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Comparison of mercury in atmospheric deposition and in Illinois and USA soils

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Abstract

It has been reported that most mercury (Hg) in USA soils is from atmospheric Hg deposition, mostly from anthropogenic sources. This paper compares the rates of atmospheric Hg deposition to amounts of Hg in Illinois and USA soils. The amounts of Hg in these soils are too great to be attributed mainly to anthropogenic atmospheric Hg deposition.

Keywords: mercury, atmospheric deposition, soil, geology, Illinois, USA

Introduction

The presumption that the amounts of mercury (Hg) in the environment are naturally low and environmentally insignificant (Borg *et al*., 1966; Harriss *et al*., 1970; Ackefors, 1971; Gardner, 1978; Johansson *et al.,* 1991; U.S. Geological Survey, 2000) has influenced scientific and public perception about the amount and influence of human activities on Hg in the environment. The finding of widespread environmentally significant amounts of Hg in landscapes (even those far removed from human activities) leads to the conclusion that atmospheric deposition of anthropogenic Hg has increased Hg to environmentally significant levels (Travis and Hester, 1991; Lindqvist, 1991; U.S. Environmental Protection Agency, 1997; Wheatley and Wyzga, 1997; Iyengar and Nair, 2000; Pilgrim *et al*., 2000a,b; Lee *et al*., 2001; United Nations Environment Programme, 2002; Meili *et al*., 2003; Watanabe *et al*., 2003).

For the North American mid-continent, Swain *et al*. (1992), assuming no geological sources of Hg in the landscape and no mobilisation of Hg in aquatic sediments (Hg remains fixed in sediment at time of deposition), estimated that anthropogenic activities have increased atmospheric Hg deposition from a background deposition rate of 37 mg ha^{-1} yr^{-1} in 1850 to 125 mg ha^{-1} yr^{-1}; most of this increase occurred after 1920. Meili (1995) reduced the background estimate to 20 mg Hg ha^{-1} yr^{-1} but subsequently, the U.S. Environmental Protection Agency (USEPA, 1997, p. 5–29) announced that the mean background atmospheric Hg deposition level for mid-continental North America may be even lower than Meili's revised estimate because Hg pollution of the atmosphere began before 1850. Also, Hg in Illinois and USA soils comes mainly from atmospheric deposition (USEPA, 1997, p. 5-33, 6-2; U.S. Geological Survey, 2000; Dreher *et al*., 2003b).

States in mid-continental North America have issued mercury advisories. For example, the Illinois Department of Public Health (2003), in its statewide advisory about high Hg levels in fish, states that Hg exists naturally in the environment in small amounts. The Wisconsin Department of Natural Resources (2001) considers Hg in the environment to be primarily of human origin. Although studies of Hg loading to rivers draining the upper Mississippi River drainage basin and other USA rivers show that the primary sources of Hg are from eroded soil and terrestrial plant materials, the unexamined assumption is that Hg associated with these materials is substantially anthropogenic (Balogh *et al*., 1998; 2003; Hurley *et al*., 1998). Mercury associated with sediments carried by the Mississippi River are reported to be primarily responsible for Hg fisheries advisories in the lower Mississippi River.

For the USA, 520,000 river kilometres are reported to be under fish and wildlife advisories (Watanabe *et al*., 2003).

This paper briefly examines the hypothesis that Hg in Illinois and USA soils is predominantly of anthropogenic atmospheric origin.

Methods

The approach used to test the hypothesis about the anthropogenic source of soil Hg is to compare rates of atmospheric Hg deposition with soil and Earth crust Hg content, assuming soil retention of all deposited Hg. The Hg content of Illinois soils (Table 1) was calculated using soil data sampled by the Illinois State Geological Survey (ISGS) at 51 soil sites in 45 counties covering the southern third of Illinois (Dreher *et al*., 2002, 2003a,b). These ISGS data are exceptional in that soils were sampled intensively in a relatively tight grid (32 km) at multiple depths throughout the soil profiles (Table 1). Topsoil was defined as the uppermost soil horizon sampled except for soil sites 12, 18, and 19 where topsoil soils depths of 24.4, 24.4, and 18.3 cm were used, respectively. Topsoil Hg content (g ha^{-1}) was determined by multiplying the ISGS Hg concentration data by topsoil depth by topsoil bulk density (assumed to be 1.3 g cm^{-3}). Total soil depth was defined as the depth of soil sampled except for soil site 29 where depth was assumed to be the top of the bottom-most layer sampled, 366 cm. Total soil Hg content was determined by multiplying ISGS whole soil arithmetic mean Hg concentration values by total soil depth by bulk density, assumed to be 1.5 g cm^{-3} below the topsoil.

The Hg concentration of USA soils used is the average reported for the 1318 samples taken by the U.S. Geological Survey's 80-km grid of the conterminous USA and sampled to a depth of about 20 cm (Shacklette and Boerngen, 1984). The quantity of Hg in average USA soil was calculated, assuming a soil depth of 20 cm and a bulk density of 1.3 g cm^{-3}. Average world soil Hg concentration used was that reported by Andren and Nriagu (1979). Average soil content of 1,434 g Hg ha^{-1} was derived by dividing the total amount of Hg in the Earth's soil and, assuming that land area equals soil area, dividing this Hg value by the Earth's land area (Andren and Nriagu, 1979). Average soil depth used to derive the global average soil Hg ha^{-1} value was estimated to be 140 cm. This estimate was calculated by dividing global soil mass by global land area (Andren and Nriagu, 1979), assuming an average bulk density of 1.3 g cm^{-3} for the top 20 cm and 1.5 g cm^{-3} for the underlying soil.

Atmospheric Hg deposition for Illinois was defined as the sum of wet and dry Hg deposition. Wet Hg deposition is measured in Illinois by the U.S. Mercury Deposition Network (MDN). For the 1999–2001 period, MDN reports that the average annual measured wet Hg deposition in Illinois ranged from 90 to 96 ha^{-1} yr^{-1} with an average of 92 mg ha^{-1} yr^{-1} (National Atmospheric Deposition Program, 2003). The USEPA (1997, p. 5-23) reports that dry Hg deposition in Illinois ranges from 10 to 100 mg ha^{-1} yr^{-1}. A total deposition value of 184 mg Hg ha^{-1} yr^{-1} for Illinois was derived by assuming that dry deposition equals wet deposition. Total average atmospheric deposition of 88.4 mg Hg ha^{-1} yr^{-1} for the conterminous USA was calculated from the USEPA estimate that an average total of 79.6 metric tons Hg yr^{-1} is deposited on the conterminous USA (USEPA, 1997, p. 5-1). The Hg concentration and content of the Illinois soils (Table 1) were compared with data from the literature for USA soils, world soils and the Earth's crust. Average Hg contents in USA and the Illinois soils were compared to estimated natural background rates of atmospheric Hg deposition and average total annual Hg deposition rates for the USA and Illinois.

Results and discussion

On the global scale, Hg is a trace element: Mason and Moore (1982, pp. 42, 47) reported that the Earth's crust averages

Table 1. Concentration and content of mercury in southern Illinois soils.

Sample	*Hg concentration (μg kg^{-1})*			*Soil depth (cm)*		
	median	*mean*	*range*	*median*	*mean*	*range*
Topsoil	28	34	18–104	19.8	19.8	9.14– 30.5
Whole soil	29	31	16–58	381	380	181–579
	Hg content (g ha^{-1})					
Topsoil	72	85	47–151	—	—	—
Whole soil	1630	1720	514–3980	—	—	—

but 80 μg Hg kg^{-1}. Shacklette and Boerngen (1984) reported that the average concentration of Hg in conterminous USA soils is 86 μg kg^{-1} (top ~20 cm) and Andren and Nriagu (1979) reported that the average concentration of Hg in world soils is 71 μg kg^{-1} (140 cm calculated soil depth).

The average concentration of Hg in the Illinois soils is even less than concentrations reported above for the Earth's crust, average USA soil and average world soil. The median and mean (average) concentrations of Hg for the topsoil (~20 cm) from the Illinois soils are only 28 and 34 μg kg^{-1}, respectively. Median and average topsoil Hg concentrations are not much different from those of the underlying ~360 cm of soil (Table 1). Nevertheless, the amount of Hg in these Illinois soils is large relative to atmospheric Hg deposition. Quantitatively, assuming that all atmospherically deposited Hg is retained in the top ~20 cm of soil, the average amount of Hg in topsoil is equivalent to ~400 years of the current estimated rate of total Hg deposition (184 mg Hg ha^{-1} yr^{-1}) and equivalent to ~4000 years of a background level of total atmospheric Hg deposition value of 20 mg Hg ha^{-1} yr^{-1}. Assuming that all atmospherically deposited Hg is retained in the ~380 cm-deep average whole soil profile, the average amount of Hg in whole soil is equivalent to ~9000 years of the current estimated rate of total atmospheric Hg deposition rate and equivalent to ~90 000 years of the background rate of total atmospheric Hg deposition.

These quantities of Hg in the Illinois soils are too great to be attributed mainly to anthropogenic atmospheric Hg deposition.

The reported average Hg concentration of USA soils is about 2.5 times greater than that of the Illinois soils, whereas average USA total atmospheric Hg deposition is reported to be about half that of Illinois. Nevertheless, the USEPA (1997, p. 5-33, 6-2) concluded that most Hg in USA soils is anthropogenic by reporting that prior atmospheric anthropogenic Hg deposition USA soils contained only in the order of 10 μg kg^{-1}. Assuming that all deposited Hg remains in the top 20 cm of soil, such an increase of Hg in the top 20 cm of average USA soil would require ~2000 years of total atmospheric Hg deposition at its current average USA rate of 88.4 mg ha^{-1} (USEPA, 1997, pp. 5-28 to 5-33). Assuming that the top 140 cm of USA soil now has the above reported world average soil, or the crustal Hg content and its natural Hg content was 10 μg kg^{-1}, it would take ~14 000 years or ~16 000 years, respectively, for the current average estimated rate atmospheric Hg deposition to account for the Hg content of the soil if all deposited Hg remained in the soil.

These quantities of Hg in USA soils are too great to be attributed mainly to anthropogenic atmospheric Hg deposition.

When widespread Hg pollution first became a popular concern, global anthropogenic Hg was compared to global soil Hg (Wollast *et al*., 1975; Andren and Nriagu, 1979) as part of a larger literature that criticised the common presumption that the principle source of Hg in the environment is anthropogenic (e.g. Bertine and Goldberg, 1971; Goldwater, 1971; Hammond, 1971; Barber *et al.,* 1972; Knauer and Martin, 1972; Miller *et al*., 1972; Goldberg, 1975; Ketchum *et al*., 1975). Regarding world soil Hg content, these early analyses reported that anthropogenic activities could have increased world soil Hg content by 0.02 percent (Wollast *et al*., 1975; Andren and Nriagu, 1979). Despite this early seminal literature and a persistent stream of similar publications in following decades (e.g. Varekamp and Buseck, 1981; Fitzgerald *et al.,* 1984; Kabata-Pendias and Pendias, 1984, pp. 92, 116–125; Siegel and Siegel, 1984; Wolf and Peel, 1985; Morrison and Therein, 1991; Vandal *et al.,* 1995; Roulet *et al*., 1998; 2000; Gustin *et al*., 2000; Lechler *et al*., 2000; Mason and Sheu, 2002; Gustin, 2003), the presumption that anthropogenic Hg is the principal source of Hg in the soils that mantle landscapes is still common and exerts a powerful effect on scientific and public perception of the role of anthropogenic atmospheric Hg deposition on the environment of Illinois and the USA.

Conclusion

The hypothesis that most Hg in Illinois and the USA soils is of anthropogenic origin is rejected. Whereas Hg is a trace element — its concentration is low compared to that of other Earth elements — Hg concentrations and contents of Illinois and USA soils are too great to be accounted for by atmospheric anthropogenic Hg deposition. This finding does not mean that atmospheric Hg pollution does not contribute to environmental Hg. Nor does it mean that there are situations where conditions are such that most Hg does come from anthropogenic atmospheric deposition. It does indicate, however, that because environmentally significant amounts of natural Hg are generally found in soils, research is needed to investigate the mobility and fate of natural and anthropogenic Hg in terrestrial and aquatic environments.

References

Ackefors, H., 1971. Mercury pollution in Sweden with special reference to conditions in the water habitat. *Proc. Roy. Soc. Lond. B,* **177**, 365–387.

Andren, A.W. and Nriagu, J.O., 1979. The global cycle of mercury. In: *Topics in Environmental Health: Volume 3, The Biogeochemistry of Mercury in the Environment*, J.O. Nriagu (Ed.). Elsevier/North-Holland Biomedical Press, Amsterdam, The Netherlands. 1–21.

Balogh, S., Meyer, M. and Johnson, K., 1998. Diffuse and point source mercury inputs to the Mississippi, Minnesota, and St. Croix Rivers. *Sci. Total Envir*., **213**, 109–113.

Balogh, S.J., Huang, Y., Offerman, H.J., Meyer, M.L. and Johnson D.K., 2003. Methylmercury in rivers draining cultivated watersheds. *Sci. Total Envir*., **304**, 305–313.

Barber, R.T., Vijayakumar A. and Cross, F.A., 1972. Mercury concentrations in recent and ninety-year-old benthopelagic fish. *Science,* **178**, 636–639.

Bertine, K.K. and Goldberg, E.D., 1971. Fossil fuel combustion and the major sedimentary cycle. *Science,* **173**, 233–235.

Borg, K., Wanntorp, H., Erne, K. and Hanko, E., 1966 Mercury poisoning in Swedish wildlife. *J. Appl. Ecol.,* **3,** suppl., 171–172.

Dreher, G.B., Follmer, L.R. and Zhang, Y., 2002. A progress report on the chemical composition of soils in Illinois: cores 1 through 10. *Illinois State Geological Survey Open-File Series* 2002-2, Champaign, IL, USA. 52pp.

Dreher, G.B., Follmer, L.R. and Zhang, Y., 2003b. A progress report on the description and chemical composition of soils in Illinois: cores 11 through 26. *Illinois State Geological Survey Open-File Series* 2003-1, Champaign, IL, USA. 99pp.

Dreher, G.B., Follmer, L.R. and Zhang, Y., 2003a. A progress report on the description of the geology and chemical composition of soils in Illinois: cores 27 through 51. *Illinois State Geological Survey Open-File Series* 2003-3, Champaign, IL, USA. 128pp.

Fitzgerald, W.F., Gill, G.A. and Kim, J.P., 1984. An equatorial Pacific source of atmospheric mercury. *Science* **224**, 597–599.

Gardner, D., 1978. Mercury in fish and waters of the Irish Sea and other United Kingdom fishing grounds. *Nature,* **272**, 49–51.

Goldberg, E.D., 1975. Man's role in the major sedimentary cycle. In: *The Changing Global Environment*, S.F. Singer (Ed.). D.Reidel Publishing, Dordrecht, The Netherlands. 275–294.

Goldwater, L.J., 1971. Mercury in the environment. *Sci. Amer*., **224**(5), 15–21.

Gustin, M.S., 2003. Are mercury emissions from geologic sources significant? A status report. *Sci. Total Envir*., **304**, 153–167.

Gustin, M.S., Lindberg, S.E., Austin, K., Coolbaugh, M., Vette, A. and Zhang, H., 2000. Assessing the contribution of natural sources to regional atmospheric mercury budgets. *Sci. Total Envir*., **259**, 61–71.

Hammond, A.L., 1971. Mercury in the environment: natural and human factors. *Science,* **171**, 788–789.

Harriss, R.C., White. D.B. and Mcfarlane, R.B., 1970. Mercury compounds reduce photosynthesis by plankton. *Science,* **170**, 736–737.

Hurley, J.P., Cowell, S.E., Shafer, M.M. and Hughes, P.E., 1998. Tributary loading of mercury to Lake Michigan: importance of seasonal events and phase partitioning. *Sci. Total Envir*., **213**, 129–137.

Illinois Department of Public Health, 2003. *Facts about Illinois' Methylmercury Advisory*. Illinois Department of Public Health, Springfield, IL, USA. 3. Website: http://www.idph.state.il.us/envhealth/fishadv/fishadvisory_qa.htm

Iyengar, G.V. and Nair, P.P., 2000. Global outlook on nutrition and the environment: meeting the challenges of the next millennium. *Sci. Total Envir*., **249**, 331–346.

Johansson, K., Aastrup, M., Andersson, A., Bringmark, L. and Iverfeldt, A., 1991. Mercury in Swedish forest soils and waters — assessment of critical load. *Water Air Soil Pollut*., **56**, 267–281.

Kabata-Pendias, A. and Pendias, H., 1984. *Trace Elements in Soils and Plants*. CRC Press, Boca Raton, FL, USA. 315pp.

Ketchum, B.H., Zitko, V. and Saward, D., 1975. Aspects of heavy metal and organohalogen pollution in aquatic ecosystems. In: *Ecological Toxicology Research: Effects of Heavy Metals and Organohalogen Compounds: Proceedings of a NATO Science Committee Conference*, A.D. McIntyre and C.F. Mills (Eds.). Plenum Press, New York, USA. 75–90.

Knauer, G.A. and Martin, J.H., 1972. Mercury in a marine pelagic food chain. *Limnol. Oceanogr*., **17,** 868–876.

Lechler, P.J., Miller, J.R., Lacerda, L.D., Vinson, D., Bonzongo, J.C., Lyons, W.B. and Warwick, J.J., 2000. Elevated mercury concentrations in soils, sediments, water, and fish of the Madeira River basin, Brazilian Amazon: a function of natural enrichments? *Sci. Total Envir*., **260**, 87–96.

Lee, D.S., Fowler, D. and Nemitz, E., 2001. New directions: the European Air Quality Framework Directive and atmospheric mercury: the wrong tool for the job? *Atmos. Environ*., **35**, 5855–5857.

Lindqvist, O. (Ed.), 1991. Mercury as an environmental pollutant: refereed papers from the international conference held in Gavle, Sweden, June 11-13, 1990. *Water Air Soil Pollut*., **56**, 1–847.

Mason, B. and Moore, C.B., 1982. *Principles of Geochemistry. Fourth Edition.* Wiley, New York, USA. 344pp.

Mason, R.P. and Sheu, G.R., 2002. Role of the ocean in the global mercury cycle. *Global Biogeochem. Cycles* **16**, 40-1—40-14.

Meili, M., 1995. Preindustrial atmospheric deposition of mercury — uncertainty rates from lake sediment and peat cores. *Water Air Soil Pollut*., **80**, 637–640.

Meili, M., Bishop, K., Bringmark, L., Johansson, K., Munthe, J., Sverdrup, H. and de Vries, W., 2003. Critical levels of atmospheric pollution: criteria and concepts for operational modelling of mercury in forest and lake ecosystems. S*ci. Total Envir*., **304**, 83–106.

Miller, G.E., Grant, P.M., Kishore, R., Steinkruger, F.J., Rowland, F.S. and Guinn, V.P., 1972. Mercury concentrations in museum specimens of tuna and swordfish. *Science,* **175**, 1121–1122.

Morrison, K.A. and Therien, N., 1991. Experimental evaluation of mercury release from flooded vegetation and soils. *Water Air Soil Pollut*., **56**, 607–619.

National Atmospheric Deposition Program, 2003. Mercury Deposition Network, Illinois State Water Survey, Champaign, IL, USA. Website: http://nadp.sws.uiuc.edu/mdn/maps/

Pilgrim, W., Poissant, L. and Trip, L., 2000a. The Northeast States and Eastern Canadian Provinces mercury study: a framework for action: summary of the Canadian chapter. *Sci. Total Envir*., **261**, 177–184.

Pilgrim, W., Schroeder, W., Porcella, D.B., Santos-Burgoa, C., Montgomery, S., Hamilton, A. and Trip, L., 2000b. Developing consensus: mercury science and policy in the NAFTA countries (Canada, the United States and Mexico). *Sci. Total Envir*., **261**, 185–193.

Roulet, M., Lucotte, M., Saint-Aubin, A., Tran, S., Rheault, I., Farella, N., De Jesus Da Silva, E., Dezencourt, J., Passos, C.J.S., Soares, G.S., Guimaraes, J.R.D., Mergler, D. and Amorim, M., 1998. The geochemistry of mercury in central Amazonian soils developed on the Alter-do-Chao formation of the lower Tapajos River Valley, Para state, Brazil. *Sci. Total Envir*., **223**, 1–24.

Roulet, M., Lucotte, M., Canuel, R., Farella, N., Courcelles, M., Guimaraes, J.R.D., Mergler, D. and Amorim, M., 2000. Increase in mercury contamination recorded in lacustrine sediments following deforestration in the central Amazon. *Chem. Geol*., **165**, 243–266.

Shacklette, H.T. and Boerngen, J.G., 1984. Element concentrations in soils and other surficial materials of the conterminous United States. *U.S. Geological Survey Professional Paper* 1270. U.S. Geological Survey, Alexandria, VA, USA. 105pp.

Siegel, S.M. and Sieleg, B.Z., 1984. First estimate of annual mercury flux at the Kilauea main vent. *Nature,* **309**, 146–147.

Swain, E.B., Engstrom, D.R., Brigham, M.E,, Henning, T.A. and Brezonik, P.L., 1992. Increasing rates of atmospheric deposition in midcontinental North America. *Science,* **257**, 784–787.

Travis, C.C. and Hester, S.T., 1991. Global chemical pollution. *Environ. Sci. Technol*., **25,** 814–819.

United Nations Environment Programme, 2002. *Global Mercury Assessment*. UNEP Chemicals, Geneva, Switzerland. 258pp.

U.S. Environmental Protection Agency, 1997. *Mercury Study Report to Congress. Volume III: Fate and Transport of Mercury in the Environment*. EPA-452/R-97-005. U.S. Environmental Protection Agency, Washington, DC, USA. various paging.

U.S. Geological Survey, 2000. *Mercury in the Environment*. U.S. Geological Survey Fact Sheet 146-00. U.S. Geological Survey, Reston, VA, USA. 6pp.

Vandal, G.M., Fitzgerald, W.F., Boutron, C.F. and Candelone, J.P., 1995. Mercury in ancient ice and snow from the Antarctic. In: *Ice Core Studies of Global Biogeochemical Cycles: Proc. of the NATO Advanced Research Workshop "Ice Score Studies of Global Biogeochemical Cycles," held in Annecy, France, March 26-31, 1993*, R.J. Delmas (Ed.). Springer, Berlin, Germany. 401–415.

Varekamp, J.C. and Buseck, P.R., 1981. Mercury emissions from Mount St Helens during September 1980. *Nature,* **293**, 555–556.

Watanabe, K.H., Desimone, F.W., Thiyagarajah, A., Hartley, W.R. and Hindrichs, A.E., 2003. Fish tissue quality in the lower Mississippi River and health risks from fish consumption. *Sci. Total Envir*., **302**, 109–126.

Wheatley, B. and Wyzga, R. (Eds.), 1997. Mercury as a global pollutant: human health issues, fourth international conference on mercury as a global pollutant, Hamburg, Germany, 4-8 August 1996. *Water Air Soil Pollut*., **97**, 1–198.

Wisconsin Department of Natural Resources, 2001. Controlling mercury a top priority at the DNR. *DNR News*, April 24, 2001. 11-14. Website: http://www.dnr.state.wi.us/org/caer/ce/news/on/2001/ON010424.htm

Wolff, E.W. and Peel, D.A., 1985. The record of global pollution in polar snow and ice. *Nature,* **313**, 535–540.

Wollast, R., Billen, G. and MacKenzie, F.T., 1975. Behavior of mercury in natural systems and its global cycle. In: *Ecological Toxicology Research: Effects of Heavy Metals and Organohalogen Compounds: Proceedings of a NATO Science Committee Conference*, A.D. McIntyre and C.F. Mills (Eds.). Plenum Press, New York, USA. 145–166.