

1 **Five hundred years of anthropogenic mercury: Spatial and temporal release**
2 **profiles**

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37 **May 23, 2019**

38 **1.0 Methodology for Estimating Time-Varying Emission Factors**

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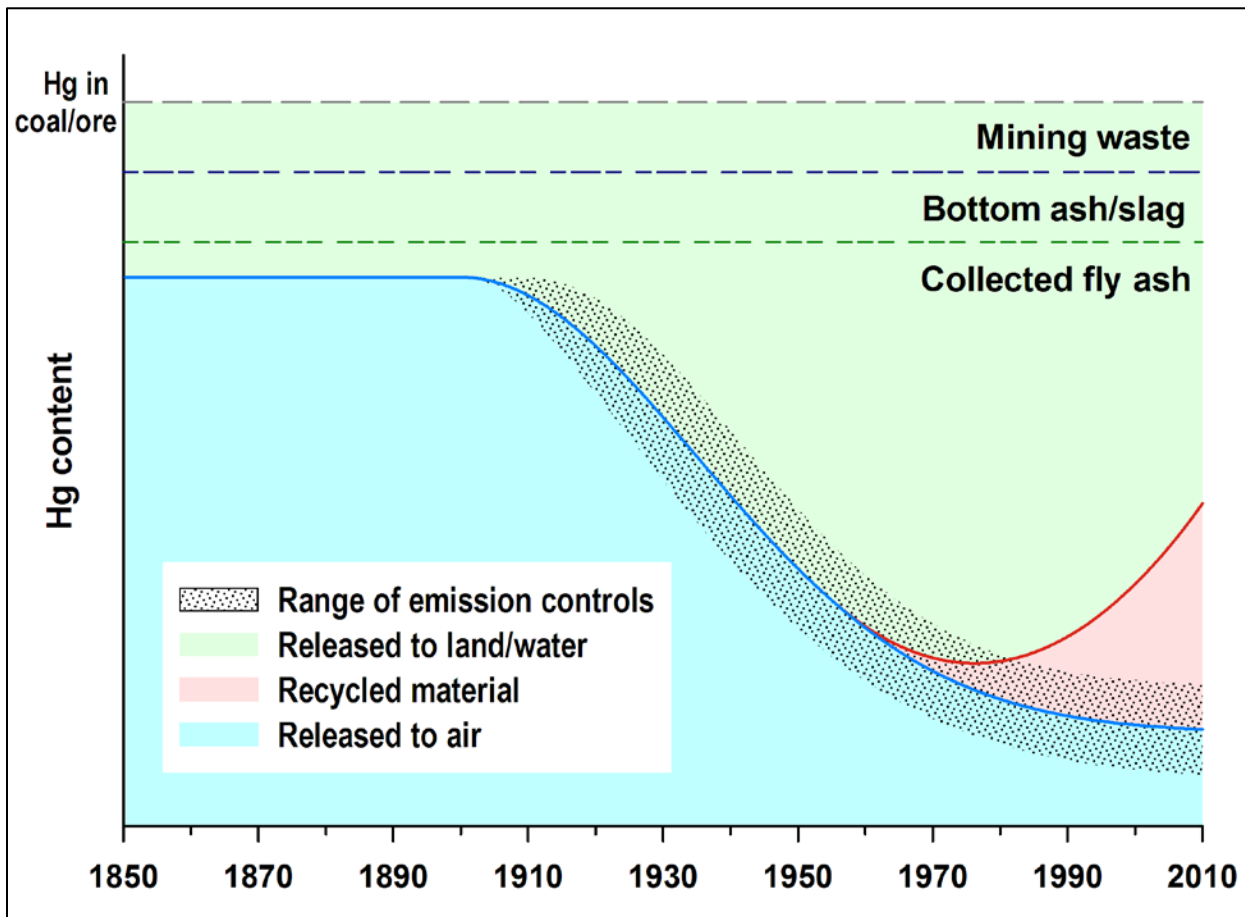
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This section is adapted from previous published documentation [1,2] of the methods used for the determination of sector-specific Hg emission factors over time (shown here from 1850 to the present). Figure 1 presents a conceptual diagram of the methodology used to estimate the time variation of Hg emissions to the environment for source types that involve combustion or metal-extraction techniques. The total Hg that is released in the combustion of a ton of coal or the production of a ton of silver, for example, is constrained by the Hg content of the raw coal or the silver ore. The relationship between these parameters determines an upper bound on the amount of Hg that can have been released in the all-time combustion of coal or the production of silver.



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Figure 1. Conceptual diagram of the methodology used to estimate the time-varying composition of Hg releases to air and land/water per unit of fuel combusted or metal produced, as a function of the Hg content of the raw material (gray dashed line), the increased penetration of emission control technologies and waste treatment systems over time (solid blue line), and the recent trend toward capturing and re-using Hg (solid red line).

54 The partitioning of emissions between air, land, and water is driven largely by the
 55 implementation of emission control technology. Before 1900 there were few attempts to limit air
 56 pollution, and so the release of Hg to the air was at a maximum per unit of activity. As time went
 57 on, there was a transition from old, small-scale, uncontrolled processes to modern, large-scale
 58 industrial processes with emission controls, and therefore the air emissions per unit of coal
 59 combusted or silver produced declined (Figure 1). Consequently, more Hg was released to land
 60 and water. The production of desirable materials has increased continuously, but at the same time
 61 process technology has improved and pollution controls have been adopted, so the resulting level
 62 of Hg releases at any given time is determined by competition between production growth and
 63 technology improvement. The partitioning between air and land/water is similarly determined.

64 We use the following transformed normal distribution function to estimate the change of air
 65 emission factors over time and hence the boundary between air and land/water emissions, as
 66 shown in Figure 1:

$$67 \quad y_{r,p,t} = (a_{r,p} - b_{r,p})e^{(-t^2/2s_{r,p}^2)} + b_{r,p}$$

68 where

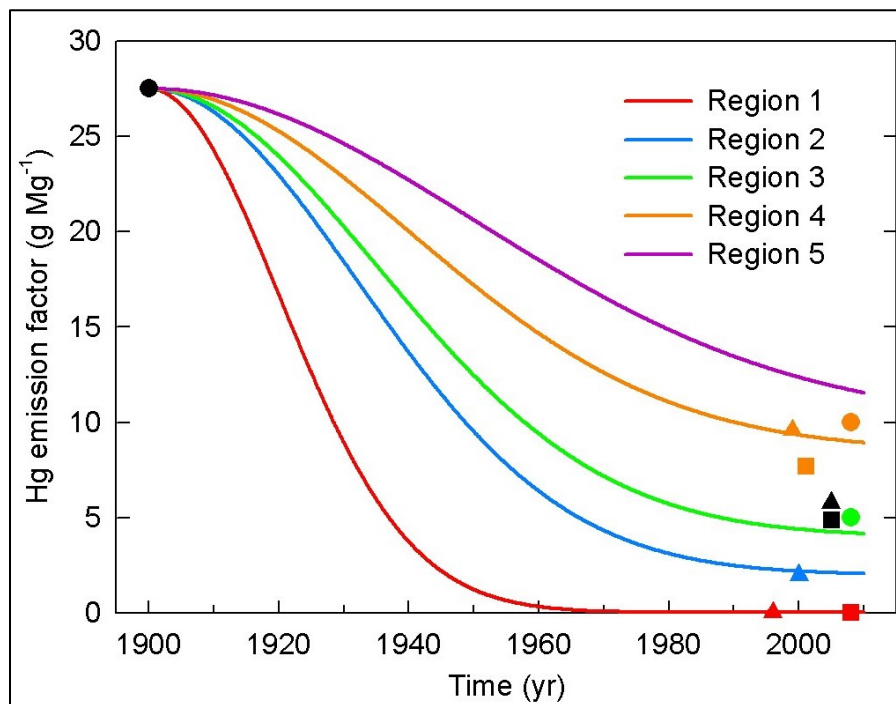
- 69 $y_{r,p,t}$ = air emission factor in region r for process p in year t (g Mg^{-1});
 70 $a_{r,p}$ = pre-1850 emission factor (g Mg^{-1}) in region r for process p ;
 71 $b_{r,p}$ = best emission factor achieved in region r for process p today (g Mg^{-1}); and
 72 $s_{r,p}$ = shape parameter of the curve for region r and process p .

73 The use of such sigmoid curves to simulate the dynamics of technology change has been
 74 previously applied to energy and emission control technology, carbon sequestration, and
 75 automobile technology. By selecting values of the parameters a , b , and s to correspond to the
 76 known or inferred time development pathway of relevant technologies, we can estimate the value
 77 of emission factor y at any point in time t .

78 Figure 1 shows that the Hg not directly released to air is composed of Hg remaining in the
 79 waste left over from the extraction and processing of the raw coal or ore, Hg left in discarded
 80 bottom ash and slag during the combustion/smelting process, and Hg contained in fly ash that is
 81 collected at the facility. Historically, and still today to some extent, these waste products have

82 accumulated at sites contaminated by Hg such as waste piles, storage ponds, and adjacent rivers.
83 In recent years, greater efforts have been taken to secure these wastes in controlled landfills, to
84 recycle the Hg and to re-use the collected wastes (in products such as cement, gypsum, and
85 sulfuric acid), as indicated in Figure 1. The total Hg released to land/water can be calculated by
86 subtraction of the air emissions from the total Hg content of the raw or processed material, by
87 direct calculation of the amount of collected fly ash, or by the ratio of air to land/water releases.

88 Figure 2 illustrates the use of this technique for estimating atmospheric Hg emission factors
89 for copper smelters (the solid blue line in Figure 1). We have divided the world regions into five
90 distinctive types to represent different emission factor trajectories. Each world region is
91 comprised of countries with similar levels of technology development, ranging from most
92 developed (Region 1) to least developed (Region 5). Emission factors for each world region were
93 determined from a review of reported emission rates in representative countries and used to
94 anchor each trajectory [1]. The Supporting Information for Reference 1 presents and documents
95 emission factor ranges for each industrial activity for 1850, 1930, and 2008 and provides
96 citations for the studies used in the development of the emission factor curves.



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98 **Figure 2.** Time development of Hg emission factors for copper smelters in five world regions.
99 Each world region is comprised of countries with similar levels of technology development.

100 **References**

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102 [1] Streets, D.G., Devane, M.K., Lu, Z., Bond, T.C., Sunderland, E.M., Jacob, D.J., 2011. All-
103 time releases of mercury to the atmosphere from human activities. *Environ. Sci. Technol.*
104 **45** 10485–10491

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106 [2] Streets, D.G., Horowitz, H.M., Jacob, D.J., Lu, Z., Levin, L., ter Schure, A.F.H., Sunderland,
107 E.M., 2017. Total mercury released to the environment by human activities. *Environ. Sci.*
108 *Technol.* **51** 5969–5977

109 **2.0 Decadal Mercury Emissions Data by Major Source Regions, 1510–2010**

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(A) 1510–1600

Long-term regional Hg releases (Mg Hg)	1510	1520	1530	1540	1550	1560	1570	1580	1590	1600
North America:										
Air	0.0	0.0	0.4	0.7	1.0	1.3	1.6	1.8	2.1	2.4
Land/Water	0.0	0.0	10.1	20.0	29.9	39.8	49.7	59.6	69.5	79.4
Total Hg	0.0	0.1	10.5	20.7	30.9	41.1	51.2	61.4	71.6	81.8
South America:										
Air	0.0	0.0	1.3	5.1	7.8	42.0	46.1	50.3	54.5	58.9
Land/Water	0.0	0.0	31.7	112.6	182.0	354.7	417.5	480.6	543.9	607.6
Total Hg	0.0	0.0	33.0	117.7	189.8	396.7	463.5	530.9	598.5	666.4
Europe:										
Air	26.9	30.9	35.0	39.4	43.9	44.6	45.3	45.9	44.9	41.6
Land/Water	78.3	87.9	98.2	109.1	120.7	122.4	124.2	125.9	125.1	120.9
Total Hg	105.2	118.8	133.2	148.5	164.6	167.0	169.4	171.8	170.0	162.5
Former USSR:										
Air	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Land/Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Hg	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Africa/Middle East:										
Air	1.5	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.3	1.3
Land/Water	2.2	2.2	2.2	2.1	2.1	2.1	2.1	2.0	2.0	2.0
Total Hg	3.7	3.6	3.6	3.6	3.5	3.5	3.4	3.4	3.3	3.3
Asia:										
Air	5.1	5.5	5.8	6.2	6.6	6.9	7.3	7.7	8.0	9.3
Land/Water	7.7	8.2	8.8	9.3	9.8	10.4	10.9	11.5	12.0	13.9
Total Hg	12.8	13.7	14.6	15.5	16.4	17.3	18.2	19.1	20.0	23.1
Oceania:										
Air	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Land/Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Hg	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Global:										
Air	33.5	37.9	44.1	52.8	60.7	96.2	101.6	107.1	110.9	113.4
Land/Water	88.2	98.4	150.9	253.1	344.5	529.4	604.3	679.5	752.5	823.7
Total Hg	121.7	136.3	195.0	305.9	405.2	625.6	705.9	786.6	863.4	937.1

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(B) 1610–1700

Long-term regional Hg releases (Mg Hg)	1610	1620	1630	1640	1650	1660	1670	1680	1690	1700
North America:										
Air	3.1	3.1	3.3	3.3	3.6	3.6	3.9	3.9	4.2	4.2
Land/Water	102.9	102.9	111.7	111.7	120.6	120.7	129.4	129.4	139.6	139.7
Total Hg	105.9	106.0	115.0	115.1	124.2	124.3	133.2	133.2	143.8	143.8
South America:										
Air	58.4	58.0	57.7	57.3	56.9	55.8	54.8	53.7	52.7	51.7
Land/Water	579.8	552.0	524.3	496.6	469.0	438.8	408.6	378.5	348.5	318.5
Total Hg	638.2	610.1	582.0	553.9	525.9	494.6	463.4	432.2	401.2	370.2
Europe:										
Air	44.3	48.5	58.3	70.2	75.0	62.0	52.9	45.4	39.1	33.9
Land/Water	137.9	159.9	193.9	235.2	251.6	205.6	173.3	146.4	124.0	105.4
Total Hg	182.2	208.4	252.2	305.4	326.7	267.6	226.2	191.8	163.1	139.3
Former USSR:										
Air	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Land/Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Hg	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Africa/Middle East:										
Air	1.2	1.2	1.1	1.0	1.0	0.9	0.8	0.8	0.7	0.7
Land/Water	1.9	1.8	1.7	1.6	1.5	1.4	1.2	1.1	1.1	1.1
Total Hg	3.1	2.9	2.8	2.6	2.4	2.3	2.1	1.9	1.9	1.8
Asia:										
Air	10.5	11.8	13.0	14.3	15.5	16.8	18.0	19.3	20.5	21.7
Land/Water	15.7	17.6	19.5	21.4	23.2	25.1	27.0	28.8	30.7	32.6
Total Hg	26.3	29.4	32.5	35.6	38.7	41.9	45.0	48.1	51.2	54.3
Oceania:										
Air	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Land/Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Hg	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Global:										
Air	117.6	122.6	133.4	146.2	152.0	139.1	130.4	122.9	117.2	112.3
Land/Water	838.2	834.2	851.0	866.4	865.9	791.5	739.5	684.3	644.0	597.2
Total Hg	955.8	956.8	984.5	1012.6	1018.0	930.6	869.9	807.2	761.2	709.5

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(C) 1710–1800

Long-term regional Hg releases (Mg Hg)	1710	1720	1730	1740	1750	1760	1770	1780	1790	1800
North America:										
Air	6.1	6.2	8.6	8.7	11.3	11.3	13.7	13.8	20.9	20.9
Land/Water	207.5	207.5	292.3	292.4	381.3	381.3	464.1	464.1	712.1	712.2
Total Hg	213.6	213.7	300.9	301.0	392.5	392.6	477.8	477.9	732.9	733.1
South America:										
Air	49.7	48.0	46.5	45.2	44.2	48.6	53.3	58.4	63.8	56.7
Land/Water	324.4	331.4	339.2	347.9	357.3	385.7	415.1	445.8	477.8	466.0
Total Hg	374.1	379.3	385.7	393.1	401.5	434.3	468.5	504.2	541.6	522.7
Europe:										
Air	44.8	59.1	77.7	102.4	135.1	152.2	171.1	192.3	214.1	218.9
Land/Water	140.6	187.3	249.5	332.6	443.8	499.7	562.5	632.9	709.2	725.3
Total Hg	185.4	246.4	327.3	435.0	579.0	651.9	733.6	825.2	923.3	944.2
Former USSR:										
Air	0.6	1.2	1.9	2.6	2.9	3.2	3.5	3.9	4.2	4.5
Land/Water	0.9	1.9	2.9	3.9	4.3	4.8	5.3	5.7	6.2	6.7
Total Hg	1.4	3.1	4.8	6.4	7.2	8.0	8.8	9.6	10.4	11.2
Africa/Middle East:										
Air	0.7	0.7	0.7	0.7	0.6	0.6	0.6	0.6	0.6	0.6
Land/Water	1.1	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9	0.9
Total Hg	1.8	1.7	1.7	1.7	1.6	1.6	1.6	1.6	1.6	1.6
Asia:										
Air	0.8	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.9	0.9
Land/Water	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.3	1.3	1.3
Total Hg	2.0	2.0	2.0	2.0	2.1	2.1	2.1	2.2	2.2	2.2
Oceania:										
Air	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Land/Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Hg	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Global:										
Air	102.8	116.0	136.3	160.4	195.0	216.8	243.2	269.8	304.5	302.6
Land/Water	675.6	730.3	886.0	978.9	1188.9	1273.7	1449.1	1550.8	1907.6	1912.3
Total Hg	778.4	846.3	1022.3	1139.3	1383.9	1490.5	1692.4	1820.6	2212.1	2215.0

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(D) 1810–1900

Long-term regional Hg releases (Mg Hg)	1810	1820	1830	1840	1850	1860	1870	1880	1890	1900
North America:										
Air	21.4	12.9	11.5	14.6	87.8	121.2	495.5	976.0	1374.2	1052.8
Land/Water	703.0	398.2	339.4	424.0	304.1	456.6	2336.4	3139.5	2414.8	2008.6
Total Hg	724.5	411.1	350.9	438.6	391.9	577.9	2831.9	4115.5	3789.0	3061.3
South America:										
Air	27.2	17.3	10.5	12.0	11.2	11.8	12.2	30.9	31.7	49.3
Land/Water	355.3	314.5	292.7	276.1	301.5	302.2	311.3	659.2	709.4	1048.8
Total Hg	382.5	331.7	303.2	288.0	312.6	314.1	323.5	690.0	741.0	1098.2
Europe:										
Air	207.7	199.1	196.9	226.0	260.8	316.5	411.6	631.1	749.6	605.9
Land/Water	676.1	632.9	595.8	654.3	714.4	795.0	991.6	1593.8	1997.0	1476.5
Total Hg	883.8	831.9	792.7	880.3	975.2	1111.6	1403.2	2224.9	2746.5	2082.4
Former USSR:										
Air	6.7	8.0	9.8	15.7	21.7	22.1	27.1	30.5	86.2	88.3
Land/Water	9.8	11.6	14.3	23.0	32.0	32.9	40.2	44.9	234.7	239.5
Total Hg	16.6	19.6	24.1	38.7	53.7	55.0	67.3	75.4	320.9	327.8
Africa/Middle East:										
Air	0.6	0.5	0.3	1.2	0.1	0.2	0.7	2.7	16.7	22.9
Land/Water	1.0	0.7	0.5	0.5	0.2	0.4	1.3	3.9	24.8	33.2
Total Hg	1.6	1.2	0.8	1.7	0.2	0.6	2.0	6.6	41.5	56.1
Asia:										
Air	1.4	2.3	6.3	12.0	1.3	2.7	5.0	23.9	42.0	72.7
Land/Water	1.5	2.5	3.4	4.3	2.4	5.2	9.9	36.6	63.2	104.3
Total Hg	3.0	4.8	9.7	16.3	3.7	7.9	14.8	60.5	105.2	177.0
Oceania:										
Air	0.0	0.0	0.0	0.0	5.2	39.8	33.6	26.7	159.6	278.3
Land/Water	0.0	0.0	0.0	0.0	7.7	59.4	50.0	39.6	236.3	410.5
Total Hg	0.0	0.0	0.0	0.0	12.9	99.2	83.5	66.4	395.9	688.7
Global:										
Air	265.1	240.0	235.2	281.5	388.1	514.5	985.6	1721.8	2460.0	2170.2
Land/Water	1746.8	1360.3	1246.0	1382.2	1362.3	1651.8	3740.7	5517.6	5680.2	5321.4
Total Hg	2011.9	1600.3	1481.3	1663.7	1750.4	2166.3	4726.3	7239.4	8140.2	7491.5

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(E) 1910–2010

Long-term regional Hg releases (Mg Hg)	1910	1920	1930	1940	1950	1960	1970	1980	1990	2000	2010
North America:											
Air	632.3	381.1	400.0	447.8	371.3	502.8	782.2	492.4	324.2	172.8	109.3
Land/Water	1201.5	724.0	955.0	1415.9	1050.0	1313.1	1805.5	2092.2	1776.2	1247.3	1033.7
Total Hg	1833.8	1105.1	1354.9	1863.7	1421.4	1815.9	2587.7	2584.6	2100.4	1420.1	1143.0
South America:											
Air	223.1	132.3	97.6	113.4	58.6	104.1	62.4	74.2	154.6	239.0	263.6
Land/Water	333.0	201.7	162.9	240.8	123.9	230.1	203.4	233.9	536.2	769.3	843.1
Total Hg	556.1	334.0	260.4	354.2	182.5	334.2	265.8	308.1	690.8	1008.4	1106.7
Europe:											
Air	691.1	396.1	430.4	614.8	318.3	559.0	1036.6	508.7	309.8	155.3	85.7
Land/Water	1677.2	909.5	915.6	1489.7	723.2	1188.8	2126.0	1959.6	1864.9	895.3	597.6
Total Hg	2368.3	1305.6	1345.9	2104.5	1041.5	1747.8	3162.5	2468.3	2174.7	1050.6	683.3
Former USSR:											
Air	63.6	36.6	90.7	197.1	194.3	252.9	198.4	213.0	188.5	114.9	86.5
Land/Water	101.1	70.6	216.0	452.6	485.8	584.0	551.3	646.5	799.0	520.3	427.1
Total Hg	164.8	107.2	306.8	649.7	680.1	836.8	749.7	859.5	987.5	635.2	513.6
Africa/Middle East:											
Air	220.6	212.1	252.5	349.1	243.6	374.3	413.1	368.1	371.8	365.3	383.2
Land/Water	336.7	345.3	465.9	728.2	547.6	962.4	1344.1	1265.6	1300.7	1083.9	887.4
Total Hg	557.3	557.4	718.3	1077.3	791.1	1336.7	1757.1	1633.7	1672.5	1449.2	1270.6
Asia:											
Air	137.2	169.6	219.6	435.5	130.6	624.1	516.5	314.5	585.2	886.9	1255.5
Land/Water	208.5	308.2	477.4	1102.6	292.7	1778.0	1757.1	831.5	1623.2	2217.2	3170.6
Total Hg	345.7	477.8	697.0	1538.1	423.2	2402.1	2273.6	1146.0	2208.4	3104.1	4426.1
Oceania:											
Air	210.1	28.1	23.7	28.7	12.9	13.3	15.3	11.7	26.4	28.5	25.6
Land/Water	308.2	42.6	31.8	63.5	37.4	51.1	61.3	76.0	298.5	397.4	372.0
Total Hg	518.2	70.7	55.5	92.2	50.3	64.4	76.6	87.7	325.0	425.9	397.6
Global:											
Air	2178.0	1355.9	1514.4	2186.4	1329.6	2430.4	3024.4	1982.6	1960.6	1962.7	2209.4
Land/Water	4166.2	2601.9	3224.5	5493.2	3260.6	6107.5	7848.7	7105.4	8198.7	7130.8	7331.4
Total Hg	6344.2	3957.7	4738.9	7679.6	4590.2	8538.0	10873.1	9088.0	10159.3	9093.6	9540.9

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