Chinese Science Bulletin 2004 Vol. 49 No. 19 2068—2072

Landfill is an important atmospheric mercury emission source

FENG Xinbin[1], TANG Shunlin[1,2], LI Zhonggen[1,2], WANG Shaofeng[1,2] & LIANG Lian[3]

1. State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China;
2. Graduate School of Chinese Academy of Sciences, Beijing 100039, China;
3. Cebam Analytical, INC. 3927 Aurora Ave, Seattle, WA 98103, USA
Correspondence should be addressed to Feng Xinbin (e-mail: Xinbin@hotmail.com)

Abstract **Since municipal wastes contain refuses with high mercury contents, incineration of municipal wastes becomes the major anthropogenic atmospheric mercury emission source. In China, landfills are however the main way to dispose of municipal wastes. Total gaseous mercury (TGM) concentrations in landfill gas of Gaoyan sanitary landfill located in suburb of Guiyang City were monitored using a high temporal resolved automated mercury analyzer, and mono-methylmercury (MMHg) and dimethylmercury (DMHg) concentrations in landfill gas were also measured using GC coupled with the cold vapor atomic fluorescence (CVAFS) method. Meanwhile, the TGM exchange fluxes between exposed waste and air and the soil surface of the landfill and air, were measured using low Hg blank quartz flux chamber coupled with high temporal resolved automated mercury analyzer technique. TGM concentrations in landfill gas from half year filling area averaged out at 665.52 ±291.25 ng/m^3, which is comparable with TGM concentrations from flue gas of a small coal combustion boiler in Guiyang. The average MMHg and DMHg concentrations averaged out at 2.06±1.82 ng/m^3 and 9.50±5.18 ng/m^3, respectively. It is proven that mercury emission is the predominant process at the surfaces of both exposed wastes and soil of landfill. Landfills are not only TGM emission source, but also methylmercury emission source to the ambient air. There are two ways to emit mercury to the air from landfills, one is with the landfill gas through landfill gas duct, and the other through soil/air exchange. The Hg emission processes from landfills are controlled by meteorological parameters.**

Keywords: mercury, landfills, MMHg, DMHg, soil-air exchange, mercury flux.

DOI: 10.1360/04wd0038

Due to the special physical and chemical properties, mercury is a global pollutant which could be aerially transported cross the borders[1,2]. Both natural processes and human activities emit mercury to the air. The major anthropogenic mercury emission source categories are coal combustion, waste incineration, chlorine-alkali plant, metal smelting and refining and so on[1−3] . Human activities emit not only elemental mercury (Hg^0), which has a long lifetime in the air, but also reactive gaseous mercury (RGM) and particulate mercury, which live short in the air. Mercury is also released into the atmosphere by a number of natural processes, including outgassing of the earth's mantle/crustal material, evasion from surficial soils[4−8], water bodies[9,10], vegetation surfaces[11], volcanoes[12], wild fires[13,14], and geothermal sources[15]. Mercury is thought to be released from natural sources mainly as Hg^0 vapor[1]. Though many efforts have been recently diverted to the estimation of total mercury emission to the atmosphere, there are still large errors and uncertainties on the estimations mainly due to different accuracies of data from different regions. At present, total annual natural mercury emission rate is estimated to range from 2500 to 29325 t[2,16,17]; while the total annual anthropogenic mercury emission rate is estimated to vary from 910 to 11000 t[2,18,19]. In addition, some potential atmospheric mercury emission sources such as landfills have not been paid enough attention to, and only a few studies were carried out globally[20−23].

Mercury concentrations in wastes are relatively high, and total mercury concentrations in US wastes before 1994 was as high as 4 mg/kg, of which 80% came from battery and remaining portion came from fluorescence light, electronic switches and thermal meters. Mercury concentrations in alkaline batteries made in China reach up to 1 to 5 %, while mercury concentration in neutral batteries are about 0.025%, and the annual mercury consumption related to battery production reached dozens of tons. The restriction of mercury uses in battery only started in 2001 in China[24]. After being buried, the wastes are in anaerobic conditions, and hydro-carbon compounds in wastes will be degraded into carboxylic acids first and into CH_4 and CO_2 finally with a series of microbiological activities[25]. At such reducing conditions, inorganic compounds in wastes will not only be reduced into volatile Hg^0, but also be converted into more toxic volatile methyl mercury compounds. Those volatile mercury compounds will be emitted into air through landfill gas conducts and soil. In developed countries, waste incineration is the major way to dispose of municipal wastes, but this method is just introduced to China. On the whole, direct landfills are the major way to dispose of municipal wastes in China[26], and this method disposes of more than 70% of total wastes[74]. The total annual production of municipal wastes in China in 1999 reached 120000000 t, and the annual production increased with a rate of 10% each year since then. According to national statistical data, the total production of waste so far reached 6.0 billion tons, and occupied a land area of more than 500 km^2. Thus it is of great importance to study mercury emission from landfills in China.

From November 21 to 30, 2003, we conducted an intensive field measurement campaign at Gaoyan landfill

in suburb of Guiyang to measure TGM, MMHg and DMHg concentrations in landfill gas and to measure TGM exchange flux between the surface of landfill and air.

1 Experimental

Gaoyan landfill is the most modern one in Guiyang, and it disposes of 800 t wastes each day. It occupies a land area of 8.79×10^5 m^2, and has gone into operation for two years. The depth of soil covered in the landfill is about 20 cm. Fig. 1 shows the distribution of landfill gas conducts and the locations of sampling sites. According to the landfilling ages, the landfill can be divided into half-year filling area, one-year filling area and two-year filling area. Since the half year filling area occupies the most area of the landfill, we chose a representative landfill gas conduct to measure TGM, MMHg and DMHg concentrations in landfill gas. Meanwhile, we also measured TGM flux between exposed wastes and air, and between soil surface of the landfill and air.

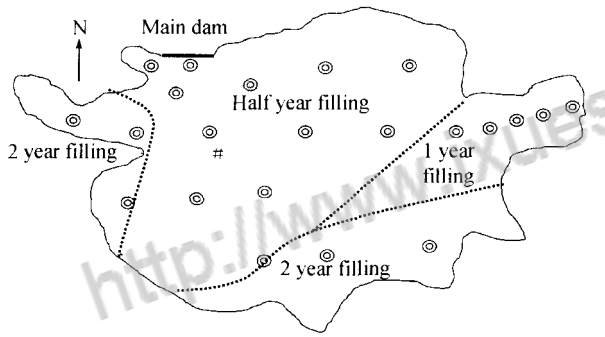

Fig. 1. The distribution of landfill gas conducts and sampling site location. # Sampling site.

TGM concentrations in landfill gas were monitored using a high temporal resolved (5 min) automated mercury vapor analyzer (Tekran 2537A) with a detection limit of 0.67 ng/m^3. MMHg was collected in two impingers in a series containing 45 mL 0.5% (*V/V*) HCl with a sampling flow rate of 0.3 L/min, and a sampling time of more than 2 h[28,29]. The analysis of MMHg was performed using distillation followed by aqueous ethylation, GC separation and CVAFS detection method[30]. DMHg was pre-concentrated onto two Carbotraps™ which are connected in series with a sampling flow rate of 0.3 L/min and a sampling time of more than 2 h[30]. DMHg was analyzed using thermal desorption coupled with GC separation and CVAFS detection method[30]. TGM exchange fluxes between exposed waste and air, and the soil surface of the landfill and air were measured using low Hg blank quartz flux chamber coupled with high temporal resolved automated mercury analyzer Tekran 2537A technique[9]. While measuring Hg flux, air temperature, surface soil temperature at 5 cm in depth, relative humidity, wind direction, wind speed and intensity of solar radiation were also monitored synchronously with Hg flux measurement using a portable mini-weather station (Global Ⅲ, USA) to examine the influence of meteorological parameters on mercury flux.

2 Results and discussion

(ⅰ) Distribution of TGM in landfill gas. TGM concentrations in a landfill gas conduct were monitored continuously for 24 h, and the result is presented in Fig. 2. A clear TGM distribution pattern that TGM concentrations are higher during daytime than that during night was obtained, implying that TGM concentrations in landfill gas are controlled by surface meteorological conditions. The preliminary result showed that the average TGM concentrations in landfill gas from half-year filling area is 665.52 ± 291.25 ng/m^3 (with a range from 175.22 to 1406.0 ng/m^3, n = 305), which is about 400 times higher than the global TGM background concentration in ambient air that is 1.5 ng/m^3 and also about two orders of magnitudes higher than the average TGM concentrations in ambient air of Guiyang where is seriously contaminated with atmospheric mercury (8.4 ng/m^3)[31,32]. TGM concentrations in landfill gas are comparable with that reported in flue gas from a small coal combustion boiler in Guiyang (690 ng/m^3)[33], indicating that landfill gas is an important atmospheric mercury emission source.

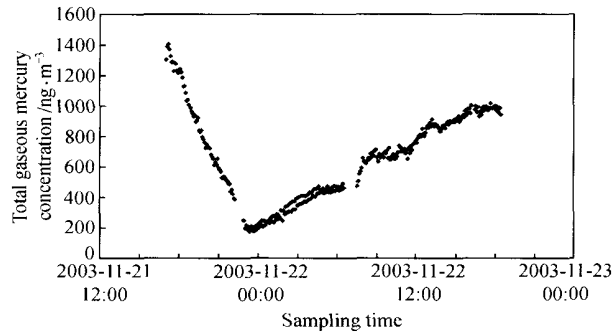

Fig. 2. The diurnal distribution of TGM in landfill gas from half year filling area.

(ⅱ) Methylmercury in landfill gas. Only a few data on MMHg concentrations in ambient air are available from the open literature at present, and the limited data showed that MMHg concentrations in ambient air are usually less than <20 pg/m^3 [28,29,34], but so far the sources of MMHg in ambient air are not quite clear. The MMHg concentrations measured from November 20 to 26, 2003 are listed in Table 1. The average MMHg concentration is 2.06 ± 1.82 ng/m^3, which is about two orders of magnitude higher than the reported concentrations in ambient air. This indicated that landfill is an important atmospheric MMHg emission source.

The measurement results of DMHg concentrations in landfill gas are listed in Table 2. The average DMHg concentration is 9.50 ± 5.18 ng/m^3, which is higher than that

Table 1 Measurement results of MMHg in landfill gas from a landfill gas conduct with a half year filling time

Sample #	Sampling date	Sampling time	Sample volume/m^3	MMHg concentration/$ng \cdot m^{-3}$
1	2003-11-20	11∶28—13∶15	0.032	1.17
2	2003-11-20	13∶40—15∶40	0.036	6.37
3	2003-11-20	16∶45—18∶20	0.029	2.65
4	2003-11-21	07∶33—09∶36	0.037	1.25
5	2003-11-21	10∶20—18∶10	0.105	1.75
6	2003-11-21	18∶38—23∶38	0.180	0.84
7	2003-11-22	23∶38—08∶00	0.301	0.85
8	2003-11-22	08∶13—19∶36	0.408	1.02
9	2003-11-23	03∶20—18∶37	0.275	1.10
10	2003-11-23-24	23-21∶10—24-11∶35	0.260	1.05
11	2004-11-26	09∶50—12∶20	0.045	4.64
		Average concentration		2.06

Table 2 Measurement results of DMHg in landfill gas from a landfill gas conduct with a half year filling time

Sample #	Sampling date	Sampling time	Sample volume/m^3	DMHg concentration/$ng \cdot m^{-3}$
1	2003-11-23	21∶05—23∶47	0.050	8.81
2	2003-11-24	10∶04—12∶10	0.039	11.15
3	2003-11-24	12∶13—14∶31	0.041	15.58
4	2003-11-24	14∶31—16∶31	0.036	14.58
5	2003-11-24	16∶45—18∶42	0.035	16.40
6	2003-11-24	19∶18—21∶18	0.036	13.92
7	2003-11-24	21∶38—23∶38	0.036	5.59
8	2003-11-25	09∶48—12∶11	0.045	2.54
9	2003-11-25	16∶30—19∶20	0.051	9.94
10	2003-11-25	19∶30—21∶30	0.036	1.64
11	2003-11-26	07∶30—09∶30	0.036	3.58
12	2003-11-26	15∶35—17∶40	0.038	10.24
		Average concentration		9.50

of MMHg in landfill gas. DMHg is an extremely toxic compound, and a US chemist died after being exposed with this compound[35]. DMHg is not however stable in ambient air, because it will be degraded to MMHg by OH, NO_3 and O_3[36]. From our measurement data it can be seen that landfill is also an important atmospheric DMHg emission source.

Landfill is one of atmospheric methylmercury emission sources discovered in terrestrial ecosystem, which could well account for the sources of the recent discovered methylmercury in the ambient air and precipitation.

(**iii**) TGM exchange flux between landfill and ambient air. Hg flux measurement results from exposed wastes and soil of landfill are summarized in Table 3. The mercury exchange fluxes are bi-directional at both exposed wastes and over soil of landfill, namely both mercury emission from soil or waste surface and mercury deposition to the surfaces occurred. On the whole, however, mercury emission is the predominant process at both occasions. It is showed that the emission fluxes from the exposed waste are much stronger than that from soil over landfill. This is mainly because the exposed wastes are

Table 3 The statistical summary of mercury flux measured at exposed waste site and at landfill with a half year filling time

Sampling site	Exposed waste	Landfill
Sampling time	2003-11-21 21∶10—2003-11-24 09∶10	2003-11-24 19∶00—2003-11-26 15∶20
Min	–286.2	–72.48
Max	5609.6	308.7
Average	502.4	55.2
SD	1206.1	74.0
Sample number	164	105

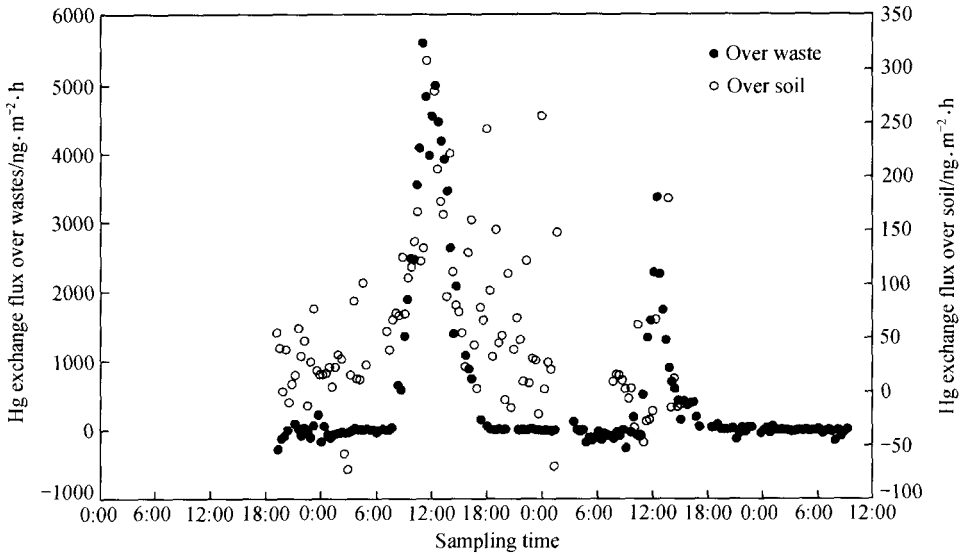

Fig. 3. The diurnal pattern of Hg exchange flux over exposed wastes and soil from landfill.

much better aerated than soil, which will facilitate mercury diffuse to the air.

As showed in Fig. 3 a consistent diurnal pattern of TGM exchange flux was observed at both exposed waste and landfill sampling sites. During daytime mercury emission is the predominant process and the emission flux reached maximum at noon, and during night mercury emission flux decreased and mercury deposition occurred. This diurnal distribution pattern is consistent with TGM distribution pattern in landfill gas, indicating that the process of mercury emission from landfill is controlled to some extent by TGM concentration in landfill gas. In comparison with mercury exchange flux at background soil site[37,38], mercury emission flux from both exposed wastes and landfill are 2 to 3 orders of magnitudes higher. It is obvious that landfills in China may become potential atmospheric emission sources.

It is revealed that TGM flux measured at both exposed waste site and landfill site correlated significantly with solar radiation and air temperature. This indicated that the formation of TGM in landfill gas is driven in a way by the meteorological parameters. Studies[5,6,37,38] have showed that divalent mercury in soil can be transferred to Hg^0 by photo-reduction processes, and solar radiation is the driving force of mercury emission from soil. Therefore our results also indicated that solar radiation is the main driving force of mercury emission from landfill.

3 Conclusions

Since the municipal wastes contain mercury, incineration of municipal waste is one of the largest anthropogenic mercury emission sources in developed countries[19]. Landfills are however the major way to dispose of municipal wastes in China. Our study showed that landfills are also potential atmospheric mercury emission source. There are two ways to emit mercury to the air from landfills, one is with the landfill gas through landfill gas duct, and the other through soil/air exchange.

Due to its special physical and chemical conditions, landfill emits not only Hg^0 with a long lifetime in the air, but more toxic MMHg and DMHg to the air. Landfill is one of a few terrestrial systems proven to be atmospheric MMHg emission source, which could well explain the recent discovery of MMHg in the air and precipitation at some terrestrial sampling sites.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant Nos. 40203009 and 40173037) and the "Hundred Talent Program" by the Chinese Academy of Sciences.

References

1. Schroeder, W. H., Munthe, J., Atmospheric mercury—An overview, Atmospheric Environment, 1998, 32: 809—822.
2. Linqvist, O., Johansson, K., Aastrup, M. et al., Mercury in the Swedish environment—Recent research on causes, consequences and corrective methods, Water Air and Soil Pollution, 1991, 55: 1—261.
3. Lin, Y., Guo, M., Gan, W., Mercury pollution from small gold mines in China, Water Air and Soil Pollution, 1997, 97: 233—239.
4. Feng, X. B., Chen, Y. C., Zhu, W. G., A study of mercury emission flux from soil, Environmental Sciences (in Chinese), 1996, 17(2): 20—22.
5. Carpi, A., Lindberg, S. E., Application of a Teflon™ dynamic flux chamber for quantifying soil mercury flux: Tests and results over background soil, Atmospheric Environment, 1998, 32(5): 873—882.
6. Carpi, A., Lindberg, S. E., The sunlight mediated emission of elemental mercury from soil amended with municipal sewage sludge, Environmental Science and Technology, 1997, 31: 2085—2091.
7. Ferrara, R., Maserti, B. E., Andersson, M. et al., Mercury degassing

rate from mineralized areas in the Mediterranean basin, Water Air and Soil Pollution, 1997, 93: 59—66.
8. Gustin, M., Lindberg, S., Austin, K. et al., Assessing the contribution of natural sources to regional atmospheric mercury budgets, The Science of the Total Environment, 2000, 259: 61—71.
9. Feng, X. B., Sommar, J., Gardfeldt, K. et al., Exchange flux of total gaseous mercury between air and natural water surfaces in summer season, Science in China, Ser. D, 2002 , 45(3): 211—220.
10. Costa, M., Liss, P. S., Photoreduction of mercury in seawater and its possible implication for Hg^0 air-sea fluxes, Marine Chemistry, 1999, 68: 87—95.
11. Lindberg, S. E., Ganson, P. J., Meyers, T. P. et al., Air/surface exchange of mercury vapor over forests—The need for a reassessment of continental biogenic emissions, Atmospheric Environment, 1998, 32: 895—905.
12. Nriagu, J., Becker, C., Volcanic emissions of mercury to the atmosphere: global and regional inventories, The Science of the Total Environment, 2003, 304(1-3): 3—12.
13. Sigler, J. M., Lee, X., Munger, W., Emission and long-range transport of gaseous mercury from a large-scale Canadian boreal forest fire, Environmental Science and Technology, 2003, 37 (19): 4343—4347.
14. Friedli, H. R., Radke, L. F., Prescott, R. et al., Mercury emissions from the August 2001 wildfires in Washington State and an agricultural waste fire in Oregon and atmospheric mercury budget estimates, Global Biogeochemical Cycles, 2003, 17(2): Art. No. 1039.
15. Nakagawa, R., Estimation of mercury emissions from geothermal activity in Japan, Chemosphere, 1999, 38(8): 1867—1871.
16. Nriagu, J. O., A global assessment of natural sources of atmospheric trace metals, Nature, 1989, 338: 47—49.
17. Mason, R., Fitzgerald, W. F., Morel, M. M., The biogeochemical cycling of elemental mercury: Anthropogenic influences, Geochimica Cosmochimica Acta, 1994, 58: 3191—3198.
18. Nriagu, J. O., Pacyna, J. M., Quantitative assessment of worldwide contamination of air, water and soil by trace metals, Nature, 1988, 333: 134—139.
19. Pirrone, N., Keller, G.. J., Nriagu, J. O., Regional differences in worldwide emissions of mercury to the atmosphere, Atmospheric Environment, 1996, 30: 2981—2987.
20. United States Environmental Protection Agency (US EPA), Products containing mercury in municipal solid waste in the US, USEPA Office of Solid Waste, 1992, 1—121.
21. Lindberg, S. E., Wallschlager, D., Prestbo, E. M. et al., Methylated mercury species in municipal waste landfill gas sampled in Florida, USA, Atmospheric Environment, 2001, 35(23): 4011—4015.
22. Kim, K. H., Kim, M. Y., Lee, G., The soil-air exchange characteristics of total gaseous mercury from a large-scale municipal landfill area, Atmospheric Environment, 2001, 35(20): 3475—3493.
23. Kim, K. H., Kim, M. Y., Mercury emissions as landfill gas from a large-scale abandoned landfill site in Seoul, Atmospheric Environment, 2002, 36(31): 4919—4918.
24. Cai, W. J., Countermeasure, waste disposal and pollution of municipal waste in Chinese cities, Railway Labor Safety, Hygiene and Environmental Protection (in Chinese), 2001, 28(1): 8—14.
25. Bogner, J. E., Spokas, K. A., Burton, E. A., Temporal variations in greenhouse gas emissions at a midlatitude landfill, Journal of Environment Quality, 1999, 28: 278—288.
26. Liu, X. Y., The status of municipal waste and disposal countermeasure in China, Chongqing Environmental Science (in Chinese), 1994, 16(2): 38—41.
27. Duan, S. J., The problem of municipal waste and management countermeasure in China, Journal of Hebei University (in Chinese), 2001, 26(1): 83—87.
28. Brosset, C., Lord, E., Methylmercury in ambient air, Method of determination and some measurement results, Water Air and Soil Pollution, 1995, 82: 739—750.
29. Lee, Y. H., Wangberg, I., Munthe, J., Sampling and analysis of gas-phase methylmercury in ambient air, The Science of Total Environment, 2003, 304: 107—113.
30. Liang, L., Horvat, M., Bloom, N. S., An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection, Talanta, 1994, 41: 371—379.
31. Feng, X., Tang, S., Shang, L. et al., Total gaseous mercury in the air of Guiyang, PR China, The Science of the Total Environment, 2003, 304: 61—72.
32. Feng, X., Shang, L., Wang, S. et al., Temporal variation of Total gaseous mercury in the air of Guiyang, PR China, Journal of Geophysical Research-Atmospheres, 2004, 109, D03303, doi:10.1029/2003JD004159.
33. Tang, S., Feng, X., Shang, L. et al., Mercury speciation in the flue gas of a small-scale coal-fired boiler in Guiyang, PR China, Journal DE Physique IV, 2003, 107: 1287—1290.
34. Bloom, N. S., Fitzgerald, W. F., Determination of volatile mercury species at the pictogram level by low temperature gas chromatography with cold-vapor atomic fluorescence detection, Analytica Chimica Acta, 1988, 208: 151—161.
35. Nierenberg, D. W., Nordgren, R. E., Chang, M. B. et al., Delayed cerebellar disease and death after accidental exposure to dimethylmercury, New England Journal of Medicine, 1998, 338(23): 1672—1676.
36. Sommar, J., Hallquist, M., Ljungstrom, E., Rate of reaction between the nitrate radical and dimethyl mercury in the gas phase, Chemical Physical Letters, 1996, 257 (5-6): 434—438.
37. Wang, S., Feng, X., Qiu, G. et al., Comparison of air/soil mercury exchange between warm and cold season in Hongfeng reservoir region, Environmental Science (in Chinese), 2004, 25(1): 123—127.
38. Wang, S., Feng, X., Qiu, G. et al., A preliminary study of airborne gaseous mercury exchange flux between soil and air in Hongfeng Reservoir region during summer season. Buuetin of Mineralogy, Petrology and Geochemistry (in Chinese), 2004, 23 (1): 19—23.

(Received January 30, 2004; accepted July 8, 2004)