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TOTAL GASEOUS MERCURY IN THE AREA OF SOUTHERN BALTIC AND IN THE COASTAL ZONE OF THE GULF OF GDAŃSK DURING SPRING AND AUTUMN

Total gaseous mercury (TGM) concentration was measured over the offshore waters of the Gdańsk Deep during spring and autumn in the years 1999–2006. The results obtained were compared with TGM concentrations recorded at the same time in the air of the coastal zone of Gdynia and Sopot. Both offshore and in coastal zone, higher Hg(g) concentrations were measured in autumn than in spring. When analyzing mean Hg(g) concentrations in subsequent hours of the day, solar radiation effect on mercury level in the air was evident. Mercury levels in the air seemed to be controlled also by the presence of dissolved organic matter in the seawater, which is responsible for mercury complexation and for algae detoxification processes.

1. INTRODUCTION

Mercury presence in the air might be responsible for many nervous system dysfunctions of both adults and children. In Europe, during the last decade of the twentieth century, mercury emissions were reduced more than twofold. Despite this fact, mercury concentration in the atmosphere and mercury deposition did not decrease. One of the reasons of this situation is the reemission of mercury from land and sea surfaces. High mercury concentrations in air have been reported, for example, in the vicinity of closed down paint factories and in the close vicinity of construction sites, during excavation and concrete pouring [1]. High mercury reemission was also recorded in coastal areas – in the area of the Vistula Mouth (from 6.9 $ng \cdot m^{-2} \cdot h^{-1}$ to 19.3 $ng \cdot m^{-2} \cdot h^{-1}$) and close to the Mechelinki sewage treatment plant (7.1 $ng \cdot m^{-2} \cdot h^{-1}$–7.7 $ng \cdot m^{-2} \cdot h^{-1}$). Significantly higher mercury emission

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from the sea to air were frequently observed in the area of Gdynia and Gdańsk harbors' fairwater (up to 60.5 ng·m^{-2}·h^{-1}). Reemission from offshore waters reached up to 5.9 ng Hg·m^{-2}h^{-1} in spring, and up to 4.0 ng Hg· m^{-2}h^{-1} in autumn [2]. The aim of the current study was to assess the variability of mercury concentration in inhaled air and to explain the role of site, season, time of the day and meteorological conditions in controlling the magnitude of this variability.

2. MATERIALS AND METHODS

Total gaseous mercury measurements in the air of the offshore area (the Gdańsk Deep – φ = 54°50' N; λ = 19°07' E) were performed in six periods, i.e. in autumn (29.09–03.10. 2002; 26.09–04.10. 2004; 19.10–21.10. 2006) and in spring: (19.05–27.05. 1999; 08.05–12.05.2003; 23.04–27.04.2006). Gaseous mercury level has been recorded at 10 m AMSL by means of an automated gaseous mercury analyzer GARDIS 3. The detection limit of the analyzer (AAS) was established at 0.5 pg Hg. Simultaneously, meteorological parameters and solar radiation intensity in UV-A, UV-B and PAR bands were measured. The results obtained were compared with TGM levels in the coastal zone of the Gulf of Gdańsk in Sopot (calendar spring and autumn of 1999) and Gdynia (autumn 2001, November 2007, calendar spring 2002 and March–April 2008) [3].

3. RESULTS AND DISCUSSION

In the offshore area, total gaseous mercury concentration in the air varied from 0.5 ng·m^{-3} (both in spring and autumn) to 6.8 ng·m^{-3} (in spring) (table 1). In autumn 2004, mean TGM concentrations of 1.3 ng·m^{-3} and in 2002 and 2006 of 1.6 ng·m^{-3} were recorded. During the spring, the concentration changes were bigger – from 1.0 ng·m^{-3} (2006) to 2.9 ng·m^{-3} (1999) (table). In the same periods, mean gaseous mercury concentration in the coastal zone of the Gulf of Gdańsk was similar to that found offshore.

The lowest gaseous mercury concentration in the air above the offshore waters of the Gdańsk Basin was recorded in 2006, after a long and severe winter. In that year, the growing season was delayed several weeks. 55% of Hg(g) concentration measurements did not exceed 1.5 ng·m^{-3} (figures 1 and 2). However, in spring of 1999 and 2003, higher TGM concentration values were measured. More than a half of the results fitted did not exceed 3.0 ng. Similar changes were observed in the coastal zone of Gdynia and Sopot, where in most cases concentration values did not exceed 3.0 ng, but the maximum values observed there were several times higher than those found offshore [3].

Statistical characteristics of total gaseous mercury [ng·m^{-3}]
recorded in spring and autumn in the air of the offshore area of Gdańsk Deep
in years 1999, 2002, 2003, 2004, 2006

Area	Season	Mean TGM [ng·m^{-3}]	Reference
Gdańsk Deep	spring 1999	2.9	this study
	spring 2003	2.7	this study
	spring 2006	1.0	this study
	autumn 2002	1.6	this study
	autumn 2004	1.3	this study
	autumn 2006	1.6	this study
Sopot	spring 1999	2.8	[3]
	autumn 1999	1.5	[3]
Gdynia	spring 2002	3.0	[3]
	March 2008	1.2	this study
	autumn 2001	1.7	this study
	November 2007	1.2	this study

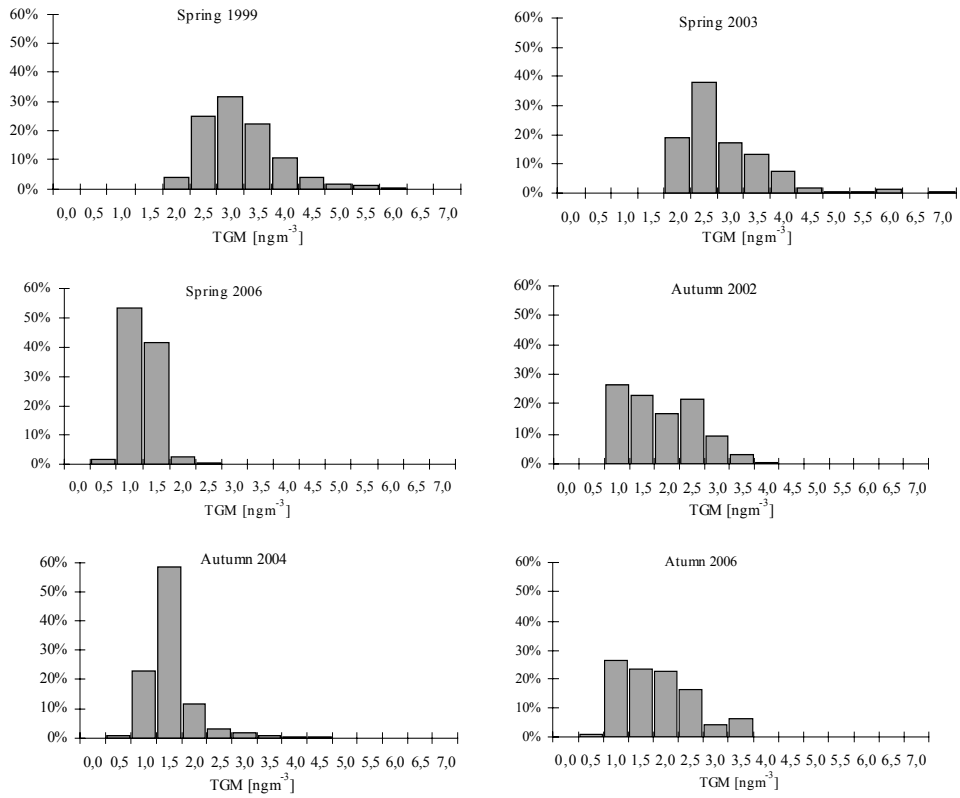

Fig. 1. Histograms of total gaseous mercury concentrations [ng·m^{-3}]
recorded in spring and autumn in the air above Gdańsk Deep (1999–2006)

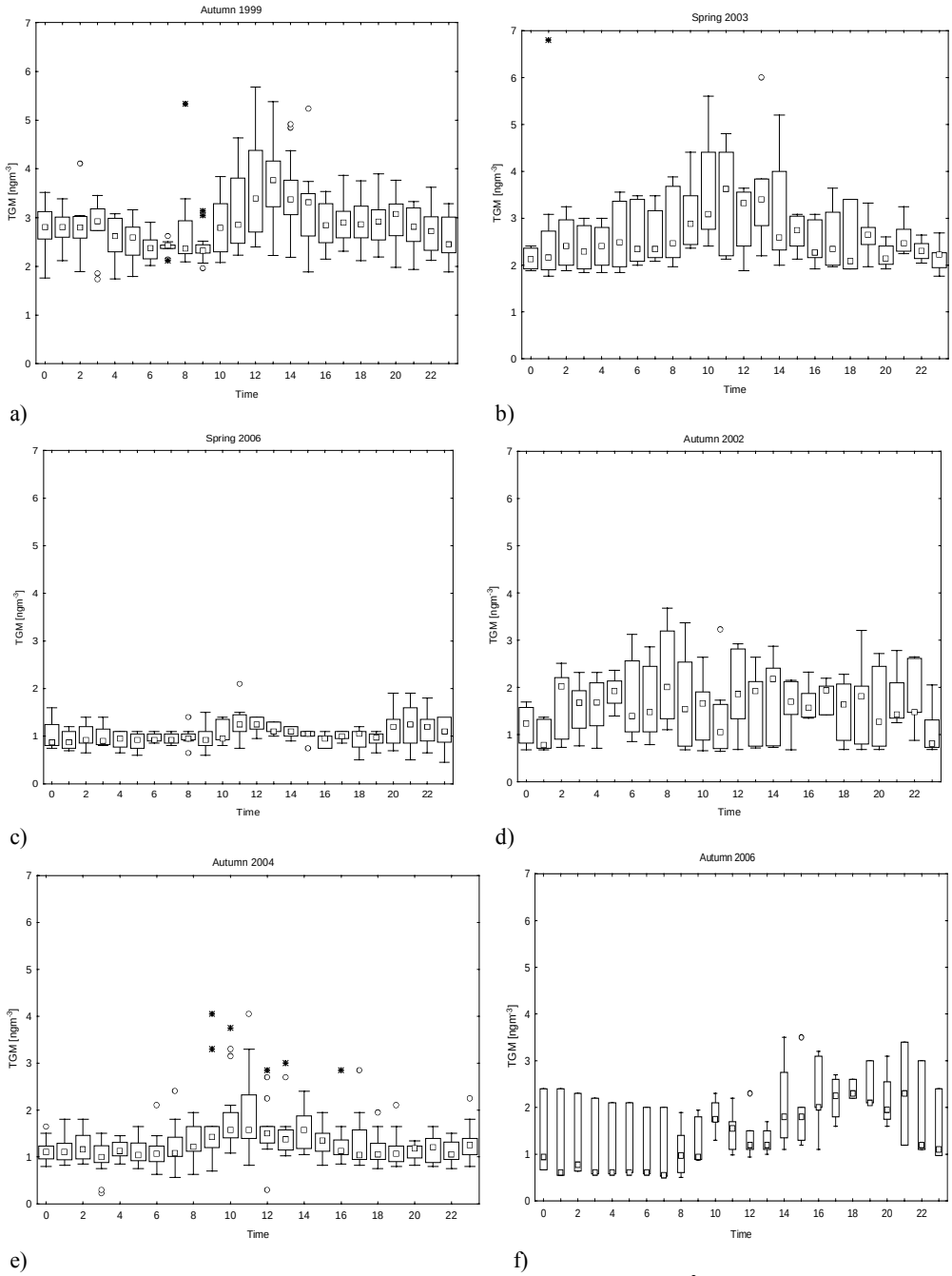

Fig. 2. Hourly averages of total gaseous mercury concentration [ng·m^{-3}] in the air of Gdańsk Deep area, calculated based on all results recorded: a) in spring in 1999 year; b) in spring in 2003 year; c) in spring in 2006 year; d) in autumn in 2002 year; e) in autumn in 2004 year; f) in autumn in 2006 year

In autumn, mean TGM concentration at the Gdańsk Deep in most cases did not exceed 2.0 ng·m^{-3}. In 2004, more than a half of the measurements (59%) of Hg(g) concentration fitted in narrower range (from 1.0 ng·m^{-3} to 1.5 ng·m^{-3}) than in the other periods of measurements (figure 1). In autumn, at the coastal stations in Gdynia and Sopot the majority of results did not exceed 1.5 ng·m^{-3} [3]. At this time of the year solar radiation intensity is too low to stimulate mercury vaporization from land and water surfaces, as it does in late spring and summer. In the offshore area, higher gaseous mercury concentration in the air might result from organic matter-induced Hg(II) reduction to Hg(0) and reemission of the latter (4–5).

In the offshore air, aside from seasonal variability, diurnal variability of TGM concentration was observed. In spring season, elemental mercury concentration has been rising from the morning, proportional to solar radiation intensity, reaching its maximum values around noon (figure 2). In this season, solar radiation intensity of: PAR – 1393 μmol/m^2/s^1; UV-B up to 1.1 W/m^2; 1.00 UV-A to 19.1 W/m^2, was high enough to stimulate both mercury–dissolved organic matter (DOM) complex formation and its reduction in the water to dissolved gaseous mercury (DGM). By exuding DOM outside of the cell, phytoplankton is able to detoxicate itself. This process leads to an increase of DGM concentration and hence to oversaturation of the surface microlayer with gaseous mercury, from where it is emitted to the atmosphere [4]–[5].

In autumn, in the Gdańsk Deep area, as in the coastal zone of the Gulf of Gdańsk [3], an increase of TGM concentration has been observed in the morning. This phenomenon might have resulted from photochemically induced reduction of Hg(II) to Hg(0) (figure 2). However, a further increase of solar radiation intensity favoured mercury complexation with organic matter, hence inhibiting mercury release from the water. This hypothesis is supported by the negative correlations between TGM concentration and solar radiation intensity: TGM/UV-A, $r = –0.4$; TGM/UV-B, $r = –0.5$; TGM/PAR, $r = –0.5$. This occurred only when the complexation capacity of organic matter was exceeded, hence the reduction of mercury and its emission to the atmosphere took place. Such a situation has been observed at afternoon, in many cases during warm days in autumn at coastal stations, when inland winds prevailed. TGM concentration increase was accompanied by the rise in air temperature [3].

4. CONCLUSIONS

Both in the offshore and coastal areas, TGM concentrations in the air were similar. In both areas the seasonal changes of TGM concentration showed similar pattern; however, in the places close to the land, high values of Hg(0) concentration were found more often. In spring, the offshore TGM has risen proportionally to solar radiation, whereas in the coastal zone of the Gulf of Gdańsk, where phytoplankton blooms are more frequent than in the Gdańsk Deep area in the spring season, mercury accu-

mulation by dissolved organic matter prevailed, which prevented mercury release from the water at noon. After exceeding organic matter complexation capacity at afternoon, the reduction of Hg(II) to Hg(0) occurred, which resulted in the emission of the latter to the atmosphere. Similar dependencies were observed in autumn in offshore areas. In the early autumn, TGM concentrations over the land varied in a narrower range, even in the case where air temperature was quite high.

REFERENCES

[1] EBINGHAUS R., TURNER R. R., de LACERDA L. D., VASILIEV O., SALOMONS W., *Mercury contaminated sites*, Springer, New York, 1999, 1–51.

[2] BEŁDOWSKA M., FALKOWSKA L., SIUDEK P., GAJECKA A., LEWANDOWSKA A., RYBKA A., ZGRUNDO A., *Atmospheric mercury over the coastal zone of the Gulf of Gdansk*, Oceanological and Hydrobiological Studies, 2007, 36, 3, 9–18.

[3] BEŁDOWSKA M., FALKOWSKA L., LEWANDOWSKA A., *The gaseous mercury concentration level in the breathed air of the coastal zone of the Gulf of Gdansk*, Ochrona Powietrza w Teorii i Praktyce, 2006, tom 2, 13–22.

[4] COSTA M., LISS P., *Photoreduction and evolution of mercury from seawater*, The Science of the Total Environment, 2000, 261, 125–135.

[5] BONZONGO J.-C.J., DONKOR A.K., *Increasing UV-B radiation at the earth's surface and potential effects on aqueous mercury cycling and toxicity*, Chemosphere, 2003, 52, 1263–1273.

RTĘĆ W POWIETRZU NAD WODAMI POŁUDNIOWEGO BAŁTYKU I W STREFIE BRZEGOWEJ ZATOKI GDAŃSKIEJ

Stężenie całkowitej gazowej rtęci (TGM) w powietrzu mierzono nad otwartym morzem w rejonie Głębi Gdańskiej wiosną i jesienią w latach 1999–2006. Wyniki porównano ze stężeniami TGM rejestrowanymi w tym samym czasie w strefie brzegowej nad Gdynią i Sopotem. Zarówno z dala od lądu, jak i w powietrzu strefy brzegowej Zatoki Gdańskiej zmierzone stężenia Hg(g) były wyższe wiosną niż jesienią. Analizując średnie stężenia Hg (g) w poszczególnych godzinach doby, nad Głębią Gdańską i na stacjach brzegowych zaobserwowano wyraźny wpływ natężenia radiacji słonecznej na poziom stężenia rtęci w powietrzu. Oprócz natężenia radiacji słonecznej ważnym czynnikiem, wpływającym na stężenie rtęci, była prawdopodobnie rozpuszczona materia organiczna, z którą należy łączyć kompleksowanie rtęci i detoksyfikację glonów.