Development of Mercury Speciation Factors for EPA's Air Emissions Modeling Programs, Technical Support Document
Version 1

Contacts: Janice Godfrey, Eric Goehl, Madeleine Strum, and Art Diem
of the EPA's Office of Air Quality Planning and Standards (OAQPS)
April 2020

I. Purpose

This document describes the development of mercury (Hg) speciation factors for the U.S. Environmental Protection Agency's (EPA's) air emissions modeling programs. Atmospheric mercury is a global environmental issue due to its toxicity, persistence, and long-range transportability. Mercury speciation plays an important part in the toxicity and exposure of mercury to living organisms. Speciation also has a considerable influence on the fate and transport of mercury within and between environmental compartments, including the atmosphere and oceans, among others. Moreover, speciation affects the controllability of mercury emissions.[1,2]

II. Background

Mercury is emitted in three main forms: elemental gaseous mercury (Hg^0), gaseous divalent mercury (Hg^{2+}), and particulate-bound divalent mercury (Hg_P). Oxidation Hg^0 to Hg^{2+} occurs in the flue gas for certain industrial processes, with a portion of Hg^{2+} adsorbed onto fly ash to form Hg_P. Mercury removal and transformation also occurs when it passes through air pollution control devices (APCDs). As described in more detail below, mercury speciation can differ between sectors due to differences in fuel type, APCDs, operating procedures, and other factors, some of which are not yet fully understood. This demonstrates the need for additional data for a variety of point sources of emissions, such as smelters and waste incinerators; especially as sources, fuels, feedstocks, and control techniques change.

Many factors affect mercury speciation. For example, coal type, and chlorine content are important factors in the speciation and capture of mercury with different types of air pollution control technologies.[3] In the U.S., bituminous coals tend to have relatively high concentrations of chlorine (Cl). This can result in the oxidization of Hg^0 to Hg^{2+} (primarily $HgCl^2$). The Hg^{2+} can be adsorbed onto fly ash carbon and captured in an electrostatic precipitator (ESP) or fabric filter (FF). On the other hand, mercury in the exhausts of plants burning other types of coal tends to be predominately Hg^0. [The capture of mercury from the flue gas from these plants tends to be

[1] AMAP/UNEP, 2002.
[2] Streets, D. et al., 2019.
[3] US EPA, 2004.

lower, whether the units are equipped with an ESP, FF, dry flue gas desulfurization (FGD) scrubber, or wet FGD scrubber.[4]]

III. General Approach for Developing Speciation Profiles for Source Categories

We conducted a literature review to find available data and information regarding the forms of mercury emitted from various sources. One of the main documents identified through this search is the 2008 Global Atmospheric Mercury Assessment.[5] In this assessment, the United Nations Environment Programme (UNEP) cooperated with the Arctic Monitoring Assessment Programme (AMAP) to produce the 2008 Global Atmospheric Mercury Assessment (AMAP/UNEP 2008). The AMAP/UNEP review includes data from several mercury studies from around the world and was prepared by expert groups engaged by AMAP and UNEP. Information submitted by governments, intergovernmental and non-governmental organizations, as well as other available scientific information, were used to prepare the report.

A more recent study (Muntean, 2018), compared speciated mercury gridded emissions inventories with chemical transport models and concentration measurements to investigate the effectiveness of mitigation measures and the mercury cycle in the environment.[6] The authors developed three emissions scenarios based on different hypotheses of the proportion of mercury species in the total mercury emissions for each activity sector. The study used the GEOS-Chem 3-D mercury model to explore the influence of speciation shifts, to reactive mercury forms, in particular, on regional wet deposition factors. Scenario 1 used speciation factors from AMAP/UNEP, which reflects a generic power plant mercury profile (Hg^0 = 50%, Hg^{2+} = 40%, and Hg_P = 10%). Scenario 2 used speciation factors from AMAP/UNEP, but substituted factors for the power generation sector with EPA data derived from an information collection request (ICR) done in conjunction with the Clean Air Mercury Rule (CAMR). Unlike the AMAP/UNEP speciation factors for power generation, the CAMR speciation factors are specific to the type of fuel and APCD used. Scenario 3 used speciation factors gleaned from recent, small studies, mainly carried out in Asia. The study shows that using the Scenario 2 emissions of reactive mercury, can improve wet deposition estimates near sources and therefore give us more confidence in the profiles developed from the AMAP/UNEP and CAMR ICR.

Although several recent smaller studies have been carried out in Asia, we decided, given that most of these studies were focused on a small number of facilities in a limited region, to generally use speciation factors derived for the AMAP/UNEP 2008 report. The exception to this is where the EPA collected emission tests for mercury speciation for coal-fired power plants for the CAMR, which was documented in the Mercury Air Toxics Standard (MATS), as well as,

[4] AMAP/UNEP, 2002.
[5] AMAP/UNEP, 2008.
[6] Muntean, M. et al., 2018.

other sectors where sufficient industry data (*i.e.,* test reports) or sector specific literature sources are available. Industry data are used for the coal-fired power plant Portland Cement and Chlor-Alkali production profiles. Sector specific literature sources are used for geothermal power and mobile sources profiles. Where data are insufficient to develop sector-specific speciation factors, we developed factors using an average of the source categories for which we have determined a speciation profile.

Once a set of speciation factors are established, they are assigned a speciation profile code to facilitate the speciation process for air emissions modeling. The speciation profile codes are also added to EPA's SPECIATE database. Profile codes are summarized in Appendix A.

IV. Mercury Speciation for Specific Source Categories

Coal

As mentioned above, mercury speciation that occurs after emissions leave the boiler and before they reach the APCD is mainly determined by coal properties, specifically chlorine, mercury, and ash contents. For example, larger availability for chlorine in coal causes larger formation of Hg^{2+} compared to H^0. Higher concentrations of fine particles in exhaust gases improve conditions for gas-to-particle conversion of gaseous mercury, resulting in higher proportions of Hg_P.[7]

In 2010, about 16% of global anthropogenic mercury emissions (unspeciated) were attributed to commercial coal-fired power plants.[8] In the 2014 National Emissions Inventory (NEI), which covers the United States, coal combustion from electric generating units was the largest mercury source category, contributing an estimated 44% of the estimated 52 tons emitted.[9] (Note that the NEI doesn't estimate mercury from fires but does include some nonpoint sources, such as dental amalgam and fluorescent light breakage, as well as a small amount from mobile sources.)

For the MATS rule, the EPA compiled documentation on mercury speciation for EGUs in the United States. The speciation approach applied for the final MATS rule was developed as part of the CAMR and based on a 1999 ICR. Eighty mercury emissions tests were collected from 69 facilities. These data include inlet and outlet speciated mercury concentration measurements for Hg_P, Hg^{2+}, and Hg^0. All emissions tests were conducted using the Ontario Hydro method and included three sampling runs. Only the outlet data (measurements after the last control device) were used to develop the mercury speciation profiles. Forty-three mercury speciation profiles were developed from these data (see Table 1). Additional information on these profiles is

[7] Pacyna and Pacyna, 2002.
[8] AMAP 2013.
[9] 2014 US EPA National Emissions Inventory (NEI).

available in the "Electric Generating Utility Mercury Speciation Profiles for the Clean Air Mercury Rule"[10] and the workbook "EGU_Hg_Speciation_Data_CAMR.xls," which are available in the regulations.gov docket EPA-HQ-OAR-2009-0234, document ID 19910. A profile code is assigned to each bin as follows: "EGUBIN" concatenated with the bin number.

Petroleum Coke (pet coke) is an additional fuel combustion profile derived from the average of bins 2, 23, 25, 38, and 43 (*i.e.,* $Hg_P = 0.10$, $Hg^{2+} = 0.30$, and $Hg^0 = 0.60$). The resultant speciation factors are assigned the profile code HGPETCOKE. For coal-fired power plants that were not a part of the MATS analysis, and for which we do not have sufficient information to include in one of the MATS bins, we intend to use the speciation factors from AMAP/UNEP for combustion emissions from power plants (see Table 2).

Table 1. Electric Generating Utility Mercury Speciation Profiles for the Clean Air Mercury Rule

Bin Type	Fuel, Boiler, Emission control device(s)	Percent Speciation		
		Particulate Hg	Oxidized Hg	Elemental Hg
0	Bituminous Coal, Coal Gasification	0.51%	8.47%	91.02%
1	Bituminous Coal, PC Boiler with ESP-CS	6.11%	68.20%	25.70%
2	Bituminous Coal and Pet. Coke, PC Boiler with ESP-CS	1.17%	46.56%	52.27%
3	Bituminous Coal, PC Boiler with SNCR and ESP-CS	20.32%	27.12%	52.56%
4	Bituminous Coal, PC Boiler with ESP-HS	4.90%	57.84%	37.26%
5	Bituminous Coal, PC Boiler with PM Scrubber	1.80%	19.51%	78.69%
6	Bituminous Coal, PC Boiler with Dry Sorbent Injection and ESP-CS	0.16%	67.10%	32.74%
7	Bituminous Coal, PC Boiler with FF Baghouse	3.98%	62.58%	33.44%
8	Bituminous Coal, PC Boiler with SDA/FF Baghouse	9.17%	28.86%	61.97%
9	Bituminous Coal, PC Boiler with SCR and SDA/FF Baghouse	5.06%	46.04%	48.90%
10	Bituminous Coal, PC Boiler with ESP-CS and Wet FGD	0.22%	7.78%	92.00%
11	Bituminous Coal, PC Boiler with ESP-HS and Wet FGD	0.63%	20.68%	78.70%
12	Bituminous Coal, PC Boiler with FF Baghouse and Wet FGD	6.48%	33.00%	60.52%
13	Subbituminous Coal, PC Boiler with ESP-CS	0.16%	30.83%	69.01%

[10] Bullock and Johnson, 2011.

Bin Type	Fuel, Boiler, Emission control device(s)	Percent Speciation		
		Particulate Hg	Oxidized Hg	Elemental Hg
14	Subbituminous Coal, PC Boiler with ESP-HS	0.06%	12.52%	87.41%
15	Subbituminous Coal, PC Boiler with FF Baghouse	1.49%	82.83%	15.68%
16	Subbituminous Coal, PC Boiler with PM Scrubber	1.45%	5.11%	93.44%
17	Subbituminous Coal, PC Boiler with SDA/ESP	0.32%	3.82%	95.86%
18	Subbituminous Coal, PC Boiler with SDA/FF Baghouse	0.99%	4.35%	94.67%
19	Subbituminous Coal, PC Boiler with ESP-CS and Wet FGD	0.43%	2.94%	96.63%
20	Subbituminous Coal, PC Boiler with ESP-HS and Wet FGD	1.17%	4.46%	94.37%
21	Lignite Coal, PC Boiler with ESP-CS	0.09%	3.62%	96.29%
22	Subbituminous Coal, Cyclone Boiler with PM Scrubber	2.34%	5.75%	91.91%
23	Subbituminous Coal/Pet. Coke, Cyclone Boiler with ESP-HS	0.93%	7.52%	91.55%
24	Lignite Coal, Cyclone Boiler with ESP-CS	0.04%	16.99%	82.97%
25	Bituminous Coal/Pet.Coke, Fluidized Bed Combustor with SNCR and FF Baghouse	42.44%	27.87%	29.70%
26	Not Used			
27	Bituminous Waste, Fluidized Bed Combustor with FF Baghouse	2.12%	38.81%	59.07%
28	Lignite Coal, Fluidized Bed Combustor with ESP-CS	1.37%	11.64%	87.00%
29	Lignite Coal, Fluidized Bed Combustor with FF Baghouse	0.42%	71.18%	28.40%
30	Anthracite Waste, Fluidized Bed Combustor with FF Baghouse	3.01%	37.30%	59.70%
31	Bituminous Coal, Stoker Boiler with SDA/FF Baghouse	19.96%	17.94%	62.11%
32	Not Used			
33	Lignite Coal, PC Boiler with ESP-CS and FF Baghouse	0.19%	64.49%	35.32%
34	Lignite Coal, PC Boiler with SDA/FF Baghouse	0.36%	12.62%	87.02%
35	Lignite Coal, PC Boiler with PM Scrubber	0.16%	2.98%	96.86%
36	Lignite Coal, PC Boiler with ESP-CS and Wet FGD	0.82%	13.45%	85.74%

Bin Type	Fuel, Boiler, Emission control device(s)	Percent Speciation		
		Particulate Hg	Oxidized Hg	Elemental Hg
37	Bituminous Coal, Cyclone Boiler with Mechanical Collector	18.75%	42.74%	38.51%
38	Bituminous Coal/Pet. Coke, Cyclone with ESP-CS and Wet FGD	0.07%	11.30%	88.63%
39	Lignite Coal, Cyclone Boiler with SDA/FF Baghouse	9.95%	17.07%	72.98%
40	Subbituminous Coal, Fluidized Bed Combustor with SNCR and FF Baghouse	0.27%	3.42%	96.32%
41	Subbituminous Coal/Bituminous Coal, PC Boiler with ESP-CS	0.88%	42.82%	56.30%
42	Subbituminous Coal/Bituminous Coal, PC Boiler with ESP-HS	2.86%	49.11%	48.03%
43	Bituminous Coal/Pet. Coke, PC Boiler with FF Baghouse	2.20%	78.41%	19.39%
44	Bituminous Coal/Subbituminous Coal, PC Boiler with FF Baghouse	5.95%	42.10%	51.95%

Portland Cement

The EPA received mercury speciation data for four U.S. Portland Cement companies (7 facilities) for its 2018 Residual Risk and Technology Review.[11] In the summary analysis, there was a wide range of values for the elemental (Hg^0) to oxidized (Hg^{2+}) split of mercury emissions – from a low of 28% to as high as 97% Hg^0. Industry stated that this wide range reflects the reality that multiple factors determine the mix of mercury species emitted by a kiln. These factors include the concentration of mercury in the raw materials (namely limestone), operating stack temperature, and type of APCDs used. The data support an estimate that, on average, 66% of mercury emissions from kilns is Hg^0 and 34% is Hg^{2+}.[12] These data reflect the use of continuous emission monitoring systems (CEMS) and the presence of controls for mercury emissions. Mercury control devices include activated carbon injection, wet scrubbers, or both. We assign this mercury profile to any Portland cement operation having kiln exhaust. The profile code for the Portland cement profile is HGCEM.

Mercury emissions from the kiln that were in the particulate form (not measured by CEMS) were considered inconsequential and were not included in the mercury speciation for kilns. Because mercury is usually completely volatilized in the kiln, mercury is typically not emitted from the clinker cooler. However, the data on metal content of clinker showed a small amount of mercury. For the purposes of speciating mercury emissions from the clinker cooler[13] and other post-kiln Portland cement product storage and handling operations, it is assumed mercury emissions are 100 percent in the form of particulate emissions and are assigned the

[11] US EPA, 2018.
[12] Portland Cement Association, 2016.
[13] US EPA, 2018

profile code HGCLI. For raw material operations that take place before the kiln, any mercury emissions are presumed to be in elemental form and are assigned the profile code HGELE.

A separate source monitoring study conducted in Florida in the year 2000 determined emission profiles that support the Portland cement industry speciation profiles. The study can be found in the EPA Technical Report EPA/600/R-00/102. The study found that Hg^{2+} represented less than 25 percent of the total mercury emissions from Portland cement kilns. The ratio of Hg^{2+} to Hg^0 was just under 1:3. The analytical procedures for determination of mercury from stack sampling followed EPA guidelines in 40 CFR 60, Appendix A, Method 29. Since the study only included limited monitoring from one kiln, we cannot conclude these numbers are representative of all Portland cement facilities. Regardless, the study may be helpful as supplementary information.

Other Anthropogenic Source Categories

As discussed above, given that most of the more recent studies were focused on a small number of facilities in a limited region (Asia), we concluded that it was more representative to use the AMAP/UNEP 2008 mercury speciation factors generally for several source categories (as shown in table 2). However, for future modeling assessments for any given source category, if the EPA obtains additional source category specific mercury speciated data, it would probably be appropriate to use the new data in lieu of, or in combination with, the speciation factors presented in this technical support document. Nevertheless, it is important to note that there is uncertainty in using one set of speciation factors for a given industry as mercury speciation can vary due to differences in fuel type, control devices, operating procedures, and other factors. The estimates presented in Table 2 were determined on the basis of data on mercury in exhaust gases from various sources collected by Pacyna et. al.[14] over two decades prior to their publication in 2002 entitled "Global Emission of Mercury from Anthropogenic sources in 1995".

Table 2. Speciation Profiles from the 2008 Global Atmospheric Mercury Assessment

Sector	Hg^0	Hg^{2+}	Hg_P
Combustion emissions from power plants	0.5	0.4	0.1
Combustion emissions from residential heating	0.5	0.4	0.1
Combustion emissions from industrial/commercial/residential boilers	0.5	0.4	0.1
Iron and steel production	0.8	0.15	0.05
Non-ferrous (Cu, Zn, Pb) metal production	0.8	0.15	0.05
Large-scale gold production	0.8	0.15	0.05
Waste incineration	0.2	0.6	0.2
Cremation emissions	0.8	0.15	0.05
Artisanal and small-scale gold mining*	1.0	0.0	0.0

[14] Pacyna and Pacyna, 2002.

AMAP (2008)

* We are not aware of any artisanal or small-scale gold mining in the U.S., but we have included it here for completeness.

Additionally, the EPA has some limited test data available for the Iron and Steel Production Sector, the Electric Arc Furnace Sector, mercury-cell chlor-alkali plants and waste incineration that are discussed below.

Discussion of Source Categories Other than Electric Generating Units and Portland Cement

Below we discuss briefly how speciation occurs within the flue gas from each source category. We also mention shortcomings in the use of the AMAP/UNEP 2008 numbers, as well as other possible considerations when applying speciation factors. There are several source categories within the EPA's Risk and Technology Review program that do not fall into one of the categories in Table 2 (*e.g.,* paper mills). Therefore, we developed a default industrial profile to use where the mercury emissions are not a result of fuel combustion and for which we do not identify any other appropriate surrogate profile. This profile is an average of the non-fuel combustion categories (*i.e.,* $Hg^0 = 0.73$, $Hg^{2+} = 0.22$, and $Hg_P = 0.05$). This profile was derived by averaging the following source categories: Iron and Steel Production; Non-Ferrous (Cu, Zn, Pb) Metal Production; Large-Scale Gold Production; Chlor-Alkali Industry (caustic soda production), Hydrochloric Acid (HCl) Production facilities; Waste Incineration; Cremation Emissions; Portland cement; Electric Arc Furnaces; and Elemental Mercury (See Appendix A for profile details). The profile code for this default industrial profile is HGIND.

Combustion Emissions from Industrial/Commercial/Residential Boilers

Mercury speciation for industrial, commercial, and residential boilers may differ significantly from power plants due to varying fuel types, control devices, and operating procedures. For example, the APCDs applied for industrial coal combustion generally have a lower Hg^{2+} removal efficiency than those applied for coal-fired power plants.[15] The speciation profile for combustion emissions from industrial/commercial/residential boilers is composed of the AMAP/UNEP 2008 mercury speciation factors for combustion and is assigned the profile code HGCMB.

Iron and Steel Production and Coke Ovens

Mercury is vaporized in high-temperature facilities, including coke oven, sintering machine, blast furnace, and convertor facilities. Mercury in the flue gas is oxidized homogeneously and heterogeneously. A portion of the mercury is removed in dust collectors (*e.g.,* ESPs and baghouses) and flue gas desulfurization devices, and the remaining mercury in

[15] Zhang, L. et al., 2016.

flue gas is emitted into the atmosphere. The EPA has very limited test data available for this category. The Michigan Department of Environmental Quality required mercury speciation tests at the Severstal facility in Dearborn, Michigan. Tests performed by NTH Consultants, Ltd. showed that the average speciation factors for this iron and steel facility were Hg^0 = 80%, Hg^{2+} = 15% and Hg_P = 5%.[16] Tests were performed with both a basic oxygen furnace (BOF) with an ESP and BOF with a bag house. This test compares well with the AMAP/UNEP speciation profile for Iron and Steel Production. The speciation profile code used for iron and steel production and coke ovens is HGMET.

Electric Arc Furnaces (EAFs)

EAFs produce steel from metal scrap, which is melted and refined by passing an electric current between electrodes and through the scrap. Much of the mercury in this source category comes from the elemental mercury in automobile switches built before 2004. The National Vehicle Mercury Switch Recovery Program is a partnership between the EPA, environmental organizations, the Environmental Council of the States, and several industry trade associations. Two trade associations—the American Iron and Steel Institute and the Steel Manufacturer Association—are among the participating entities. The goal of this initiative is the removal of mercury-containing light switches from scrap vehicles before the vehicles are flattened, shredded, and melted to make new steel. Begun in 2006, the national initiative will help cut mercury air emissions by up to 75 tons over the 15-year span of the project.[17]

Due to the characteristics of the raw materials, we determined that the source category most like EAFs is the Iron and Steel Production source category. Therefore, we intend to use the Iron and Steel Production AMAP/UNEP 2008 speciation profile for the EAF category, as it aligns with what we would expect from the EAF source category given that most of the mercury originates from mercury-containing light switches in the scrap metal from automobiles. Test data for speciation of the mercury from the EAF source category is limited. Eagle Mountain Scientific performed an annual compliance test including speciated mercury for Gerdau Ameristeel in St. Paul, Minnesota. Test reports show most of the mercury is elemental with an average speciation profile of Hg^0 = 76%, Hg^{2+} = 24%, and Hg_P = 0.0%.[18] This test lends support to the use of the AMAP/UNEP 2008 speciation profile for Iron and Steel Production for the EAF category, as 76% of the mercury is in the form of Hg^0, which is similar to the profile described above for Iron and Steel Production (i.e., 80% elemental mercury). The speciation profile code used for EAFs is HGMET.

Non-Ferrous Metal Smelters

[16] NTH Consultants, Ltd, 2009.
[17] https://archive.epa.gov/mercury/archive/web/html/index-4.html.
[18] Eagle Mountain Scientific, Inc., 2008.

Mercury speciation for non-ferrous metal smelters is mostly estimated from the smelting and roasting stage, where the majority of mercury is emitted. However, mercury emissions also come from the slag dehydration and volatilization stages. Elemental gaseous mercury (Hg^0) tends to be the principal form in the flue gases emitted from non-ferrous metal smelters. Catalytic metallic components and high particulate matter (PM) concentrations in flue gases are the two primary causes. Mercury reclaiming towers in non-ferrous metal smelters preferentially release Hg^0 to downstream flue gases. The speciation profile code used for non-ferrous metals smelters is HGMET.

As with the other categories, there are a number of uncertainties in Hg speciation for this category. More recent studies in China have shown speciation splits for Hg^{2+} to be closer to 50 to 60 percent, thereby reducing the splits for Hg^0 and Hg_P.[19] However, these data are from a limited number of facilities in a limited geographical area. Studies from across the world suggest that the deviation in speciation for non-ferrous metal production to be on the order of $\pm$ 30 percent.[20] It should also be noted that in the previous (2002) AMAP the speciation for non-ferrous metals was Hg^0 = 60%, Hg^{2+} = 30%, and Hg_P = 10%.[21]

Chlor-Alkali Industry

Major points of mercury release in the mercury cell process of chlor-alkali production include: byproduct hydrogen stream, end box ventilation air, and cell room ventilation air. Typical devices/techniques for removal of mercury in these points are: (1) gas stream cooling to remove mercury from hydrogen stream, (2) mist eliminators, (3) scrubbers, and (4) adsorption on activated carbon and molecular sieves.[22] Mercury cell chlor-alkali plants (MCCAPs) were estimated to be the largest non-combustion anthropogenic sources of atmospheric mercury in the U.S. in the early 1990s, emitting 6.5 megagrams/year from the 14 operating plants in 1994–1995 (US EPA, 1997). However, most facilities have closed or converted to non-mercury processes since that time. Furthermore, the few remaining facilities have reduced emissions pursuant to the MACT standards promulgated in 2003 (68 FR 70904, December 19, 2003). The mercury emissions from this source category today are substantially lower than they were in the 1990s.

A February 2000 industrial source monitoring study at a chlor-alkali plant in Augusta, Georgia found a high fraction of mercury emitted as Hg^0 gas in the production of chlorine and caustic soda (mercury-based chlor-alkali production). This 9-day field sampling campaign study is available from the EPA Technical Report EPA/600/R-02-007a. The results of this study showed an average Hg^0 emission rate of 0.36 grams/minute from the roof ventilator. A separate

[19] Zhang, L. et al., 2015.
[20] Pacyna and Pacyna, 2002.
[21] AMAP/UNEP, 2002.
[22] Pacyna and Pacyna, 2002.

report[23] based on this same monitoring study stated that the measurements in the cell building roof vent of Hg^{2+} constituted approximately 2.1±0.7% of the concurrently measured Hg^0. The percent Hg^{2+} was substantially lower than the 30% Hg^{2+} estimate utilized by the EPA to model the impact of MCCAPs for the 1997 Mercury Report to Congress and shown in Table 2. Therefore, because these studies, based on measurements of mercury at a U.S. facility, are likely to be a better representation of mercury speciation from the remaining domestic chlor-alkali sources in the U.S. than the 2008 AMEP/UNEP report speciation, we are using a mercury speciation of 97.3% Hg^0 and 2.7% Hg^{2+} for this industry. The 2.7% Hg^{2+} value was computed by conservatively considering the error bound about the estimate from this measurement. The profile code for chlor-alkali production is HGHCL.

Waste Incineration

Mercury speciation from waste incineration is another category where fluctuations can depend on the type of waste burned, APCDs, and operational practices. The major incineration types are municipal solid waste (MSW) incineration, medical waste incineration and industrial and/or hazardous waste incineration. Based on a study by Park et al, a significant proportion of mercury (80 to 96 percent) in the MSW releases from the incinerator into the flue gas is in the form of Hg^0 at 850–1000°C[24]. High chlorine content in the waste results in higher Hg^{2+} proportion in the flue gas. Limestone slurry or powder sprayed in dry flue gas deacidification (SD-FGD or D-FGD) absorbs a large amount of Hg^{2+} and activated carbon adsorbs a large amount of both Hg^0 and Hg^{2+}. Particles from SD-FGD and activated carbon injection (ACI) are captured by the downstream FF. Hg_P is removed by all types of dust controllers. The high Hg^{2+} formation rate due to the oxidative condition in flue gas and the high Hg^{2+} removal rate by APCDs (especially SD-FGD, FF and ACI) cause significant variation in mercury speciation profiles for incinerators.[25] The profile code for waste incineration is HGINC.

An industrial source monitoring study conducted in Florida in the year 2000 found emission profiles that support the fractions displayed in Table 2. This study can be found in the EPA Technical Report EPA/600/R-00/102. For waste incineration, this study found nearly all mercury emissions to be in the form of Hg^{2+} gas from a medical waste incinerator (MWI) and a resource recovery incinerator (RRI). The analytical procedures for determination of mercury from stack sampling followed EPA guidelines in 40 CFR 60, Appendix A, Method 29. Hg^{2+} was the dominant form of mercury at the RRI and the MWI, accounting for more than 75 percent and 98 percent, respectively, of the total mercury (somewhat higher than the split for Hg^{2+} shown in Table 2). The ratio of Hg^{2+} to Hg^0 for RRI was 3.4:1 and for MWI was 51.6:1. Since this study only included limited monitoring from two sources, we cannot conclude these

[23] Landis, M. et al., 2003
[24] Park, K. S. et al., 2008
[25] Zhang, L. et al., 2016.

numbers are representative of all waste incineration. Regardless, the study may be helpful as supplementary information.

Cremation Emissions

Extremely large uncertainties exist in this sector due to the diversity of mercury content in human body and dental amalgam. Sectors that include cremation emissions should be further examined for specific combustion practices. Cremation emissions are currently not a regulated source of hazardous air pollutant emissions in the United States.[26] The HGCRE profile code is assigned to this category.

Mercury Production

Mercury has not been produced as a principal mineral commodity in the United States since 1992.[27] In 2018, mercury was recovered as a byproduct from processing gold-silver ore at several mines in Nevada; however, production data were not reported.[28]

Artisanal and Other Gold Mining

No U.S. emissions reported.

Other Mining

The EPA will evaluate other source categories within the category of mining (*e.g.,* taconite), as needed. Where possible we intend to use source specific data. Where no information is available, we plan to use the AMAP/UNEP Non-Ferrous (Cu, Zn, Pb) Metal Production profile (HGMET).

Geothermal Power Plants

Mercury is present in geothermal vents used for electric generation. Geothermal power production equipment types that emit mercury to the atmosphere include off-gas steam ejectors and cooling tower exhaust. Mercury speciation from these equipment types are documented in the paper titled Mercury Emissions from Geothermal Power Plants[29] EPA averaged the 3 speciation values from ejector off-gases and the 2 speciation values from cooling tower exhaust

[26] Mari, M and Domingo, J., 2009.
[27] USGS Minerals Yearbook, 2019.
[28] USGS Minerals Yearbook, 2019.
[29] Robertson, D.E. et al., 1977

air for profile code HGGEO, resulting in mercury speciation percentages of 87.0 percent for Hg^0, 13.0 percent for Hg^{2+}, and 0.0 percent for Hg_P.

Mobile Sources

Mercury speciation of mobile sources is not addressed in the AMAP/UNEP 2008 report. However, small amounts of mercury from mobile sources are included in the EPA's NEI. In the 2014 NEI mobile sources contribute less than 2 percent of the total mercury emissions. The speciation factors for mobile sources are derived from source testing done at the EPA. Onroad mobile source emission factors are documented in the EPA Technical Report EPA-420-R-16-016, titled *Air Toxic Emissions from On-road Vehicles in MOVES2014*. Emission factors for Hg^0, Hg^{2+}, and Hg_P were obtained from a 2005 test program at the EPA's National Exposure Research Laboratory (NERL). In this program mercury samples in raw exhaust were collected from 14 light-duty gasoline vehicles and two heavy-duty diesel vehicles. Data collected included elemental and total gas-phase mercury and particulate mercury. The emission rates were computed in grams/mile (g/mi). Gaseous divalent mercury was computed by subtracting Hg^0 from total gas-phase mercury. The emission factors for gasoline vehicles are 1.1×10^{-7} g/mi Hg^0, 9.9×10^{-9} g/mi Hg^{2+} and 4×10^{-10}g/m Hg_P, resulting in mercury speciation percentages of 91.5, 8.2 and 0.3 for Hg^0, Hg^{2+}, and Hg_P, respectively. The emission factors for diesel vehicles are 6.2×10^{-9} g/mi Hg^0, 3.2×10^{-9} g/mi Hg^{2+} and 1.6×10^{-9}g/m Hg_P, resulting in mercury speciation percentages of 56, 29 and 15 for Hg^0, Hg^{2+}, and Hg_P, respectively. The mobile gasoline profile is assigned the code HGMG, and the mobile diesel profile is assigned the code HGMD.

For nonroad engines, emission factors are documented in the EPA Technical Report EPA-420-R-18-011, titled *Speciation Profiles and Toxic Emission Factors for Nonroad Engines in MOVES2014b*. Nonroad gasoline and diesel vehicle emission factors for mercury (all phases) were derived from onroad air toxics factors discussed above (EPA-420-R-16-016), converting gram per mile emission factors to gram per gallon emission factors using fuel economy estimates.

Elemental Mercury Categories

Dental Alloy Production[30], Bench Scale Reagents, Fluorescent Lamp Breakage[31], and Portland cement raw material handling operations prior to kilning[32] are assumed to be entirely elemental gaseous mercury (Hg^0). These categories are assigned the profile code HGELE.

[30] Goodrich, J. et al., 2016.
[31] Johnson, N. et al., 2008.
[32] US EPA, 2018 (p. 16 of 199, and Table 6)

V. Concluding Remarks

Based on our analysis, we conclude the speciation factors shown in Table 2 should generally be used as the default factors for most source sectors in the absence of source category specific data. However, for electric generating power plants that were included in the MATS analysis, we recommend the factors used in the Mercury Air Toxics Standard (MATS) analyses, and for other sectors where sufficient source category specific data are available (*e.g.,* Portland Cement) those data should be used to determine the speciation splits. For source categories not specifically listed in Table 2 or in Appendix A, and for which insufficient information is available to assign a surrogate source category profile, we recommend the use of an average of the source categories for which we have determined a speciation profile, as described above and listed in Appendix A.

Nevertheless, as mentioned above, there are uncertainties and data gaps. Future studies on mercury speciation would be helpful for gaining a better understanding of the environmental and human health risks from mercury. Conventional mercury measurement methods must be carefully performed to effectively determine the speciation distribution. In addition, CEMS intended to provide a direct determination of either total Hg^0 and/or Hg^0 and Hg^{2+} are currently under development and evaluation in the field. The factors presented here reflect limited insight and generally should not be used when more specific data is available.

VI. References

AMAP/UNEP, 2002. Technical Background Report to the Global Mercury Assessment. Artic Monitoring and Assessment Programme/UNEP Chemicals Branch (2002). http://www.eurocbc.org/final-assessment-report-25nov02.pdf (last accessed April 2020)

AMAP/UNEP, 2008. Technical Background Report to the Global Mercury Assessment. Artic Monitoring and Assessment Programme/UNEP Chemicals Branch (2008). https://www.amap.no/documents/doc/technical-background-report-to-the-global-atmospheric-mercury-assessment-2008/755 (last accessed April 2020)

Arctic Monitoring and Assessment Programme/United Nations Environment Programme, 2013. Technical Background Report for the Global Mercury Assessment. AMAP, Oslo, Norway/UNEP Chemicals Branch, Geneva, Switzerland. https://www.amap.no/documents/doc/technical-background-report-for-the-global-mercury-assessment-2013/848

Bullock, D., Johnson, S., 2011. Electric Generating Utility Mercury Speciation Profiles for Clean Air Mercury Rule, EPA-454/R-11-010. EPA. https://www.regulations.gov/document?D=EPA-HQ-OAR-2009-0234-19910

Eagle Mountain Scientific, Inc., 2008. Results of the Annual Compliance Test Including Speciated Mercury, Prepared for Gerdau Ameristeel, Report #902508.

Goodrich, J. et al., 2016. Exposures of Dental Professionals to Elemental Mercury and Methylmercury, *Expo Sci Environ Epidemiol.,* 26(1), 78-85.

Johnson, N. et al., 2008. Mercury Vapor Release from Broken Compact Fluorescent Lamps and In Situ Capture by New Nanomaterial Sorbents, *Environmental Science & Technology* 42(15), 5772-5778.

Landis, M. et al., 2003. Divalent inorganic reactive gaseous mercury emissions from a mercury cell chlor-alkali plant and its impact on near-field atmospheric dry deposition, *Atmospheric Environment*, 38 (2004), 613–622.

Mari, M. and Domingo, J., 2009. Toxic emissions from crematories: A review, Environment International 36 (2010), 131–137.

Muntean, M. et al., 2018. Evaluating EDGARv4.tox2 speciated mercury emissions ex-post scenarios and their impacts on modelled global and regional wet deposition patterns, *Atmospheric Environment*, 184 (2018), 56-68.

NTH Consultants, Ltd, 2009. Performance Test BOF ESP and BOF Secondary Baghouse Severstal North America, prepared for Michigan Department of Environmental Quality, Project No. 74-080094-08.

Pacyna, E., Pacyna, J., 2002. Global emission of mercury from anthropogenic sources in 1995, *Water Air Soil Pollut*., 137, 149-165. https://doi.org/10.1023/A:1015502430561

Park, K. S. et al., 2008. Emission and speciation of mercury from various combustion sources, *Powder Technol*., 180, 151–156.

Portland Cement Association, 2016. Email from Elizabeth Horner, Portlandtabl Cement Association, to Sharon Nizich and Keith Barnett, OAQPS, U.S. EPA. "Mercury Speciation," Additional Requested Changes to Default Assumptions in Portland Cement RTR Modeling File, October 28, 2016. EPA-HQ-OAR-2016-0442-0116. https://www.regulations.gov/document?D=EPA-HQ-OAR-2016-0442-0116

Robertson, D.E. et al., 1977. Mercury Emissions from Geothermal Power Plants, *Science*, Vol. 196, No. 4294 (Jun. 3, 1977), 1094-1097.

https://doi.org/10.1126/science.860131

Streets, D. et al., 2019. Global and regional trends in mercury emissions and concentrations, 2010–2015. *Atmospheric Environment*, 201 (2019), 417-427.

US EPA, 1997. Mercury Study Report to Congress, Vol. 3, EPA-452/R-97-003. Office of Air Quality Planning and Standards, Office of Research and Development, Washington, DC. (Chapter 4).

US EPA Technical Report EPA/600/R-00/102. 2000. South Florida mercury monitoring and modeling pilot study.

US EPA Technical Report EPA/600/R-02-007a. 2002. Characterization of mercury emissions at a chlor-alkali plant.

US EPA Technical Report EPA-600/R-04/147. 2004. Selective Catalytic Reduction Mercury Field Sampling Project.

US EPA, 2018. Residual Risk Assessment for the Portland Cement Manufacturing Source Category in Support of the 2018 Risk and Technology Review Final Rule, Office of Air Quality Planning and Standards, EPA-HQ-OAR-2016-0442-0222. https://www.regulations.gov/document?D=EPA-HQ-OAR-2016-0442-0222

US EPA Technical Report EPA-420-R-16-016. 2016. Air Toxic Emissions from On-road Vehicles in MOVES2014**.** Office of Transportation and Air Quality.

US EPA Technical Report EPA-420-R-10-011. 2018. Speciation Profiles and Toxic Emission Factors for Nonroad Engines in MOVES2014b. Office of Transportation and Air Quality.

USGS Minerals Yearbook, 2019. Mineral Commodities Summary – Mercury. https://prd-wret.s3-us-west-2.amazonaws.com/assets/palladium/production/atoms/files/mcs-2019-mercu.pdf

Zhang, L. et al., 2015. Updated Emission Inventories for Speciated Atmospheric Mercury from Anthropogenic Sources in China. *Environmental Science & Technology* 49, 3185-3194.

Zhang, L. et al., 2016. Mercury transformation and speciation in flue gases from anthropogenic emission sources: a critical review. *Atmos. Chem. Phys.*, 2417-2433.

Appendix A

The following list includes the speciation codes given to each of the categories used in the EPA's air emissions modeling programs.

Profile Code	Profile Description	Profile (Hg^0, Hg^{2+}, Hg_P)
EGUBIN00	Bituminous Coal, Coal Gasification	0.9102, 0.0847, 0.0051
EGUBIN01	Bituminous Coal, PC Boiler with ESP-CS	0.2570, 0.6820, 0.0611
EGUBIN02	Bituminous Coal and Pet. Coke, PC Boiler with ESP-CS	0.5227, 0.4656, 0.0117
EGUBIN03	Bituminous Coal, PC Boiler with SNCR and ESP-CS	0.5256, 0.2712, 0.2032
EGUBIN04	Bituminous Coal, PC Boiler with ESP-HS	0.3726, 0.5784, 0.0490
EGUBIN05	Bituminous Coal, PC Boiler with PM Scrubber	0.7869, 0.1951, 0.0180
EGUBIN06	Bituminous Coal, PC Boiler with Dry Sorbent Injection and ESP-CS	0.3274, 0.6710, 0.0016
EGUBIN07	Bituminous Coal, PC Boiler with FF Baghouse	0.3344, 0.6258, 0.0398
EGUBIN08	Bituminous Coal, PC Boiler with SDA/FF Baghouse	0.6197, 0.2886, 0.0917
EGUBIN09	Bituminous Coal, PC Boiler with SCR and SDA/FF Baghouse	0.4890, 0.4604, 0.0506
EGUBIN10	Bituminous Coal, PC Boiler with ESP-CS and Wet FGD	0.9200, 0.0778, 0.0022
EGUBIN11	Bituminous Coal, PC Boiler with ESP-HS and Wet FGD	0.7870, 0.2068, 0.0063
EGUBIN12	Bituminous Coal, PC Boiler with FF Baghouse and Wet FGD	0.6052, 0.3300, 0.0648
EGUBIN13	Subbituminous Coal, PC Boiler with ESP-CS	0.6901, 0.3083, 0.0016
EGUBIN14	Subbituminous Coal, PC Boiler with ESP-HS	0.8741, 0.1252, 0.0006
EGUBIN15	Subbituminous Coal, PC Boiler with FF Baghouse	0.1568, 0.8283, 0.0149
EGUBIN16	Subbituminous Coal, PC Boiler with PM Scrubber	0.9344, 0.0511, 0.0145
EGUBIN17	Subbituminous Coal, PC Boiler with SDA/ESP	0.9586, 0.0382, 0.0032
EGUBIN18	Subbituminous Coal, PC Boiler with SDA/FF Baghouse	0.9467, 0.0435, 0.0099
EGUBIN19	Subbituminous Coal, PC Boiler with ESP-CS and Wet FGD	0.9663, 0.0294, 0.0043
EGUBIN20	Subbituminous Coal, PC Boiler with ESP-HS and Wet FGD	0.9437, 0.0446, 0.0117

Profile Code	Profile Description	Profile (Hg^0, Hg^{2+}, Hg_P)
EGUBIN21	Lignite Coal, PC Boiler with ESP-CS	0.9629, 0.0362, 0.0009
EGUBIN22	Subbituminous Coal, Cyclone Boiler with PM Scrubber	0.9191, 0.0575, 0.0234
EGUBIN23	Subbituminous Coal/Pet. Coke, Cyclone Boiler with ESP-HS	0.9155, 0.0752, 0.0093
EGUBIN24	Lignite Coal, Cyclone Boiler with ESP-CS	0.8297, 0.1699, 0.0004
EGUBIN25	Bituminous Coal/Pet. Coke, Fluidized Bed Combustor with SNCR and FF Baghouse	0.2970, 0.2787, 0.4244
EGUBIN26	Not Used at this time	
EGUBIN27	Bituminous Waste, Fluidized Bed Combustor with FF Baghouse	0.5907, 0.3881, 0.0212
EGUBIN28	Lignite Coal, Fluidized Bed Combustor with ESP-CS	0.8700, 0.1164, 0.0137
EGUBIN29	Lignite Coal, Fluidized Bed Combustor with FF Baghouse	0.2840, 0.7118, 0.0042
EGUBIN30	Anthracite Waste, Fluidized Bed Combustor with FF Baghouse	0.5970, 0.3730, 0.0301
EGUBIN31	Bituminous Coal, Stoker Boiler with SDA/FF Baghouse	0.6211, 0.1794, 0.1996
EGUBIN32	Not used at this time	
EGUBIN33	Lignite Coal, PC Boiler with ESP-CS and FF Baghouse	0.3532, 0.6449, 0.0019
EGUBIN34	Lignite Coal, PC Boiler with SDA/FF Baghouse	0.8702, 0.1262, 0.0036
EGUBIN35	Lignite Coal, PC Boiler with PM Scrubber	0.9686, 0.0298, 0.0016
EGUBIN36	Lignite Coal, PC Boiler with ESP-CS and Wet FGD	0.8574, 0.1345, 0.0082
EGUBIN37	Bituminous Coal, Cyclone Boiler with Mechanical Collector	0.3851, 0.4274, 0.1875
EGUBIN38	Bituminous Coal/Pet. Coke, Cyclone with ESP-CS and Wet FGD	0.8863, 0.1130, 0.0007,
EGUBIN39	Lignite Coal, Cyclone Boiler with SDA/FF Baghouse	0.7298, 0.1707, 0.0995
EGUBIN40	Subbituminous Coal, Fluidized Bed Combustor with SNCR and FF Baghouse	0.9632, 0.0342, 0.0027
EGUBIN41	Subbituminous Coal/Bituminous Coal, PC Boiler with ESP-CS	0.5630, 0.4282, 0.0088
EGUBIN42	Subbituminous Coal/Bituminous Coal, PC Boiler with ESP-HS	0.4803, 0.4911, 0.0286

Profile Code	Profile Description	Profile (Hg^0, Hg^{2+}, Hg_P)
EGUBIN43	Bituminous Coal/Pet. Coke, PC Boiler with FF Baghouse	0.1939, 0.7841, 0.0220
EGUBIN44	Bituminous Coal/Subbituminous Coal, PC Boiler with FF Baghouse	0.5195, 0.4210, 0.0595
HGCEM	Portland Cement Kiln Exhaust	0.66, 0.34, 0.0
HGCLI	Cement Clinker Cooler	0.0, 0.0, 1.0
HGCMB	Fuel Combustion	0.50, 0.40, 0.10
HGCRE	Cremation (humans and animals)	0.80, 0.15, 0.05
HGELE	Elemental (dental alloy, reagents, fluorescent lamp breakage, Portland cement raw material handling operations, artisanal scale gold mining)	1.0, 0.0, 0.0
HGGEO	Geothermal power plant (non-binary)	0.87, 0.13, 0.0
HGGLD	Large-scale gold production	0.80, 0.15, 0.05
HGHCL	Chlor-Alkali Plants	0.973, 0.027, 0.0
HGINC	Waste Incineration	0.20, 0.60, 0.20
HGIND	Industrial (average of non-comb. profiles)	0.73, 0.22, 0.05
HGMD	Mobile Diesel	0.56, 0.29, 0.15
HGMET	Metal Production (iron and steel production, non-ferrous metal production)	0.80, 0.15, 0.05
HGMG	Mobile Gasoline	0.915, 0.082, 0.003
HGMWI	Medical Waste Incineration	0.20, 0.60, 0.20
HGPETCOKE	Petroleum Coke Combustion	0.60, 0.30, 0.10