Pol. J. Environ. Stud. Vol. 22, No. 3 (2013), 759-771

Original Research

The Estimation of Total Gaseous Mercury Concentration (TGM) Using Exploratory and Stochastic Methods

Grzegorz Majewski[1]*, Piotr O. Czechowski[2], Artur Badyda[3], Wioletta Rogula-Kozłowska[4]

[1]Division of Meteorology and Climatology, Warsaw University of Life Sciences,
Nowoursynowska 166, 02-776 Warszawa, Poland
[2]Information Systems Department, Gdynia Maritime University, Morska 83, 81-225 Gdynia, Poland
[3]Environmental Engineering Faculty, Warsaw University of Technology,
Nowowiejska 20, 00-653 Warszawa, Poland
[4]Institute of Environmental Engineering of the Polish Academy of Sciences, Department of Air Protection,
M. Skłodowskiej-Curie 34, 41-819 Zabrze, Poland

Received: 16 April 2012
Accepted: 8 January 2013

Abstract

Our paper presents the results of the first one-year measurement series of total gaseous mercury collected at an automatic air quality monitoring station in the village of Granica (Granica-KPN). The measurement series of mercury concentrations was used to estimate the model that identifies the influence of selected measurement results, both imission and meteorological ones, on the concentration of gaseous mercury in the air. Such a model can be a useful tool for the estimation of gaseous mercury concentration over a certain area, and for the estimation of the mercury deposition rate, as well as for the reduction of costs of expensive measuring devices used for recording concentration of that air pollutant.

The advantage of the presented method for mercury concentration identification is the relatively low cost of acquiring precise results, when meteorological conditions are known and the measurements of imission are significantly connected with mercury.

Such a low cost is related, first of all, to the computation time and the software, assuming that the considered analytical system is fully functional. The disadvantages include the need to have measurement series without gaps in data. It is a practical problem for which the solution is stochastic interpolations as proposed in this paper. In order to obtain precise resultant estimations of a variable we need to have high-quality input data - in a sense it is a truism that is often not sufficiently implemented in practice. For this reason, a detailed diagnosis of measurement data is required, including stochastic- exploratory tools, which were presented in this paper in their most effective implementation. It is essential not to include in calculations those data that contain errors, e.g. having an influential or atypical character in relation to other distributions or measurements.

These errors in the data will be transferred onto results unless they are identified in the initial phase of modeling.

Mean annual TGM concentration was equal to 1.52 $ng \cdot m^{-3}$ and was considerably lower than in other parts of Poland. Seasonal variability of TGM concentration was observed, and the TGM concentration was higher in the winter period than in summer. Mean concentration of TGM in the winter period (heating season)

*e-mail: grzegorz_majewski@sggw.pl

was equal to 1.65 ng·m^{-3}, but in the summer it reached 1.40 ng·m^{-3}. The TGM concentration at the Granica-KPN station was influenced mostly by local emission sources, in both warm and cold periods of the year. The analysis of fluxes of total gaseous mercury proved that the state of air pollution with mercury in the surroundings of the station also was influenced by the sources of a high emission rate in the winter period, located in WSW, W, and WNW sectors.

Keywords: total gaseous mercury (TGM), pollution plume, exploratory and stochastic methods

Introduction

Mercury is a heavy metal of toxic properties, significantly affecting the environment and human health. Mercury in the air comes both from natural and anthropogenic sources, primary and secondary ones [1]. Anthropogenic sources of mercury include the combustion of fossil fuels (refineries, heat and power plants, power industry, household heating), metallurgy, ore purification plants, other branches of industry, and waste incineration plants [2]. Poland belongs to a group of countries of high anthropogenic Hg emissions. In 2000 it ranked second in this respect in Europe behind Russia, slightly ahead of Germany and Spain [3].

In the atmospheric air mercury occurs mainly in a form of vapors of Hg^0 (GEM – gaseous element mercury), but also in an ionic form, as Hg^{2+} (GDM – gaseous divalent mercury) and rarely as Hg^+; as an unstable form it easily undergoes oxidation to Hg^{2+} [4]. A small amount of atmospheric mercury is combined with solid particles (P-Hg) [5]. Hg^0 constitutes, depending on the source of emission, 60-90% of the total concentration of gaseous mercury in the air (TGM – total gaseous mercury) [6]. The duration of elemental mercury vapor remaining in the air is assessed to be on average about 1 year, which means that it is a transboundary pollutant [7, 8].

The compounds of divalent mercury, frequently called reactive gaseous mercury (RGM), constitute a small share (about 3%) in the total concentration of mercury occurring in the air in a gaseous form [9]. Mercury in suspended dust (P-Hg) is an effect of direct emission, adsorption of mercury present in the air in a gaseous phase, dissolution of Hg compounds in humid aerosols, and inclusion of minerals containing Hg in the particles of aerosols [10]. The duration of RGM and P-Hg remaining in the air is much shorter in comparison to elemental mercury: it lasts only from several days to several weeks [11, 12].

With reference to the data contained in the literature, total gaseous mercury (TGM) in non-polluted areas is within a range from 0.5 ng·m^{-3} to 10 ng·m^{-3} (on average 1.5 ng·m^{-3}) and in the areas with emission sources the content may even reach 20 μg·m^{-3} [13-15].

Research on the level of mercury concentration in different parts of the world has been conducted for many years. So far in Poland measurements of mercury vapors in the air have been made sporadically. In Mazovia Province measurements of total gaseous mercury (TGM) were started as late as from 1 January 2010.

Our work presents first results of a one-year series of systematic measurements of total gaseous mercury in the air on the basis of measurement data from the only automatic measurement station of the Voivodeship Inspectorate of Environmental Protection (WIOŚ) in Mazovia Province, located in the village of Granica (the Granica-KPN station) in Kampinos National Park. The measurements series of mercury concentration was used to estimate the model identifying the influence of selected measurement results, both imission and meteorological ones, on the concentrations of gaseous mercury in atmospheric air. Such a model can be a useful tool for the estimation of the concentration of gaseous mercury over a certain area and mercury deposition flux. Also, it can reduce costs of expensive measuring devices of the analyzed pollutant.

Material and Methods

The measurement data used in the study came from an automatic air quality monitoring station of the Voivodeship Inspectorate of Environmental Protection in Warsaw, located in the village of Granica (Granica-KPN). The Granica-KPN station (λ_E 20º27'20" φ_N 52º17'09.088", 72.0 m above sea level) is situated in the southwestern part of Kampinos National Park (KPN). Area representativeness of the station is a diameter of several dozen kilometers. The parameters measured at the station, apart from meteorological conditions, are: concentrations of sulfur dioxide, nitrogen dioxide, ozone, and PM_{10} dust. Since 2010 measurements of total gaseous mercury (TGM) at the station are conducted with the use of a Tekran 2537 A analyzer. The analyzer performs a continuous measurement of total gaseous mercury in the atmospheric air with an update rate of 2.5 minutes. A detection limit is less than 0.1 ng·m^{-3} (12 parts per quadrillion).

The air quality in Granica is affected by emissions from nearby towns: Warsaw in the east, Sochaczew in the southwest, Żyrardów in the south. At a distance of about 2 km south of the measurement station runs Regional Road 580. Local sources of emission include the village of Koszówka, about 2 km south-east of the station, and the buildings of the KPN administration.

The analysis took into consideration the measurement results of total gaseous mercury concentration (1-h, 24-h) and other air pollutants measured at the station in Granica. The assessment of pollutant dispersion conditions took into account meteorological parameters.

An important element of the study is the identification of air inflow directions over the examined area and an attempt at indicating the emission sources polluting air with total gaseous mercury. To achieve this goal, pollution windroses were drawn up. This method only allows finding which wind directions bring the highest concentrations. However, a relatively high average value of pollutant concentration may result from an incidental occurrence of raised concentration values in a given sector. Circle diagrams of pollutant concentration percentiles are a better graphical representation of the distribution of concentration values with different wind directions [16].

In order to obtain the information about dust inflow directions over the examined area and about the intensity of the sources of air pollution with mercury, the study analyzed pollution fluxes [17, 18]. A pollution flux is a vector. The scalar of this vector is equal to the amount of pollution flowing in a unit of time through a unit of surface area orthogonal to the flow direction. This is a flux rate [ng·m^{-2}·s^{-1}], which constitutes a measure of inflow and outflow of a substance through a unit of surface area in space [19]. After calculating the pollution fluxes, circle diagrams of their percentiles of p = 50, 70, 95, and 98 were prepared.

A sequence of mercury measurements was used to estimate the model identifying the influence of selected measurement results, both imission and meteorological ones, on concentrations of gaseous mercury in the atmospheric air. Before building the model the data were tested to eliminate gross errors and other potential anomalies such as information transmission errors. Detailed analyses of the synergy of components in frequency domain and of the delay in time domain were carried out. A short duration of a series of measurement results (a year), which determines selection of quantitative research methodology, was a limitation of all the analyses.

Table 1. Descriptive statistics of one-year measurement series of air pollutants at Granica station.

Statistical parameter	Pollutant concentration (24-h)				
	Gaseous mercury TGM	PM_{10}	SO_2	NO_2	O_3
	[ng·m^{-3}]	[μg·m^{-3}]			
Year					
Arithmetic mean	1.52	31.0	5.5	8.6	49.7
Minimum	0.86	3.2	0.9	1.4	4.9
Maximum	2.50	143.3	36.1	42.3	87.9
Median	1.48	25.0	3.5	6.4	51.2
Standard deviation	0.30	21.7	5.2	6.8	18.3
Warm half-year					
Arithmetic mean	1.40	20.3	2.8	4.6	56.9
Minimum	0.86	3.2	0.9	1.4	17.3
Maximum	2.28	47.7	6.7	13.0	87.9
Median	1.38	18.8	2.6	4.1	58.1
Standard deviation	0.19	8.3	1.1	2.2	15.3
Cold half-year					
Arithmetic mean	1.65	41.7	8.4	12.6	42.7
Minimum	0.86	6.6	0.9	2.5	4.9
Maximum	2.50	143.3	36.1	42.3	81.3
Median	1.67	35.7	6.3	10.5	44.5
Standard deviation	0.33	25.3	6.2	7.4	18.4

Research Results and Discussion

The measurement results of concentrations of gaseous mercury and other pollutants measured at the measuring station were presented in Table 1.

Mean daily, gaseous mercury concentration changed during the whole measurement period from 0.86 ng·m^{-3} to 2.50 ng·m^{-3}. Seasonal variability of TGM concentration was observed, in winter TGM concentration was higher than in summer. Mean concentration of TGM in the winter season (heating season) amounted to 1.65 ng·m^{-3}, and in summer to 1.40 ng·m^{-3}.

Mean annual concentration of TGM amounted to 1.52 ng·m^{-3} and was much lower than those recorded in other regions of Poland. At the stations in Hel, Sopot, and Gdynia mean TGM concentration from 1997-2002 amounted to 2.3 ng·m^{-3} [2]. Much higher TGM concentrations were obtained from measurements performed at the background station in Katowice, i.e. 3.1 ng·m^{-3} [20], and in towns of the Upper Silesia agglomeration where it equaled from 2.4 ng·m^{-3} at the station in Tychy (the town with the highest availability of heat supply in the region) to 4.6 ng·m^{-3} at the station located in Dąbrowa in an industrial estate [21].

Mean concentration of TGM at Granica station is very similar to background values of TGM, measured in other European countries [22].

Measurements conducted beyond Europe, e.g. in China, show that TGM concentrations are at a much higher level than at the stations in Poland, on average from 8.1 to 34.9 ng·m^{-3} [23-25].

In Fig. 1 showing mean hourly TGM concentrations during 24 hours, one can observe the occurrence of a distinct cycle of daily variability of mercury concentration, with one local peak in the morning, about 10-11 a.m., taking into account the fact that the hour of its occurrence changes in the course of the year. In winter the maximum concentration occurs during later morning hours than in summer. A considerable decrease in mercury concentration is observed in the daytime after 1 p.m. with a night minimum at about 5 a.m.

In order to identify the directions of mercury inflow, circle diagrams of the percentiles of mercury influx concentrations and rates were prepared and analyzed in relation to particular sectors of a wind-rose (Figs. 2 a, b). In these figures one can see a difference in the distribution of percentiles in particular sectors between the summer and the

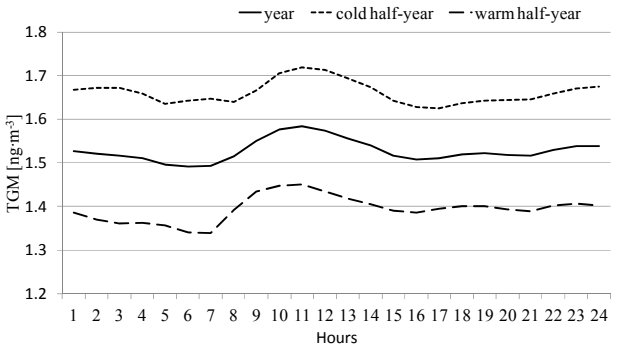


Fig. 1. Mean daily course of TGM concentration at the Granica station, 2010.

winter season. In summer they are regular, which may show the effect of pollution sources located in different directions around the measuring point. The mercury levels at Granica station in the warm half-year are shaped by a different kind of emission sources and different conditions of pollutant dispersion than in the cold season of the year. In the warm half-year the heating industry emits less pollution, and weather conditions are less conducive to the transport of pollutants over long distances, so the mercury pollution plume is mainly shaped by the local sources with a large contribution of transport.

In the warm half-year the distribution of mercury concentration percentiles of 50-95% was even in all sectors. The course of the 98th percentile shows slightly higher concentrations with the air inflow from SE and SSW, but it is only 10% higher than concentrations in the remaining sectors. This is evidence of the influence of the sources scattered in different directions around the measuring station on the pollution plume. It results from the analysis of pollution fluxes that the sources of the highest emission rate in that period were located in the sector 202-270ºN. As much as the flux distribution of the 50th and the 70th percentiles is almost even in relation to the directions of air mass inflow, the distributions of the 95th and the 98th percentiles show an especially strong flux of dust inflow from SSW, with an almost twice as high rate (above 5.5 $ng \cdot m^{-2} \cdot s^{-1}$) than with the inflow from the eastern sectors. On average, the flux intensities from the sector 202-270ºN were higher by 60% than the remaining ones.

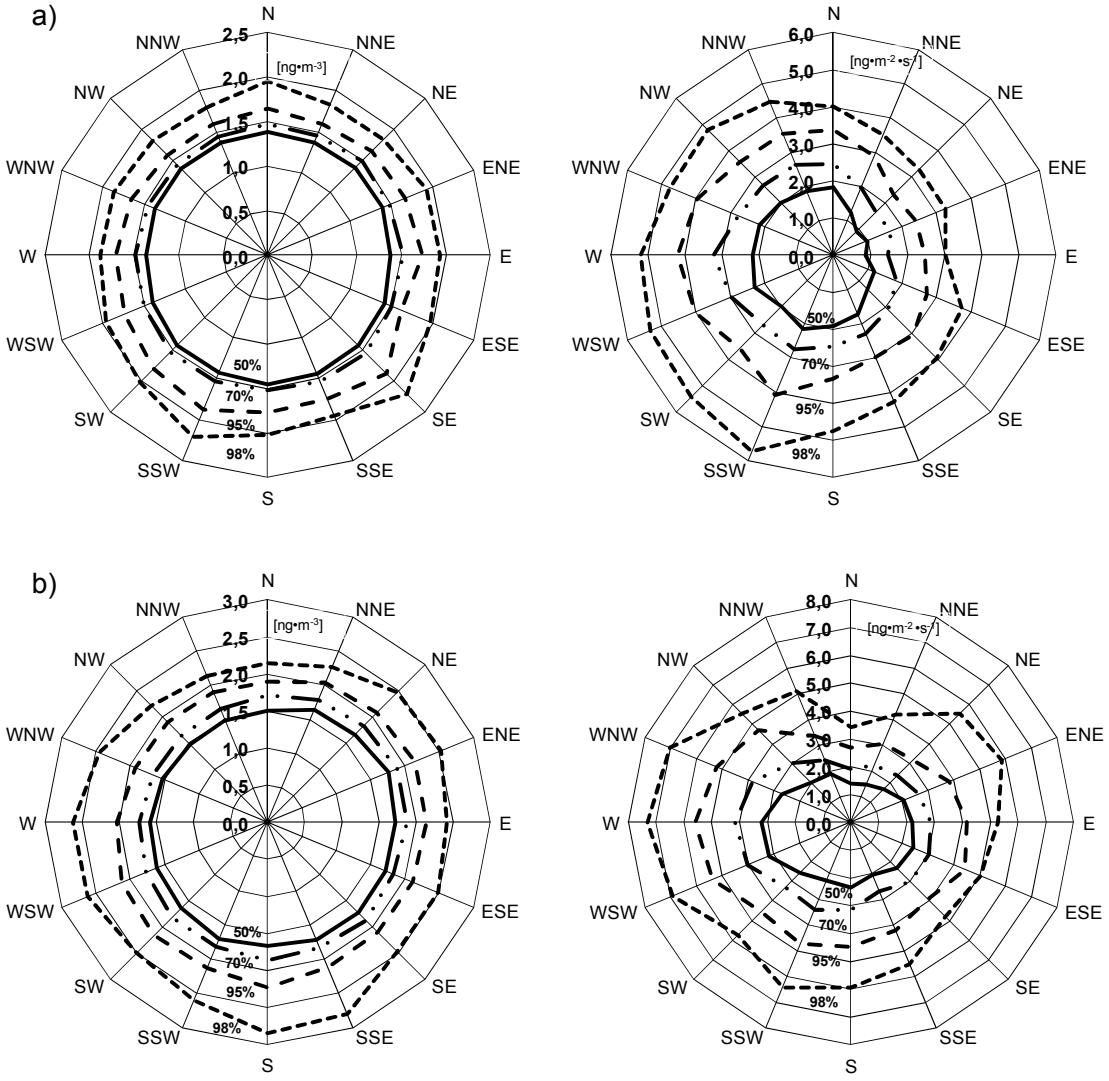


Fig. 2. Circle diagrams of the percentiles of total gaseous mercury concentrations and the total gaseous mercury fluxes in the warm (a) and the cold (b) half-year at Granica station, 2010.

Table 2. Distributions of the series of data gaps.

Length of data gaps series	Mercury	PM_{10}	SO_2	NO_2	O_3	Temp	Velocity	Humid.	Rad.	Pressure
x_i bd	n_i bd									
1	1	3	1	1	1	1	1	1	1	1
2	1	3	1	2	2	1	1	1	1	1
4			1							
10	1									
Total	13	9	7	5	5	3	3	3	3	3

Temp. – air temperature, Velocity – wind velocity, Humid. – relative air humidity, Rad. – solar radiation intensity, Pressure – atmospheric pressure

Table 3. Characteristics of one-dimensional distributions of measurement results. classical statistical measurements.

Variable	N	Minimum	Maximum	Standard deviation unbiased	Mean X0	Winsorised mean X0w (10%; 10%)	Trimmed mean X0u (10%; 10%)	Alpha 3 biased
Mercury	334	0.86	2.5	0.3	1.51	1.50	1.49	0.59
PM_{10}	334	3.2	143.3	20.21	29.19	27.10	25.68	2.19
SO_2	334	0.9	36.1	4.56	4.95	4.46	3.97	2.78
NO_2	334	1.4	42.3	5.7	7.60	7.05	6.56	1.77
O_3	334	4.9	87.9	17.43	51.78	51.88	52.59	-0.38
Temp	334	-20.9	26.8	9.35	8.29	8.54	8.72	-0.47
Rad.	334	5	519	143.74	192.17	187.04	181.27	0.48
Pressure	334	970.0	1,025.58	9.42	998.34	998.50	998.64	-0.69

In the cold half-year, the distribution of mercury concentration percentiles of 50-75% was almost even in all sectors. Fig. 2b shows that the highest concentrations occurred with the air inflow from sectors 157-202°N and 247-270ºN (the value of a percentile of 98% in the sectors SSE and S was higher by 20% than in the remaining ones), which could indicate the effect of big point emission sources.

The distribution of the percentiles of mercury fluxes in particular sectors of wind directions looks completely different. In the cold half-year the highest flux intensities occur with air mass inflow from sectors 247-292ºN, and also from ENE, SSE, S, and SSW. The distribution of the 98th percentile shows a particularly strong mercury flux from the west, with a rate over two times higher (more than 7 $ng \cdot m^{-2} \cdot s^{-1}$) than with the inflow from the northern sectors.

Equating the directions of inflow with straight line trajectories, one can state that they determine the areas in which the sources of a high emission rate are located [26].

Such a pattern of pollutant inflow is connected with the location of the station on the southern boundary of Kampinos National Park. Southwest of the station are larger villages such as Kampinos and Leszno, and also regional and national roads of high traffic density. Analysis of the fluxes shows that the level of mercury imission at the Granica station is affected not only by the local sources of pollutant emission but also by the inflow from more distant towns and villages, e.g. Sochaczew, which are located southwest of the station or from Warsaw situated west of the station.

Quantitative Analysis

Preliminary Data Analysis

The sequences of measurement results with data gaps were subjected to interpolation to allow conducting model calculations [27]. The distributions of data gaps enabled interpolation with the use of a simple method of the arithmetic mean and linear interpolation from end points in the case of a ten-observation series of mercury (Table 2).

The calculations were made with the use of the system Statistica and Eco Data Miner, an analytical system for environmental engineering [28].

a. <u>One-dimensional approach</u>

The preliminary analysis involved a general and a detailed analysis of measurement data quality. The general analysis was conducted on the basis of assessing the influence of the Winsorized distribution and the trimmed distribution on the initial distribution (Tables 2-4).

Table 4. Characteristics of one-dimensional distributions of measurement results. Robust statistical measurements.

Variable	N	Percentile 1	Percentile 99	Median	Percentile deviation	A(x0)	A(perc)
Mercury	334	0.87	2.33	1.46	0.73	1.04	1.04
PM_{10}	334	6.73	101.27	23.4	47.27	0.67	0.67
SO_2	334	1	20.27	3.4	9.63	0.63	0.63
NO_2	334	1.73	26.67	5.75	12.47	0.49	0.49
O_3	334	12.73	85.5	53.4	36.39	-0.59	-0.59
Temp	334	-15.82	24.74	9.15	20.28	0.21	0.21
Rad.	334	6.33	498.02	171	245.85	1.29	1.29
Pressure	334	971.92	1,022.31	998.33	25.2	0.82	0.82

Both trimming and Winsorization were conducted on the basis of 10% symmetric distribution edges. Appropriate means: the trimmed one and the Winsorized one were accepted as the basis of calculations.

In none of the measurement series was strong influence of extreme values on the initial distribution observed. The strongest influence, for the Winsorized mean, was observed in the case of measurement results of SO_2 (Table 5), namely -9.9%. In the case of the trimmed mean, the share of the difference between the trimmed and the classical mean at the average level amounted to -20%. Both results show a relatively low impact of extreme values on the distribution, which in turn might suggest lack of strong anomalies. It should be stressed that in the case of SO_2 measurements, the elimination of extreme values influences the distribution most strongly, which may suggest the occurrence of outlying values [29].

The confirmation comes from a detailed analysis of outliers, conducted on the basis of DFITS, Cook's Distance and the Mahalanobis Distance, where a point of reference is Fourier's Harmonic Regression Model.

The goal of the detailed assessment of measurement data quality is to help detect potential deviated values. The final decision about eliminating an observation from a set of data is taken by a researcher. The idea of the method was based on the analysis of a character of deviated observations (influential, outlying, or atypical).

Table 5. General estimation of the influence of extreme values on the mean level (based on the trimmed and the Winsorized means).

Variable	(X0w-X0)/X0	(X0u-X0)/X0
Mercury	-0.7%	-1.3%
PM_{10}	-7.2%	-12.0%
SO_2	-9.9%	-19.8%
NO_2	-7.2%	-13.7%
O_3	0.2%	1.6%
Temp.	3.0%	5.2%
Rad.	-2.7%	-5.7%
Pressure	0.0%	0.0%

The suggested method enables detecting an occurrence which is not consistent with the nature of a phenomenon, and evaluating the influence of elimination of atypical observations on the entire distribution of pollutant concentration in a one-dimensional approach. A multi-dimensional approach enables specifying if natural causes occur (e.g. influence of atmospheric factors) that might affect the occurrence of a concentration value that is not consistent with its nature.

The essence of the solution is the estimation of three major measures that enable classifying the causes of observation identification as incorrect: DFITS shows a strong atypicality of an observation without pointing to the cause. The Mahalanobis Distance enables evaluating a distance at which a measurement indicated by DFITS is located in relation to the distribution of a dependent variable (e.g. concentration). It allows answering the question whether the cause of identification lies in the distribution of a dependent variable. Finally, Cook's Distance enables evaluation of a distance at which a measurement is located in relation to the centroid being a point of reference in the multi-dimensional space of independent variables (e.g. meteorological measurements, data from balance models, or predictors identifying periodicity). This enables answering the question whether the cause of identification lies in independent variables.

Detailed analysis confirmed the preliminary conclusions. In the measurement results of SO_2, one measurement was observed whose character the QAAH1 analysis classified as outlying [28]. The results of the analysis confirmed high quality of the data; atypical values of diverse characteristics did not occur.

b. Relationships and correlations of components between mercury and the remaining measurement results

Before approaching the model identification it is necessary to conduct a preliminary analysis of relationships and then a correlation of components so that in the identification process one could precisely indicate the cause-and-effect structure.

Table 6. Total correlations of mercury measurement results with other measurement results.

	PM_{10}	SO_2	NO_2	O_3	Temp.	Velocity	Humidity	Rad.	Pressure
Mercury	0.6893	0.7130	0.7231	0.0304	-0.4980	0.0942	0.0411	-0.3639	-0.0930
	p=0.00	p=0.00	p=0.00	p=0.616	p=0.000	p=0.120	p=0.499	p=0.000	p=0.125

c. Total correlations

The results of mercury measurements are most strongly correlated, in pairs, with the measurements of NO_2 (0.72), SO_2 (0.71), and PM_{10} (0.69). Out of meteorological factors the strongest relationship can be observed with air temperature (-0.49) and solar radiation intensity (-0.36). Other relationships are not statistically significant (Table 6).

These interdependencies are variable in time, which is shown in Fig. 3. For NO_2 concentrations, this interdependence varies from 0.24 in April to 0.76 in June. Strong fluctuations also were observed for the correlation of mercury with O_3 (from -0.48 in May to +0.56 in July), and air temperature (from -0.26 in January to +0.65 and + 0.64 in June and July and +0.61 in March).

Such high amplitudes of changes show a potentially strong influence of seasonality in the monthly approach and during measurement periods (warm and cold). The results show the necessity to pay attention to this phenomenon in the model. To confirm the fact and to be able to precisely identify seasonality, it is necessary to have measurement series from at least three to five cycles, which in the case of annual measurements denotes at least three years of measurements. At present, as this is the first research study of this kind, the length of a series does not exceed twelve months. It seems to be justifiable to recommend further measurements to be able to verify in the future all the theses put forth in the present study, which could be emblematically called a pilot study.

Principal Component Analysis – PCA

The preliminary analysis displayed a significant role of seasonality. Another step is answering the question about the correlation of components, both the "closest" one, i.e. primary one, and further correlations which may show the occurrence of either non-linear relationships or a strong influence of seasonality, which would confirm our preliminary conclusions.

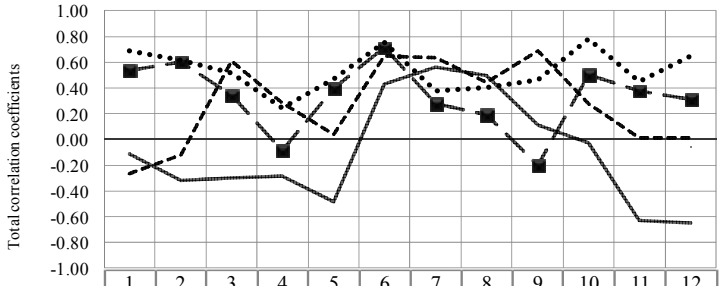
The index of the phenomenon (Table 7, Component 1) confirms preliminary conclusions. The results of mercury concentrations are most strongly, in direct proportion, correlated with the results of concentration measurements of NO_2, SO_2, and PM_{10}, and inversely proportional to air temperature and solar radiation intensity. Increases in mercury concentration are accompanied by an increase in concentrations of PM_{10}, SO_2, and NO_2, with a decrease in air temperature and solar radiation intensity. They form a principal correlation that explains more than 40% of the total variability of a measuring system.

A secondary correlation is a contrast between air humidity (-0.86) and solar radiation intensity (+0.59) and ozone (+0.67), which accounts for slightly more than 21.5% of variability. Radiation plays an important role both in the first and the second component (0.71 and 0.59, respectively).

The third component, based on both Kaiser criterion (eigenvalue > 1) and Cattell criterion (a break point), is a third important correlation. To a large extent, it is formed by a contrast of measurements of atmospheric pressure (-0.58) against wind velocity (0.83) and ozone (0.49). The most distinct is wind velocity measurements.

Finally, the fourth and the last significant correlation is a relationship between atmospheric pressure (0.63) and other measurements. It is hard to distinguish here a clear structure. This correlation is connected with particular measurements that use appropriate weights with variables, in proportion to the modulus of the value.

The first principal component displays combustion as the most important source, the second one gas conversion into a particle with participation of ozone, the third and the fourth one: atmospheric conditions.



	1	2	3	4	5	6	7	8	9	10	11	12
PM10	0.54	0.60	0.35	-0.09	0.40	0.71	0.28	0.19	-0.20	0.5	0.38	0.31
NO2	0.69	0.61	0.52	0.24	0.47	0.76	0.37	0.40	0.47	0.78	0.45	0.65
O3	-0.11	-0.32	-0.30	-0.29	-0.48	0.43	0.56	0.50	0.11	-0.03	-0.63	-0.65
Temp	-0.26	-0.12	0.61	0.29	0.04	0.65	0.64	0.44	0.69	0.28	0.01	0.01

Fig. 3. Total correlations of mercury measurement results with other measurement results for individual months of 2010.

Table 7. Identification of component correlations (PCA model). From the left: correlations of component loadings with real variables and eigenvalues along with the determination of the variance by individual principal components.

	Component 1	Component 2	Component 3	Component 4
Mercury	**-0.710**	0.274	0.304	-0.358
PM_{10}	**-0.780**	0.416	-0.121	-0.137
SO_2	**-0.834**	0.393	0.092	0.047
NO_2	**-0.881**	0.191	-0.136	-0.161
O_3	0.394	**0.666**	0.490	0.010
Temp	**0.819**	0.032	-0.003	-0.415
Velocity	-0.031	-0.084	**0.827**	0.470
Humidity	-0.350	**-0.863**	-0.018	-0.081
Rad.	**0.710**	0.594	-0.129	-0.201
Pressure	0.002	0.419	-0.570	0.626
Ex. var.	4.038	2.164	1.400	1.007
Percentage	40.4%	21.6%	14.0%	10.1%

Ex. var. – Explainable variance

	Eigenvalue	% total variance	Cumulative eigenvalue	Cumul. %
1	4.038	40.38	4.04	40.38
2	2.164	21.64	6.20	62.02
3	1.400	14.00	7.60	76.02
4	1.007	10.07	8.61	86.09

In total, the first four components account for slightly more than 86% of the variance of the whole system, which is a significant value and shows their key importance in the phenomenon.

Such a weight distribution may show, as it was assumed initially, non-linearity of the relationships and the influence of seasonality on the phenomenon of the identification of the model of cross-relationships between mercury and the other factors.

An illustration of the model is a projection of a ten-dimensional space onto a plane, where all correlations are clearly shown (Fig. 4).

Model Construction

An initial stage of model identification is the analysis of lags of measurement results having the following form: mercury ≤ other measurement results. It was not possible to make an analysis based on the autocorrelation and the partial autocorrelation functions (Ljung-Box Q statistics) or the analysis of Almon distributed lags because of too short series of measurements and a potential absence of measurement stability. The study made an attempt to estimate lags not longer than 5 periods with the use of classical estimators of the total correlation. It enabled more effective identification of the model through a possibility of comparing autocorrelation results when choosing a final model.

a. Analysis of lags

The obtained estimates show significant correlations between the sequence of mercury and the sequences of measurement results of PM_{10}, SO_2, NO_2, air temperature, solar radiation intensity and atmospheric pressure; the memory of lags not greater than two periods back was limited a priori. In Table 8 the strongest among the significant coefficients are underlined. These results proved to be valuable guidelines in the model identification process.

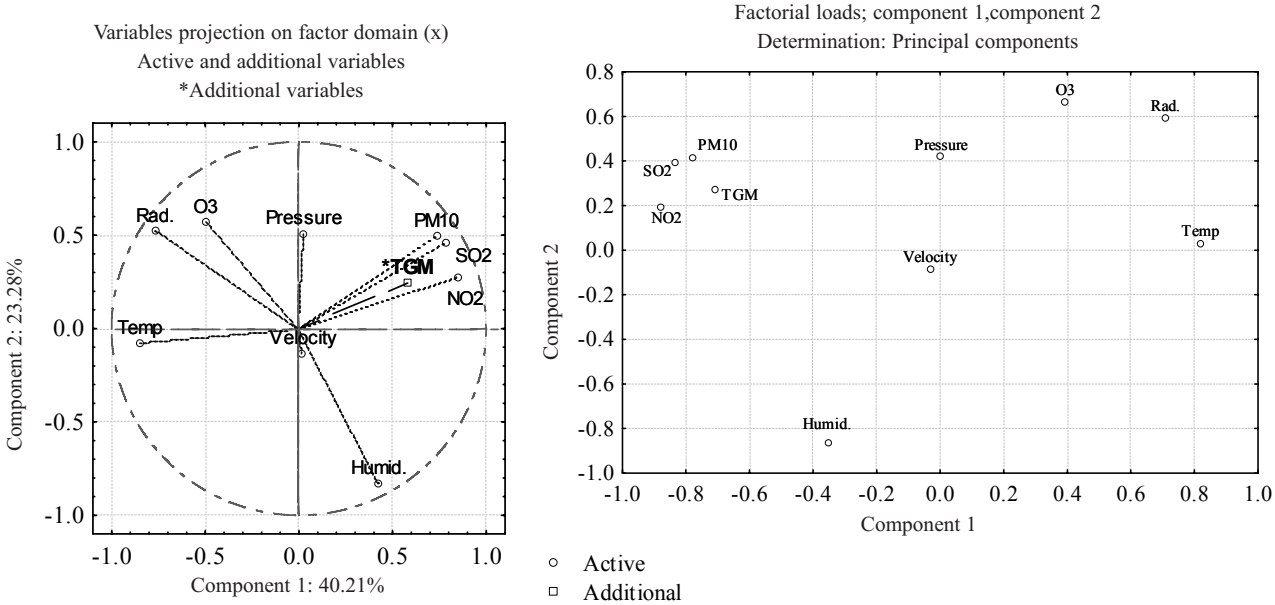


Fig. 4. Projection of component assumptions of PCA model on two-dimensional space; no rotation.

Table 8. Initial analysis of the cross-autocorrelations of mercury measurement results with other measurements: Mercury (+*t*) – a shift in time by *t* periods.

Mercury	PM_{10}	SO_2	NO_2	O_3	Temp.	Velocity	Humidity	Rad.	Pressure
	0.61	**0.66**	**0.66**	0.05	-0.38	0.08	0.06	**-0.31**	-0.16
Mercury (+1)	0.61	0.61	0.60	0.08	-0.42	0.02	0.00	-0.27	-0.11
Mercury (+2)	0.50	0.59	0.52	0.09	**-0.47**	0.06	0.02	-0.27	-0.08
Mercury (+3)	0.47	0.56	0.49	0.11	**-0.48**	0.09	0.03	-0.29	-0.07
Mercury (+4)	0.44	0.56	0.45	0.08	**-0.49**	0.08	0.03	-0.29	-0.03
Mercury (+5)	0.44	0.56	0.44	0.08	**-0.49**	0.10	0.02	-0.29	0.01
	PM_{10}	SO_2	NO_2	O_3	Temp	Velocity	Humidity	Rad.	Pressure
	t-1	t	t	-	t-2	-	-	t	-

Table 9. Model identification process for mercury measurement results.

Subsequent models	Adjusted R^2	Number of effects	SO_2	NO_2	O_3	Temp	Rad.	Pressure	PM_{10} (t-1)
1	0.601525	7	0.279864	0.455942	0.252250	0.184605	-0.203212	-0.162854	0.157303
2	0.592401	6	0.205273	0.450291	0.248867		-0.102214	-0.202841	0.151773
3	0.590983	6	0.351405	0.498458	0.280835	0.177226	-0.213760	-0.173716	
4	0.588107	6	0.267393	0.449709	0.178669	0.054778		-0.216607	0.167465
5	0.587971	5	0.236194	0.448545	0.193809			-0.222661	0.162638
6	0.582991	6		0.594241	0.304866	0.090653	-0.190993	-0.157558	0.224835
7	0.582715	5	0.277277	0.491589	0.276617		-0.116306	-0.211792	
8	0.581389	5		0.570089	0.294977		-0.135463	-0.181078	0.211468
9	0.581250	6	0.269961	0.464379	0.275179	0.278788	-0.301707		0.176478
10	0.576586	4	0.318735	0.492979	0.215626			-0.235306	

b. General regression model (GRM) identification

In order to identify the influence of imission and meteorological conditions on gaseous mercury concentration a generalized regression model (GRM) was applied. It is an identification method that enables conducting stepwise regression taking the methods of general linear model into consideration. It allows building models pertaining to the systems that contain the effects of many degrees of freedom for qualitative predictors, as well as pertaining to the systems containing the effects of single degrees of freedom for continuous predictors. GRM incorporated the techniques of model identification by a stepwise method and a method of the best regression subset for the systems of analysis of variance (ANOVA), regression analysis, and analysis of covariance (ANCOVA). In a general linear model, GRM uses the least squares method to identify models and to estimate and test hypotheses concerning the effects considered in the final model.

The results of the model identification process with the use of a best subset method for mercury are presented in Table 9. The adjusted coefficient of determination R^2 was accepted as a criterion.

The estimation results of the model are presented in Table 10 and Fig. 5. The model of the form below (1) was regarded as the best:

$$\begin{aligned} \text{Mercury} = {} & 6.11756331 + 0.018188865 \cdot SO_2 + \\ & + 0.023735704 \cdot NO_2 + 0.004295008 \cdot O_3 + \\ & + 0.005869468 \cdot \text{Temp} - 0.00042 \cdot \text{Rad} + \\ & - 0.00514800 \cdot \text{Pressure} + 0.002310011 \cdot PM_{10(t-1)} \end{aligned} \quad (1)$$

The identified model fits the empirical data well. The adjusted R squared amounts to 0.60, which means that about 60% of the total variability of measurement results are accounted for by the formation of independent variables. The empirical data differ from theoretical ones, shown by the model, on average by 0.04 $ng \cdot m^{-3}$, which is presented in Fig. 6. The identified structure of interdependencies of components confirms the correctness of the model.

c. Model testing

The identified model fulfills the assumptions of stationarity and normal distribution of residuals (Fig. 7). During

Table 10. Resultant model for a mercury measurement series, along with the estimation of parameters and the assessment of fit.

	Mercury Param.	Mercury Statistical error.	Mercury t	Mercury p	-95.00% Confidence limit.	+95.00% Confidence limit	Mercury Beta (ß)	Mercury Statistical error. ß	-95.00% Confidence limit	+95.00% Confidence limit
Absolute term	6.117563	1.229782	4.97451	0.000001	3.698226	8.536900				
SO_2	0.018189	0.004524	4.02027	0.000072	0.009288	0.027089	0.279864	0.069613	0.142914	0.416813
NO_2	0.023736	0.003239	7.32875	0.000000	0.017364	0.030107	0.455942	0.062213	0.333551	0.578333
O_3	0.004295	0.000800	5.36679	0.000000	0.002721	0.005869	0.252250	0.047002	0.159783	0.344716
Temp	0.005869	0.002017	2.90933	0.003872	0.001901	0.009838	0.184605	0.063453	0.059775	0.309435
Rad.	-0.000420	0.000121	-3.46076	0.000611	-0.000659	-0.000181	-0.203212	0.058719	-0.318729	-0.087695
Pressure	-0.005148	0.001228	-4.19371	0.000035	-0.007563	-0.002733	-0.162854	0.038833	-0.239249	-0.086458
PM_{10} (t-1)	0.002310	0.000745	3.10224	0.002089	0.000845	0.003775	0.157303	0.050706	0.057549	0.257057

Mercury	Multiple R	Multiple R^2	Adjusted R^2	SS Model	df Model	MS Model	SS Residual	df Residual	MS Residual	F	p
	0.780978	0.609926	0.601525	17.87467	7	2.553525	11.43162	325	0.035174	72.59651	0.00

testing, two measurements (Nos. 27 and 28) raised reservations. For them the DFITS coefficient assumed values below -1, which is caused by high values of residuals (Fig. 8). It may show, like in the case of the value of determination coefficient (0.6), the need to search for a more precise model. However, as was noted above, to do that it is necessary to have a much longer measurement series. Undoubtedly, they would enable considering in the model a bigger number of elements, such as different types of periodic changes, which in turn would be reflected in a higher estimation precision of the model itself. In light of the assumed goals of the study, the obtained results are more than satisfying and the identified model is effective and helpful in practice.

Conclusions

The study presented the results of a one-year measurement series of total gaseous mercury in the atmospheric air from the only station that carries out such measurements in Mazovia province, the Granica-KPN station.

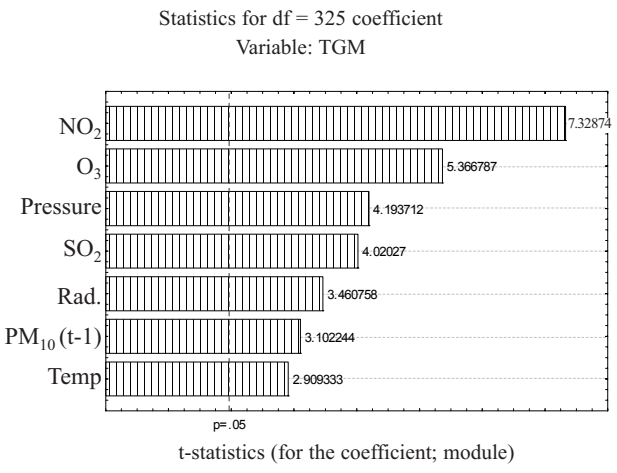


Fig. 5. Pareto chart: t-statistics for estimating model parameters.

Mean annual concentration of TGM amounted to 1.52 $ng \cdot m^{-3}$ and was much lower than those recorded in different regions of Poland and comparable to the concentration of TGM at the background station of EMEP in Diabla Góra. Seasonal variability of TGM concentration was observed; in the winter TGM concentration was higher in comparison to the summer season. Mean TGM concentration in the winter season (heating season) amounted to 1.65 $ng \cdot m^{-3}$, and in summer 1.40 $ng \cdot m^{-3}$.

The level of concentrations recorded at Granica station was affected mainly by local sources of emission, both in the warm and cold seasons of the year. The analysis of TGM fluxes showed that the state of air pollution with mercury in the vicinity of the station was influenced in the winter also by the sources of a high emission rate located in sectors WSW, W and WNW.

Operating since 2010, the only station measuring gaseous mercury in the Mazovia province is insufficient to precisely determine the mercury pollution plume and also should cover the towns in which the level of pollutant emission is much higher than around the analyzed measuring station. Most of all, it concerns the following district towns, e.g.: Warsaw, Radom, Siedlce, Żuromin, and Ciechanów. In these towns the recorded levels of PM_{10} dust as well as other pollutants are a few times higher than at the station in Granica [18, 30], so the level of mercury imission can be considerably higher. This may be indicated by interdependence analysis in the static and dynamic approach. A basic measure of interdependence is the total correlation coefficient, values of which may indicate strong relationships of mercury with the other pollutants analyzed at the station: mercury concentration with PM_{10} (R=0.69), with SO_2 (R=0.71), and with NO_2 (R=0.72). It is worth mentioning at this point that there is a higher rate of respiratory system

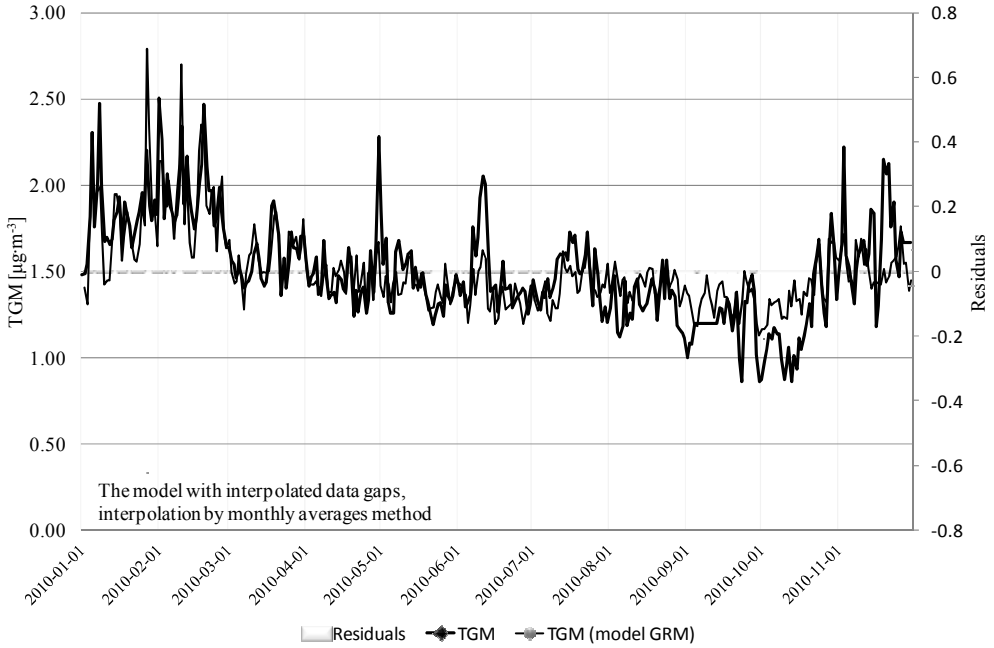


Fig. 6. Series of empirical measurements of mercury concentration. The model series and the residuals.

disease incidence in urban conditions in comparison to rural areas. It is proved, e.g. by the results of the research conducted in Warsaw [31], showing a much higher rate of incidence of respiratory system disease symptoms, especially among non-smoking people living near busy traffic routes, where the levels of pollutants such as PM_{10} or NO_2 are particularly high. It seems to be advisable to simultaneously monitor mercury concentrations also in these places, especially that its negative effect on human health has been known for a long time.

Interdependencies in the dynamic approach, measured by Pearson correlation coefficients in months, as they are highly vary in time. For NO_2 concentrations this interdependency varies from 0.24 in April to 0.76 in June. Strong fluctuations can be also observed in the correlation of mercury with O_3 (from -0.48 in May to +0.56 in July; although total correlation is not statistically significant, at a level of 0.05) and with air temperature (from -0.26 in January to +0.65 and + 0.64 in June and July and +0.61 in March).

The conclusions are confirmed by the results of synergies of components, which clearly indicate strong, directly proportional correlations of mercury with imissions of NO_2, SO_2, and PM_{10} as the most important and strongest element of the index of the whole phenomenon.

The conducted GRM identification confirmed all preliminary conclusions. In the model, mercury as an endogenous variable is strongly and significantly correlated, apart from meteorological measurements, also with imissions, which are exogenous variables.

However, it should be remembered that the obtained research results, after taking further measurements, should be estimated again, as only three- to five-year series make possible obtaining stable estimations, e.g. after using a spectrum model (the Fourier transform), and will enable conducting a deeper lag analysis.

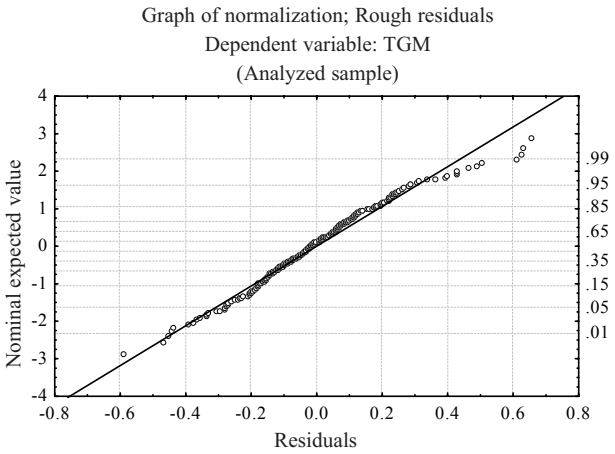


Fig. 7. Estimation of the distribution of mercury model residuals.

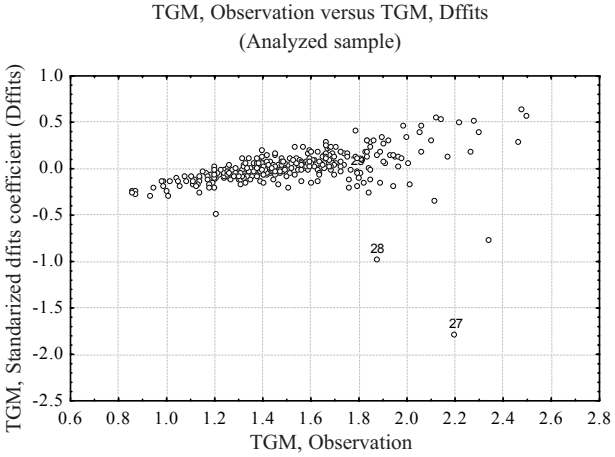


Fig. 8. Testing mercury model residuals – DFITS coefficient.

High and significant values of correlation coefficients, with such a big number of series enable stating that there are potential strong relationships of imissions of NO_2, SO_2, and O_3 with mercury, which is a valuable indication for future model estimations of mercury concentrations using information about imission.

An advantage of the presented method for mercury concentration identification is the relatively low cost of obtaining exact results, when meteorological conditions are known and imission measurements are significantly correlated with mercury. This low cost is mainly connected with the time of computation and the software, assuming that the analytical system is fully functional.

This method does not require purchasing sometimes very costly measuring instruments. At present, without sufficiently long measurement series which allow estimating the precision of obtained results, research studies should be continued in this direction.

The disadvantages of the solution include the need to have measurement series without gaps in the data. It is a practical problem, whose solution is stochastic interpolations, which were used in the study.

It is worth noting that when determining a model for long measurement series, in the future, the model may also serve an interpolation function. It also will enable making a comparative analysis with the measurement results of actual mercury concentrations.

To obtain precise output estimations it is necessary to have high-quality input data; in a sense it is a truism, but sometimes in practice it is not sufficiently implemented.

Therefore, a detailed diagnosis of measurement data is indispensable, including a diagnosis with the use of stochastic and exploratory tools that were presented in the study in one of the most effective implementations. Data with errors, e.g. having an influential or atypical character in relation to other measurements or distributions, cannot be included in calculations. These errors may be transferred onto the obtained results unless they are identified at an early stage of modelling.

At present, the dedicated software makes possible identification of such risks and their elimination. It is not always possible to obtain it in an automatic way, but the workload connected with it does not appear to be big.

References

1. HŁAWICZKA S. Mercury in atmospheric environment. Works and Studies, Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze **73**, 1, **2008** [In Polish].
2. BEŁDOWSKA M., FALKOWSKA L., LEWANDOWSKA A. The gaseous mercury concentration level in the breathed air of the coastal zone of the gulf of Gdańsk. Air Protection in Theory and Practice. The Institute of Environmental Engineering, Zabrze, **2**, 13, **2006** [In Polish].
3. PACYNA J.M., PACYNA E.G., FUDAŁA J., STRZELECKA-JASTRZĄB E., HŁAWICZKA S., PANASIUK D. Mercury emissions to the atmosphere from anthropogenic sources in Europe in 2000 and their scenarios until 2020. Sci. Total Environ. **370**, 147, **2006**.
4. SCHRODER W. H., MUNTHE J. Atmospheric mercury – an overview. Atmos. Environ. **32**, (5), 809, **1998**.
5. KEELER G.J., DVONCH T.J. Atmospheric mercury: a decade of observations in the Great Lakes. In: Dynamics of Mercury Pollution on Regional and Global scales: atmospheric processes and human exposures around the world. Springer, New York, pp. 611-636, **2005**.
6. PACYNA E., PACYNA J.M., PIRRONE N. Atmospheric mercury emissions in Europe from anthropogenic sources. Atmos. Environ. **35**, 2987, **2001**.
7. SLEMR F., SCHUSTER G., SEILER W. Distribution, speciation, and budget of atmospheric mercury. J. Atmos. Chem., **3**, 407, **1985**.
8. LINDBERG S., BULLOCK R., EBINGHAUS R., ENGSTROM R., FENG X., FITZGERALD W., PIRRONE N., PRESTBO E., SEIGNEUR C. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. Ambio **36**, (1), 19, **2007**.
9. BULLOCK JR. O. R. Current methods and research strategies for modeling atmospheric mercury. Fuel. Process. Technol. **65-66**, 459, **2000**.
10. MALCOLM E. G, KEELER G.J Evidence for a sampling artifact for particulate-phase mercury in the marine atmosphere. Atmos. Environ. **41**, 3352, **2007**.
11. LINDQVIST O., RODHE H. Atmospheric Mercury-a review. Tellus **37B**, 136, **1985**.
12. SANIEWSKA D., BEŁDOWSKA M., BEŁDOWSKI J., FALKOWSKA L. Atmospheric deposition of mercury to the coastal zone of the southern Baltic sea. Air Protection in Theory and Practice. The Institute of Environmental Engineering, Zabrze, **2**, 303, **2010** [In Polish].
13. BOSZKE L., SIEPAK J. Selected aspects of mercury speciacion in ambient air. Ecology and Technology **3**, 67, **2002** [In Polish].
14. HORVAT M., JERAN Z., SPIRIC Z., JACIMOVIC R., MIKLAVCIC V. Mercury and other elements in lichens near the INA Naftaplin gas treatment plant, Molve, Croatia. J. Environ. Monit. **2**, 139, **2000**.
15. LYNAM M.M., KEELER G.J. Source-receptor relationships for atmospheric mercury in urban Detroit, Michigan, Atmos. Environ. **40**, 3144, **2006**.
16. KLIŚ CZ., MATEJCZYK M. Assessing the impact of sources on air quality in the light of the act on 'Environment Protection Law'. Air Protection and Waste Problems **36**, (3), 95, **2002** [In Polish].
17. KLIŚ CZ., ŻEGLIN M. Identification of air pollution inflow directions using measurements with a short averaging time. Environment Protection Archives **27**, (2), 47, **2001** [In Polish].
18. MAJEWSKI G., PRZEWOŹNICZUK W. Study of Particulate Matter Pollution in Warsaw Area. Pol. J. Environ. Stud. **18**, (2), 293, **2009**.
19. STULL R.B. Meteorology Today For Scientists and Engineers, West Publishing Comp. New York, 1, **1995**.
20. ZIELONKA U., NOWA B. Changes of TGM (total gaseous mercury) and the mercury absorbed by particulate matter (TPM) at the monitoring station in Katowice. Mercury in environment. Identification of threats to human health. Eds. L. Falkowska. Gdańsk University Development Foundation, Gdańsk, **2**, 23, **2010** [In Polish].
21. PYTA H., ZAJUSZ R., GRZEGORCZYK M. Total gaseous mercury and particulate mercury in the air of the upper Silesia. Air Protection in Theory and Practice. The Institute of Environmental Engineering, Zabrze, **2**, 257 **2010** [In Polish].

22. WÄNGBERG I., MUNTHE J. Atmospheric mercury in Sweden, Northern Finland and Northern Europe. Results from National Monitoring and European Research. Report IVL, Göteborg, Sweden 1, **2001**.
23. LIU S., NADIM F., PERKINS C., CARLEY R.J., HOAG G.E., LIN Y., CHEN L. Atmospheric mercury monitoring survey in Beijing, China. Chemosphere **48**, 97, **2002**.
24. FANG F., WANG Q., LI J. Urban environmental mercury in Changchun, a metropolitan city in northeastern China: source, cycle, and fate. Sci. Total Environ. **330**, 159, **2004**.
25. FU X., FENG X., ZHU W., WANG S., LU J. Total gaseous mercury concentrations in ambient air in the eastern slope of Mt. Gongga, South-Eastern fringe of the Tibetan plateau, China. Atmos. Environ., **42**, (5), 970, **2008**.
26. KLIŚ CZ. Methods for analyzing the air pollution inflows. Air Protection and Waste Problems **37**, (1-2), 22, **2003** [In Polish].
27. CZECHOWSKI P.O. Statistical interpolation of measurement data gaps; 2003 report on atmospheric pollution state in Gdańsk Agglomeration, Gdańsk, 1, **2004** [In Polish].
28. CZECHOWSKI P.O., KRASZEWSKI A., BADYDA A., MAJEWSKI G. Air pollution measurement data quality assessment: selected classical quantitative methods and robust methodology comparative study. Air Protection in Theory and Practice. The Institute of Environmental Engineering, Zabrze, **2**, 51, **2010** [In Polish].
29. CZECHOWSKI P.O. Mechanisms of measurement data quality assessment in the concept of Eco Data Miner analytical system; The Institute of Marine Transport, Gdańsk, 1, **2009** [In Polish].
30. LASZUK O. The analysis of different emission sources influence on air quality status in the Mazovia Voivodship. Master thesis. Faculty of Civil and Environmental Engineering, WULS, Warsaw, 6, **2011** [In Polish].
31. BADYDA A., LUBIŃSKI W. The influence of air pollution on pulmonary function test results in people living close to busy roads. Pol. J. Environ. Stud. **18**, (3A), 7, **2009**.