Environment Protection Engineering

Vol. 32 2006 No. 3

MAGDALENA BEŁDOWSKA*,**, LUCYNA FALKOWSKA*,
PATRYCJA SIUDEK*, MARTA OTREMBA*

INFLUENCE OF BUILDING ACTIVITIES AND HIGH-TEMPERATURE PROCESSES ON THE CONCENTRATION OF GASEOUS MERCURY IN AIR

Total gaseous mercury (TGM) concentration in the air has been recorded continuously by means of an automated gaseous mercury analyzer GARDIS 3. In winter, when the reemission of gases from land and sea is restricted, the concentration of TGM increases several times as a result of building activities, such as: ground works, foundation building, and road asphalting. A similar increase in the TGM concentration has been observed in air masses flowing over exhaust fume emitters. The phenomena observed can affect the health of the inhabitants of Gdynia, workers and tourists, as the respiratory system is the main route for mercury to enter a human organism.

1. INTRODUCTION

In recent years, the percentage of people with cancer and brain dysfunction has increased significantly. One of the reasons of these diseases is an increase in mercury concentration in the environment. It is claimed to be responsible for autism, schizophrenia, Alzheimer disease, depression, multiple sclerosis, arthritis and chronic fatigue syndrome [1], [2]. Most recent research proves that induction of brain malfunction can be caused by the concentration of mercury being 10 times lower than the one considered dangerous by the World Health Organization (WHO). One of the ways in which mercury penetrates into human organism is a respiratory system.

Main sources of gaseous mercury (Hg(g)) emitted into the atmosphere are: fossil fuel combustion, smelting, refineries and other industrial plants utilizing mercury compounds in production [3]. In warm seasons, i.e., late spring, summer and early

* University of Gdańsk, Institute of Oceanography, Department of Marine Chemistry and Marine Environmental Protection, Al. Marszałka Piłsudskiego 46, 81-378 Gdynia, Poland. Tel: +48 58 660 1606.

** Corresponding author: Tel.: +48 58 600 16 09, fax: +48 58 660 16 78. E-mail address: ryba@sat.ocean.univ.gda.pl (Magdalena Bełdowska)

autumn, when solar radiation intensity and air temperature are high, the reemission of mercury from land and sea surfaces is considered to be the process contributing to an increase of its atmospheric concentration. A significant example of reemission in Europe could be Chemische Werke Buna, a chemical plant in Schkopau, Germany, that ceased its operation. Many years after the plant closure an elevated concentration of gaseous mercury in the air has been observed in the area [4]. Similarly, after several hundred years of mercury release to the environment, its reemission can be observed from water bodies and land surfaces [5].

In this study, we demonstrate the influence of short-term human activities (foundation construction, excavation, road surface replacement, replacement of sewage pipes, fossil fuel combustion) on an increase in mercury concentration in the air. The measurements have been conducted during the winter, when mercury reemission is quite low, which enabled precise identification of source processes.

2. MATERIALS AND METHODS

Sampling station has been situated in Gdynia, Poland ($\varphi = 54^\circ5'$, $\lambda = 18^\circ5'$), at the height of 3 m amsl (above mean sea level) in the year 2001 (October–December) and at the height of 20 m amsl in 2005 (February–March) and 2006 (February–March). Total gaseous mercury (TGM) concentration in the air has been recorded continuously with the resolution of 30 min by the means of an automated gaseous mercury analyzer GARDIS 3. The analyzer (an automated atomic absorption (AAS)) has the detection limit of 0.5 pg Hg being is comparable to that of AFS detectors or even better [6]. The experiments were preceded the analyser calibration at a room temperature. The results of TGM were automatically recorded by a computer [7]. For the trajectories of air masses, an HYSPLIT on-line Transport and Dispersion Model, provided by air resources laboratory NOAA, has been used [8], [9].

3. RESULTS AND DISCUSSION

Average concentrations and maximum values of total gaseous mercury (Hg(g)) in air during a cold season, when its reemission from land and sea was restricted, in the years 2001 and 2006 were comparable, i.e., 1.1 ngm^{-3}–1.7 ngm^{-3} and 16.2 ngm^{-3}–17.0 ngm^{-3}, respectively (table 1). During winter 2005 average TGM concentration was almost ten times as high as these in the remaining cold periods. In the season mentioned, maximum mercury concentration and standard deviation were almost 20 times as high as these in the years 2001 and 2006 (table 1). Multiannual observations proved that the concentration of TGM in the air in the area of our interest was usually higher in warm seasons (late spring, summer, early autumn) than in the colder seasons [10], [11] (table 2). Similar observations

have been made in other areas of Europe [12], [13]. In the coastal zone of the Gulf of Gdańsk as well as in other coastal areas (table 2), both primary and secondary sources of mercury are present, i.e., municipal waste dumps, area of the former fluorescent lamp replacement workshops and various water bodies. With an increase in the air temperature, evaporation of gaseous mercury improves, which is responsible for its higher concentration in air in warm seasons. In the cold seasons (late autumn, winter, early spring), low air temperature, weak solar radiation and high humidity inhibit evaporation, hence the reemission of mercury from land and water surfaces. Due to intensive combustion of fossil fuels in the heating season, the concentration of mercury in the atmosphere increases. However, in the period of its emission, gaseous mercury is quickly transported together with warm air to great heights, which prevents the immediate vicinity of the emitters from its higher concentration [14]. Due to a long residence time, reaching up to 24 months, Hg(g) can be transported together with air masses to remote areas, i.e, to Scandinavia [15]. Mercury use in industry has been very rigorously reduced in Sweden, which has lowered its emission from 150.0 tonnes year^{-1} to 1.5 tonnes year^{-1} [16], 17]. Elimination of mercury sources and the remediation of mercury reemission have resulted in a decrease in gaseous mercury concentration in the air during summer (table 1). However, the increased concentrations of gaseous mercury in winter, as suggested by LINDQVIST [18], might be due to its atmospheric transport from the polluted areas as a result of coal combustion in heating systems.

Table 1

Statistical characterization of the concentration of total gaseous mercury in Gdynia during cold seasons in 2001, 2005, 2006

Parameter	October–December 2001	February–March 2005	February–March 2006
Mean	1.7	9.7	1.1
Median	1.4	5.4	0.8
Standard deviation	1.3	21.6	1.1
Range	15.3	304.0	16.9
Minimal	0.9	2.0	0.1
Maximal	16.2	306.0	17.0

The influence of fossil fuel combustion on an increase in gaseous mercury concentration in a close vicinity of emitters has been observed by the end of the winter (the 1st of March 2006) when the masses of air coming from the area of the refinery (78 h prior the observation) came there from Silesia (42 h before) (figure 1). Air masses flowing over the largest mercury emitters in Poland can carry this element to remote areas. Therefore TGM concentration measured in the air above the Gulf of Gdańsk was as high as 18.0 ngm^{-3} (average concentration in winter – 1.3 ngm^{-3}, table 2). As a result, mercury level in the atmosphere during the light phase of the day has increased four times during the

period of interest, reaching an average value of 4.0 ngm^{-3} (figure 2).

Table 2

Concentration of total gaseous mercury (TGM) [ngm^{-3}] in different regions during summer and winter

Region	Season	TGM [ngm^{-3}]
Mt. Amiata (Italia) [12]	summer winter	20 10
Kagoshima (Japan) [13]	summer winter	14.8 4.4
Hel (Poland) [10]	summer winter	2.2 1.9
Sopot (Poland) [11]	summer winter	3.3 1.9
Gdynia (Poland) [11] (this paper)	summer winter	2.6 1.3
Sweden [18]	summer winter	1.5–2 3–4

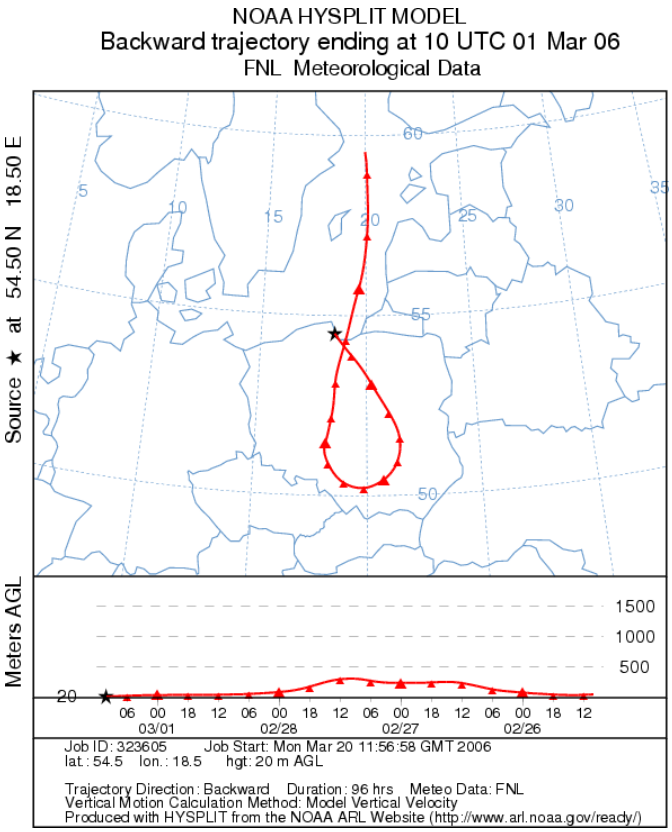
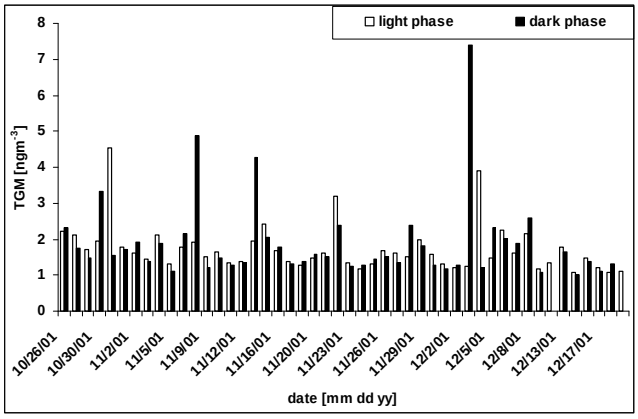


Fig. 1. Backward trajectory ending on March 1st 2006 [8], [9]

a)



b)

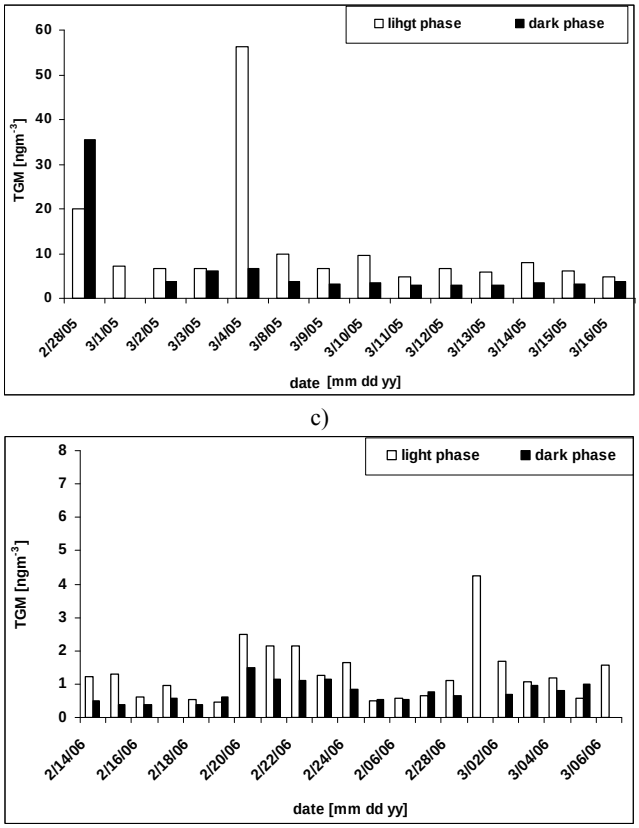


Fig. 2. Average total gaseous mercury (TGM) [ngm^{-3}] concentration during light and dark phases of the day during winter: a) 2001, b) 2005, c) 2006

High concentration of total gaseous mercury has been observed in the air over Gdynia a year before – in March 2005, during the construction activities pursued at a distance of 15 m from the sampling station. Because of a high volatility, the highest mercury concentration has been observed during concrete pouring, while the foundation of the 6-storey building was built. Average TGM concentration in this period was 9 times as high (9.7 ngm^{-3}) as an average mercury concentration observed in the winter in this area (table 1). Volatile Hg(g) has migrated quickly to the height of 20 m, which led to the increase in the average TGM concentration up to 60.0 ngm^{-3} (daytime) and 35.0 ngm^{-3} (nighttime) (figure 2).

Building works connected with street repair conducted in the fourth quarter of the year 2001 were also responsible for pollution of the air over Gdynia with mercury. In this time, the road surface replacement has been carried out on the Świętojańska street, located 100 m from the sampling station. Average mercury concentra-

tion in the air recorded 3 m amsl has been twice as high as that recorded during winter in other years, when sampling has been performed (table 2, figure 2). In the year 2001, the winter was warmer than usually (temperature above 0 °C). During that winter street repairs were conducted in Gdynia. Mercury present in asphalt and tar [19] as well as ground works conducted due to sewage pipes replacement could contribute to an increase in TGM concentration in air. It could be due to reemitting Hg(g) from soil or replacing old sewage pipes or covering a road with hot asphalt or tar outgassing. The concentration of Hg(g) rose from an average value of 2.3 ngm^{-3} to 6.4 ngm^{-3} (table 2, figure 3). The concentration of gaseous mercury increased several times during cold seasons of the year 2006, which could be also caused by the Świętojańska street repairs (figure 3). In 2001, the mercury concentrations were lower, probably because of a longer distance between the place of repair activities and the sampling station (1.5 km) and low air temperature, which did not favour the emission of gases.

4. CONCLUSIONS

The air flowing over the emitters of fossil fuel exhaust fumes has contributed to more than tenfold increase in Hg(g) concentration. Comparing the well-known gaseous mercury sources (e.g., fossil fuel combustion) to these that are based on different building activities (ground works, foundation building and asphalting) it can be claimed that the latter present themselves an efficient local source of mercury. In their immediate vicinity (15 m), the increase in mercury concentration in the air was more than 10 times bigger, and at the distance of 100 m the mercury concentration increased several times. The influence of building activities on mercury concentration in air might be of even more importance in the warm seasons, when gas emissions are stronger.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for providing us with the HYSPLIT transport and dispersion model and the READY website (http://www.arl.noaa.gov/ready.html).

LITERATURE

[1] BERNARD S., ENAYATI A., REDWOOD L., ROGER H., BINSTOCK T., *Autism: a novel form of mercury poising*, Medical Hypotheses, 2001, 56(4), 462–471.

[2] HOCK C., DRASCH G., GOLOMBOWSKI S., MÜLLER-SPAHN, WILLERSHAUSEN-ZÖNNCHEN, SCHWARZ P., HOCK U., GROWDON J.H., NITSCH R.M., *Increased blood mercury levels in patients with Alzhei-*

mer's disease, J. Neural Transmission, 1998, 105, 59–68.
[3] EBINGHAUS R., TURNER R.R., DE LACERDA L.D., VASILIEV O., SALOMONS W. (eds), *Mercury contaminated sites, characterization, risk assessment and remediation*, Springer-Verlag, Berlin, Heidelberg, 1999, 1–51.
[4] KRÜGER O., EBINGHAUS R., KOCKS H.H., RICHTER-POLITZ I., GEILCHUFE C., *Estimation of gaseous mercury emissions in Germany: Inverse modeling of source strengths at the contaminated industrial side BSL Werg Schopau*, [in:] R. Ebinghaus, R.R. Turner, L.D. de Lacerda, O. Vasilev, W. Salomons, (eds), *Mercury contaminated sites, characterization, risk assessment and remediation*, Springer-Verlag, Berlin–Heidelberg, 1999, 249–257.
[5] MASON R.P., FITZGERALD W.F., *Sources, sinks and biogeochemical cycling of mercury in the ocean*, [in:] W. Baeyens, R. Ebinghaus, O. Vasiliew (eds.), *Global and regional mercury cycles: sources, fluxes and mass balances*, NATO-ASI- Series 2, Environment 21, Kluwer, Dordrecht, The Netherlands, 1996, 249–272.
[6] URBA A., KVIETKUS K., SAKALYS J., XIAO Z., LIDQVIST O., *A new sensitive and portable mercury vapour analyzer Gardis-1A*, Water, Air and Soil Pollut., 1995, (80), 1305–1309.
[7] FALKOWSKA L., BEŁDOWSKA M., *Rtęć w powietrzu, w wodzie morskiej i w aerozolach*, [in:] J. Siepak (ed.), *Problemy analityczne oznaczania rtęci i jej form specjacyjnych w próbkach środowiskowych*, BETAGRAF, Poznań, 2003, 55–74.
[8] DRAXLER R.R., ROLPH G.D., *HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html)*,. NOAA Air Resources Laboratory, Silver Spring, MD, 2003.
[9] ROLPH G.D., *Real-time Environmental Applications and Display sYstem (READY) Website (http://www.arl.noaa.gov/ready/hysplit4.html)*, NOAA Air Resources Laboratory, Silver Spring, MD, 2003.
[10] MARKS R., BEŁDOWSKA M., *Air–sea exchange of mercury vapor over the Gulf of Gdańsk and southern Baltic Sea*, Journal of Marine Systems, 2000, 739, 1–10.
[11] BEŁDOWSKA, M., *Morze jako magazyn i jako źródło atmosferycznej rtęci (na przykładzie Basenu Gdańskiego)*, PhD Thesis, Department of Marine Chemistry and Marine Environmental Protection, Institute of Oceanography, University of Gdańsk (in Polish), 2004, 163 pp.
[12] FERRARA R., *Mercury mines in Europe: Assessment and environmental contamination*, Environmental Science, 1999, 49–70.
[13] TOMIYASU T., NAGANO A., SAKAMOTO H., YONEHARA N., *Background levels of atmospheric mercury in Kagoshima City, and influence of mercury emission from Sakurajima Volcano, Southern Kyushu, Japan*, The Science of the Total Environment, 2000, 259, 231–237.
[14] BEŁDOWSKA M., FALKOWSKA L., MARKS R., *Total gaseous mercury over the coastal zone of the Gulf of Gdańsk*, Oceanological and Hydrobiological Studies, 2003, 22(3), 3–18.
[15] LINDQUEST O., RODHE H., *Atmospheris – a reviev*, Tellus B, 1985, (37), 136–159.
[16] PACYNA J.M., PACYNA E.G., *An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic source worldwide*, Environmental Reviews, 2001, (9), 1–30.
[17] WREMBEL H.Z., *Mercury in the Baltic Sea*, Pedagogical University in Słupsk, 1997, p. 390.
[18] LINDQVIST O., *Mercury in the Swedish Environment*, Kluwer Academic Publishers, 1991, 33–40.
[19] VAN METRE P.C., MAHLER B.J., *The contribution of particles washed from rooftops to contaminant loading to urban streams*, Chemosphere, 2003, (52), 1727–1741.

WPŁYW DZIAŁAŃ BUDOWLANYCH I PROCESÓW WYSOKOTEMPERATUROWYCH NA POZIOM STĘŻENIA GAZOWEJ RTĘCI W POWIETRZU

Pomiary stężenia całkowitej gazowej rtęci (TGM) w powietrzu prowadzono w Gdyni z zastosowa-

niem automatycznego analizatora rtęci gazowej GARDIS 3. Zimą, gdy procesy reemsji gazów z powierzchni lądu i wody są ograniczone, obserwowano kilkukrotny wzrost stężenia TGM podczas prowadzonych działań remontowych i budowlanych takich jak: wykopy, powstawanie fundamentów, smołowanie, wylewanie asfaltu. Zmierzono również kilkunastokrotnie wyższe stężenie Hg(g) w masach powietrza przemieszczających się nad emiterami spalin. Ma to duże znaczenie zarówno dla pracowników, mieszkańców, jak i turystów, gdyż układ oddechowy jest główną i bezpośrednią drogą wnikania rtęci do organizmu człowieka.