in wastes (10.0 Mg annually) originate from dental practice. Majority of mercury contained in dental amalgam is re-collected in dental clinics and stored safely. However load 2.9 Mg is transferred to infectious medical wastes and later incinerated in industrial plants and stored safely.

M.O.1.1A-2

TRACE OF PM_{2.5} SOURCES BY USING MERCURY ISOTOPE IN TEN MEGACITIES OF CHINA

LIU, Chen; FU, Xuewu

Both PM_{2.5} and total gaseous mercury (TGM) serve as an important atmospheric pollutant in urban areas and pose a health risk to human. Because PM_{2.5} and PBM are strongly bounded, and different mercury isotope signature could be observed from different source. So mercury isotope can be used as a tracer for PM_{2.5} sources. TGM and particulate bound mercury (PBM) were collected in summer and winter for ten megacities of China including: Shanghai, Beijing, Wuhan, Chengdu, Guiyang, Shijiazhuang, Lanzhou, Jinan, Guangzhou, Zhengzhou. Two sampling sites were selected including urban and suburban stations for each of the city. Diurnal TGM and PBM concentrations were 2.89±1.28 ng•m⁻³, 170.05±270.52 pg•m⁻³ (1SD) in summer and 2.93±1.52 ng•m⁻³, 127.66±336.79 pg•m⁻³ in winter, respectively. Mass-independent fractionation (MIF) of TGM were $\Delta^{199}\text{Hg} = -0.09 \pm 0.07\%$ (2SD, n = 28) in winter and $-0.04 \pm 0.05\%$ (2SD, n = 30) in summer. Only minor seasonal variations were observed as $\Delta^{199}\text{Hg}$ is 0.05% negative than summer. This may cause by different anthropogenic sources as coal heating contribute much mercury in winter which gave much negative $\Delta^{199}\text{Hg}$ value by fossil fuel burning. Northern cities have significantly higher (t-test, P<0.05) MIF of $\Delta^{199}\text{Hg}$ ($-0.09 \pm 0.06\%$, 2SD, n = 35) than southern cities ($-0.03 \pm 0.04\%$, 2SD, n = 23) due to their difference in energy and industrial structures. Because coal-fired power plants are the major mercury source of north-

ern area whereas more mixed industrial source in the south such as chemical plants and ore mining. Positive matrix factorization (PMF) results, by making use of the combined data sets of total gaseous mercury (TGM), particulate bound mercury (PBM), OC, EC, hydrophilic ions, trace elements and meteorological parameters, suggested that atmospheric combustion source, crustal material source, secondary pollution source (>80%) is the most important sources of PM_{2.5} in these cities. The research could guide the government to take better policies to control urban pollution sources.

M.O.1.1A-3

UPDATED GAS-PARTICLE PARTITIONING MODEL FOR ATMOSPHERIC OXIDIZED MERCURY

WU, Qingru¹; WANG, Shuxiao¹

(1)Tsinghua University, China

Gas-particle partitioning of reactive gaseous mercury (RGM) is one significant process impacting mercury transportation in the air. Multi-pollutants observation in three Chinese sites indicated gas-particle partitioning coefficient (K_p) is impacted by surrounding mercury emissions, temperature, relative humidity and particle composition (mainly water content (AWC), Na⁺, Cl⁻). By using Generalized Additive Model, functions describing the relationship between K_p and temperature, water content under different relative humidity were developed. When relative humidity is lower than 60%, K_p is mainly dominated by temperature according to the regression analysis, $\lg(1/K_p) = -3021(1/T) + 11$ (R²=0.43). Otherwise, K_p is under the joint impact of temperature, particle composition and relative humidity temperature. However, the value of K_p finally relied on temperature and water content based on Akaike's Information Criterion (AIC) and R² values for each analysis, $\lg(1/K_p) = -2302(1/T) + 3010\lg(\text{AWC}) + 12$ (R²=0.65). In both conditions, R² value of the regression model will be improved by 0.5-1.2 when excluding the point under the impact of emission sources, because the model has not accounted for different mercury speciation profile of the emitted sources. The use of local observation data to parameterize RGM partitioning in the proposed models potentially improves the estimation of mercury cycling in chemical transport models and elsewhere.

M.O.1.1A-4

MERCURY EMISSIONS AND POSSIBLE AIRBORNE PHOTOCHEMICAL REDUCTION OF OXIDIZED MERCURY OBSERVED DURING AIRCRAFT MEASUREMENTS IN THE EMISSIONS PLUMES OF ALBERTA OIL SANDS FACILITIES

MCLAGAN, David¹; STEFFEN, Alexandra²; STUPPLE, Geoffrey W.²; WHEELER, Michael²; LI, Shao-Meng²; WENTZELL, Jeremy J.B.²; LIGGIO, John²; DARLINGTON, Andrea²; HAYDEN, Katherine²

(1)Technical University of Braunschweig

(2)Environment and Climate Change Canada

In 2018, Environment and Climate Change Canada (ECCC) conducted an aircraft monitoring campaign of the industrial mining facilities of the Athabasca Oil Sands in Alberta, Canada. The National Research Council of Canada's Convair-580 was equipped with an array of atmospheric gas and particulate contaminant and meteorological instruments for the characterization of emissions and chemistry processes occurring directly in and around emissions plumes of these facilities. Among these instruments was a Tekran 2537X setup to measure gaseous elemental Hg (GEM). The system was fitted with a 0.45µm Polytetrafluoroethylene (PTFE) filter and a soda-lime trap to remove gaseous oxidized mercury (GOM) and particulate bound mercury (PBM). 30 flights were completed in total and included emissions "box" flights (multi-height, box flight paths circumnavigating an entire facility), used for determining emissions strength, and "transformation" screen flights (a series of

multi-height screens that track the plume at increasing distance from the facilities), used to determine contaminant concentration changes in ageing plumes associated with photochemistry, dilution, and deposition. Significant positive correlations between GEM and primary pollutants (e.g. black carbon, ultra-fine particulate counts, SO₂, NO_x) observed in box flights showed there were minor, but detectable emissions of GEM being released from the facilities. GEM emissions were strongest at In Situ (steam-assisted gravity drainage) facilities, which is a heat-driven extraction process used for deeper bitumen deposits that may have the tendency to liberate more mercury from bitumen than surface mines. Gaseous oxidized mercury (GOM) or particulate bound mercury (PBM) measurements were not made on these flights, but these species make up a much higher proportion of atmospheric mercury near industrial sources. Thus, considering the observed GEM emissions, we could also expect emissions of GOM and PBM. Transformation flights generally showed increasing GEM concentrations on the edges of emissions plumes and as the plume aged. The positive correlation with ozone, a tropospheric contaminant generated photochemically, was highly significant during these flights, while primary pollutants were significantly, but inversely, correlated. A possible mechanism for the elevated GEM concentrations observed on plume edges and in aged plumes at greater distance from the facilities is the photochemical reduction of GOM and/or PBM to GEM. This process is an expected reaction mechanism in surface waters, yet until recently it was not thought to occur in the atmosphere. These results add to an emerging body of research that suggest photochemical generation of GEM could also be an important atmospheric process.

M.O.1.1A-5

MULTI-CENTURY RECONSTRUCTION OF ATMOSPHERIC Hg(0) TRENDS IN NORTHERN CANADA USING TREE-RINGS.

LEHNHERR, Igor¹; PORTER, Trevor¹; CLACKETT, Sydney¹; GHOTRA, Avneet¹

(1)Department of Geography, University of Toronto

The atmospheric Hg(0) reservoir plays a key role in the global Hg cycle, facilitating long-range transport, and contributing a significant input of Hg to many ecosystems. An improved quantitative understanding of the atmospheric Hg(0) pool and historical anthropogenic emissions is key to be able to predict how regulatory action (i.e., the Minamata Convention on Mercury) will affect Hg concentrations in various environmental compartments and foodwebs, and thus exposure risk in human populations. Due to the limited temporal duration of the instrumental atmospheric Hg record, natural Hg archives such as lake sediments, peat cores and ice cores have been used to infer long term temporal trends in atmospheric Hg(0) concentrations and Hg deposition. Tree-rings have recently been suggested as potential archives of past atmospheric Hg(0). Tree-rings have numerous advantages over other archives, for example, they are annually resolved with excellent dating control, span centuries to millennia, and provide extensive spatial coverage over large areas of Earth's surface. We present an annually-resolved tree-ring Hg record from the Klondike Goldfields, where the gold-Hg amalgam method was used to recover fine gold from placer ore, to demonstrate that Hg concentrations in white spruce tree rings are consistent with the history of local mining activity. Given that white spruce tree-rings faithfully record atmospheric Hg(0), we use this approach to reconstruct temporal trends in atmospheric Hg(0) spanning from 1600 AD to present-day, from various regions in northern Canada, including continental sites (central Yukon, northern Yukon) and coastal sites (Mackenzie River Delta, Northwest Territories). While regional differences exist in the timing of the initial increase attributed to anthropogenic emissions and the timing of maximum Hg(0), the fastest rate of increase in Hg concentrations occurs between 1850 and the mid 20th century at all sites. Furthermore, the enrichment factor in modern Hg(0) relative to the pre-industrial baseline estimated from tree rings appears to be somewhat lower compared to enrichment factors similarly calculated from sediment and peat cores. Important

methodological considerations such as replication and the need to calculate adjusted Hg concentrations to account for systematic inter-tree differences will also be discussed. Overall, tree-rings show tremendous promise for various applications such as validating emission inventories and refining atmospheric Hg models.

M.O.1.1A-6

PHYTOMANAGEMENT OF CHLOR-ALKALI TAILINGS DUMPS USING TREES: TRANSFER OF Hg, PLANT PRODUCTIVITY AND IMPACT ON MICROBIAL COMMUNITIES

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Hg is a contaminant classified within the quantitatively most important pollutant groups known as trace elements (TEs). It is highly persistent in the soil environment and is classified as a "priority hazardous substance" by the Agency for Toxic Substances and Disease Registry (ATSDR) due to its toxicity, mobility, and long residence time in the atmosphere. Here we have explored the fate of Hg within tree plantation and its accompanying vegetation, as well impact of Hg on microbial communities at a chlor-alkali tailings dump located in the North East of France. We first demonstrated that most of the Hg detected in the aboveground parts of Salicaceae trees collected at that site had entered the poplar leaves through exclusively through an atmospheric pathway. We further characterized aboveground and belowground microbial populations in the environment of planted trees. Aboveground and belowground poplar habitats host completely different fungal communities, as highlighted by the core microbiome of the four habitats that represent only reduced to 5.9% of the total OTUs. Leaf and stem habitats were characterized by few dominant OTUs such as those from the Dothideomycete class producing mutual exclusion with other OTUs. *Aureobasidium pullulans*, one of the dominating OTUs, was further isolated from the leaf habitat, in addition to *Nakazawaea populi* species, which were found to be Hg resistant. We also studied the accompanying vegetation under the poplar trees that can be valorized within industrial processes and the transfer of Hg into this vegetation, with nettle as the dominant species. The nettle biomass yields are lower than or equal to the lower range of the values obtained when using traditional nettle crop cultivation practises. The properties obtained in this study are equal to or better than those of hemp and flax and make this nettle biomass very promising for composite application. Altogether, these findings provide an improved point of reference for research on vegetation, associated microbes and insects in the phytomanagement of chlor-alkali tailings dumps.

1.3A Regional and local scale stable isotope studies in mercury biogeochemical cycling and bioaccumulation

M.O.1.3A-1

MERCURY CYCLING IN THE PACIFIC OCEAN AS REVEALED BY MERCURY STABLE ISOTOPES

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14

The photochemical decomposition of methylmercury (MeHg) in the surface ocean is an important pathway in the biogeochemical cycle of the global pollutant mercury (Hg), because it limits the amount of Hg available for bioaccumulation in marine organisms. Despite the crucial importance of this pathway there are many unanswered questions about photochemical reaction mechanisms and the relative importance of various MeHg species that lead to Hg incorporation into the food web. Numerous studies have shown that the dominant cause of odd mass independent isotope fractionation (MIF) of Hg in marine foodwebs is due to the partial photochemical decomposition of MeHg, with the residual MeHg containing a distinct MIF fingerprint incorporated into low trophic level organisms and bioaccumulated without additional MIF. Based on this understanding we investigated the photochemical degradation, uptake, and bioaccumulation of MeHg using Hg stable isotope analyses of various components of the marine food web in the Central Pacific Ocean. The isotopic signatures of MeHg from photochemistry experiments, measurements of marine particles, zooplankton, and pelagic fish demonstrate that there are two important photochemical degradation pathways that directly impact the pool of MeHg available for uptake into the marine foodweb. We will discuss the relationship between the isotopic composition of marine MeHg subjected to photochemical decomposition and the Hg stable isotope signatures preserved in marine particles, zooplankton, and fish. These Hg isotope measurements shed light on abiotic and biotic production and degradation of MeHg throughout the marine water column, and emphasize the importance of marine particles and zooplankton in the vertical transport of Hg.

M.O.13A-2

USING MERCURY STABLE ISOTOPES TO UNRAVEL METHYLMERCURY SOURCE ORIGIN AND DISTRIBUTION IN TUNA FROM THE SOUTH WESTERN PACIFIC OCEAN

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In the tropical Pacific Ocean, tuna contribute significantly to the livelihoods, food and economic security of many island nations. Tuna fisheries from the South Western Pacific Ocean (WCPO) account for a significant fraction of the world tuna catches representing a landing value of several billion US\$. Mercury concentrations in bigeye (BET), albacore (ALB) and yellowfin tuna (YFT) increase in the following order BET-ALB-YFT. This species-specific pattern is assumed to reflect a relative difference of foraging depth among the three-tuna species, with YFT occupying a more epipelagic habitat compared to mesopelagic BET in the WCPO. At the species level, spatial gradients not explained by fish size have also been observed with increased mercury concentrations at southern latitudes (10S-20S) relative to the equatorial regions (0-10S), with BET exhibiting the strongest latitudinal gradient. To investigate if changes in foraging ecology, and/or differences in marine MeHg biogeochemistry and sources contribute to the geographical trends observed, mercury stable isotopes ($d^{202}\text{Hg}$, $D^{199}\text{Hg}$) and additional trophic tracers ($d^{13}\text{C}$, $d^{15}\text{N}$) were determined at high spatial resolution on YFT, ALB, and BET samples from the WCPO. Complementary samples including pelagic prey items, mollusks from local hydrothermal vents and deep sediments were also considered for analysis. Finally, high resolution MeHg oceanic profiles collected along the OUTPACE cruise will also be shown, providing an oceanographic Hg context to this study. High resolution regional Hg isoscapes ($d^{202}\text{Hg}$ and $D^{199}\text{Hg}$)

between 20N and 20S will be presented for both YFT and BET. These isoscapes exhibit significant geographical trends, ranging for $d^{202}\text{Hg}$ between 0.5 and 1.3pm for YFT and between 0.3 to 1pm for BET, and for $D^{199}\text{Hg}$ between 2.4 to 3.2pm for YFT, and between 1.3 to 2.5pm for BET, respectively. These results indicate that Hg stable isotopes in tuna vary significantly with geography. Mercury concentrations anomalies not explained by size differences among the different individuals sampled across this large oceanic region are related to spatial changes in the $D^{199}\text{Hg}/d^{202}\text{Hg}$ ratio, with a stronger latitudinal gradient for BET relative to YFT. These results will be discussed in the context of spatial changes in marine Hg biogeochemistry, and with considering variations in tuna foraging ecology reflecting changes in physical oceanography across this region.

M.O.13A-3

ENERGY BUT MERCURY: PINNIPED CONSUMPTION INCREASES MERCURY EXPOSURE FOR THE GREAT WHITE SHARK.

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Methylmercury (MeHg) is known to have deleterious effects on the health of marine organisms. This contaminant is bioaccumulated over time and biomagnified along trophic chains. Because sharks are long-lived species at the top of food webs, they are particularly prone to MeHg contamination, potentially participating to their decline worldwide. The great white shark *Carcharodon carcharias* is a threatened species with some of the highest mercury (Hg) concentrations within marine top-predators, almost exclusively under the MeHg form. Sub-adult and adult white sharks aggregate seasonally near coastal pinniped colonies in several parts of the globe, while they spend the rest of the year in oceanic habitats. As predators themselves, pinnipeds have higher MeHg concentrations in muscle than pelagic and mesopelagic prey. However, fat can represent up to 40% of the body weight of pinnipeds and contains low Hg concentrations, mostly in inorganic form and therefore poorly bioavailable. In this context, the aim of this study was to evaluate the contribution of pinnipeds compared to pelagic and mesopelagic prey in trophic mercury exposure for the great white shark. For this purpose, 60 white sharks and 10 northern elephant seal *Mirounga angustirostris* were sampled in a Northeastern Pacific aggregation site (Guadalupe Island, off the coasts of Mexico). Shark subdermal tissues and seal hairs were analyzed for total mercury concentration (THg) and isotopes of Hg, carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$). Our results were compared to the values of pelagic and mesopelagic organisms already published in the same area. White sharks had $\Delta^{199}\text{Hg}$ values similar to both mesopelagic squids and the northern elephant seals, but $\delta^{202}\text{Hg}$ values closer to the elephant seals. Moreover, a positive correlation was found between THg and $\delta^{202}\text{Hg}$ values as well as between THg and $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ values, reflecting an increase in mercury contamination with the consumption of elephant seals. Our study thus revealed that (i) white sharks are mainly feeding on pinnipeds near aggregation sites and to a lesser extent on mesopelagic squids, (ii) pinnipeds are the main source of mercury for sharks at the population scale during the coastal season, (iii) pinniped consumption increases mercury exposure for sharks at the individual scale. Overall, this work demonstrates that mercury isotopes are relevant tracers of both diet and mercury source, and provide a better understanding of the trophic exposure to a major contaminant during the migratory life cycle of an iconic marine predator.

INVESTIGATING ENVIRONMENTAL ORIGINS AND BIOACCUMULATION OF METHYLMERCURY IN A SUBARCTIC ESTUARY

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Methylmercury (MeHg) is a potent toxicant that can lead to adverse health effects in human and wildlife. The primary route of MeHg exposure for most human populations is seafood consumption. Northern indigenous populations are particularly at risk of high exposures to MeHg due to their traditional diets primarily composed of fish and marine mammals. To better understand the mercury (Hg) biogeochemical cycling in northern coastal ecosystems that provide important hunting and fishing territory, we measured mercury concentrations, stable isotopes of Hg ($\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, $\Delta^{200}\text{Hg}$, and $\Delta^{201}\text{Hg}$), carbon ($\delta^{13}\text{C}$), and nitrogen ($\delta^{15}\text{N}$) of a variety of environmental samples from a large subarctic estuary (Lake Melville), including plankton, shellfish, fish, seals, and humans. We compare Hg isotopic composition of hair samples from indigenous populations with those of environmental samples to further assess the environmental origins of MeHg for northern communities. Results show methylation varies across seasons and geographic locations. Mammals and humans have enriched $\delta^{202}\text{Hg}$ values compared to their diet, probably due to the preferential demethylation and elimination of lighter Hg isotopes. The presentation will also discuss how Hg isotopes provide insight into the major environmental origins of MeHg in northern populations.

SEABIRD HG ISOTOPIC SIGNATURES DOCUMENT INTERANNUAL CHANGING DYNAMICS OF THE HG CYCLE IN THE PERUVIAN COAST

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Along the coasts of Peru, the persistent coastal upwelling system, known as the Northern Humboldt Current System, is one of the most productive of the world ocean. Covering 0.1% of the surface of the global ocean it accounts for >10% of global fisheries, with in particular the anchovy (*Engraulis ringens*) production. This upwelling system off Peru drives one of the most extensive and shallow oxygen minimum zones (OMZ) (upper limit at ~20–100 m). At interannual time scales, this region is mainly affected by the warm phases of the El Niño southern oscillation (ENSO), which result in the reduction of the upwelling efficiency, reducing drastically nutrient inputs to the surface layers. Under these conditions, primary productivity is reduced, impacting the whole ecosystem up to fish and top predators. ENSO is also suspected to influence the Hg cycle, in particular methylmercury production and transformations. The Peruvian coastal region is therefore an interesting case study to explore the potential evolution of the global marine Hg given the predicted expansion of oceanic OMZ in a warming ocean. Because Hg isotopic signatures are a powerful tool to investigate Hg sources and reactivity within marine compartments, we analyzed Hg isotopic composition in time series of seabird blood samples, which are widely used as effective bioindicators of Hg contamination of the marine food webs. Blood samples from two seabird species, the Peruvian boobies (*Sula variegata*) and the Guanay Cormorants (*Leucocarbo bou-*

gainvillii), were collected in the breeding period from 2009 to 2016. Both seabird species shared similar temporal patterns between mass dependent ($\delta^{202}\text{Hg}$) and mass independent ($\Delta^{199}\text{Hg}$) fractionation signatures, suggesting interannual changes in Hg biogeochemical dynamics rather than strong trophic shifts (that were assessed by simultaneous $\delta^{15}\text{N}$ analyses). The most significant interannual variations were observed for $\Delta^{199}\text{Hg}$ values (1.85 ± 0.02 to 2.57 ± 0.04 ‰), suggesting important interannual differences in the extent of Hg photochemical processes. Variable $\delta^{202}\text{Hg}$ values were also observed between years (1.00 ± 0.21 to 1.36 ± 0.11 ‰), suggesting different extent of methylation/demethylation processes and/or an influence of changing vertical mixing of different Hg sources. Overall, this work demonstrates that Hg isotopic variations recorded in seabird samples help to explore the link between the Hg cycle and climatic factors influencing the ocean dynamics of the Humboldt upwelling system and its impact on the epipelagic communities of the Peruvian coast.

VARIATIONS OF MERCURY ISOTOPE COMPOSITIONS IN PENGUIN GUANO DEPOSITS DURING THE LITTLE ICE AGE IN ANTARCTICA

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Penguin guano deposits are important records of penguin ecological history, providing valuable information for penguin population, dietary change, migration, and environmental changes in Antarctica. Guano deposits are also excellent proxy of the marine cycling of trace elements, including mercury (Hg). Hg in guano is primary transferred by penguins from the ocean in Antarctica. Previous studies on guano deposits on Ross Island revealed significant changes in penguin population during the Little Ice Age (LIA, ~1500-1850AD), a period characterized by colder climate, stronger katabatic winds, cooler sea surface temperature and larger polynyas (open water surface surrounded by sea ice) than today. However, it is not clear how the climate change during LIA affected the biogeochemical cycle of Hg. Here we studied Hg isotope compositions in two guano sediment cores located at Cape Bird, Ross Island (CB2) and near Zhongshan Station (RNL2), Antarctica, respectively, and investigated the potential link between Hg isotope signals and climate change. Both cores showed significant variations in $\Delta^{199}\text{Hg}$ only at the onset of the LIA (~1500-1650AD), but with different patterns. The RNL2 core showed relatively low $\Delta^{199}\text{Hg}$ at the onset of LIA and increased gradually during 1500-1650AD, along with increases of Hg concentration and other bio-elements such as P, Cu and Ni, suggesting an increase of penguin population and penguin-sourced Hg input. Thus the increase of $\Delta^{199}\text{Hg}$ is likely caused by the increased input of marine-derived Hg, which may have more positive mass independent fractionation (MIF) signals due to marine photochemistry than atmospheric or terrestrial Hg inputs. In contrast, the CB2 core showed relatively high $\Delta^{199}\text{Hg}$ during 1500-1650AD, and then decreased gradually at ~1650AD, and stayed relatively constant afterwards. Such variation of $\Delta^{199}\text{Hg}$ is unlikely caused by changes in Hg sources because both Hg concentration and %P showed little change during 1500-1650AD, suggesting that the penguin population and Hg input from penguin remained relatively stable during this period. Therefore, we hypothesize that the change of $\Delta^{199}\text{Hg}$ at the onset of LIA was most likely caused by changes in marine photochemistry of Hg, which may have been enhanced due to enlarged or more persistent polynya. This observation is consistent with our previous study on another guano core on Ross Island (MB6), which also showed higher $\Delta^{199}\text{Hg}$ values during ~1500-1650AD. Therefore, Hg MIF in penguin guano may serve as a potential proxy of Hg marine photochemistry, which may provide further insights into the climate change and penguin activities in Antarctica.

1.8 Mercury methylation: contrasting microbial and geochemical constraints

M.O.1.8-1

THIOL FUNCTIONAL GROUPS ASSOCIATED WITH NATURAL ORGANIC MATTER AND BACTERIAL MEMBRANES: CONCENTRATIONS AND THERMODYNAMIC STABILITIES OF COMPLEXES FORMED WITH MERCURY(II)

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Thiol functional groups associated with natural organic matter (NOM-RSH) and bacterial cell membranes (Mem-RSH) play an important role in bioavailability, cellular uptake and biotic transformations of Hg(II). Thermodynamic stability constants ($\log K$) of Hg(II) complexes formed with thiol groups of Suwannee River NOM (2R101N) and membranes of the Hg(II) methylating bacteria *Geobacter sulfurreducens* PCA and *Desulfovibrio desulfuricans* ND132 were determined by competitive ligand-exchange. Cysteine (Cys) was used as the competing ligand and the equilibrium concentration of the formed Hg(Cys)₂ complex was determined by a mass spectrometry. Side-reactions between Cys and NOM, as well as the potential formation of mixed ligand complexes, Hg(Cys)(NOM-RSH), were examined by isotope labelled ¹³C-Cys. To determine concentrations of NOM-RSH and Mem-RSH functional groups, and to characterize structures formed with Hg(II), we used Hg LIII-edge EXAFS. We determined the concentration of thiol groups in Suwannee River NOM and in membranes of *G. sulfurreducens* and *D. desulfuricans* to be 7.5 ± 0.4 , 121 ± 12 and $144 \pm 5 \mu\text{mol g}^{-1}$, respectively. The thermodynamic stability constant ($\log K \pm \text{SD}$) for the formation of Hg(NOM-RS)₂ [$\text{Hg}^{2+} + 2\text{RS}^- = \text{Hg}(\text{NOM-RS})_2$] and the mixed complex structure Hg(Cys)(NOM-RS) [$\text{Hg}^{2+} + \text{Cys}^- + \text{RS}^- = \text{Hg}(\text{Cys})(\text{RS})$] was determined to be 40.0 ± 0.2 and 38.5 ± 0.2 , respectively. The $\log K$ for the structure Hg(Mem-RS)₂ [$\text{Hg}^{2+} + 2\text{Mem-RS}^- = \text{Hg}(\text{Mem-RS})_2$] of *G. desulfuricans* and *D. sulfurreducens* was 39.1 ± 1.2 and 38.4 ± 0.9 , respectively. It should be noticed that $\log K$ for Hg(Cys)₂ [$\text{Hg}^{2+} + 2\text{Cys}^- = \text{Hg}(\text{Cys})_2$] was set to 37.5 according to previous study; and the pK_a values of RSH (here RSH denote any thiol group in Cys, NOM and membranes *G. desulfuricans* and *D. sulfurreducens*) were set to 8.6, 10.0, 9.5 and 9.3, respectively. A key finding of this study is that, at pH < 7 when all thiol groups are protonated, the $-\log K$ values for all complexes of Hg(RS)₂ [$\text{Hg}^{2+} + 2\text{RSH} = \text{Hg}(\text{RS})_2 + 2\text{H}^+$] are very similar, close to 20.0. Together with data on $\log K$'s of 15 low molecular mass (LMM) thiols that have been previously determined by the same method, our results offer an internally consistent thermodynamic data set for modelling the speciation and distribution of Hg(II) among NOM, LMM and bacterial membrane associated thiols. It will thereby provide a new basis for an improved molecular scale understanding of the processes of bacterial uptake, reduction/oxidation and methylation of Hg(II).

M.O.1.8-2

FERMENTATIVE BACTERIA DOMINATE MERCURY-METHYLATING COMMUNITY IN THE WATER COLUMN OF A SULFATE-ENRICHED FRESHWATER LAKE

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Methylmercury is produced from inorganic mercury by microorganisms living in anoxic environments. Understanding the timing and location of methylmercury production is crucial to understanding methylmercury uptake into the foodweb. Water column methylation in freshwater lakes is a potentially critical source of methylmercury to food webs in some systems due to the volume of anoxic habitat and proximity to phytoplankton at the base of the food web, but has been studied less than methylmercury production in sediments or periphyton. Known methylating organisms are phylogenetically and metabolically diverse, but in many systems, sulfate-reducing organisms are described as primarily responsible for methylmercury production. In this study, we sought to identify likely hotspots for methylmercury production in a lake with elevated sulfate levels and to identify methylators from samples with different redox conditions using genome-resolved metagenomics.

Lake Mendota is a eutrophic, sulfate-enriched lake with a high methylmercury to total mercury ratio in the anoxic hypolimnion. We collected depth-discrete geochemical and bacterial samples throughout the stratified season. Mercury speciation profiles suggested increased methylation potential near the oxic/anoxic interface during late season stratification. To investigate the methylating community at this time point, we performed shotgun metagenomic sequencing and searched for hgcA homologs (a known marker for methylation capabilities) in the assembled contigs. We identified many hgcA sequences in the assembly that clustered with hgcA sequences from known methylators. However, the hgcA+ population was dominated by non-canonical hgcA sequences. Genomic reconstructions revealed that the hgcA+ genome bins were dominated by fermentative Verrucomicrobia, Bacteroidetes, and Firmicutes in all of our metagenomes. Desulfobacterota, most of them with the capability for sulfate reduction, were also found throughout our metagenomes, albeit at a markedly lower abundance. Methanogenic Archaea and Syntrophobacteriales bins were most prevalent in high-sulfide portions of the water column. Metal-reducing *Geobacter* bins were rare and only identified near the oxic/anoxic interface. Using these bins, we can begin to probe how the ecophysiology of the methylating organisms serve to link biogeochemical cycles to methylmercury production. This study is further evidence that methylmercury production in high sulfate freshwater systems is not driven by sulfate-reducing organisms. Instead, the hgcA+ population is dominated by non-canonical fermentative organisms. This provides support for future studies that will further characterize the links between biogeochemical redox cycling and methylmercury production in freshwater lakes.

M.O.1.8-3

MICROBIAL BIOSYNTHESIS OF THIOL COMPOUNDS: IMPLICATIONS FOR SPECIATION, CELLULAR UPTAKE AND METHYLATION OF HG(II)

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Cellular uptake of inorganic divalent mercury (Hg(II)) is a key step in the microbial production of neurotoxic methylmercury (MeHg). The uptake mechanisms are not identified but low molecular mass thiol (LMM-RSH) compounds play important roles. Here we show that the iron reducing bacterium *Geobacter sulfurreducens* produces and exports several LMM-RSH compounds to concentrations exceeding 100 nM in the assay medium. These compounds control the chemical speciation and rates for cellular uptake and methylation of Hg(II) via the formation of Hg(LMM-RS)₂ complexes (primarily with cysteine) in assays without added thiols. We characterized and quantified microbially produced LMM-RSH compounds during Hg(II) methylation to gain new insights about the role of these compounds for MeHg formation. Our results show that Hg(II) complexes with weaker thermodynamic binding stabilities such as those of mixed ligation with LMM-RSH, Cl⁻ and OH⁻ were

methylated at higher rates than the stronger Hg(LMM-RS)₂ species. We further demonstrate that moderate differences in chemical structure of LMM-RSH compounds can cause significant differences in methylation rate for the different corresponding Hg(LMM-RS)₂ complexes. We also find that high nM concentrations of certain LMM-RSH compounds promote significant increases in Hg(II) methylation via unknown mechanisms which cannot be explained by either thermodynamic modelling or chemical structure alone. Combined, our results form a refined basis for understanding Hg(II) availability for microbial methylation and elaborate on the multiple effects of LMM-RSH compounds for MeHg formation.

M.O.1.8-4

THE ROLES OF MERCURY CHEMICAL SPECIATION AND BIOLOGICAL PRODUCTION OF LOW MOLECULAR MASS THIOLS FOR METHYLMERCURY FORMATION IN BOREAL WETLANDS

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The importance of the chemical speciation of dissolved Hg(II) for MeHg formation has been demonstrated in laboratory experiments on model systems. There is however a lack of studies investigating this relation in natural environments. In this work, we established a comprehensive chemical speciation model for Hg(II) and determined Hg(II) methylation rate constants, *k_{meth}*, in boreal wetland soils which have been identified as major sources of MeHg. The speciation model included Hg(II) complexes with inorganic sulfide (S-II), polysulfides (H₂S_n), thiols associated with natural organic matter (NOM-RSH) and specific low molecular mass thiols (LMM-RSH). The prediction power of the Hg(II) model was optimized by varying stability constants of Hg-sulfide and Hg-thiol species within their published values. The concentration of NOM-RSH(aq) shows a significant correlation ($p < 0.001$, $R^2 = 0.69$) with the measured Hg(II)(aq) concentration in porewater for the samples containing low S-II(aq) concentration ($< 1 \mu\text{mol L}^{-1}$), but not for the medium and high S-II(aq) concentration ($> 1 \mu\text{mol L}^{-1}$) ($p > 0.05$, $R^2 = 0.13$). Thus, it seems NOM-RSH(aq) controls the Hg(II) solubility below, but not above, $1 \mu\text{mol L}^{-1}$ of S-II(aq). The modeling results suggest that in these wetland soils Hg(SH)₂(aq) is the most important species for cellular uptake and methylation of Hg(II) at sulfidic conditions of $> 0.4 \mu\text{M H}_2\text{S(aq)}$. Eight specific Hg(LMM-RS)₂(aq) complexes were included in the speciation model and these are likely to be more important than Hg(SH)₂(aq) for Hg(II) uptake and methylation at ferruginous conditions when H₂S(aq) is less than 40 nM. A significant correlation ($R^2 > 0.65$, $p < 0.001$) was observed between total concentrations of biologically produced LMM thiol compounds and *k_{meth}*. We propose that these LMM thiols are produced by anaerobic microbes, and that the correlation with *k_{meth}* is reflecting a relation between microbial activity and MeHg formation.

M.O.1.8-5

ROLES OF MICROBIAL COMMUNITIES IN REGULATING MERCURY METHYLATION IN PADDY SOILS

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Rice ingestion has been recognized as an important route of dietary exposure to neurotoxic methylmercury (MeHg) that is usually synthesized in rice paddy soils. Although certain anaerobic microorganisms are known to convert inorganic mercury (Hg) to MeHg and the discovery of a two-gene cluster *hgcAB* has linked Hg methylation to several phylogenetically diverse groups of microorganisms, the prevalence and diversity of Hg methylators in microbial communities of rice paddy soils remain unclear; we also lack understanding of the role of non-Hg methylating

communities in MeHg accumulation. Here, we collected 141 paddy soil samples from main rice-producing areas across China to identify the diversity of Hg methylator, and associations between bacterial community composition (including both Hg and non-Hg methylators), and Hg methylation efficiency (proxy as %MeHg). Results showed that %MeHg in the paddy soils varied from 0.005 to 2.838% at a national spatial scale, which can be explained by the variations of soil microbial community composition across different areas. We show that Hg methylating communities are diverse, with iron-reducing bacteria (i.e., *Geobacter*) and methanogens as the dominant taxa likely involved in Hg methylation in the soil. Phylogenetic analysis also uncovered some *hgcAB* sequences closely related to three novel Hg methylators, *Geobacter anodireducens*, *Desulfuromonas* sp. DDH964, and *Desulfovibrio* sp. J2 in these paddy soils. Our structure equation modeling suggested a much stronger link between bacterial community composition and %MeHg, compared to the abundance of methylating gene (*hgcA*) and edaphic properties. More importantly, random forest models suggested a more important role of non-Hg methylators in predicting variations of soil %MeHg than Hg methylators. Further analysis of microbial network revealed strong co-occurrence patterns between non-Hg and Hg methylators, suggesting their interactions may affect MeHg production in paddy soils. These findings shed new light on microbial community composition and major clades driving Hg methylation in rice paddy soils. Our work highlights the important role of both Hg and non-Hg methylating communities in predicting MeHg production in paddy fields.

M.O.1.8-6

ASSESSMENT OF MICROBIAL COMMUNITIES AND GEOCHEMICAL PARAMETERS DETERMINING THE MERCURY METHYLATION IN SUBMARINE CANYON SEDIMENTS (ATLANTIC OCEAN, SW FRANCE)

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Microbial mercury (Hg) methylation transforms the inorganic mercury (Hg(II)) to the neurotoxin methylmercury (MeHg) in anoxic marine sediments. Both geochemical parameters and microbial activities constrain the net MeHg production, and were studied in the Capbreton Canyon. Twenty-three deep sea surface sediments were investigated within the first 30 km of this Canyon. A multidisciplinary approach combining geochemical parameters (e.i. organic carbon content (OC) and grain size), Hg(II) and MeHg concentrations (by ID-GC-ICP-MS) with microorganisms taxonomic diversity (16S DNA by MiSEQ) were investigated in all locations. Strong positive correlations have been found between geochemical parameters (OC and fine grain size) and mercury species concentrations. Both Hg(II) and MeHg levels increased in deep sea sediment, especially in the furthest location reaching 972 ng g⁻¹ dw and 2.1 ng g⁻¹ dw, respectively. Data showed that the MeHg proportion decreased along this canyon suggesting higher methylation production in coastal sediments. Sediment slurry incubations using mercury isotopic tracers performed under biotic and abiotic conditions demonstrated that methylation potential was mainly mediated by microbial processes and was the highest for the coastal station, whereas demethylation potential was similar for all stations. The taxonomic diversity demonstrated the presence of two main families of Deltaproteobacteria, Desulfobulbaceae and Desulfobacteraceae, suggesting sulfate reducing bacteria were involved in the Hg methylation. The Hg methylators using *HgcA* gene (by cloning and SANGER sequencing) were investigated in the sediments. Deltaproteobacteria, notably Desulfovibrionaceae, dominated the *HgcA* carrying communities, showing sulfate reducers constituted the main Hg methylators in those submarine sediments. Those results suggested the mercury-methylating microbial communities are constrained by the environmental parameters promoting the sulfate reducing bacteria activities.

2.6 Communities affected by Mercury Pollution

M.O.2.6-1

THE RESPONSE OF THE DEHCHO FIRST NATIONS (CANADA) FOLLOWING FISH CONSUMPTION NOTICES RELEASE AND INCREASED MERCURY LEVELS MEASURED IN ENVIRONMENTAL DATA.

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The Dehcho region in the Northwest Territories, in subarctic Canada, is the land of over 3000 Dene members. Under the Dehcho First Nations (DFN) organization, Dene people aim to self-govern their region to increase the sustainability of their lifestyle so the next generations can benefit from the wealth and health of people and Lands. This objective was sought through local initiatives including the implementation of the first Indigenous protected area in Canada, the Guardian program to monitor environmental and wildlife parameters, and several research initiatives to investigate trends in environmental monitoring.

Since 2014, the Government of the Northwest Territories has emitted Site Specific Fish Consumption Advice in several areas. Currently, 10 water bodies in the Dehcho are associated with advice to limit the consumption of certain fish species. The traditional diet of Dene, which was assessed in 1994 and 2016-2017, includes local fish consumption. Lake trout, the second most consumed fish in the region, is one of the species identified as having elevated mercury concentrations.

The DFN initiated a program to collect long-term mercury data to understand the impact of this contaminant on the Dene lifestyle. Mercury data in water and fish, as well as complementary environmental data, are collected as part of an ongoing program facilitating community-based water monitoring: the Aboriginal Aquatic Resources and Oceans Management. Additionally, academic collaborative projects measuring mercury in traditional foods, as well as human hair, blood and urine were developed. These initiatives are essential to understanding the impact of climate change, including changes to the permafrost and nutrition transitions in the region.

A comprehensive community strategic plan was developed to ensure ongoing monitoring of the water and land. The findings will lead to a strategy to cope with climate change challenges, improve resilience, and build community-led solutions to preserve the traditional Dene lifestyle while not increasing the risk to people's health.

M.O.2.6-2

MERCURY HAZARDS AWARENESS PROGRAM AMONG DIFFERENT COMMUNITIES PARTICULARLY EMPHASIS ON SCHOOL CHILDREN IN HISAR, HARYANA, INDIA

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Objectives were achieved by having different expert lectures at school level as well as at central points in the city. These lectures were followed by a discussion session sensitizing the brain at the end both at school level as well as community level. This further include film screening and power point presentation regarding the hazards of mercury. The interactive nature sessions were proved to be effective and provided lot of discussion amongst students and teachers post every session. The students were put into an hypothetical situation which may lead to mercury spill at different places of their use and what mitigation they can have in the situation. The Mercury Awareness Programme was also carried out in the communities. Seeking the maximum participation of the people the, local leaders, local other NGO, influential persons

and key person of the community were contacted. The lecture cum discussion, screening of films on the usage and hazards of Mercury, animated film on spill management and participatory question answer session were the key methods used for disseminating the information. The Information and communication material on Mercury was also distributed; such as posters and handbills. Important data was collected and calculated from the masses including schools regarding the instruments they use at home, gender and age sensitization towards mercury pollution and it was found that females in the age group of 14-26 were keener to learn the things about mercury pollution. Only 5% of the total group of students are aware of mitigation strategy after the spill of mercury at home and most of them put their responsibility to their elders in case of an mercury accident. Education level has a great impact on the paradigm of mercury pollution and the people having qualification above metric are more versatile towards the hazards of mercury pollution then the illiterate people. Furthermore, epistolary exchange has more effect as compared to verbal exchange and film screening. This is something peculiar due to retaining capacity of written literature like pamphlets etc. Further studies on these lines are in progress and our society's aim is to not only create awareness amongst the different sections of the society but on the basis of our observation, we can help the policy maker also regarding the waste management in the city.

M.O.2.6-3

MANAGING MERCURY EXPOSURE THROUGH CONSUMPTION ADVISORIES IN CANADA – SUCCESS OR FAILURE?

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When evaluating mercury exposure through the consumption of foods, Health Canada currently provides advice based on the assumption that 100% of total mercury is methylated, bioavailable, bioaccessible, and absorbed. These assumptions are typically made in human health risk assessments due to a lack of scientific data. As a result, the risk posed to human health from mercury in country foods may be overestimated, which can lead to consumption advisories which may or may not be necessary. Managing mercury exposure by issuing consumption advisories has historically been a standard risk management strategy in Canada primarily for hydroelectric developments, but also for any other industrial activity that may in the future or has previously resulted in increased MeHg levels in fish which may be consumed by people (including Indigenous communities). Unnecessary consumption advisories can have negative impacts on human health, specifically among Indigenous communities, as they deter individuals from consuming country foods and this may result in the consumption of potentially less nutritious commercial foods and influence longer-term food security and consumption patterns. This disconnect can result in issues related to the nutritional status and the overall practice of traditional activities of Indigenous peoples.

This presentation examines the extent of consumption advisories issued in Canada and their linkages to industrial developments or other disturbances. Using fish consumption advisories as an example, the presentation discusses the procedural differences in issuing advisories within Canada. It will provide information on how varying assumptions in advisories as well as the subsequent response(s), compliance and awareness are assessed. Where surveyed, the uptake and efficacy of these advisories are examined, and effects on the Indigenous communities in Canada discussed. Consumption surveys as a method to reduce mercury exposure from traditional foods are compared to other approaches. These include establishing realistic hazard quotients taking into account for differences in Hg concentrations in different species, muscles and organs, the level of mercury methylation, actual consumption levels (including seasonal variation in consumption), and differing levels of bioavailability, bioaccessibility and absorption. Methods of food preparation and the influence of other considerations (such as the influence of selenium) are also discussed.

3.6A Mercury Emissions Reductions – A Challenge to Industry

M.O.3.6A-1

MERCURY CONTROL IN LIGNITE AND COAL FIRED POWER PLANTS BY STATIONARY SORBENT MODULES

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The GORE™ Mercury and SO₂ Control System (GMCS) (see http://www.gore.com/en_xx/products/filtration/mercury/mercury-control-coal-fired-boiler.html for details) has been proven in more than 30 power plants and incinerators in the US since 2012. Three pilot plants are operated in EU power plants.

In August 2018 a German industrial scale lignite based power plant installed the system to control mercury emissions and improve SO₂ reduction.

This system is based on sorbent polymer composite (SPC) material housed within discrete modules which provide passive, continuous mercury control with minimal pressure drop. As a result, no injection of any sorbents or chemicals are required. The modules will capture and retain mercury for many years of operation, resulting in an exceedingly easy-to-operate mercury control system, and very low ongoing operating costs. Modules can be installed inside of a wet flue gas desulfurizer (wFGD), which requires no additional footprint on site. Unlike systems that inject oxidizing chemicals such as calcium bromide, this system presents no risk of air preheater corrosion, and does not impact the waste water treatment system on the scrubber effluent stream. The system is unaffected by SO₂/SO₃ concentrations, which makes it very suitable for high sulfur coal sources, and may provide fuel flexibility options to a plant operator. In addition, the system can provide protection against scrubber re-emissions in a way that doesn't impact gypsum quality or the waste water treatment system. The modules also carry a co-benefit of SO₂ removal, which can help meet tighter SO₂ emissions limits and possibly avoid a scrubber upgrade.

Results from the pilot plants and the full-scale installation in Germany will be provided.

M.O.3.6A-2

MERCURY EMISSION – CHALLENGES FOR COAL-BASED POWER GENERATION SECTOR

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Electricity production, which is the main source of mercury emission to the atmosphere, is based mainly on combustion of solid fuels, such as hard coal and lignite. In Poland, the anthropogenic emission of mercury is estimated at 11.8 Mg, of which 9.1 Mg (over 77%) results from solid fuels combustion. The average mercury content in coal in Poland, according to tests carried out by Wojnar and Wisz was 0.100 mg / kg for hard coals and 0.250 mg/ kg for lignite (Wojnar and Wisz 2006).

From August 2021, the Polish coal-based power generation sector will have to meet stricter requirements introduced by Commission Implementing Decision (EU) 2017/1442 of 31 July 2017 (BAT Conclusions), including mercury emission requirements in flue gases.

New requirements can be fulfilled not only by equipping power units with dedicated mercury emission reduction installations, but also by optimised utilisation of capacities of existing environmental protection installations, in particular by possibility to remove mercury in electrostatic precipitators and bag filters while dedusting flue gases, as well as during nitrogen oxides removal in catalytic selective (SCR) and non-catalytic (SNCR) processes of nitrogen oxides reduction. Flue gas desulphurisation processes, such as semi-dry and wet flue gas desulphurisation, offer high mercury removal potential. Flue gas dedusting processes allow to reduce mercury emissions from 5 to 60%, mainly mercury that is carried

by fly ash particles. Installations for NO_x emission reduction (first of all SCR) also have positive effect on the emission reduction, they allow to increase the share of oxidised mercury in flue gases.

A significant mercury emission reduction effect is possible to achieve through a combination of various environmental protection installations. Regardless of applied secondary measures, proper fuel mix prepared for combustion in the boiler is of key importance in the process of mercury emission reduction.

Tests of mercury emissions carried out on power units of TAURON Wytwarzanie SA indicate that levels of this emission in all tested cases are in the range defined in BAT Conclusions.

In case of new power units, emission levels allow them also to meet emission limits set for new units. It is clear from this that construction of large modern power units burning Polish hard coal can significantly reduce mercury emissions from the power generation sector.

M.O.3.6A-3

REDUCING MERCURY WITH NEWLY DEVELOPED POWDERED ACTIVATED CARBONS AT COAL FIRED POWER PLANTS

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(1)Solution provider

Powdered Activated Carbon (PAC) is used as a dry sorbent to remove mercury and other impurities from flue gases of various combustion process, amongst other, at coal fired power plants. Based on more than 20 years of experience in this application, Cabot Norit activated carbon develops constantly improved grades for the removal of mercury both in oxidized or elemental form, from the flue gas.

New developed 3rd generation grades are suitable to use at high concentrations of elemental mercury and/or organic (oxidized) mercury as well as at elevated sulfur trioxide concentration. DARCO HG activated carbon types are also developed to operate and perform at the various flue gas processes in operation. Recent pilot and full-scale extended trials have demonstrated effective mercury emission reduction at a variety of sites with both elevated sulfur trioxide and other gas chemistry challenges.

These newly developed powder activated carbon sorbents, DARCO® Hg-LH EXTRA SP and SR as well as DARCO® Hg EXTRA, are capable at low sorbent injection rates of reducing mercury emissions sufficiently for compliance with both national and international pollution regulations (i.e. MATS, BREF and the Minamata Convention) even at the most stringent composition of the flue gas. With high sulfur combustion fuel and process feedstocks likely to be in use for the foreseeable future, DARCO® Hg-LH EXTRA SP and SR as well as DARCO® Hg EXTRA allow cost-effective mercury emission control and reduced balance-of-plants concerns.

M.O.3.6A-4

NOVEL METHOD OF MERCURY REDUCTION IN FLUE GASES OF LIGNITE FIRED POWER PLANTS BY DEDICATED BROMINE SALTS MIXTURES

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The method of mercury reduction based on implementation of dedicated mixture of bromine salts to lignite before combustion process was investigated. The novelty of the method in comparison to well-known technology of dosing the halogenated additives in the fuel or its injection to the furnace lies in an appropriate selection of bromine salts additives, taking into account the composition of the burnt lignite i.e. content of halides, concentration of calcium and sulfur compounds. Another important issues are the activation of bromine salts and fuel and the selection of dosage place. The predefined quantity of the mixture is added directly into the lignite before mills. In the process of grinding the

mixture of bromine salts and coal are homogenized. Further, in the process of combustion, mercury is oxidized to bromine salt and sulfur oxides are bound, which increases absorption reactivity of the ashes.

The technology was investigated in selected units in Power Plants Belchatów and Turów belonging to PGE GiEK S.A. The tests lasting six months performed under normal operating conditions of the units (without fuel selection and shutdowns) confirmed the achievement of emission limits imposed by BREF/BAT conclusions, which will be binding starting from 17th of August 2021.

The method of mercury reduction by dedicated bromine salt mixtures is characterized by low capital expenditure due to simple dosing installation and relatively low operating costs compared to other mercury emission reduction methods.

M.O.3.6A-5

REDUCTION OF MERCURY EMISSIONS FROM A 900MW COAL-FIRED POWER PLANT THROUGH MERCURY STABILIZATION AND ADSORPTION DURING A WET-FLUE GAS DESULPHURIZATION (WFGD)

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In 2010, 24 % of global anthropogenic mercury emissions were generated by fossil-fired power. Hence, German regulations stipulate coal-fired power plant mercury emissions to a daily mean value of 30 µg/m³ STP (standard temperature and pressure) and yearly mean value of 10 µg/m³ STP. In the BAT Reference Document for Large Combustion Plants (BREF-LCP), an average annual emission by existing hard coal-fired power plants with a rated thermal input ≥ 300 MWth of <1 to 4 µg/m³ STP was identified using the best available technology.

The aim of this project is to develop a process for reducing coal-fired power plant mercury emissions well below the upper range of the BREF-LCP bandwidth without affecting gypsum, fly-ash and waste water quality. Based on a detailed analysis of operational data over several months, an approach combining different mercury reduction mechanisms has been detected as a possible solution.

After successfully testing at laboratory scale, the approach has been implemented at industrial scale at unit 9 of Grosskraftwerk Mannheim, Germany.

The overall procedure consists of 3 steps:

1. Increasing the chloride concentration in the WFGD absorber suspension to 25 g/L:

At this concentration, oxidized mercury absorption from flue gas is promoted. The adsorbed mercury forms water soluble complexes which stabilize the mercury inventory within the WFGD system. Thus, mercury concentration in the solid phase of the WFGD suspension and the re-emission rate of mercury from the WFGD into the gas phase is decreased.

2. Raising the WFGD water discharge volume flow:

This increases the waste water treatment plant mercury discharge. The overall mercury inventory within the WFGD system as well as the mercury emissions at the stack are reduced.

3. Consecutive dosing of three different additives, straight or as a mix, within the WFGD:

By adsorbing the mercury, they suppress mercury re-emissions. One additive can be completely separated from the WFGD gypsum in a hydro cyclone classifier. Mercury concentration in gypsum is not increased by additive dosing. The additive with the adsorbed mercury is discharged with the sludge of the waste water treatment plant.

By following the above-described strategy the industrial scale experiments demonstrate: mercury concentration at unit 9 is reduced in all

filtrates along the WFGD and increased in the solids discharged into the waste water sludge. Mercury emissions at the stack are significantly decreased. Values <4µg/m³ STP according to the upper range of BREF-LCP bandwidth can be safely achieved under all operating conditions.

M.O.3.6A-6

NOVEL HYBRID TECHNIQUE FOR MERCURY REDUCTION IN FLUE GASES

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A major source of environmental mercury is the combustion of fossil fuel used to produce energy. Based on the actual and planned European directive, the emission of mercury might be limited to a value near 1 µg/dNm³ at 6% oxygen. Nowadays the regulations concerning mercury concentration in flue gases are getting more strict. Thus there is a need to propose an efficient and economically justified mercury reduction technique. To achieve the required deep reduction of mercury will not be easy for power plants which burn only hard coal, and it will be even more difficult for lignite fired boilers, which usually contain larger amounts of mercury relative to hard coal.

To meet this request an innovative system for mercury removal from flue gases is proposed. The developed process is based on the combination of injection of brominated powdered activated carbon, dispensing of fuel additives and use of the innovative polymeric membrane material. The idea of the hybrid technique was to provide the possibility to reduce mercury emission without the necessity of introducing many significant modifications into the flue gas treatment system. Up to now, the injection of an activated carbon into the flue gases and the use of fuel additives are commonly used for mercury reduction. Those methods are characterized by low investment but high operational costs. Here, the application of polymer material is considered as a part of reduction system. Polymer material is expensive to buy but has almost none operational costs. To find the proper combination of mentioned techniques both laboratory tests and a pilot scale facilities were used to collect all necessary information. Laboratory tests focused mainly on the behavior of the polymer material under various conditions including pre-saturation of the material with mercury. Pilot installations were used to test various combinations of number of layers of polymer modules together with different fuel additives and mercury sorbents injected to flue gases. The collected data were used to develop a predictive numerical model. The model was implemented into the Ansys Fluent code, using a set of user defined functions combined with the solution procedure. The developed mode will be used to tailor the proposed approach for any particular installation.

4.1 Evaluating the effectiveness of the Minamata Convention

M.O.4.1-1

USING INDICATORS TO EVALUATE THE EFFECTIVENESS OF THE MINAMATA CONVENTION ON MERCURY

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This research focuses on the potential use of outcome and process indicators for the periodic evaluations of the Minamata Convention

on Mercury that are mandated under Article 22. These evaluations, which will start no later than 2023, must consider whether the Minamata Convention is meeting its overall objective, as expressed in Article 1, to "protect the human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds." This research draws from insights from previous effectiveness evaluations of other international environmental agreements, including the Stockholm Convention on Persistent Organic Pollutants, as well as the existing academic literature. Ideally an effectiveness evaluation would (a) collect and use comprehensive information about the changes in emissions and releases of mercury and mercury compounds that are attributable to measures taken under the Convention (b) directly connect these changes to observed changes in environmental concentrations of mercury, and (c) subsequently link the environmental concentrations to changed exposure levels for key human populations and wildlife receptors. However, because the current state of mercury science cannot definitively attribute observed global changes in mercury concentrations in the environment and humans to specific actions under the Minamata Convention, the use of such outcome indicators will at least initially have to play a secondary role in effectiveness evaluation. Instead, evaluations conducted in the near term will have to rely largely on process indicators that reflect the scope and intensity of actions taken by parties under the Minamata Convention, and associated reductions in inputs to the environment, as proxies for reduction in risks to human health and the environment. We propose a specific set of process indicators that are both small enough in number to be manageable and comprehensive enough to provide policy-relevant information across the full life-cycle of Minamata Convention provisions on supply, trade, use, storage, disposal, emissions, and releases. To the extent feasible, we propose that this information can be supplemented by modelling of key scenarios, to provide insights into how changes in emissions and releases could be predicted to affect environmental levels and exposures. As mercury science improves in the future, monitoring data may be able to provide a more direct gauge of effectiveness of the Minamata Convention.

M.O.4.1-2

MERCURY STABLE ISOTOPES FOR THE EFFECTIVENESS EVALUATION OF THE MINAMATA CONVENTION ON MERCURY

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As a part of the Minamata Convention, specific provisions are set-out for a global monitoring program (GMP; Article 22(2)) and the convention effectiveness evaluation (EE; Article 22(3)). While the precise scope of the GMP and EE are being discussed, these objectives share common opportunities and challenges. The major opportunity is that they stimulate scientific advancements to better measure mercury in the environment. The major challenges are establishing an internationally comparable performance indicator that can ascertain changes in mercury sources subject to regulation and distinguishing between policy signal and noise, which may be interfered by climate change and other human activities. By tracking atmospheric emissions to ecosystem fate, we illustrate how measurements of mercury stable isotopes can help address the challenges of the GMP and EE. Among the atmospheric samples (total gaseous mercury; TGM, precipitation, particulate bound mercury; PBM), we find that isotopic compositions of TGM are effective for distinguishing between long-range transport ($d202Hg = -0.39$ to $+0.93\%$, $D199Hg = -0.22$ to -0.01% , $n=11$) and anthropogenically influenced mercury sources ($d202Hg = -2.03$ to 0.19% , $D199Hg = -0.16$ to $+0.15\%$, $n=49$). In terrestrial environment, the most important factors governing the differences in mercury isotopic compositions between foliage and soil are the types of atmospheric mercury

sources and the organic matter content, respectively. Foliage collected at various locations of the U.S. and China show $\sim 1\%$ deviation, depending on mercury sources that influence the foliage. Urban, mineral, and organic soil collected from a wide range of environment show a significant negative relationship between mercury isotopic compositions and the total organic matter content, rather than sources that contaminate the soil. For the first time, we compare mercury isotopic compositions of sediments ($n=887$) by differentiating between point source impacted, non-point source influenced, and pre-anthropogenic and between ecosystem type (river, lake, coastal, marine). We find increasing trends in $D200Hg$ and $D199Hg$ with decreasing anthropogenic mercury influence from coastal and marine sediments. Lake sediments show decreasing $D199Hg$ trends with decreasing anthropogenic influence, given that soil runoff characterized by low $D199Hg$ acts as an important mercury source to many remote lake systems. All in all, our study suggests that the measurements of mercury isotopes in various environment samples (TGM, foliage, sediment) can aid the interpretation of mercury sources and processes at a large spatial scale. We also suggest that our data can be used for forming a baseline and for evaluating changes in mercury sources under the implementation of the Minamata Convention.

M.O.4.1-3

GLOBAL MONITORING OF HUMAN EXPOSURE TO MERCURY AND ITS COMPOUNDS: ARE WE READY?

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Assessment of human exposure to mercury and its compounds is critical for planning of targeted measures to reduce risks for human health and to monitor progress. Harmonized approach for collecting this information at global level brings a number of benefits: collection of reliable and comparable data; identification of highly exposed populations at different levels – national, regional and global; more effective use of human, technical and financial resources for exposure assessment; and, in total, for an assessment of effectiveness of global efforts to protect human health from negative impact of mercury. The requirement to monitor mercury compounds and their trends in vulnerable populations using harmonised methodologies is included in the Minamata Convention (Art 19 and Art 22).

To ensure feasibility of global monitoring of human exposure to mercury, WHO developed a series of standard operating procedures for sampling and analysis of mercury, and a tool for the development of national protocols for the assessment of mercury risks to developing organisms (foetus), during critical windows of exposure. The tool includes technical details relevant for planning, designing and implementation of national surveys, both at a countrywide level and in contaminated sites.

The pilot national HBM surveys, implemented in China, Ghana, India, Mongolia, Kyrgyzstan, and the Russian Federation, using the WHO methodology and following the WHO ethical principles, confirmed the applicability of the technical documents and the feasibility of mercury HBM studies in countries with different level of economic development. The pilot surveys also demonstrated that capacities for reliable assessment of exposure to mercury using HBM exist, or can be built in developing countries and countries with economies in transition.

The analysis of the data obtained in the pilot surveys on mercury HBM confirmed the earlier scientific findings that populations with high level of consumption of marine and fresh waters fish and other contaminated food (such as rice) are more exposed to mercury. Populations living in the areas of ASGM and other highly contaminated sites are also populations at higher mercury risks. This confirms robustness of the WHO methodology for identification of populations at risks globally and for an assessment of effectiveness of risk reduction measures, including in the Convention framework.

Thus, scientific, technical and methodological basis for global monitoring of mercury exists and global monitoring of human exposure to mercury is possible.

M.O.4.1-4

PROGRESS ON IMPLEMENTATION OF MINAMATA CONVENTION IN CHINA

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In order to protect human health and the environment from the common hazards of anthropogenic emissions and releases of mercury and mercury compounds, the international community has worked hard to reach the Minamata Convention on Mercury. The Minamata Convention is another legally binding time-limited Convention following the Stockholm Convention and the Climate Change Convention in the past 15 years. It is an important milestone in the history of human environmental protection. As an economic developing and transforming country, China is actively facing enormous pressures and challenges of environmental protection. It is committed to ecological civilization construction and environmental protection, and attach great importance to mercury prevention and control. China is one of the first signatories of the Minamata Convention, and the Ministry of Ecology and Environment actively coordinates and promotes domestic ratification. On April 28, 2016, the Standing Committee of the 12th National People's Congress approved the Convention, and on August 31 of the same year, it deposited the instrument of ratification and became the 30th ratifying country. The Convention entered into force on August 16, 2017. From August 2017 to August 2018, in the first year of the implementation of the Convention, China has made great progress. First, the National Coordinating Group for the Implementation of the Mercury Convention, constituted by 17 Ministries, and a compliance coordination mechanism was established. Second, China officially launched the preparation of the National Implementation Plan, strengthened the top-level design and continued to promote the implementation of the Convention. Third, to strictly fulfill the obligations stipulated in the Convention, the "Announcement on the Entry into Force of the Convention on Water Margins" was promulgated, and the "List of China's Strictly Restricted Toxic Chemicals" and the "List of Priority Control Chemicals (First Batch)" were issued. Important documents such as the application for the discharge permit and the technical specifications for the issuance of key industries were published as well. At this stage, China will continue to increase the management of mercury pollution prevention and control, continuously improve the mercury pollution prevention policies, regulations and standards, gradually improve the ability and overall level of mercury pollution prevention, and actively strengthen the foundation for the compliance of the Convention.

M.O.4.1-5

USING SOILS AND BIOTA TO EVALUATE THE EFFECTIVENESS OF THE MINAMATA CONVENTION ON MERCURY

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The Minamata Convention on Mercury (Hg) was recently ratified and entered into force in August, 2017. As noted in the Convention text, fish are an important source of nutrition to consumers worldwide and several species represent important links in the global source-receptor dynamics of monomethylmercury (MeHg). However a coordinated global program for biota, and soils, using accredited laboratories, reproducible data and reliable models is still lacking. Hg science has evolved significantly with its use of advanced technologies and computational models to address this complex and ubiquitous environmental and public health issue. These advances have made it essential that transparency be enhanced to ensure that Hg biomonitoring studies used in support of the Convention are scientifically sound, robust and reproducible. Here we outline a sampling framework based on existing and planned monitoring of key biota and soils. In biota, measurements comprise total Hg, MeHg and stable isotopes (SIA) of Hg, carbon (C) and nitrogen (N). For soils the same Hg and SIA measurements will be made with the addition of bulk estimates of C, N, sulfur and pH. Soil sampling will focus on organic surface horizons to assess integrated deposition loads of Hg and we will also identify biases related to the effects of microbial activity on soil methylation-demethylation dynamics. The biological sampling will focus on key marine fish species including, but not limited to, bluefish (*Pomatomus saltatrix*), sardinella (*Sardinella* spp.) and hake (*Merluccius* spp.) and other globally-distributed species including birds, freshwater fish, such as perch (*Perca fluviatilis*) and salmonids (*Salmonidae*), invertebrates, sea turtles, and selected marine mammals. Sampling will follow existing frameworks and will occur at a global scale; biota will be selected based on information and guidance from the Conference of Parties (COP) and as stated in Articles 19 and 21 of the MCM text. All work will utilize accredited laboratories and established protocols and will cooperate with existing international, local and regional biomonitoring programs. Inter-laboratory comparisons and analytical chemistry guidance will be provided by IAEA in support of the Convention's biomonitoring goals. Challenges and obstacles to developing a successful global Hg biomonitoring program in support of the MCM will also be discussed. Data will be stored in an interoperable, web-based, data platform and standardized spatiotemporal analyses in soils and selected taxa, as guided by the COP, will be conducted to evaluate the effectiveness of the Minamata Convention on Mercury. ©2017, ©2018, ©2019 U.S. Copyright Number 1-7492662211

M.O.4.1-6

HOW CLOSELY DO MERCURY TRENDS IN AQUATIC WILDLIFE TRACK THOSE IN THE ATMOSPHERE? – IMPLICATIONS FOR EVALUATING THE EFFECTIVENESS OF THE MINAMATA CONVENTION

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The Minamata Convention to reduce anthropogenic mercury (Hg) emissions entered into force in 2017, and attention is now on how to best monitor its effectiveness at reducing Hg exposure to humans. To address this, a key question is how closely Hg concentrations in the human food chain, especially in fish and other aquatic wildlife, will track the changes in atmospheric Hg that are expected to occur following anthropogenic emission reductions. As part of the United Nations Environment Programme (UNEP)'s Global Mercury Assessment (GMA), we investigated this question by evaluating several regional groups of case studies where Hg concentrations in aquatic biota have been monitored continuously or intermittently for several decades. Our analysis shows that in most cases Hg time-trends in biota did not agree with concurrent Hg trends in atmospheric deposition or concentrations, and the divergence between the two trends have become more apparent

over the past two decades. An over-arching general explanation for these results is that the impact of changing atmospheric inputs on biotic Hg is masked by two factors: 1) The aquatic environment also contains a large inventory of legacy emitted Hg that remains available for bio-uptake leading to a substantial lag in their response time to a change in external inputs; and 2) Biotic Hg trends reflect the dominant effects of changes in multi-causal, local and regional processes (e.g., aquatic or terrestrial biogeochemical processes, feeding ecology, climate) that control the speciation, bioavailability, and bio-uptake of both present-day and legacy emitted Hg. Globally climate change has become the most prevalent contributor to the divergence. A wide range of biotic Hg outcomes can thus be expected as anthropogenic atmospheric Hg emissions decline, depending on how these processes operate on specific regions and specific organisms. Therefore, evaluating the effectiveness of the Minamata Convention will require biomonitoring of multiple species that represent different trophic and ecological niches in multiple regions of the world.

1.2A Biogeochemical cycling of mercury in the aquatic ecosystems

M.O.1.2A-1

METABOLOMICS UNCOVERS PHYTOPLANKTON RESPONSES TO HG COMPOUNDS IN AQUATIC ENVIRONMENT

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Metabolomics, the youngest among -omics technologies, characterizes low-molecular-weight molecules involved in different biochemical reactions and provides an integrated assessment of the physiological state of an organism. This feature makes the metabolomics well suited to study organism – environment interactions. Nonetheless, very few studies use the metabolomics approach to explore the contaminant-induced metabolic perturbation in phytoplankton and to the best of our knowledge, no such studies exist for mercury.

The present pilot study aimed at getting new insights into the basic mechanisms determining cellular responses during mercury exposure. To this end, untargeted liquid chromatography – mass spectrometry (LC-MS) metabolomics was employed to follow the metabolic variations in green alga *Chlamydomonas reinhardtii* and cyanobacterium *Synechocystis* sp., as representatives of two important phytoplankton groups. Both hydrophilic and lipophilic compounds were determined in the microorganisms exposed to 1 or 10 nM inorganic (IHg) or methylmercury (MeHg) and compared with unexposed controls. The untargeted metabolomics approach resulted in approximately 900 signals from both hydrophobic and hydrophilic extracts of *C. reinhardtii* or *Synechocystis* sp. However only about one third were annotated. Supervised and unsupervised multivariate methods provided an information on most influential metabolites, which were further used to identify the most important metabolic pathways affected by Hg or MeHg exposure. The results revealed an alteration of multiple pathways for both cyanobacteria and green alga when exposed to IHg or MeHg, including carbohydrate metabolism, energy and lipid metabolism, amino acid metabolism, metabolism of cofactors and vitamins. Globally Hg species induced metabolic perturbations in green algae were more important than those found in cyanobacteria, which corresponds to higher sensitivity of the green algae to mercury. The annotated metabolites showed that IHg and MeHg affected similar pathways, however for comparable exposure concentrations in some cases MeHg-induced perturbations were more pronounced or specie-specific. For example among different hydrophobic molecules the most pronounced decrease was found in the diacylglycerylhomoserines (DGTSS) class involved in glycerophospholipid metabolism of *C. reinhardtii* during MeHg expo-

sure. However, DGTSSs were not detected in *Synechocystis* sp. The results demonstrated the promise of metabolomics in uncovering Hg-induced perturbations in the two model phytoplankton species and underlying biochemical mechanisms. However they have also revealed some drawbacks mainly due to the relatively high metabolic variability, corresponding to normal operation range of the microorganisms, which could hide the subtle changes in metabolite concentrations, as well as the lack of phytoplankton-specific metabolite information in the existing databases which limits the metabolite identification.

M.O.1.2A-2

BIOGEOCHEMISTRY OF MERCURY SPECIES IN THE WATER COLUMN OF HIGH ALTITUDE LAKES OF THE WESTERN PYRENEES (FRANCE / SPAIN)

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While Hg is a major concern in all aquatic environments where methylation and biomagnification take place, very few studies consider Hg cycling in remote alpine lakes and their use as proxies of global environmental changes. This work presents an integrated investigation conducted in twenty high altitude pristine lakes from Western Pyrenees. Subsurface water samples were collected in June/October 2017/2018 for Hg speciation analysis (iHg, MMHg, DGM) to investigate spatial and seasonal variations. DGM provided information on biotic and photoreduction of Hg as well as atmospheric re-emission extents. In June/October 2018, a more in-depth study was performed in lakes Gentau, Arratille and Sabocos, by sampling at different depths along the day. Besides, in situ incubation experiments using isotopically enriched Hg species (¹⁹⁹iHg, ²⁰¹MMHg) were conducted to investigate Hg transformation mechanisms in the water column (methylation, demethylation, reduction). Comparison between filtered (<0.2µm) and unfiltered samples highlighted significant differences in most of the samples. While iHg did not show seasonal variations, MMHg was significantly higher in autumn, except for bottom anoxic waters (Gentau and Sabocos). For the unfiltered samples, concentrations of MMHg in surface waters were low in Gentau, respectively 8±1pg/L (2% of HgTOT) in spring and 29±5pg/L in autumn (9% of HgTOT). Similar values were found in Sabocos, 19±3pg/L (3% of HgTOT) and 29±5pg/L (5% of HgTOT), and Arratille, 7±1pg/L (3% of HgTOT) and 17±3pg/L (3% of HgTOT). Bottom waters in Gentau exhibits higher MMHg concentrations, 426±59pg/L in spring (36% of HgTOT) and 388±67pg/L in autumn (50% of HgTOT). These values are higher than in Sabocos, 60±8pg/L (10% of HgTOT) and 26±5pg/L (3% of HgTOT), and Arratille, 9±1pg/L (3% of HgTOT) and 14±2pg/L (6% of HgTOT). Results from the incubation experiments highlighted an important demethylation yield in Gentau (44±11%/day in spring, 42±25%/day in autumn). In bottom waters, methylation rate is 2.4±1.8%/day (spring) and 1.9±2.6%/day (autumn) for Gentau whereas methylation rates are about 0.7±0.5%/day in both seasons for Sabocos (below LOD=0.04%/day in Arratille). Overall, drastic environmental changes occurring daily and seasonally in alpine lakes are providing conditions that can both promote Hg methylation (stratified anoxic waters) and MMHg demethylation (intense UV light). Both climate change (warming) and human impact (through eutrophication) may have important implications on those pathways and the fate of Hg in these remote lakes.

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MERCURY SPECIES IN SURFACE WATER IN MIDDLE AND NORTHERN TIBETAN PLATEAU

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Climate change and human activities affect the cryospheric characteristics and hydrological changes of the rivers originating from the Tibetan Plateau (TP). Mercury (Hg) is a global pollutant and methylmercury (MeHg) can be more toxic due to the bioaccumulation and biomagnification effect in the food chain. There is an increasing concern on Hg in TP since the high sensitivity of the pristine environment to the long-distance-travelled Hg. To better understand the Hg distribution and its impact factors, the concentrations of Hg species in surface water were investigated in Three River Source Region (TRS) and Qi Lian Mountain (QLM), which is located in the middle and northern TP, respectively. In 2018, water samples were collected in the rivers or lakes in TRS and QLM. Total Hg (THg), dissolved Hg (DHg), particulate Hg (PHg), total MeHg (TMeHg), dissolved MeHg (DMeHg) and particulate MeHg (PMeHg) were analyzed according to EPA method 1631 and 1630. THg in TRS ranged from 0.51 to 7.48 ng·L⁻¹, which were slightly lower than those in QLM (0.94-7.93 ng·L⁻¹). TMeHg in TRS and QLM ranged from 0.05-0.31 ng·L⁻¹ and 0.04-0.49 ng·L⁻¹, respectively. Nonparametric tests of the TMeHg showed no significant difference between both sites. THg and TMeHg were comparable to the previous results in TP and the arctic area, which represent the background levels in river systems. The ratios of TMeHg/THg in TRS and QLM were 7.31±3.00% and 5.22±2.63%, respectively. The ratios were consistent with previous observation in Yarlung Zangbo River (5±2%) in southern TP, but much higher than Yukon River (1%) which is located in Arctic and Subarctic. In TRS, a positive correlation was observed between DOC and THg, DHg, DMeHg values ($r=0.466$, $p<0.01$; $r=0.591$, $p<0.01$; $r=0.477$, $p<0.01$), and PHg was positively correlated with altitude ($r=0.416$, $p<0.05$), indicating that DOC and altitude mainly affected the migration and transformation of Hg. In QLM, THg and PHg was significantly correlated with the TSP ($r=0.386$, $p<0.05$; $r=0.423$, $p<0.01$), and TMeHg, PMeHg was significantly correlated with THg and PHg ($p<0.01$). This indicates that Hg in QLM were affected by particulate matter. In comparison with Hg in other rivers of TP which were mainly in TSP-associated species, PHg decreases with altitude and higher DOC in TRS indicating that continued warm likely increasing the potential release of DOC-bound Hg.

PROPAGATION OF THE MERCURY CONTAMINATION IN CASCADE RESERVOIRS IMPACTED BY A CHLOR-ALKALI PLANT, OLT RIVER, ROMANIA

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The chlor-alkali industry is a major contributor of local to regional mercury contamination of aquatic environments. Mercury released into

surface waters by this industry is mainly bound to the particulate phase and therefore more likely to rapidly deposit in standing waters such as lakes and reservoirs. However, a fraction of that mercury can be associated with very fine inorganic and organic particles, which can travel longer distances. Here we report the propagation of the mercury released by a chlor-alkali plant into the Olt River, the largest Romanian tributary of the Danube River, as recorded in sediments of five cascade reservoirs. Both mercury concentration and deposition flux histories, together with sedimentological parameters, have been determined in 137Cs-radiodated sediment cores collected in the deepest zones of one upstream (Valcea, reference reservoir) and four downstream reservoirs (Babeni, Ionesti, Zavideni, and Dragasani). The maximum mercury concentration – 44.5 mg/kg, representing more than 300 times the background level – was recorded in a sediment layer deposited in 1987 in the Babeni reservoir, which is directly impacted by the plant effluent. The history of the contamination was similarly recorded in the three other downstream reservoirs, with decreasing maximum concentrations of 36, 13.5 and 7.4 mg/kg, respectively. Likewise, the maximum mercury specific fluxes decreased in the four cascade reservoirs, from 146 to 4.3 $\mu\text{g cm}^{-2} \text{y}^{-1}$. These results showed a significant reduction of the mercury inputs into the lower reservoirs. However, the mean mercury concentrations recorded during the 1980-2013 period did not show such an important reduction down the cascade reservoirs. The decrease in the mean mercury concentration was only by a factor 2 between the most impacted Babeni reservoir (4.4 mg/kg) and the Dragasani reservoir, the farthest we studied in the cascade (2.1 mg/kg), more than 35 km downstream the contamination source. This relatively low decrease rate is due to the concomitant effects of i) a very high sediment load (3.3 $\text{g cm}^{-2} \text{y}^{-1}$) from tributaries in the Babeni reservoir that "dilute" mercury compared to the low sediment load in the downstream reservoirs (0.6 $\text{g cm}^{-2} \text{y}^{-1}$ in Dragasani); and ii) the transport of mercury through the reservoirs by fine inorganic and organic particles delivered by the tributaries and less prone to settle. These associated effects result in an extended contamination of the reservoir sediments in a long reach of this river, a favorable environment for methylation.

TEMPORAL MERCURY DYNAMICS THROUGHOUT THE RICE CULTIVATION CYCLE: AN INTEGRATIVE APPROACH

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During the last few decades, the input of mercury to the environment resulting from anthropogenic activities has increased. This can translate into effects to both wildlife and humans.

For the last fifty years, a chlor-alkali plant situated at the locality of Flix (NE Spain), ca. 100 km above the Ebro river mouth, has dumped mercury-loaded residues into the river. The residues have been transported throughout the river reaching its delta ecosystems (e.g., rice fields, flood plains, marshes, lagoons). The Ebro Delta (ca. 30000 ha of wetlands) is a highly important site of rice production with more than 75% of its area intended to this activity. Moreover, it constitutes one of the largest wetlands of the Mediterranean being also relevant from the conservation point of view, as it is the breeding habitat for several bird species. Rice paddies are considered a potential 'hotspot' for methylmercury due to the biotic methylation activities of soils, as well as a source of methylmercury for both aquatic and terrestrial food webs.

In this context, we studied temporal changes in mercury dynamics throughout the rice cultivation season (early-, mid-, late-season) in both abiotic (water, sediments) and biotic compartments. Rice plants (*Oryza sativa*) and fauna (vertebrates and invertebrates) belonging to the rice-paddies food webs have been analyzed for total mercury (THg). Furthermore, we assessed the effect of different agricultural management practices (ecological vs. conventional) associated to various flooding patterns (flooded cultivation vs. dry cultivation) to the mercury levels present in the plants and fauna. We found that different agricultural practices and/or flooding patterns did not influence as much as expected the mercury levels observed in rice plants or rice paddies food webs. We observed a clear evidence of mercury biomagnification through the food web of the studied systems.

M.O.1.2A-6

IMPACT OF SEDIMENT MERCURY SPECIATION ON MERCURY CYCLING IN THE ST. LOUIS RIVER ESTUARY

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The St. Louis River Estuary (SLRE) is a freshwater estuary at the terminus of the second largest tributary of Lake Superior that exhibits complex Hg biogeochemistry. Fish and other aquatic biota in the estuary often contain high levels of methylmercury compared to the upstream river or Lake Superior. The downstream estuarine area contains some high mercury legacy sediment contamination from previous industrial activities. Despite remediation efforts, some sediments still contain concentrations of total Hg well above background levels for the area, which implicates them as a potential source for MeHg. In this study, we focus on the impact of sediment chemistry and solid-phase mercury speciation on inorganic- and methyl-mercury bioavailability and partitioning in relation to methylmercury production in the estuary. Sediment cores and porewater were collected from three geochemically distinct locations within the estuary and analyzed for total and methylmercury, carbon (sediment and porewater), and acid volatile sulfide or dissolved sulfide. In addition, selective extractions were used to separate solid phase mercury compounds into behavioral classes. Results indicate that more mercury is retained in sediments with high concentrations of carbon and sulfide. Methylmercury production and porewater methylmercury is lowest in sediment with the highest sulfide to carbon ratio, suggesting both inorganic and methylmercury availability are partially controlled by solid phase carbon and sulfide. Selective extraction results indicate that sediments with more strong acid soluble species have larger portions of inorganic- and methyl-mercury in the sediment, while sediments with more organic-chelated Hg species have larger portions of inorganic- and methyl-mercury in the porewater. Our results suggest that sediment with low total mercury concentrations may contribute more methylmercury and bioavailable inorganic mercury to the porewater and eventually the lower portions of the food web than sediment with high total mercury concentrations.

1.4A Mercury cycling and bioaccumulation in polar regions

M.O.1.4A-1

ENHANCED ARCTIC RIVER PARTICULATE HG EXPORT AT THE PERMAFROST THAWING FRONT

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Arctic permafrost soils contain large amounts of organic carbon and mercury (Hg). Arctic warming and associated changes in hydrology, biogeochemistry and ecology risk mobilizing soil carbon and Hg, yet little is known about the quantity, timing and mechanisms involved. We investigated seasonal particulate Hg (PHg) and organic carbon (POC) export in 32 small and medium rivers across a 1700km latitudinal permafrost transect of the western Siberian Lowland (WSL). The WSL transect covers absent, isolated and sporadic permafrost in the south to discontinuous and continuous permafrost in the north. PHg and POC levels strongly correlated and decreased with river watershed size, suggesting Hg mobilization from organic (peat) rather than mineral soil layers. Maximum PHg concentrations; run-off and export fluxes were located in rivers of the sporadic permafrost zone. We suggest this reflects enhanced Hg mobilization at the permafrost thawing front, due to maximal active layer depth. Both the maximal thickness of the active layer and maximal PHg run-off progressively move to the north during the summer and fall seasons, thus leading to maximal PHg export at the latitudinal thawing front. The discharge-weighted PHg:POC ratio in WSL rivers (2.7 ± 0.5) extrapolated to the whole Ob River basin yields a PHg flux of 1.5 ± 0.3 Mg y⁻¹, consistent with previous estimates. Using a substituting space for time approach for climate warming and permafrost thaw scenario in WSL, we predict that a northward shift of permafrost boundaries and increase of active layer depth may enhance the PHg export by WSL rivers to the Arctic Ocean by a factor of two over the next 10-50 years.

M.O.1.4A-2

3-D MODELING OF ATMOSPHERIC BOUNDARY-LAYER MERCURY DEPLETION EVENTS ACROSS THE SPRING-TIME ARCTIC

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Gas-phase bromine radical chemistry is the main driver for the frequent and concurrent depletion of ozone and mercury (Hg) in the polar boundary layer during the spring. Sea ice and its overlying snow cover are broadly understood as the key elements in the production of reactive bromine in polar spring. However, a full characterization remains unsettled on how physicochemical state of snow and ice influence the release of bromine into the atmosphere. Uncertainties in the kinetics and reaction mechanisms of Hg redox chemistry add further complexity to accurately assessing the behavior of Hg during its depletion from air. Three-dimensional (3-D) models developed to simulate the impact of bromine chemistry on Hg oxidation in the Arctic, have generally relied upon indirect representations of the sources, sinks and photochemical transformation of bromine radical species in the polar atmosphere.

This study presents development of a process-oriented representation for the coupled bromine-ozone-Hg chemistry and the exchange of bromine, ozone and Hg species between air and snow/ice surface within Environment and Climate Change Canada's air-quality model, GEM-MACH-Hg. The model simulations are performed at 15-km horizontal resolution in a limited-area domain of the Arctic. The model captures the evolution of high BrO column densities associated with synoptic weather disturbances during polar sunrise as can be seen from satellite. The concurrent depletion of ozone and Hg is simulated by consistent model formulation, where the release of reactive bromine from the frozen surfaces is facilitated by the presence of ozone in air. Extensive model evaluation is performed using measured ambient concentrations

of ozone and speciated Hg, total Hg in snow and the vertical column densities of BrO retrieved from ground stations and buoys floating on the ice-covered ocean at fine temporal scale. The model framework for simulating the reactive bromine release from the snow/ice cover is found to work reasonably well for the representation of ozone and Hg depletion events across the Arctic over synoptic and seasonal time scales. The deposition of oxidized Hg from the atmosphere is found to be enhanced particularly under the disturbed weather conditions, as a result of the vertical and horizontal inflow of ozone and gaseous elemental Hg. The model is applied to estimate springtime deposition, re-emission and accumulation of mercury in the Arctic.

M.O.1.4A-3

EURASIAN RIVER SPRING FLOOD OBSERVATIONS SUPPORT NET ARCTIC OCEAN MERCURY EXPORT TO THE ATMOSPHERE AND ATLANTIC OCEAN

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Midlatitude anthropogenic mercury (Hg) emissions and discharge reach the Arctic Ocean (AO) by atmospheric and oceanic transport. Recent studies suggest that Arctic river Hg inputs have been a potentially overlooked source of Hg to the AO. Observations on Hg in Eurasian rivers, which represent 80% of freshwater inputs to the AO, are quasi-inexistent, however, putting firm understanding of the Arctic Hg cycle on hold. Here, we present comprehensive seasonal observations on dissolved Hg (DHg) and particulate Hg (PHg) concentrations and fluxes for two large Eurasian rivers, the Yenisei and the Severnaya Dvina. We find large DHg and PHg fluxes during the spring flood, followed by a second pulse during the fall flood. We observe well-defined water vs. Hg runoff relationships for Eurasian and North American Hg fluxes to the AO and for Canadian Hg fluxes into the larger Hudson Bay area. Extrapolation to pan-Arctic rivers and watersheds gives a total Hg river flux to the AO of 44 ± 4 Mg per year (1 σ), in agreement with the recent model-based estimates of 16 to 46 Mg per year and Hg/ dissolved organic carbon (DOC) observation-based estimate of 50 Mg per year. The river Hg budget, together with recent observations on tundra Hg uptake and AO Hg dynamics, provide a consistent view of the Arctic Hg cycle in which continental ecosystems traffic anthropogenic Hg emissions to the AO via rivers, and the AO exports Hg to the atmosphere, to the Atlantic Ocean, and to AO marine sediments.

M.O.1.4A-4

IDENTIFYING THE SOURCES AND FATE OF WINTER-TIME MERCURY DEPOSITION TO A NORTHERN ALASKA COASTAL WATERSHED USING MAJOR IONS AND MERCURY STABLE ISOTOPES

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Snow deposited to Polar coastal locations during springtime atmospheric mercury depletion events (AMDEs) commonly has highly elevated mercury concentrations (>200 ng Hg/L). During AMDEs gaseous elemental mercury (GEM) is photochemically oxidized to reactive gaseous mercury by halogen-mediated reactions and the Hg is deposited to the snowpack. The reactive mercury is then either photochemically reduced back to GEM and re-emitted from the snowpack to the atmosphere or it remains until spring snowmelt. GEM can also be deposited to the snowpack and tundra vegetation by reactive surface uptake (dry deposition) from the atmosphere by processes that also occur at lower latitudes. The proportion of Hg attributable to AMDEs versus dry deposition that is released in spring runoff has not been quantified. We conducted extensive sampling campaigns in late winter and during snowmelt for two years at a small (2.5 ha) watershed on the Arctic coastal plain near Utqiagvik (formerly Barrow), Alaska. Airborne LiDAR and GPS surveys were used to delineate the watershed area to cm scale accuracy. Snowpack, meltwater, and stream channel water were sampled and analyzed for total dissolved Hg, Hg stable isotopes, major ions, and stable oxygen and hydrogen isotopes. Permafrost peat cores were collected and analyzed for Hg concentrations and Hg isotope ratios. We identified an "ionic pulse" of mercury and major ions in runoff during both snowmelt seasons, with total dissolved Hg in runoff up to 14.3 (+/- 0.7) mg/ha. This runoff flux is five to seven times higher than what has been reported from other arctic watersheds and from lower latitudes. We calculate that up to three quarters of the snowpack Hg was exported with snowmelt runoff. Hg isotope measurements indicate the majority of this snowmelt Hg originated as GEM oxidized in the snowpack by reactive halogens in a process similar to reactive surface uptake of GEM into the leaves of trees in temperate forests. This GEM-sourced Hg is the dominant Hg we measured in the spring snowpack and in the tundra peat. We calculate that ~75% of the Hg exported from the watershed in snow melt came from non-AMDE sources while ~25% is attributable to AMDE deposition. Projected future warming in the Arctic will produce an increasingly dynamic sea ice regime with more first year ice and open sea ice leads. This will likely enhance the source of reactive halogens, promote GEM oxidation, and lead to greater Hg deposition to coastal and marine snowpacks.

M.O.1.4A-5

MERCURY IN THE BERING SEA FOOD WEB

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The Southeastern Bering Sea (SEBS) supports one of the most productive and economically important fisheries in the world. Mercury (Hg) is projected to rise in the North Pacific and possibility in the SEBS in response to increased atmospheric emissions from Asia. To date, concentrations of total Hg (THg) and methylmercury (MeHg) in the SEBS seawater and plankton are lacking; thus, Hg transfer in the SEBS food web is unknown. We investigated spatial differences in (THg) and (MeHg) concentrations in seawater, suspended particles, zooplankton and ichthyoplankton, from samples collected in the SEBS in June and September of 2018. We found that THg and MeHg showed a horizontal pattern of westward increasing concentrations in both seawater (4-100 pg/L MeHg and 36-178 pg/L THg) and copepods (3-13 ng/g dry weight MeHg). Moreover, there were significant differences between the hydrographic domains of the SEBS such that concentrations of Hg were highest in the outer domain. Our Hg data will be presented in the context of other auxiliary measurements including oceanographic (i.e., salinity, temperature, density, etc.) and biological (i.e., $\delta^{15}N$ - based trophic position and taxonomy) parameters. Data presented here represents a subset of a larger study, which will altogether illustrate the flow of THg and MeHg in the SEBS food web and, thus, inform other studies that investigate risks of MeHg exposure to marine mammals, seabirds and human consumers of locally harvested seafood.

METHYLMERCURY BIOGEOCHEMISTRY AND FATE IN DECEPTION ISLAND, (ANTARCTICA)

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In contrast to established long-term research programs in the Arctic, little is known about mercury biogeochemistry in Antarctica. Environmental studies in Deception Island (South Shetlands Archipelago) are scarce but are of great interest since it potentially represents a significant source of Hg, namely volcanic activity. Previous results showed the presence of relatively high Hg and methylmercury (MMHg) levels. Our study in this volcanic island aimed to better understand the Hg cycle in the Deception ecosystem, particularly, fluxes, speciation and bioavailability of mercury.

Sediment/soils were analysed for MMHg and for their methylation potential using enriched stable isotopes, as well as for other ancillary parameters. In the laboratory, trace element bioavailability tests were also performed. Finally, a three-dimensional hydrodynamic model was developed using the Mohid water modelling system. MMHg data was incorporated into the model to better understand the Hg and MMHg circulation in the Bay.

Mercury levels in water and sediments sampled at two fumaroles on Deception Island were up to 10000 times higher compared to the other sampling sites. Moreover, the concentrations obtained in Port Foster waters are also considerably higher than those typically observed in open waters of the Atlantic or the Southern Ocean. The proportion of MMHg (MMHg/HgT) was surprisingly high in saline waters of Port Foster (9–59%), suggesting exceptional conditions for Hg methylation processes in the water column. In fact, high abiotic (up to 3.6% of Hg) and biotic (up to 7.2% per day) methylation rates were estimated.

Additionally, the high residence time of water (ca. 1.7 yr) in the Bay contributes to creating a substantial standing pool of mercury and MMHg available for aquatic organisms. Moreover, the low capacity of sediments for Hg adsorption, (low carbon content and low superficial area (Si/Al>4)), may also contribute to keep mercury in solution and therefore increase its bioavailability. A first approach to model the circulation of Hg and MMHg was done using Lagrangian tracers, allowing visualization of their movement in the aquatic environment. The model output indicates that the tidal currents have almost no impact in the elements dispersion. Results obtained in this work pointed to a continuous input of Hg to the Deception ecosystem due to volcanic emissions. This input and the special biogeochemical conditions in Port Foster Bay water promote Hg methylation and the presence of more bioavailable Hg species that can, in fact, be taken up by aquatic organisms.

1.3B Regional and local scale stable isotope studies in mercury biogeochemical cycling and bioaccumulation

M.O.1.3B-1

TRACING MERCURY MOBILITY AND DISTRIBUTION IN THE ABBADIA SAN SALVATORE LEGACY MERCURY MINE AREA USING MERCURY ISOTOPE RATIOS AND CONCENTRATIONS

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Persistent mercury (Hg) impact from legacy mines continues to present risk to the environment and human health globally. The Monte Amiata Hg district in Southern Tuscany, Italy was one of the five largest Hg districts in the world. Mining of Hg began in the region during the Roman era with modern mining beginning in the mid-1800s and concluding in the early 1980s which resulted in the occurrence of elevated Hg in the surrounding ecosystem. The study area focused near Abbadia San Salvatore mine (ASSM) as it was the major Hg processing facility for many mines in the district and considered a primary source for elevated Hg. The extraction of Hg from cinnabar was carried out via the roasting of ore using two primary furnace types. Initially, Čermak-Špirek shaft type and tower furnaces were used which were later replaced by Gould and Pacific type furnaces. The ore was roasted at 600-700°C to volatilize Hg to gas which was recovered via condensation. Mass dependent fractionation (MDF) of Hg isotope ratios and variation in Hg concentrations resulting from the processing of cinnabar ore has been reported for mine-waste calcines. Elevated concentrations of Hg in the extensive mine-waste calcine piles in ASSM possess the potential of releasing Hg into the local environment over a sustained period of time. The differences in extraction efficiency of Hg from cinnabar ore of different grain size and different furnace types resulted in variations of Hg concentration and isotopic composition in the mine-waste calcines (Čermak-Špirek calcine d202Hg average of 0.52‰ and concentration range of 32 to 1500 ug/g; Gould and Pacific d202Hg average of -0.58 and concentration range of 25 to 130 ug/g). Mass independent fractionation (MIF) has also been reported for Hg isotope ratios and is attributed to photochemical reduction of aqueous HgII and MeHg. The contribution of Hg from chemical processes and weathering of legacy mine-waste calcine piles as well as initial Hg contribution from historical Hg ore processing has resulted in a wide range of Hg concentrations (0.48 ug/g to 1500 ug/g) and D202Hg and D199Hg isotopic compositions (-1.96‰ to 0.95‰, -0.30‰ to 0.25‰ respectively). We will present an overview of Hg distribution and mobility using concentration and isotopic composition measured for a wide range of samples (cinnabar ore, calcines, sediment, soils, geothermal water, and fish) collected in the ASSM area.

M.O.1.3B-2

IDENTIFICATION OF MERCURY SOURCES IN THROUGH-FALL USING STABLE ISOTOPE SIGNATURES

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Throughfall is one of the main pathways of mercury (Hg) loading to forest ecosystem. The sources of Hg in throughfall, however, have not been well constrained by previous studies. In this study, concentrations and isotopic compositions of Hg in throughfall were obtained at an evergreen broadleaf forest site in southwestern China and a Boreal coniferous forest site in northern Sweden for one to 12 month periods. The mean concentrations of dissolve mercury (DHg) in wet-only precipitation and throughfall were 4.24 ± 0.30 and 11.43 ± 3.59 ng/L at the broadleaf forest site in southwestern China, respectively, and they were 2.52 ± 1.90 and 8.93 ± 2.24 ng/L at the coniferous forest site in northern Sweden, respectively. The mean concentrations of particle mercury (PHg) in wet-only precipitation and throughfall were 1.06 ± 0.43 and 5.18 ± 1.94 ng/L at the broadleaf forest site in southwestern China, respectively. The increasing concentration in the throughfall indicated that Hg deposited on the canopy was wash-off by the precipitation. A significant positive correlation was observed between DHg concentrations and dissolved organic carbon concentrations ($R^2 = 0.71$, $P < 0.01$) in the throughfall. This indicates that the major form of DHg in throughfall was carbon bounded Hg. A large difference in Hg isotopic compositions was observed between throughfall and wet-only precipitation. Mean $\Delta^{199}\text{Hg}$ and $\Delta^{200}\text{Hg}$ of DHg in wet-only precipitation at the two sites were $0.72 \pm 0.32\text{‰}$ and $0.24 \pm 0.06\text{‰}$, respectively, which were much higher compared to that in throughfall (mean

$\Delta 199\text{Hg} = -0.20 \pm 0.24\text{‰}$, mean $\Delta 200\text{Hg} = 0.07 \pm 0.05\text{‰}$). Mean $\Delta 199\text{Hg}$ and $\Delta 200\text{Hg}$ of PHg in wet-only precipitation at the two sites were $-0.03 \pm 0.3\text{‰}$ and $0.16 \pm 0.05\text{‰}$, respectively, which were much higher compared to that in throughfall (mean $\Delta 199\text{Hg} = -0.66 \pm 0.1\text{‰}$, mean $\Delta 200\text{Hg} = 0.05 \pm 0.04\text{‰}$). The MIF signatures of DHg and PHg in throughfall were distinct from the values reported for atmospheric particulate bound mercury (PBM) but close to the values of atmospheric gaseous elemental mercury (GEM). A binary mixing model was applied and showed that GEM in atmosphere contributed approximately $60 \pm 14\%$ for DHg and $53 \pm 16\%$ for PHg in throughfall. We suggest that GEM deposited to vegetation leaves could be incorporated into throughfall during the wash-off processes. Overall, deposition of Hg by throughfall is more representative of GEM dry deposition.

M.O.1.3B-3

STABLE ISOTOPE FRACTIONATION INDUCED FROM MERCURY BIOGEOCHEMICAL CYCLING IN FOREST ECOSYSTEMS

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Forests mediate the mercury (Hg) biogeochemical cycling between the atmosphere and terrestrial ecosystems, while there remain substantial knowledge gaps regarding the cycling processes. Here, we determined the mass flow and isotopic compositions/fractionations associated with Hg cycling in the air-water-plant-soil compartments in an evergreen broadleaf forest site in Southwestern China to reveal mechanisms underlying the cycling of Hg. It is found that that annual Hg mass flow is $-26.8 \pm 12.7 \mu\text{g m}^{-2} \text{ year}^{-1}$ for air-foliage HgO flux, $6.7 \pm 20.5 \mu\text{g m}^{-2} \text{ year}^{-1}$ for air-soil HgO flux, $9.1 \pm 1.2 \mu\text{g m}^{-2} \text{ year}^{-1}$ for bulk Hg deposition, $31.8 \pm 10.6 \mu\text{g m}^{-2} \text{ year}^{-1}$ for throughfall Hg deposition, $0.3 \pm 0.1 \mu\text{g m}^{-2} \text{ year}^{-1}$ for stemflow Hg deposition, and $1.8 \pm 0.4 \mu\text{g m}^{-2} \text{ year}^{-1}$ for Hg runoff. Mass balance analysis using the flux data shows a $50.4 \pm 44.2 \mu\text{g m}^{-2} \text{ year}^{-1}$ net atmospheric Hg sink. Interestingly, we observed the $\delta 202\text{Hg}$ shift of 0 to -3.1‰ between air and foliage as leaf age increases, and so for the $\Delta 199\text{Hg}$ shift of 0 to -0.15‰ . The observed isotopic composition of foliage Hg and isotopic shift support re-emission of HgO occurring after reductive loss from foliage. The $\delta 202\text{Hg}$ shift caused by Hg evasion from soil in summer ranges -0.92‰ to -0.23‰ with a $\Delta 199\text{Hg}$ shift from -0.25‰ to -0.10‰ ; while in winter only $\delta 202\text{Hg}$ shift is observed with range of -0.28‰ to 0.41‰ . Given the isotopic compositions found in soil pore gas ($\delta 202\text{Hg} = -0.94 \pm 0.32\text{‰}$, $\Delta 199\text{Hg} = -0.49 \pm 0.07\text{‰}$ and $\Delta 200\text{Hg} = -0.03 \pm 0.04\text{‰}$) and ambient air ($\delta 202\text{Hg} = 0.26 \pm 0.20\text{‰}$, $\Delta 199\text{Hg} = -0.16 \pm 0.06\text{‰}$ and $\Delta 200\text{Hg} = -0.05 \pm 0.04\text{‰}$), legacy Hg re-emission is largely caused by dark reduction processes in deep soil in summer, and by photo-reduction processes in surface soil in winter. Moreover, the distinctly negative $\Delta 199\text{Hg}$ (range of -0.40‰ in Oi to -0.47‰ in Oa) and $\sim 0 \Delta 200\text{Hg}$ in organic soils indicate atmospheric HgO deposition is the dominant source of Hg in soil. Finally, we observed positive $\Delta 199\text{Hg}$ ($0.57 \pm 0.32\text{‰}$) and $\Delta 200\text{Hg}$ ($0.22 \pm 0.06\text{‰}$) in bulk precipitation, however, the $\Delta 199\text{Hg}$ and $\Delta 200\text{Hg}$ in throughfall ($-0.34 \pm 0.20\text{‰}$ and $0.06 \pm 0.05\text{‰}$), stemflow ($-0.41 \pm 0.20\text{‰}$ and $-0.04 \pm 0.08\text{‰}$) and runoff ($-0.40 \pm 0.08\text{‰}$ and $-0.02 \pm 0.04\text{‰}$) exhibit distinctly negative values. This suggests a significant atmospheric HgO source contribution in throughfall ($60 \pm 13\%$), stemflow ($96 \pm 25\%$) and runoff ($89 \pm 23\%$). Results from mass balance modeling show that atmospheric HgO deposition accounts for $\sim 75\%$ of total atmospheric Hg deposition, ~ 2 times greater than values by the estimate from air-foliage/soil flux. Overall, this study highlights the governing role of atmospheric HgO deposition and re-emission processes in Hg cycling of forest ecosystems.

M.O.1.3B-4

USING MERCURY ISOTOPES TO IDENTIFY SOURCES OF MERCURY AND METHYLMERCURY ACCUMULATING IN FOREST SOILS AND BIOTA ALONG A MONTANE ELEVATIONAL GRADIENT.

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There is growing evidence that mercury (Hg) within upland forest soils can be transformed to methylmercury and biomagnified within terrestrial food webs. However, identifying the source(s) of mercury deposited to and transformed within forested ecosystems remains challenging. In this study, we used natural abundance Hg isotope analysis to assess the pathways of Hg deposition along a montane elevational gradient, and to trace sources of atmospheric Hg into the terrestrial food web on Whiteface Mountain in the Adirondack region of New York State, USA. Mercury isotope analysis indicates that soil Hg in all forest types (deciduous, coniferous, and alpine) is predominantly derived from foliar uptake of gaseous Hg that is deposited with litterfall. This is consistent with other forest Hg isotope studies, but stands in contrast to mass balance results indicating that throughfall inputs dominate in the coniferous and alpine zones at this study site. Based on an isotope mixing model, the amount of precipitation-derived Hg accumulating in forest soils was similar to throughfall flux estimates in deciduous forests, but approximately 20-30% lower than throughfall flux estimates in coniferous and alpine zones. This discrepancy was consistent with isotopic signatures indicating increased photo-volatilization from coniferous and alpine soils, and may also suggest that a larger component of throughfall inputs in coniferous and alpine zones is derived from foliage, rather than precipitation. The fraction of precipitation-derived Hg was similar in forest soil and low trophic level soil invertebrates with low %MeHg. However, high trophic level soil invertebrates with high %MeHg typically had a greater fraction of precipitation-derived Hg. Songbird Hg isotopic signatures did not consistently overlap with soil invertebrate Hg isotope signatures, and the relative fraction of precipitation-derived Hg in songbird blood was more variable. Both of these observations suggest that songbirds may accumulate methylmercury from other sources in addition to forest soil invertebrates. Overall, our data suggest that precipitation-derived Hg is preferentially transformed to methylmercury and bioaccumulated in the food web of this forested ecosystem.

M.O.1.3B-5

MERCURY ISOTOPIC FRACTIONATION DURING FOREST BURNING IN THE AMAZON

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Biomass burning is an important source of Hg to the atmosphere, being estimated as 13 % of total terrestrial emissions. Recent studies in the emissions of Hg during coal combustion observed that this type of

process may result in Mass Dependent Fractionation (MDF), but no Mass Independent Fractionation (MIF) has been documented. However, the impacts of combustion in Hg isotopes has never been investigated during forest burning. To address that, we performed burning experiments in the Amazon rainforest, which is one of the main emitter of gases due to forest burning in the world. We chose two different localities in the Brazilian Amazon (Alta Floresta (AF) and Candeias do Jamari (CJ)) and performed two different scales of experiments. Litter, ashes and soils samples were collected before and after burning. Samples were decomposed using strong acid and oxidant mixture under controlled temperature and pressure conditions (Hot-Block and High Pressure Asher). Their Hg isotopic composition was measured through CVG-MC-ICP-MS (Nu plasma). Accuracy and precision of the methods were evaluated using QA/QC protocols and certified reference materials well documented in the literature. For AF, where small scale experiments were performed, no differences were found in the mercury isotopic composition between all the samples before and after burning. For the larger scale experiment in CJ, litter, ashes and soils before burning differed significantly from each other in terms of MDF - $\delta^{202}\text{Hg}$ ($\delta^{202}\text{Hg}$ for litter, ashes and soils before burning, respectively, $-1.63 \pm 0.16 \text{ ‰}$ (N=10); $-1.78 \pm 0.10 \text{ ‰}$ (N=9) and $-2.06 \pm 0.10 \text{ ‰}$ (N=13)). Regarding MIF, ashes and soils presented similar $\Delta^{199}\text{Hg}$ results (respectively, $-0.58 \pm 0.06 \text{ ‰}$ (N=9) and $-0.59 \pm 0.03 \text{ ‰}$ (N=13)) while litter presented greater values ($\Delta^{199}\text{Hg} = -0.37 \pm 0.05$ (N=10)). All the samples presented $\Delta^{200}\text{Hg}$ close to 0. Hg isotopic composition in soils before and after burning did not differ significantly ($P=0.89$). Similar odd-MIF pattern obtained for ashes and soils suggests that the main source of the Hg found in the ashes come from soils, while the Hg from litter is almost totally emitted to the atmosphere. In this sense, a slight enrichment of $\delta^{202}\text{Hg}$ in the ashes compared to the soils, confirm that such MDF is induced by the volatilization of lighter isotopes in burning litter. This work highlights the potential of Amazonian biomass burning to cause Hg isotopic fractionation, which directly depends on the extent of the burning process.

M.O.1.3B-6

ISOTOPIC FRACTIONATION INDUCED BY SOIL-AIR EXCHANGE OF MERCURY VAPOR IN SUBTROPICAL FOREST ECOSYSTEMS: EVIDENCE FOR LEGACY RE-EMISSION

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Uncertainties in quantifying soil-air exchange of elemental mercury vapor have limit our understanding in the contribution of terrestrial systems to global mercury (Hg) cycling. In this study, we investigated the soil-air HgO exchange in ambient air and under HgO-free gas exposures, as well as its isotopic shift caused by the exchange. It has been found that soil pore gas has $\delta^{202}\text{Hg}$ of $-0.94 \pm 0.32 \text{ ‰}$ and $\Delta^{199}\text{Hg}$ of $-0.49 \pm 0.07 \text{ ‰}$, more positive $\delta^{202}\text{Hg}$ and no significant $\Delta^{199}\text{Hg}$ compared to Hg in soil ($\delta^{202}\text{Hg} = -2.08 \pm 0.26 \text{ ‰}$; $\Delta^{199}\text{Hg} = -0.57 \pm 0.10 \text{ ‰}$). Soil-air HgO exchange flux exhibit a seasonal pattern, suggesting soil an atmospheric Hg source in summer and a sink in winter. Compared to inlet isotopic composition ($\delta^{202}\text{Hg}=0.43 \pm 0.13 \text{ ‰}$ and $\Delta^{199}\text{Hg}=-0.20 \pm 0.05 \text{ ‰}$ in summer; $\delta^{202}\text{Hg}=0.66 \pm 0.22 \text{ ‰}$ and $\Delta^{199}\text{Hg}=-0.08 \pm 0.05 \text{ ‰}$ in winter), the isotopic compositions of outlet display a significantly more negative $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ in summer ($\delta^{202}\text{Hg}=-0.15 \pm 0.23 \text{ ‰}$ and $\Delta^{199}\text{Hg}=-0.33 \pm 0.05 \text{ ‰}$, $p < 0.01$, pair t-test), but comparable values in winter ($\delta^{202}\text{Hg}=0.52 \pm 0.55 \text{ ‰}$ and $\Delta^{199}\text{Hg}=-0.10 \pm 0.04 \text{ ‰}$, $p > 0.05$, pair t-test). This suggests HgO re-emission from soils with much more negative $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ than values in air, and HgO deposition with no distinct MDF and MIF.

The HgO re-emission isotopic composition is further determined by soil HgO evasion under Hg-free gas exposure. Soil HgO evasion under Hg-free gas exposure in summer has $\delta^{202}\text{Hg}$ of $-2.20 \pm 0.63 \text{ ‰}$ and $\Delta^{199}\text{Hg}$ of $-0.36 \pm 0.04 \text{ ‰}$, while in winter $\delta^{202}\text{Hg}$ of $-3.45 \pm 0.16 \text{ ‰}$ and $\Delta^{199}\text{Hg}$ of $0.19 \pm 0.08 \text{ ‰}$. Given the isotopic compositions found in soil pore gas and ambient air, the promoted soil HgO evasion under Hg-free air in summer is mainly attributed to the diffusion of pore gas, and in winter to photo-reduction of divalent Hg in surface soil. Hence, the apparent soil-air HgO exchange represents a result of HgO deposition, HgO evasion from surface soil induced by photo-reduction and HgO diffusion from soil pore. Using an isotopic mass balance model, the estimated flux in summer is $-11.2 \pm 10.6 \text{ ng m}^{-2} \text{ h}^{-1}$ by HgO deposition, $+3.0 \pm 5.7 \text{ ng m}^{-2} \text{ h}^{-1}$ by HgO evasion from surface photo-reduction, and $+13.6 \pm 8.9 \text{ ng m}^{-2} \text{ h}^{-1}$ by HgO diffusion from soil pores. In winter, atmospheric HgO deposition and HgO evasion from photo-reduction and HgO diffusion are much weaker, with the value of $-1.9 \pm 2.8 \text{ ng m}^{-2} \text{ h}^{-1}$, $+0.4 \pm 2.8 \text{ ng m}^{-2} \text{ h}^{-1}$, and $+0.1 \pm 0.5 \text{ ng m}^{-2} \text{ h}^{-1}$, respectively. Overall, legacy Hg re-emission is largely caused by dark reaction processes in deep soil in summer, and by photo-reduction processes in surface soil in winter.

2.7 Human Exposure and Health effects of Methylmercury

M.O.2.7-2

DIETARY CORRELATES OF METHYL MERCURY IN SEAFOOD CONSUMERS AND NON-SEAFOOD CONSUMERS

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Methyl mercury (MeHg) exposure is of concern due to the neurotoxicity of MeHg, particularly among children. Fish and seafood consumption is the largest dietary source of MeHg. However, most studies have estimated correlates of total mercury, not methyl mercury, and studies assessing dietary correlates of mercury among non-seafood consumers are limited. Therefore, we determined dietary correlates of whole blood MeHg in a cross-sectional analysis of 2011-2012 United States National Health and Nutrition Examination Survey data, stratified by self-reported seafood consumption within the past 30 days. 5427 (75.4%) children and adults reported eating fish/seafood in the previous 30 days and 1770 (24.6%) did not. MeHg was determined using ICP-MS. Dietary correlates of MeHg were assessed using a 24-hour dietary recall conducted by trained interviewers. Foods which were highly correlated were combined into larger categories prior to inclusion in regression models. Multivariable regression models predicting natural-log transformed MeHg included covariates for age, sex, education, race/ethnicity and self-reported consumption of fish or shellfish (in past 24 hours); beans, nuts or soy; Asian foods; soup; mixed rice dishes; rice; red or leafy vegetables or vegetable oil; beer; wine; and liquor. Geometric mean MeHg was $0.67 \text{ } \mu\text{g/L}$ (95% confidence interval (CI): $0.57, 0.80$) and $0.17 \text{ } \mu\text{g/L}$ (95% CI: $0.16, 0.19$) among seafood consumers and non-consumers, respectively. In multivariable regression models including seafood consumers, self-reported consumption of fish/seafood in prior 24 hours (β : 1.23 ; 95% CI: $0.50, 1.96$), soup (β : 0.42 ; 95% CI: $0.10, 0.73$), rice (β : 0.35 ; 95% CI: $0.05, 0.66$), red/leafy vegetables or vegetable oil (β : 0.43 ; 95% CI: $0.08, 0.78$) and wine; (β : 1.00 ; 95% CI: $0.57, 1.43$) were significantly associated with higher blood MeHg. Among non-seafood consumers, the only food item significantly associated with MeHg was wine (β : 0.84 ; 95% CI: $0.06, 1.62$). Our results are similar to previous research which has identified rice and vegetables as potential non-seafood sources of mercury exposure. Wine was the only food category significantly associated with MeHg concentration among non-seafood consumers; additional research on wine as a potential source of MeHg exposure is recommended.

M.O.2.7-3

GENETIC DISPOSITION TO DEVELOPMENTAL METHYLMERCURY NEUROTOXICITY

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Some common heterogeneities are thought to affect methylmercury kinetics in the body and perhaps also neurodevelopmental outcomes of prenatal methylmercury exposure. We examined the suspected heterogeneities for modification of exposure-related cognitive development in 2,172 children from the Avon Longitudinal Study of Parents and Children (Bristol, UK) (ALSPAC). Prenatal methylmercury exposure was determined from the total mercury concentration of cord tissue. Neuropsychological function was determined by the Wechsler Intelligence Scale for Children Intelligence Quotient (IQ) score at age eight years. Data was available on 247 single-nucleotide polymorphisms (SNPs) within relevant genes. In this population with low-level methylmercury exposure, the log₁₀-transformed mercury concentration appeared to be positively associated with IQ, although adjustment cofactors attenuated this association. Among four SNPs found in a pilot study to exhibit interaction methylmercury neurotoxicity, one was replicated, i.e., the minor allele of rs1042838 (progesterone receptor), with a beta (95% confidence interval) of -11.8 (-23.0, -0.7) (p for interaction, 0.004). Despite the low exposure level, the PGR minor allele revealed a strong negative association between methylmercury exposure and IQ. The relevant SNPs will be determined in a Faroese birth cohort with much higher prenatal methylmercury exposures to ascertain whether the genetic predisposition can be replicated. As the PGR minor allele is fairly common in Caucasian populations, the results suggest that this genetically predisposed subpopulation carries the brunt of neurobehavioral toxicity from developmental methylmercury exposure and that current exposure limits may not provide sufficient protection for this vulnerable group.

M.O.2.7-4

THE POTENTIAL AND THE CHALLENGES OF UPDATING ASSESSMENTS OF METHYLMERCURY TOXICITY

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Multiple health agencies (Health Canada, 2007; UNEP, 2002; US EPA, 2001, 1997; ATSDR, 1999) and the US National Academy of Sciences (NRC, 2000) have established that prenatal oral exposure to methylmercury in humans causes developmental neurotoxicity (DNT). The existing US EPA quantitative assessment of methylmercury dose-response was developed by the IRIS (Integrated Risk Information System) program in 2001. That assessment derived a reference dose (RfD) based on DNT effects in children following prenatal exposure using information from 3 epidemiological cohorts in several publications. The RfD of 0.1 µg/kg-day was derived from multiple DNT measures related to cord blood concentrations of 46–79 µg/L, which the assessment estimated corresponded to maternal daily intakes of methylmercury during pregnancy of 0.86–1.47 µg/kg-day. This presentation will discuss considerations in evaluation of new data that could be used to update quantitative methylmercury assessments based on literature search results as well as an initial identification of key scientific issues. A recent literature search found more than 200 epidemiological reports published since 2000 with dose-response information on neurodevelopmental effects in humans of methylmercury exposure pre- and/or postnatally, based on dozens of epidemiological cohorts, including the 3 original ones considered in the 2001 IRIS assessment. Several scientific issues were identified on

an initial review of the literature. These include what form of mercury was evaluated in analytical measurements, which biomarkers of exposure were used in the study, and what methods were used to address confounding in epidemiological studies.

Disclaimer: The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the US EPA.

M.O.2.7-5

NEUROPSYCHOLOGICAL TESTS USED TO ASSESS METHYLMERCURY DEVELOPMENTAL NEUROTOXICITY

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Methylmercury is a well-known developmental neurotoxicant. In an effort to evaluate studies published since the release of the U.S. EPA IRIS Methylmercury Assessment in 2001, which was based on an assessment by the National Academy of Sciences (NAS) in 2000, a recent literature search was conducted for studies assessing the effects of methylmercury exposure on developmental neurotoxicity (DNT) in humans. DNT was the focus of the literature search because DNT endpoints were used to derive the Reference Dose in the 2001 Methylmercury IRIS Assessment. PubMed, Web of Science, ToxNet, and Science Direct were searched to find studies. The software tools, SWIFT[®] and Distiller[®], were used to screen the studies, which resulted in the identification of more than 200 epidemiological studies that evaluated DNT effects and provided quantitative exposure-response data.

Several neurodevelopmental endpoints were evaluated in the studies, including: cognition (e.g., verbal ability, nonverbal ability, executive functioning, attention, visual-spatial processing, learning/memory, IQ), motor function, sensory function, mood/affect/personal regulation, and clinical diagnoses of Autism Spectrum Disorder and Attention Deficit/Hyperactivity Disorder. Many different neuropsychological tests, including multiple versions of the same test (e.g., Bayley Scales) and numerous subtests (e.g., Wechsler Intelligence Scale for Children (WISC) III), were used to assess the neurodevelopmental endpoints. Some of the more common neuropsychological tests were Bayley Scales of Infant and Toddler Development-II, Brazelton Neonatal Behavioral Assessment Scale, California Verbal Learning Test, McCarthy Scales of Children's Abilities, Neurobehavioral Evaluation System 2, and WISC III. However, some tests were less common and only appeared in one study (e.g., Test of Haptic Matching), and others were commonly used tests that were adapted for non-U.S. populations (e.g., WISC III modified for Inuit children).

Many factors, such as the appropriateness of tests for other cultures and/or populations than those for which they were originally designed and the conditions under which the tests were given (e.g., distraction-free testing site and well-rested children), will need to be considered. Therefore, specific guidelines are being developed to assist in determining the validity and reliability of each test as it is used in individual studies.

Disclaimer: The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the US EPA.

M.O.2.7-6

LOW-LEVEL MERCURY EXPOSURE, NEURODEVELOPMENT AND THE ROLE OF GENETIC POLYMORPHISMS: FOLLOW-UP OF THE SLOVENIAN AND CROATIAN BIRTH COHORTS

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This prospective birth cohort study was set to investigate an association between prenatal mercury (Hg) exposure at low to moderate levels and neuropsychological performance taking into account variability in relevant genes as potential internal exposure or effect modifiers. Gene polymorphism of apolipoprotein E (APOE), brain derived neurotrophic factor (BDNF), paraoxonase (PON1), catechol O-methyltransferase (COMT), coproporphyrinogen oxidase (CPOX) has been selected due to their potential role in metal binding and/or implication in brain development processes. Mother-child pairs were recruited from the central Slovenia region (n=601) and Rijeka, on the Croatian coast of the northern Adriatic (n=243). Determination of total Hg and other elements in cord blood, Bayley Scales of Infant and Toddler Development, Third Edition (Bayley III) assessment at 18 months of age and genotyping was done in total of 361 children. In the follow-up, 179 children from Slovenia and 34 from Croatia were re-sampled at the age of 7-8 years and re-assessed for neuropsychological performance using Wechsler Intelligence Scale for Children (WISC-IV). Information on mother's and child's diet, living environment, potential exposure and maternal life-style was obtained through questionnaires. Associations between Hg levels and neuropsychological performance was evaluated using multiple linear regression, stratified by the genotype. Prenatal Hg exposure ranged from 0.16 to 10.0 ng/g (GM 1.58 ng/g) in cord blood of Slovenian children, and from 0.79 to 32.3 ng/g (GM 3.41) in Croatian children, while the exposure at 7-8 years of age from below limit of detection to 4.17 µg/L (GM 0.44 µg/L) in blood of Slovenian children, and from 0.06 to 7.05 µg/L (GM 0.68 µg/L) in Croatian children. The majority of the children had Bayley scores and Full Scale Intelligence Quotient of the WISC assessment within the normal limits. Data evaluated so far showed significant negative association between ln transformed Hg levels in cord blood and cognitive composite score ($\beta=-5.44$, $p=0.043$) in children carrying at least one APOE $\epsilon 4$ allele. Moreover, carriers of variant alleles for CPOX, BDNF and PON1 showed negative associations between prenatal Hg levels and cognitive scores, while the associations in carriers of common alleles were neutral or positive. However, none of associations was statistically significant, borderline significance was revealed for CPOX variant allele carriers only. The work is still on-going, however, the results presented indicate that stratifying for specific genotypes is crucial in identifying susceptible population groups exposed to low levels of Hg.

3.6B Mercury Emissions Reductions – A Challenge to Industry

M.O.3.6B-1

FROM TOXIC MERCURY TO NON-TOXIC MERCURY COMPOUND

SCHARRENBACH, Frank¹; FRITZSCHE, Jürgen¹

(1)New Environmental Technology GmbH

In every thermal combustion plant you can measure and detect mercury from the scrubber through the flue gas to the chimney up to the environment.

As a standard treatment, activated carbon/coke is used to adsorb the mercury. The loaded adsorbent is disposed on a landfill. In terms of gas limit values, this system works well. But not for a sustainable, holistic treatment. Mercury leach out and forms by microbiology, organic mercury.

Mercury becomes even more toxic.

For this reason, mercury must be removed as nonsoluble HgS from this cycle. HgS is a natural mineral, called cinnabar. And the only non-toxic mercury compound.

Scrubber systems have an opportunity to buffer and store mercury salts (e.g. HgCl₂/HgCl₄) in high saturation. Under normal conditions the systems are running stable, with no risk of HgO-gas blow out.

But the concentration of dissolved mercury is the magnitude of influence for a HgO-blow out event.

Of course in an event of high input of reducing agent (e.g. SO₂), the ionic(dissolved)Hg compounds transformed to elemental Hg₀. In this case a Hg-gas blow out is happened.

In case of a mercury event, the mercury breaks through the scrubber and contaminates the subsequent purification stages. Hg₀ deposits can be bleed out all the time and generate a "baseline" of Hg-emission, only a few µg below the current limits. But the environment is continuously contaminated and poisoned with tons of Hg/year.

The use of a special inorganic polymeric sulfur compound in an acidic scrubber or FGD plant produces only nonsoluble non-toxic HgS.

HgS is chemically and thermally very stable. Therefore, HgS can be treated both in a classic sewage treatment and in a spray dryer.

Here is the most efficient point for all Mercury compounds, where it's allowed to leave the plant.

As non toxic HgS

With this technology, it is made impossible to form an internal dissolved Hg cycle in the scrubber system. Unexpected events can be buffered. There're no Hg-blow outs possible.

This is an effective way to separate mercury from a scrubber system.

The special inorganic polymeric sulfur liquid (NETfloc SMF1) is easy to apply into any scrubber systems.

Regular analyzes of the mercury balance (Hg dissolved/Hg insoluble) in the scrubber help to determine the optimum dosing level for best cost efficiency.

The German Umwelt Bundesamt (UBA) has tested HgS as the best choice for deposition of mercury compound in underground dumps.

M.O.3.6B-2

BALANCING MERCURY IN THE GERMAN CEMENT INDUSTRY

HOENIG, Volker¹; HARRASS, Robin¹

(1)VDZ

In the past two decades, public awareness of mercury as a harmful environmental toxin has grown strongly and has moved into the spotlight of political and social discussion at both national and international levels. Against the background of the Minamata convention and its ongoing implementation in the EU member states, the German Environment Agency is elaborating proposals for a national abatement strategy. In the light of this, VDZ, with wide support from its member plants, has drawn up a mercury balance for the entire German cement industry to clarify the input and output pathways of mercury in cement production. It is based on more than 5,300 analysis data on solids from the incoming and outgoing raw materials, fuels and products, as well as data on air emissions, which are almost exclusively continuously monitored.

The balance result supports the cement industry's long term experience that over 60 % of the mercury input enters the process through the raw materials and less than 40 % through the fuels. About 60 % of the output of mercury occurs through the products and about 40 % through the emissions to air. The levels of mercury in the cements of 0.016 to 0.048 mg/kg (arithmetic means for CEM I-III) are low and are of the same order of magnitude as in the natural raw materials used in cement production. Stack emission concentrations were 12.9 µg/m³ as a yearly industry average. In order to ensure that emissions from cement mills do not falsify the balance result (as most German cement plants apply dust shuttling technology), long-term investigations at several cement mills (closed-circuit grinding) were performed. Their results show that the mercury concentration in the exhaust air lies at a negligibly low level in the range of uncertainty of the method of measurement (approx. 2 µg/m³).

Generally, there is always the risk of a fairly large level of uncertainty of a material balance if large mass flows are linked with very low concentrations. The main raw materials limestone, marl and chalk as well as granulated blast-furnace slag show low mercury concentrations with numerous analytical values below the limit of quantification of the respective method of analysis. Nevertheless – due to the vast number of available data – the mercury balance is essentially closed for the "most probable" average case.

M.O.3.6B-3

OPTIMIZING MERCURY CONTROLS IN COAL COMBUSTION POWER AND CEMENT PRODUCING PLANTS

MASHYANOV, Nikolay R.¹

(1)Ohio Lumex Company

Over the course of its 15 years of industry experience, Ohio Lumex has developed a variety of measurement techniques, products, and services which provide coal-fired utilities and cement kilns with effective means for reducing mercury emissions. The data provided by these measurements has been critical in helping the affected industries minimize operating costs required to meet regulatory limits, via optimization of control technologies and injected materials.

Mercury sorbent traps and portable sorbent trap analyzers allow for quick and reliable on-site and accurate determination of total mercury concentration as well as mercury oxidation ratio, in any sampling environment from the SCR inlet to the stack. Sorbent traps have become the industry standard, and are well-renowned for their self-validation criteria, ease of use, and reliability. In addition to mercury sorbent traps, Ohio Lumex has designed sorbent traps to measure a variety of common analytes of interest, such as NH₃, SO₃, HCl, HBr, Se, and As. Portable mercury speciating monitors yield real-time total and oxidized mercury data, and are designed to function for extended durations in nearly any sampling environment. Permanent mercury monitoring systems are generally installed in stacks or at the inlet to FGDs, and are equipped to send live mercury data directly to the plant's data integration system.

Hundreds of engineering studies have utilized these technologies and have demonstrably reduced the cost of mercury abatement via tuning of plant control technologies as well as optimized injection rates of activated carbon, dry sorbents, calcium bromide, sulfides and other materials.

M.O.3.6B-4

INVESTIGATION ON MERCURY EMISSION FROM CHINESE CEMENT SECTOR AND ITS WHOLE-PROCESS ASSESSMENT

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(1)China Building Materials Academy

The cement sector is the fourth biggest source of anthropogenic mercury emission. It has been estimated that the cement industry contributes with 9% or about 173 metric tons to the estimated total of 1921 metric tons per year of global anthropogenic mercury emissions according to UNEP report. China produced around 60% of the world's cement since 2012. Thus, the cement industry has become a more important source of mercury emissions even while technologically advanced new plants may have lower emission factors. The worldwide average emission factor for mercury from cement kilns is around 35 mg/t cement.

This article describes a Project Baseline Investigation of Mercury Emission from Chinese Cement Sector and Its Whole-process Control funded by UNIDO, aiming to reduce mercury emissions from cement sector in an efficient, effective and coherent manner, and to protect the human health and environment. Mercury enters in the kiln system are mainly from natural and alternative raw materials as well as conventional and alternative fuels. So, the easiest means to reduce mercury emissions may be to reduce the total inputs into the kiln system. The existing data shows that the average mercury content of raw meal is 0.031 mg/kg-clinker, in which the limestone can often account for the majority of the mercury input. The average mercury content of fossil fuels is 0.010 mg/kg. However, the concentration of mercury in raw materials and fuel can vary significantly, hence, it is important to know the mercury content of each raw material as well as its variability. In this project, it is monitored the sources of mercury from raw materials and fuels from around 30 selected representative cement plants, as well as

mercury emissions from different process outlets from 5 cement lines in different regions of China. The testing samples include limestone, raw meal, kiln feed, fuel, kiln dust, coal, clinker and cement from each cement line. Mercury levels in raw materials and fuels are determined by Automatic Isokinetic Sampler in accordance with GB30760-2014 Technical Specification for Coprocessing of Solid Waste in Cement. Mercury emission from whole process are evaluated with Ontario Hydro Method. The results will identify the mercury emission dependent on inputs of various materials and fuel and typical process, and clarify the behavior of mercury in cement clinker production process.

M.O.3.6B-5

STUDY ON THE EFFECTIVENESS OF SELECTED METHODS OF REMOVING MERCURY FROM LIGNITE FLUE GASES

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In Poland, the largest share in anthropogenic mercury emission to the atmosphere is generated by the combustion of solid fuels (electricity production), which amounts to 77.8%. Analyzing the structure of emissions in the countries of the whole European Union, this share is much lower and amounts to 63.4%.

Taking into account the structure of electricity generation, the largest share is held by lignite-based generation units. Given the higher mercury content of lignite compared to bituminous coal and the less favourable elementary composition, dedicated methods to remove mercury compounds from exhaust gases are necessary.

The methods used to remove mercury, both primary and secondary methods, have been presented on the basis of the conducted research. For secondary methods (dedicated to mercury removal), the efficacy of the methods, their advantages, disadvantages and limitations are discussed.

M.O.3.6B-6

MERCURY RELEASED FROM MERCURY CONTAMINATED STEEL DURING SMELTING

ANDREW, Mark; KIRBY, Matthew; BAKER, Stuart; BOWER, Matthew; WALLS, David

Many oil and gas producing regions that have aged assets, coupled with lower reserves of petroleum resources, has led to the implementation of decommissioning activities for these facilities.

Mercury is ubiquitous in oil and gas reservoirs and it is well documented that mercury will deposit onto the internal process infrastructure via several mechanisms including chemisorption, adsorption, precipitated scale deposits (e.g. HgS) and co-precipitation with other scale (e.g. iron oxide). Thus, aged facilities that have reached the end of their operational life and are selected for decommissioning may pose a serious risk to health and the environment.

Decommissioning offshore assets is a comprehensive process that encompasses:

- Platform preparation
- Well plugging and abandonment
- Removal of conductor casing
- Topside removal of rig / platform
- Pipeline and power cable removal
- Material disposal

The entire process needs to be sustainable with minimal impact on the environment and as much recycling of the materials as is practically possible. This presentation details work carried out to better understand the potential mercury exposure to workers and releases to the environment during the smelting of mercury contaminated scrap steel.

4.2 Global and Local policies to inform decisions making and reduce exposure

M.O.4.2-1

ANALYSIS OF NATIONAL PRIORITIES FROM MINAMATA INITIAL ASSESSMENTS

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(1)Secretariat of the Minamata Convention on Mercury, United Nations Environment Programme

One important purpose of Minamata Convention Initial Assessments (MIAs) is to identify challenges to implementation of the Minamata Convention, and capacity building, technical assistance and other needs. MIA reports are key documents in planning for capacity building and technical assistance activities, including projects funded by the Specific International Programme.

The guidance document developed by UNDP in cooperation with other intergovernmental organization recommends the submission of MIA reports to the Secretariat of the Minamata Convention. The secretariat makes submitted MIA reports available on the Convention website. As of 1 March 2019, MIA reports have been received from 26 countries: Benin, Burkina Faso, Cameroon, Comoros Costa Rica, Dominican Republic, Ethiopia, Jamaica, the Gambia, Guinea, Guyana, Lesotho, Madagascar, Mali, Mexico, Moldova, North Macedonia, Nigeria, Saint Kitts and Nevis, Saint Lucia, Senegal, the Seychelles, Tanzania, Trinidad and Tobago, Uganda and Zambia. The submitted MIA reports are a valuable source of information for identifying the global challenges and needs of the developing countries and countries with economies in transition in the implementation of the Convention.

A preliminary analysis of the national priorities described in the 26 submitted MIA reports shows that mercury-added products (Article 4), and mercury wastes (Article 11) are priorities for most countries. More than half of the countries that mentioned their priority areas also included artisanal and small-scale gold mining (Article 7) and emission (Article 8) in their priority list. Releases (Article 9), health aspects (Article 16), awareness raising (Article 18) and research and monitoring (Article 19) were also identified as priority by several countries. Many countries also listed the development of institutional and regulatory framework as one of the priority actions. Some countries identified specific sectors, such as non-ferrous metal production, cement production, waste incineration and dental amalgam. Some countries have not identified priority actions in their MIA reports.

MIA projects are still underway in more than 100 countries. As more MIA reports become available, further analysis will become possible together with their inventory data, which will contribute to the efficient allocation of resources for capacity building and technical assistance, and thus to the effectiveness implementation of the Minamata Convention.

M.O.4.2-2

THE KNOWLEDGE PLATFORM OF THE GLOBAL OBSERVATION SYSTEM FOR MERCURY (GOS4M): A PROACTIVE ENVIRONMENT FOR DECISION-MAKERS

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Provision of observational and modelled data on mercury in the environment do not fully meet the needs of decision-makers in their assessments as both observation and prediction (i.e. scenario) are most often pre-processed by domain experts. Current tools are laid out as tables, graphs, maps, and despite the introduction of the digital paradigm such tools remain static without offering a proactive environment for decision-makers.

A proactive environment is characterized by a fully interactive environment where the user can control and schedule analyses, design workflows, integrate different data sources and execute assessments. In other words there is the need to bring data to knowledge.

The Conference of Parties (COP) (and specifically the established ad-hoc group) of the Minamata Convention on Mercury (MCM) is working to prepare the effectiveness evaluation of MCM implementation. As detailed in the Report of the ad hoc group of expert on effectiveness evaluation (UNEP/MC/COP.2/INF/8, <http://www.mercuryconvention.org/Meetings/COP2>) it is necessary to provide comparable data on global basis, make them available through interoperable systems and enhance their discovery and use.

Under the activity of the Group on Earth Observation (GEO), the Flagship Global Observation System for Mercury (GOS4M) was launched, which is part of the GEO Work Programme (2016-2025).

GOS4M is aimed to support all interested Parties in the implementation of the MCM. The core objective of the GOS4M business plan is to support the Nations, MCM Secretariat, UN Environment and others interested Parties and Stakeholders to contribute to the fulfilment the COP decisions and requests related to, but not limited to, capacity-building and technical assistance to developing country Parties (Article 15), research, development and monitoring (Article 19) and Effectiveness Evaluation of the convention (Article 22). The overarching goal of GOS4M is to promote actions aiming to provide comparable global monitoring mercury data, validated modelling frameworks and assessment tools. Therefore GOS4M is developing a Knowledge Platform (G-KP), an integrated solution of high quality observational data, model output and digital tools to respond closely to specific needs, and address major knowledge gaps. The G-KP is based on five knowledge elements: i) Data Collection/Elicitation; ii) Data Formalization/Encoding; iii) Data Sharing; iv) Data Use; and v) Data Generation.

This work presents the state-of-art of the G-KP and its potential for effectiveness evaluation of MCM.

M.O.4.2-3

GLOBAL OPPORTUNITIES FOR THE LONG-TERM DEVELOPMENT OF THE ARTISANAL AND SMALL-SCALE GOLD MINING SECTOR: INVOLVING THE SCIENTIFIC COMMUNITY IN ASGM MERCURY REDUCTION EFFORTS

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(1)United Nations Environment Programme

(2)Natural Resources Defense Council

In 2016, the Global Environment Facility (GEF) approved the development of the Programme entitled: "Global Opportunities for the Long-term Development of the Artisanal and Small-Scale Gold Mining sector" or GEF-GOLD. The Programme is led by the United Nations Environment Programme (UNEP) and aims to reduce the use and emissions of mercury by the sector in eight countries: Burkina Faso, Colombia, Guyana, Indonesia, Kenya, Mongolia, Peru and the Philippines. The Programme has four components: 1) formalization of the sector 2) improving access to finance and access to formal markets for the miners 3) transfer of non-mercury alternatives and 4) knowledge management and communication. The Programme was officially launched in London, United Kingdom in February 2019.

As a collaborative initiative, GEF GOLD calls for the involvement and participation of a wide range of partners to contribute to the four main components of the Programme. During the launch in London, investors and representatives from the gold consumer industries have expressed interest in working with us. However, further engagement of the scientific community is also important to achieve the goals of the program. In particular, scientific inputs from environmental and social scientists are required to assist in the implementation and to monitor and document the achievements.

Engineering expertise and science is needed to support the technology transfer component as the ideal solutions are often very site-specific

and many options will have to be tried and evaluated. In the same vein, innovative and cost-effective tools for monitoring miners' exposure to mercury and environmental mercury concentrations at mine sites will have to be developed. The results will not only contribute to the immediate monitoring of the project but also provide data to help evaluate the fate and transport of mercury from ASGM globally. Further, the inputs of social sciences will be important for the formalization and the access to finance components. Understanding the social-economic systems that either hinder or enhance formalization, and the social and governance barriers to the adoption of mercury-free techniques, will allow the Programme to tailor intervention to address them.

M.O.4.2-4

THE USE AND IMPACT OF FLEXIBILITY MECHANISMS IN MULTILATERAL ENVIRONMENTAL AGREEMENTS – INVESTIGATING PRACTISE AND IMPACT UNDER THE MINAMATA CONVENTION ON MERCURY

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When negotiating new multilateral environmental agreements (MEAs), delegates devote significant attention to the balance between depth versus participation. A prevailing one-dimensional assumption has been that more stringent obligations imply less ratifications and vice versa. However, scholars have over the years modified this picture, claiming that the dynamics are in fact multidimensional. The specific design of the MEA, including enforcement rules, organization and function, financial assistance and dispute settlement, are all aspects that may influence participation. Under the recently adopted MEA, the Minamata Convention on Mercury (MC), exemptions were introduced as a core flexibility mechanism, allowing Parties a permanent exemption for some specific types of use and temporary exemptions for a broad range of provisions. However, the need or potential impact of such mechanisms has not previously been assessed. This paper will investigate the use and the impact of the exemption mechanism under the MC, by analysing the requests and motivations for exemptions, which countries and why they have requested an exemption, its links to participation and its potential impact on actual reductions. The study will provide an empirical perspective from the MC of how flexibility measures are being applied and how they may influence the reduction potential and overall objective of the instrument.

M.O.4.2-5

INCORPORATING DIVERSE PERSPECTIVES ON THE HUMAN HEALTH IMPACTS OF METHYLMERCURY EXPOSURE INTO REGULATORY ENVIRONMENTAL ASSESSMENT

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(1)University of British Columbia

Environmental policy choices are fraught with competing scientific, social, political, and cultural considerations. Although mercury exposure is a health risk of global concern, as evidenced by the Minamata Convention, it is not entirely evident how to translate scientific knowledge of mercury and methyl mercury exposure into policy and regulations that protect human health in a holistic manner that is relevant to local communities. This research explores how multi-disciplinary knowledge about the human health impacts of methyl mercury exposure is used in the regulatory decision-making process.

The case study of interest is the Muskrat Falls hydroelectric project in Labrador, Canada. During the project implementation phase, there was a lack of consensus among stakeholders regarding the potential

increases in exposure to methyl mercury and the subsequent health impacts – particularly for downstream Indigenous communities consuming country foods. This case illustrates how contradictory scientific evidence and competing cultural values can lead to controversial decision-making outcomes. We use qualitative discourse analysis to elicit the scientific and decision-making rhetoric surrounding the controversy from the perspectives of multiple stakeholders. Discourse analysis connects language use in text documents to broader social themes, which reveals important perceptions about whether environmental policies are adequately protecting human health from risks like mercury exposure. We use qualitative coding to elicit discourses present in the academic literature, the grey literature, news articles, and interviews with key stakeholders. Through this analysis, we explore themes such as how human health is defined by different stakeholders, what is considered adequate scientific evidence for policy-making, and the scientific and cultural thresholds of significant adverse health impacts from methyl mercury exposure. Preliminary findings indicate that health impacts included in the regulatory assessment of the project did not reflect the health concerns of the community. This work contributes to the exploration of future mercury reduction policy avenues that incorporate balanced perspectives from multiple stakeholders.

M.O.4.2-6

TRANS-PROVINCIAL HEALTH IMPACTS OF ATMOSPHERIC MERCURY EMISSIONS IN CHINA

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(2)Beijing Normal University
(3)Peking University
(4)University College London
(5)Nanjing University
(6)Tianjin University
(7)Renmin University of China

Mercury (Hg) exposure poses substantial risks to human health. Investigating the more complete chain of the biogeochemical Hg cycle from economic activities to human health can reveal the sources and critical processes of Hg-related health risks and help inform policy decisions for subsequent Hg control. We develop a more comprehensive assessment method using an emission inventory, a multi-regional input-output model, an atmospheric transport model and health impact assessments to investigate the more complete chain of the biogeochemical Hg cycle. This method is applied to mainland China – the largest Hg emitter in the world. We present a map of Hg-related health risks in China and estimate that 0.14 points of per-foetus intelligence quotient (IQ) decrements and 7,360 deaths from fatal heart attacks are related to the intake of methylmercury in 2010. This study, for the first time, reveals the considerable magnitude of the net impacts of interprovincial trade on Hg-related health risks over the whole country. For instance, interprovincial trade induced by final consumption of products prevents 0.0039 points for per-foetus IQ decrements and 194 deaths from fatal heart attacks. These findings highlight the importance of source identification and relevant policy decisions in different stages of economic supply chains to effectively reduce Hg-related health risks. Meanwhile, the spatial relocation of Hg-related health risks due to interprovincial trade highlights regional pairs/groups that can collaboratively reduce Hg-related health risks of the whole system. Final consumers such as Shanghai, Zhejiang, and Guangdong could transfer related technologies and capital to their upstream direct emitters (e.g., Henan and Gansu) to reduce their Hg-related health risks. Primary suppliers such as Shanxi and Inner Mongolia could transfer related technologies and capital to their downstream users (e.g., Gansu and Yunnan) to reduce their Hg-related health risks.



ORAL ABSTRACTS

Tuesday 10th September 2019