Biogeochemistry (2007) 85:119–123
DOI 10.1007/s10533-007-9108-0

ORIGINAL PAPER

Atmospheric mercury pollution due to losses of terrestrial carbon pools?

Daniel Obrist

Received: 14 August 2006 / Accepted: 17 January 2007 / Published online: 14 March 2007

Abstract Plants accumulate significant amounts of atmospheric mercury (Hg) in aboveground biomass, likely sequestering over 1,000 Mg of atmospheric Hg every year. This large mercury uptake could be strong enough to affect tropospheric Hg levels and might be partially responsible for seasonal variations in atmospheric Hg observed at Mace Head, Ireland. The fluctuations of Hg concentrations coincide temporally with the annual oscillation of carbon dioxide (CO_2) in the Northern Hemisphere, which is a result of seasonal growth of vegetation. Therefore, declining Hg concentrations in spring and summer may be attributed in part to plant uptake of atmospheric Hg. Further, the increase of Hg concentrations during non-active vegetation periods might partially be due to plant-derived Hg emitting back to the atmosphere during carbon mineralization. The implications of these propositions are that past and future changes in biomass productivity and organic carbon pools may have had—and may continue to have—significant effects on atmospheric Hg levels. Specifically, large losses in soil and biomass carbon pools in the last 150 years could have contributed significantly to observed increases in atmospheric Hg pollution. The roles of vegetation and terrestrial carbon pools should receive detailed consideration on how they might attenuate or exacerbate atmospheric Hg pollution.

Keywords Atmospheric mercury · Plant mercury uptake · Carbon mineralization · Mercury sequestration · Seasonality

D. Obrist (✉)
Division of Atmospheric Sciences, Desert Research Institute, Reno, NV 89512, USA
e-mail: daniel.obrist@dri.edu

Introduction

Atmospheric mercury (Hg) pollution in the last 150 years has greatly increased Hg deposition to terrestrial and aquatic ecosystems (e.g., Biester et al. 2003; Fitzgerald et al. 1998; Schuster et al. 2002). The cycling of Hg through terrestrial ecosystems includes a complex and not fully understood suite of deposition, emission, and re-emission processes of various atmospheric Hg species (e.g., Grigal 2002; Gustin et al. 2006). One important aspect is that above-ground plant biomass accumulates substantial amounts of Hg through the growing season, with reported mid-point concentrations in plant foliage of 24 μg kg^{-1} (Grigal 2002) and lower concentrations observed in woody tissues (e.g., averaging 6 μg kg^{-1}; Fleck et al. 1999; Grigal et al. 2000; Moore et al. 1995; Pang 1997; Zhang et al. 1995a, b). There is strong evidence that Hg allocated in above-ground plant compartments is of atmospheric origin while root

Hg originates mainly from soil uptake. The evidence is based on (1) limited translocation of Hg from roots to other plant compartments (Beauford et al. 1977; Godbold and Hüttermann 1988; Lindberg et al. 1979), (2) the known ability of plants to assimilate airborne Hg by stomatal uptake (Hanson et al. 1995), (3) limited xylem Hg transport (Bishop et al. 1998), (4) measured net deposition of elemental gaseous Hg to vegetated surfaces (Obrist et al. 2006), and (5) combined air/soil exposure experiments where above-ground plant Hg levels are generally a function of atmospheric Hg levels independent of soil Hg exposures (Ericksen et al. 2003; Frescholz et al. 2003; Milhollen et al. 2006a, b). Above-ground plant Hg uptake thus represents an important pathway for atmospheric Hg deposition to terrestrial ecosystems via litterfall and plant senescence (e.g., Lindberg et al. 1996; Munthe et al. 1995). Similarly, the decomposition of Hg-laden plant litter in the soil represents a potential pathway for Hg to return to the atmosphere. These two processes have not received adequate consideration in the discussion of how they may affect atmospheric Hg levels and pollution.

Results and Discussion

Globally, net primary production on land is estimated at 60 Pg of carbon per year, of which roughly half is allocated to aboveground plant compartments (Saugier et al. 2001). Based on reported plant Hg concentrations, global above-ground biomass production likely accounts for over 1,000 Mg of atmospheric Hg uptake per year (Table 1). This is a substantial part of the total atmospheric Hg burden of 5,000 Mg (Mason et al. 1994)—or of the 2500 Mg estimated to reside in the lower 5 km of the troposphere (Banic et al. 2003). Figure 1a shows seasonal patterns of published long-term atmospheric records of total gaseous Hg (TGM) and carbon dioxide (CO_2) at Mace Head, Ireland from September 1995 to November 2001 (Ebinghaus et al. 2002; Tans and Conway 2005). In the Northern Hemisphere the concentration of atmospheric CO_2 increases in winter and declines in summer as a result of seasonal growth of vegetation (Hall et al. 1975), an oscillation which is well noticeable at this remote station exposed to air masses from the North Atlantic Ocean. A corresponding oscillation occurs with atmospheric Hg, which is lowest at the end of the growing season in September, and 20% higher at the start of the northern vegetation growth period in March. The observed annual atmospheric Hg oscillation has been explained with the occurrence of higher levels of atmospheric oxidants in summer leading to removal of atmospheric pollutants and by higher fossil fuel burning during the winter months (Slemr and Scheel 1998). I propose that the observed decline in atmospheric Hg with the onset of the growing season in the Northern Hemisphere may be partially attributed to plant Hg uptake. The slope between atmospheric Hg and CO_2 (0.02 ng Hg m^{-3} per 1 ppmv change in CO_2) corresponds to 20 μg Hg kg^{-1} biomass, a value close to commonly reported plant Hg concentrations. Similar seasonal variations have

Table 1 Estimation of global annual plant Hg uptake from the atmosphere based on published tissue mercury concentration (see text) and net primary productivity (NPP) data from Saugier et al. (2001)

Annual global NPP (Pg C/yr)	60			
Annual biomass production (=NPP × 2; Pg/yr)	120			
	50% forests/shrublands		50% grasslands/others	
	60		60	
Annual above-ground biomass production (Pg/yr)	55% of 60: 33		45% of 60: 27	
	30% leaves	70% wood	100% leaves	0% wood
	9.9	23.1	27	–
Tissue Hg concentration (ppb)	24	6	24	–
Annual atmospheric Hg uptake (Mg Hg/yr)	237.6	138.6	648.0	–
Sum	1024.2			

Conversion of NPP to annual biomass production is based on 50% (w/w dry mass) carbon content in biomass

been observed in other stations in the Northern Hemisphere (Banic et al. 2003). Seasonal patterns of Hg are weak and reversed (Slemr et al. 2006)—or completely absent (Baker et al. 2003)—in the Southern Hemisphere where a smaller land mass also causes only minor CO_2 oscillations (Steele et al. 2002; Fig. 1B).

The increase in Hg during winter months in the Northern Hemisphere may be due to anthropogenic and natural Hg emissions exceeding deposition processes. However, consideration should also be given to the possibility of Hg emissions to the atmosphere due to organic carbon mineralization. Recent experimental field and laboratory studies in fact show that Hg emissions correlate with soil respiration rates in terrestrial soils, with increased soil respiration leading to increased Hg emissions (Fritsche et al. 2006, 2007; Wickland et al. 2006). A lack of plant activity in the dormant season along with Hg losses associated with carbon mineralization may impede the potential of ecosystem to sequester other emission sources resulting in higher atmospheric mercury concentrations. It is important to consider the possibility of re-emissions of atmospherically derived biomass Hg when estimating biological impacts on atmospheric Hg cycling. For example, 121 Pg of biomass and soil carbon was lost to the atmosphere during the last 150 years due to climate and land use changes (Prentice et al. 2001). If all Hg associated with this carbon pool was emitted to the atmosphere, this would have contributed more than 2,000 Mg of Hg to the atmosphere. The notion of Hg losses from biomass burning has received considerable attention before (e.g., Artaxo et al. 2000; Friedli et al. 2001; Veiga et al. 1994), including potential consequences of global-change induced alterations in the occurrence of wildfires (Turetsky et al. 2006). However, detailed study of the role of vegetation and of the fate of plant litter and soil carbon related Hg during mineralization processes is needed in light of the changes in terrestrial carbon pools that are expected to occur as a result of global environmental change. Ultimately, the size of the biomass Hg pump and the degree of Hg re-emissions during carbon losses will determine the capacity of terrestrial ecosystems to attenuate—or to exacerbate—atmospheric Hg pollution.

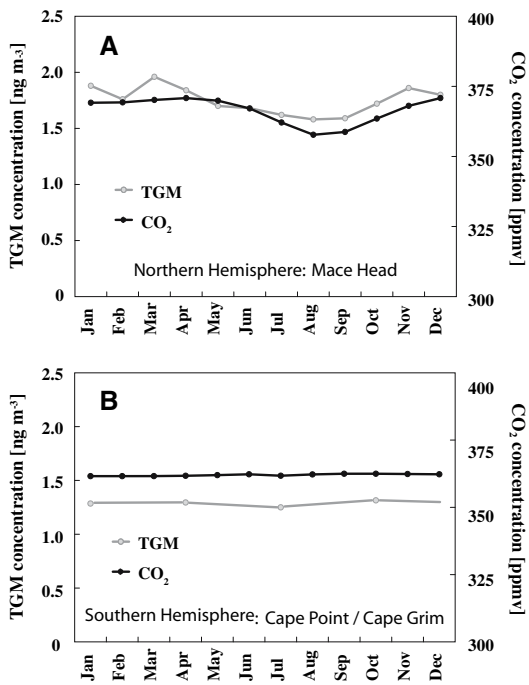

Fig. 1 (**A**) Northern hemispheric seasonal variation of total gaseous mercury (TGM) and carbon dioxide (CO_2) concentrations between September 1995 and December 2001 measured at Mace Head, Ireland (53°20′ N). Data on TGM are from Ebinghaus et al. *(2002)*. CO_2 data are from Tans and Conway *(2005)*. (**B**) TGM and CO_2 concentrations between September 1995 and June 1999 in the Southern Hemisphere. TGM data are from Baker et al. (2003) measured at Cape Point, South Africa (34°21' S) and were lumped by the authors into four seasons (Mar–May; Jun–Aug, Sep–Nov, Dec–Feb). No published data are available for CO_2 at Cape Point so CO_2 data are from Steele et al. (2002) measured at Cape Grim, Australia (40°41′ S)

Acknowledgements I would like to thank Jay Arnone, Harald Biester, Christophe Ferrari, Dale Johnson, Hans Moosmüller, and two anonymous reviewers for valuable inputs and editorial comments to this manuscript. This research was in part supported by the National Science Foundation (ATM 0632780) and by the Desert Research Institute.

References

Artaxo P, Calixto de Campos R, Fernandes ET et al (2000) Large scale mercury and trace element measurements in the Amazon basin. Atmos Environ 34:4085–4096

Baker PGL, Brunke E-G, Slemr F et al (2003) Atmospheric mercury measurements at Cape Point, South Africa. Atmos Environ 36:2459–2465

Banic CM, Beauchamp ST, Tordon RJ et al (2003) Vertical distribution of gaseous elemental mercury in Canada. J Geophys Res 108(D9): 4264

Beauford W, Barber J, Barringer AR (1977) Uptake and distribution of mercury within higher plants. Physiol Plant 39:261–265

Biester H, Martinez-Cortizas A, Birkenstock S et al (2003) Effect of peat decomposition and mass loss on historic mercury records in peat bogs from Patagonia. Environ Sci Technol 37:32–39

Bishop KH, Lee Y-H, Munthe J et al (1998) Xylem sap as a pathway for total mercury and methylmercury transport form soil to tree canopy in the boreal forest. Biogeochem 40:101–113

Ebinghaus R, Kock HH, Coggins AM et al (2002) Long-term measurements of atmospheric mercury at Mace Head, Irish west coast, between 1995 and 2001. Atmos Environ 36:5267–5276

Ericksen JA, Gustin MS, Schorran DE et al (2003) Accumulation of atmospheric mercury in forest foliage. Atmos Environ 37:1613–1622

Fitzgerald WF, Engstrom DR, Mason RP et al (1998) The case for atmospheric mercury contamination in remote areas. Environ Sci Technol 32:1–7

Fleck JA, Grigal DF, Nater EA (1999) Mercury uptake by trees: and observational experiment. Water Air Soil Poll 115:513–523

Frescholtz TF, Gustin MS, Schorran DE et al (2003) Assessing the source of mercury in foliar tissue of quaking aspen. Environ Toxicol Chem 22:2114–2119

Friedli HR, Radke LF, Lu JY (2001) Mercury in smoke from biomass fires. Geophys Res Let 28(17):3223–3226

Fritsche J, Obrist D, Alewell C (2006) Effects of microbiological activity on Hg^0 emission in uncontaminated terrestrial soils. In: Abstracts of the 8th international conference on mercury as a global pollutant, Madison, USA, August 6–11 2006

Fritsche J, Obrist D, Alewell C (2007) Evidence of microbial control of Hg^0 emissions from uncontaminated terrestrial soils. J Plant Nutr Soil Sci (in press)

Godbold D, Hüttermann A (1988) Inhibition of photosynthesis and transpiration in relation to mercury-induced root damage in spruce seedlings. Physiol Plant 74:270–275

Grigal DF (2002) Inputs and outputs of mercury from terrestrial watersheds: a review. Environ Rev 10:1–39

Grigal DF, Kolka RK, Fleck JA et al (2000) Mercury budget of an upland-peatland watershed. Biogeochem 50:95–109

Gustin MS, Marsik F, Obrist D (2006) Air-surface exchange of mercury in terrestrial ecosystems. In: Abstracts of the 8th international conference on mercury as a global pollutant, Madison, USA, August 6–11 2006

Hall CAS, Ekdahl CA, Wartenberg DE (1975) A fifteen-year record of biotic metabolism in the Northern Hemisphere. Nature 255:136–138

Hanson PJ, Lindberg SE, Tabberer TA, Owens JG, Kim K-H (1995) Foliar exchange of mercury vapor: evidence for a compensation point. Water Air Soil Poll 80:373–382

Lindberg SE (1996) Forests and the global biogeochemical cycle of mercury: The importance of understanding air/vegetation exchange processes. In: Baeyens W, Ebinghaus R, Vasiliev O (eds) Global and regional mercury cycles: Sources, fluxes and mass balances. NATOASISeries, vol 21. Kluwer Academic Publishers, Dordrecht, pp 359–380

Lindberg SE, Jackson DR, Huckabee JW et al (1979) Atmospheric emissions and plant uptake of mercury from agricultural soils near the Almaden mercury mine. J Environ Qual 8:572–578

Mason RP, Fitzgerald WF, Morel FMM (1994) The biogeochemical cycling of elemental mercury: Anthropogenic influences. Geochim Cosm Acta 58:3191–3198

Milhollen AG, Gustin MS, Obrist D (2006a) Foliar mercury accumulation and exchange for three tree species. Environ Sci Technol 40:6001–6006

Milhollen AG, Obrist D, Gustin MS (2006b) Mercury accumulation in grass and forb species as a function of atmospheric carbon dioxide concentrations and mercury. Chemosphere 65:889–897

Munthe J, Hultberg H, Iverfeldt A (1995) Mechanisms of deposition of methylmercury and mercury to coniferous forests. Water Air Soil Poll 80:363–371

Obrist D, Conen F, Vogt R et al (2006) Quantification of elemental Hg^0 exchange using $^{222}Rn/Hg^0$ accumulation in the stable nocturnal boundary layer. Atmos Environ 40:856–866

Pang SM (1997) Mercury in wood and wood fuels. Thesis, University of Minnesota, Minneapolis, MN

Prentice IC, Farquhar GD, Fasham MJR et al (2001) The carbon cycle and atmospheric carbon dioxide. In: Climate change 2001: The scientific basis. Contribution of working group I to the third assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge

Saugier BS, Roy J, Mooney HA (2001) Estimations of global terrestrial productivity: converging toward a single number? In: Roy J, Saugier B, Mooney HA (eds) Terrestrial global productivity. Academic Press, San Diego, pp 543–557

Schuster PF, Krabbenhoft DP, Naftz DL et al (2002) Atmospheric mercury deposition during the last 270 years: A glacial ice core record of natural and anthropogenic sources. Environ Sci Technol 36:2303–2310

Slemr F, Brunke E, Labuschagne C (2006) Long-term observations of total gaseous mercury at the Cape Point GAW Station, South Africa. In: Abstracts of the 8th international conference on mercury as a global pollutant, Madison, August 6–11 2006

Slemr F, Scheel HE (1998) Trends in atmospheric mercury concentrations at the summit of the Wank mountain, Southern Germany. Atmos Environ 32:845–853

Steele LP, Krummel PB, Langenfelds RL (2002) In Trends: A compendium of data on global change. Carbon dioxide information analysis center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge

Tans PP, Conway TJ (2005) In Trends: A compendium of data on global change. Carbon dioxide information analysis center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge

Turetsky MR, Harden JW, Friedli HR et al (2006) Wildfires threaten mercury stocks in northern soils. Geophys Res Let 33:L16403

Veiga MM, Meech JA, Onate N (1994) Mercury pollution from deforestation. Nature 368:816–817

Wickland K, Krabbenhoft D, Olund S (2006) Evidence for a link between soil respiration and mercury emission from organic soils. In: Abstracts of the 8th international conference on mercury as a global pollutant, Madison, August 6–11 2006

Zhang L, Qian J, Planas D (1995a) Mercury concentrations in tree rings of black spruce (Picea mariana Mill. B.S.P) in boreal Quebec, Canada. Water Air Soil Poll 81:163–173

Zhang L, Planas D, Qian J (1995b) Mercury concentrations in black spruce (Picea mariana B.S.P) and lichens in boreal Quebec, Canada. Water Air Soil Poll 81:153–161