atmosphere

Article

Submicron Particle-Bound Mercury in University Teaching Rooms: A Summer Study from Two Polish Cities

Grzegorz Majewski [1,*], Karolina Kociszewska [1], Wioletta Rogula-Kozłowska [2], Halina Pyta [2], Patrycja Rogula-Kopiec [2], Walter Mucha [3] and Józef S. Pastuszka [3]

[1] Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences, 02-787 Warsaw, Poland; karolina_cwiek@sggw.pl
[2] Institute of Environmental Engineering, Polish Academy of Sciences, 41-819 Zabrze, Poland; wioletta.rogula-kozlowska@ipis.zabrze.pl (W.R.-K.); halina.pyta@ipis.zabrze.pl (H.P.); patrycja.rogula-kopiec@ipis.zabrze.pl (P.R.-K.)
[3] Faculty of Energy and Environmental Engineering, Silesian University of Technology, 44-100 Gliwice, Poland; Walter.Mucha@polsl.pl (W.M.); Jozef.Pastuszka@polsl.pl (J.S.P.)
* Correspondence: grzegorz_majewski@sggw.pl; Tel.: +48-22-5935-3225

Academic Editors: Pasquale Avino and Robert W. Talbot
Received: 23 July 2016; Accepted: 13 September 2016; Published: 15 September 2016

Abstract: The goal of the study was to determine the concentrations of submicron particulate matter (PM_1) and of the mercury contained in it (Hg_p) in the air in two teaching rooms in two Polish cities, Gliwice and Warsaw. The levels of atmospheric particulate matter (PM) differ greatly between these two cities. The relations between the indoor (I) and outdoor (O) 24-h concentrations for each PM_1 and Hg_p were determined and, based on the conclusions, an attempt was made to identify the main sources of the indoor Hg_p in both cities. During the whole measuring period (April–June 2015), in both Warsaw and Gliwice, the 24-h outdoor PM_1 concentrations were slightly higher than the indoor ones (outdoor and indoor averages were equal to 19.3 $\mu g\ m^{-3}$ and 14.5 $\mu g \cdot m^{-3}$, respectively, in Gliwice and to 13.2 $\mu g \cdot m^{-3}$ and 9.5 $\mu g \cdot m^{-3}$ in Warsaw). In Gliwice, the indoor concentrations of Hg_p (2.4 $pg \cdot m^{-3}$ to 27.7 $pg \cdot m^{-3}$) were much higher than the outdoor ones (1.1 $pg \cdot m^{-3}$ to 6.1 $pg \cdot m^{-3}$); in Warsaw the average concentrations of Hg_p were equal to 1.4 $pg\ m^{-3}$ indoors and outdoors. The 24-h concentrations of Hg_p and the 24-h I/O ratios for Hg_p varied more intensely in Gliwice than in Warsaw throughout the whole measuring period. In Warsaw, the teaching room Hg_p came mainly from the infiltration of atmospheric (outdoor) Hg_p. In Gliwice, a part of the indoor Hg_p infiltrated into the teaching room with the outdoor PM_1 that most probably was then enriched with gaseous indoor Hg, what resulted in the relatively high indoor Hg_p concentrations.

Keywords: Hg; PM_1; indoor/outdoor; indoor air pollution; atmospheric air; Poland

1. Introduction

In comparison with the available number of studies concerning atmospheric air pollution, the problem of indoor air pollution with particulate matter (PM) and its toxic components has hardly been addressed. The concentrations and chemical composition of PM in various rooms (including teaching rooms and laboratories at schools and universities) have been studied in the world for years [1–5] and in Poland PM concentrations inside teaching rooms have already been studied as well [6–13].

It has been established beyond doubt that PM concentrations in the atmospheric air have a significant influence on the PM concentrations inside various buildings [14–22]. This impact depends on the internal sources of pollutants and indoor ventilation conditions. Indoors, basic PM sources include human skin, hair, plants, animals, cooking, building materials, tobacco smoking, heating (coal, wood and biomass combustion), cleaning agents and specific activities related to the use of a building [23–26]. The internal sources also emit other pollutants that may become PM precursors or components due to their deposition on PM particles present in the air [11,25,26].

The I/O ratio is commonly used to define the impact of atmospheric pollutants (e.g., PM) on the indoor pollutant concentration. The I/O is the ratio of the indoor concentration (I) of a compound, element, etc. to its outdoor concentration (O). Based on an analysis of the I/O ratio, it has been estimated that atmospheric air inflow may be accountable for 75% of $PM_{2.5}$ and 66% of PM_{10} concentrations [27] in offices located in Upper Silesia, Poland. Observations carried out in kindergartens have shown that the I/O ratio for $PM_{2.5}$ and PM_{10} practically depends on the activity of children in the classrooms only, as it determined the intensity of PM resuspension [28]. It has also been proven that in urban areas there is a greater threat from $PM_{2.5}$-bound metals inside kindergarten rooms than in rural areas (hence a higher I/O ratio) [11]. On the other hand, analysis of the elemental composition of PM_1, $PM_{2.5}$ and PM_{10}, and of the I/O ratio of the elements concerned, has demonstrated that significant contribution to indoor Zn, Pb and S concentrations in fine PM found in a public school in Wrocław was from the penetration of outdoor air [10]. No Polish or other European literature references have been found regarding the content of mercury (Hg) in fine PM in such buildings as schools, kindergartens and universities.

Among other substances, Hg is absorbed on the surface of ambient particles. In general, particulate mercury (mercury bound to ambient PM, Hg_p) makes up merely several per cent of the total mass of ambient mercury [29–31]. In cities situated in the urbanized southern Poland, the Hg_p in the total mass of ambient mercury can range from a few per cent to as much as 14% [30,32]. The proportion of Hg_p to total atmospheric mercury varies from one location to another, but also at the same location over time [32,33].

The main anthropogenic source of mercury in the air is the combustion of coal, oil and waste [34]. In Poland, where more than 80% of energy is produced from coal, ambient concentrations of mercury reach high levels, much higher than in other European countries. The ambient concentration of Hg_p can reach 600 $pg \cdot m^{-3}$ [35], 4800 $pg \cdot m^{-3}$ [32], and 142 $pg \cdot m^{-3}$ [36] in the central, southern and northern parts of Poland, respectively.

In the air, Hg_p may be directly emitted (as a primary pollutant, adsorbed to or constituting PM particles in the primary PM), formed through the adsorption of ambient Hg^{2+} (bound to compounds) and Hg° vapours to ambient particles, or through the dissolution of ambient Hg^{2+} in PM-bound water [37,38]. In certain circumstances, the two latter mechanisms are supposed to play as important a role in enriching PM in Hg as the primary emissions do [39].

Although it constitutes just a small contribution to the total mass of ambient mercury, Hg_p is an important part of the total Hg and is of particular interest because of its health impact. Mercury is commonly known to be harmful to human health due to its high mobility in the environment, the inability to undergo biodegradation, a high bioaccumulation potential, and a high chemical and biological activity [40,41]. When bound to airborne fine PM, whose particles penetrate deeply into the human respiratory system, and some of them even into the blood flow [42,43], Hg_p can pose a major threat to human health.

The aim of this study was to attempt an initial determination of submicron PM (PM_1) concentration and the concentration of PM_1-bound Hg (Hg_p) in two teaching rooms. The indoor (I; both rooms) and outdoor (O; atmospheric air) variability in the 24-h PM_1 and Hg_p concentrations was discussed. Additionally, the I/O ratio was analysed.

2. Materials and Methods

2.1. Sampling Sites

The research was conducted in parallel in two Polish cities: Gliwice (where the main sources of air pollution are commercial power generation, household emissions and industries) [44–47] and Warsaw (where traffic emissions prevail) [48–50]. The 24-h samples of PM_1 were collected simultaneously in a teaching room in Warsaw and in a student laboratory in Gliwice, as well as outside the two rooms. The rooms were both located on the 2nd floor (approximately 8 to 10 m above the ground level). No air conditioning or air cleaning equipment was used in those rooms. In both rooms, PM samplers were located at 6 to 9 m opposite the windows, more or less 2 m from the nearest wall and 8 to 12 m from the door. At the laboratory, classes are held two-three times a week during which chemical reagents are used, some of which may contain trace amounts of mercury. There are also flow meters, barometers and thermometers, which may be sources of mercury. On the other hand, the lecture room in Warsaw situated in an old building where mercury-in glass thermometers and barometers have been used for years might have had a history of past pollution with mercury. Therefore, before samples were collected, an assessment of short-time concentration of gaseous Hg in the ambient air was carried out at both locations using a Lumex RA915M mercury analyser (Atomic Absorption Spectrometry, AAS, with Zeeman background correction). The instrument was applied at various areas of the rooms, a few times during one day (before classes in the morning, after classes late in the afternoon and after a good airing of the rooms). The measurements were repeated during the PM sampling session, too. The ambient concentration of mercury in the Warsaw room and in the Gliwice laboratory ranged from a few to 24 $ng \cdot m^{-3}$. The concentrations inside both rooms mainly depended on the duration of airing before measurement, but they did not depend on the duration of the classes, the type of class or the number of people inside the rooms. As a result, it was assumed that no actual internal sources of ambient mercury were identifiable in the rooms and no traces of past mercury pollution were found either.

The outdoor measurements in Warsaw and Gliwice were taken at a height of approximately 4 to 5 m above the ground level. The measurement points outside the buildings in Warsaw and in Gliwice were located in campuses where vehicular traffic is limited and the impact of local pollution from the combustion of fuel is therefore limited as well. Both external measurement points were sited 50 to 70 m—in a straight line—from the internal measurement points (Figure 1). In Warsaw, the distance to the nearest residential buildings where coal is used for heating, was 850 m and in Gliwice it was 350 m. The nearest coal-fired power plants were situated at a distance of 4 km and 2.5 km in Warsaw and Gliwice, respectively. In urban areas, a substantial source of air pollution, including fine PM, is road traffic. Both external measurement points were located about 200 m from a busy road.

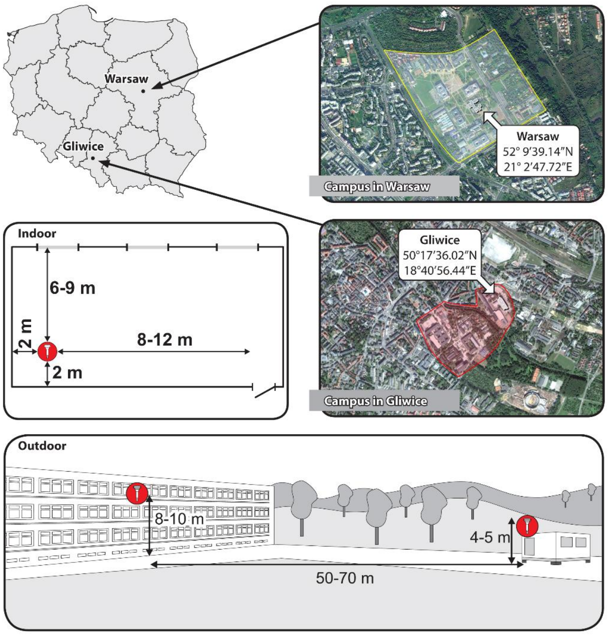

Figure 1. Measurement points in Warsaw and Gliwice (Poland).

The measurements were carried out from April 2015 to June 2015. The samples were taken from Monday through Friday, which are days when classes or lectures were held in the rooms. The months selected to carry out those initial measurements of Hg_p in rooms, were selected specifically to exclude intensive emissions of PM and Hg_p from the nearby coal stoves and coal-fired heating and power plants (i.e., the months outside the heating season). At both locations, the emissions may have a strong impact on the pollution of atmospheric air with PM and Hg_p, which can also affect the proper analysis of results.

2.2. PM_1 Sampling

Altogether, 25 measurements of 24-h concentrations of PM_1 were taken (simultaneously indoors and outdoors) in Warsaw and in Gliwice.

The same standard PM_1 sampling sets were placed at each measurement point. They comprised pumps (Zambelli, New Castle, PA, USA) and heads equipped with jet impactors (TSI) used to separate particles greater than 1 µm from the air stream. PM_1 was sampled at a stable air flow rate ($2.3\ m^3 \cdot h^{-1}$) onto 47-mm QMA quartz filters (Whatman, Maidstone, UK). Before the exposure, the clean quartz filters were specially prepared (heated at 650 °C for 2 h), conditioned in a weighing room (48 h; relative air humidity 45% ± 5%; air temperature 20 ± 2 °C) and weighed twice (at 24 h intervals) on a Mettler Toledo AT microbalance (with a resolution of 2 µg) equipped with a Haug U-ionizer. The procedures for conditioning, weighing, storage, and transport of the samples and of the blank sample preparation complied with the QA/QC procedures of the reference method for gravimetric measurements (EN 12341:2014). The weighting accuracy, determined as three standard deviations from the mean obtained from ten weightings of a blank filter (conditioning performed every 48 h), was 20.5 µg.

To prevent Hg re-volatilization, the samples were stored in a refrigerator (2–4 °C) before analysis.

2.3. Hg Analysis

The mercury content of PM_1 was determined by applying cold-vapour atomic absorption spectrometry (CVAAS) to thermally decomposed PM_1 samples; an MA-2 analyser (Nippon Instr. Co, Tokyo, Japan) was used. The PM_1 sample (a 1.5 cm^2 section of an exposed filter) and additives were placed in a quartz boat and heated in mercury-free air in the decomposition furnace to 700 °C. Then, the decomposition products were carried to the catalyst furnace and heated to 850 °C. The products of thermal decomposition from the oven, containing elemental mercury, were passed through a buffer solution (pH = 7), and then, after drying, to a gold trap where the amalgam (Hg-Au) is formed. Vaporised Hg°, released upon rapid heating of the trap, was carried to the detector, where the light absorbance of the mixture Hg/carrier gas was measured at the wavelength $\lambda = 253.7$ nm.

The calibration curve (0.1–6 ng, $R^2 = 0.999$) was prepared by analysing the calibration standard (Inorganic Ventures; Hg concentration 10 ppm). The limits of detection (LoD, 0.025 ng·Hg) and of quantitation (LoQ, 0.075 ng·Hg) were determined by iteratively analysing 25 blank samples. The method was validated using the standards SRM1633b and SRM2583 (NIST). The repeatability, computed as a standard deviation from 25 measurements, was 4.5% for an actual sample and 3.9% for SRM1633b. The average recovery of SRM1633b was 90% and for SRM2583 was 96% [51]. For each batch of five actual samples, blank samples were analysed (one blank field sample in a batch of five actual samples, separately for the outdoor and indoor measurements). The mass of Hg in a blank field sample was deducted from the mass of Hg determined in actual samples of the given batch.

3. Results and Discussion

3.1. Outdoor Concentrations of PM_1 and Hg_p—A Comparison with Earlier Studies

The outdoor PM_1 concentrations observed in April 2015–June 2015 in Gliwice were similar, and in the case of Warsaw slightly lower than the PM_1 concentrations observed earlier in Silesian cities. In Zabrze, situated 15 km west of Gliwice, the ambient concentrations of PM_1 were between

16.7 μg·m^{-3} and 60.2 μg·m^{-3} (monthly averages), while, in Katowice, 25 km west of Gliwice, 24-h concentrations of PM_1 were in the range of 8.0 μg·m^{-3} to 73.6 μg·m^{-3} [52,53]. There are no published PM_1 data regarding central Poland, where Warsaw is situated, and there are no data of PM_1-bound Hg concentrations for that area. Nevertheless, earlier research has shown that in the urban area of Poznań (central Poland, 270 km east of Warsaw), 24-h ambient concentration of $PM_{2.5}$-bound Hg can reach 77 pg·m^{-3} [35]. In Poland, the ambient concentration of PM_1-bound Hg was measured only in Zabrze before, showing the values of 7.7 pg·m^{-3} to 186.2 pg·m^{-3} [52].

Therefore, it can be stated that the average ambient concentrations of PM_1-bound Hg in April 2015–June 2015, reaching 3 pg·m^{-3} in Gliwice and 1.4 pg·m^{-3} in Warsaw, were very low. Our measurements were taken in a warm season (Table 1) and precipitation was observed on over a dozen measurement days in Warsaw and on a few measurement days in Gliwice. Thus, during the measurement period, emissions of PM and Hg from household heating must have been minimum (in Poland hard coal is mainly used for heating in local boiler plants and household stoves), and the prevailing weather conditions did not support the accumulation of pollution in the bottom layer of the atmosphere, most likely favouring wet (leaching) or dry deposition of the pollutants from the air [54]. In Poland, each summer demonstrates lower PM concentrations than in winter and hence lower concentrations of most PM components including PM-bound Hg [46,51,53]. The presented results were obtained during a short measurement period at the end of spring and the beginning of summer. Since the concentrations of PM and its components in Poland are subject to extensive seasonal fluctuations, the levels shown in this study cannot be considered typical values for the two areas. They are only values of reference to concentrations measured inside teaching rooms and as such demonstrate certain general trends in the PM air pollution in Poland.

The ambient concentrations of PM_1 and Hg_p and the Hg_p content in PM_1 were considerably higher in Gliwice than in Warsaw. This applied to the values obtained both outdoors and inside the teaching rooms. The Mann–Whitney and Wilcoxon tests (SPSS) confirmed a statistical significance of the differences between the mean values for both PM_1 and Hg_p ambient concentrations and for the Hg_p content in PM_1 in Gliwice and Warsaw ($\alpha_{\text{assump.}} = 0.05$, $p_{comp.} < 0.0002$).

Table 1. Descriptive statistics for the 24-h PM_1 and Hg_p concentrations, Hg_p content in PM_1 and meteorological parameters in Gliwice and Warsaw.

Parameter	No. of Valid Measurements	Mean Value	Minimum	Maximum	Standard Deviation
Gliwice					
Wind speed, m·s^{-1}	25	1.2	0.7	3.6	0.7
Atmospheric pressure, hPa		986.1	974.6	996.7	4.7
Air temperature, °C		13.5	6.9	19.7	3.5
Relative air humidity, %		73.0	42.3	92.6	12.7
Indoor PM_1 concentration, μg·m^{-3}		14.5	7.7	26.4	3.6
Outdoor PM_1 concentration, μg·m^{-3}		19.3	9.9	50.1	7.4
Indoor Hg_p concentration, pg·m^{-3}		6.1	2.4	27.4	5.1
Outdoor Hg_p concentration, pg·m^{-3}		3.0	1.1	6.1	1.4
Indoor Hg_p content of PM_1, ppm		0.4	0.2	1.8	0.3
Outdoor Hg_p content of PM_1, ppm		0.2	0.1	0.3	0.1
Warsaw					
Wind speed, m·s^{-1}	25	3.1	1.9	5.1	1.0
Atmospheric pressure, hPa		1004.2	997.3	1 014.3	5.2
Air temperature, °C		14.9	7.5	23.3	4.1
Relative air humidity, %		57.6	39.6	84.1	12.7
Indoor PM_1 concentration, μg·m^{-3}		9.5	4.0	24.8	5.1
Outdoor PM_1 concentration, μg·m^{-3}		13.2	5.7	37.8	6.6
Indoor Hg_p concentration, pg·m^{-3}		1.4	0.9	4.1	0.7
Outdoor Hg_p concentration, pg·m^{-3}		1.4	0.7	2.3	0.5
Indoor Hg_p content of PM_1, ppm		0.2	0.1	0.3	0.1
Outdoor Hg_p content of PM_1, ppm		0.1	0.03	0.2	0.04

3.2. Indoor–Outdoor PM_1 Concentration

In Warsaw, the 24-h PM_1 concentrations ranged from 4.0 $\mu g \cdot m^{-3}$ to 24.8 $\mu g \cdot m^{-3}$ (indoor values) and from 5.7 $\mu g \cdot m^{-3}$ to 37.8 $\mu g \cdot m^{-3}$ (outdoor values) (Table 1). In Gliwice, the PM_1 ranged from 9.9 $\mu g \cdot m^{-3}$ to 50.1 $\mu g \cdot m^{-3}$ (outdoor values) and from 7.7 $\mu g \cdot m^{-3}$ to 26.4 $\mu g \cdot m^{-3}$ (indoor values). In both cities, the 24-h PM_1 concentrations were generally higher in the atmospheric air than indoors. The differences were statistically significant (Mann–Whitney and Wilcoxon tests; $\alpha_{assump.} = 0.05$, $p_{comp.} < 0.0001$), nevertheless both in Gliwice and Warsaw, the indoor and outdoor 24-h concentrations of PM_1 were linearly correlated; the Pearson's Correlation coefficient was higher for the concentrations in Gliwice ($r = 0.9$; $\alpha = 0.05$) than in Warsaw ($r = 0.69$; $\alpha = 0.05$) (Table 2).

Table 2. Pearson's Correlation coefficients for indoor and outdoor 24-h PM_1 and Hg_p concentrations and Hg_p content in PM_1 in Gliwice and Warsaw.

Warsaw	**Indoor PM_1 Concentration**	**Outdoor PM_1 Concentration**	**Indoor Hg_p Concentration**	**Outdoor Hg_p Concentration**	**Indoor Hg_p in PM_1**	**Outdoor Hg_p in PM_1**
Indoor PM_1 concentration	1.00	0.69 *	0.51	0.12	−0.56	−0.63
Outdoor PM_1 concentration	0.69	1.00	0.24	0.29	−0.50	−0.66
Indoor Hg_p concentration	0.51	0.24	1.00	0.48	0.26	−0.07
Outdoor Hg_p concentration	0.12	0.29	0.48	1.00	0.07	0.31
Indoor Hg_p in PM_1	−0.56	−0.50	0.26	0.07	1.00	0.59
Outdoor Hg_p in PM_1	−0.63	−0.66	−0.07	0.31	0.59	1.00
Gliwice	**Indoor PM_1 Concentration**	**Outdoor PM_1 Concentration**	**Indoor Hg_p Concentration**	**Outdoor Hg_p Concentration**	**Indoor Hg_p in PM_1**	**Outdoor Hg_p in PM_1**
Indoor PM_1 concentration	1.00	0.90	0.25	0.22	0.00	−0.37
Outdoor PM_1 concentration	0.90	1.00	0.24	0.35	0.02	−0.27
Indoor Hg_p concentration	0.25	0.24	1.00	0.15	0.96	−0.03
Outdoor Hg_p concentration	0.22	0.35	0.15	1.00	0.14	0.78
Indoor Hg_p in PM_1	0.00	0.02	0.96	0.14	1.00	0.10
Outdoor Hg_p in PM_1	−0.37	−0.27	−0.03	0.78	0.10	1.00

* values marked in red are statistically significant ($\alpha = 0.05$).

Both in Gliwice and Warsaw (except for one day in Warsaw), the I/O ratio for 24-h PM_1 concentrations did not exceed 1 (Figure 2). In Gliwice, its mean value was 0.8 and ranged from 0.5 to 0.9. In Warsaw, the mean value was similar to the mean value in Gliwice (0.7) and ranged from 0.5 to 2.1. Stronger I/O value fluctuations occurred in Warsaw.

The size and properties of particles constituting PM_1 suggest that the indoor and outdoor concentrations should be balanced. If effective sources of fine particles were found inside the rooms, the indoor concentration of PM_1 could be higher than the outdoor concentrations [1–5,10,11]. Balanced levels of PM_1 concentration indoors and outdoors (or higher indoor values at most) are so much more likely, considering that the timing of the measurements fell on a spring/summer season, when the weather conditions were conducive to frequent airing, and the selected rooms were not equipped with an air cleaning or air conditioning system. It seems that the reason for such a surprising relationship between the indoor and outdoor PM_1 concentrations at both sites was the location of the measurement points outside the teaching rooms. Perhaps the higher outdoor concentrations of PM_1 were a result of the outdoor location of the measuring heads at a lower height (4 m) than in both rooms (2nd floor). Closer to the ground, the influence of resuspension of settled particles on ambient concentrations of PM is possible. Similar phenomena and their reasons have already been reported in previous studies [55,56]. On the other hand, the meteorological conditions present during the spring-summer period, such as a high level of insolation, little breeziness and high ozone concentrations in the air [57], favoured the intensive formation of secondary aerosol in the urban atmosphere [54]. During the summer season, the secondary matter make up to 50% of the PM_1 mass [46,52]. Even if gaseous precursors of secondary PM occurred at the same concentration at both rooms as in the outdoor air, the indoor secondary PM formation was definitely limited.

The mentioned observations allow a hypothesis that the migration of PM_1 from atmospheric air may have been the main source of indoor air pollution both inside the laboratory in Gliwice and the teaching room in Warsaw. In other words, it can be assumed that there were no significant internal PM and/or PM gaseous precursor sources in either of the rooms.

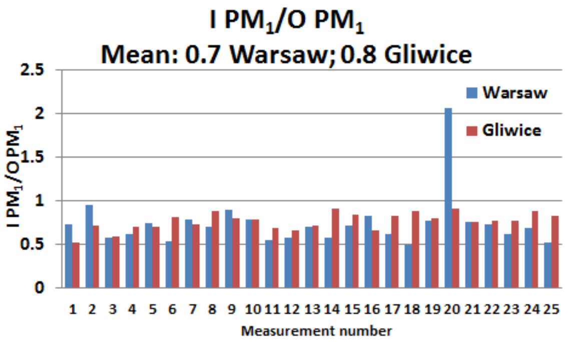

Figure 2. Ratio of the 24-h indoor (I) and outdoor (O) PM_1 concentrations in Gliwice and Warsaw.

3.3. Indoor-Outdoor Hg_p Concentration

In Warsaw, the mean Hg_p concentration over the entire measurement period was the same indoors and outdoors, 1.4 pg·m^{-3}. The 24-h concentrations of Hg_p were in the range of 0.9 pg·m^{-3} to 4.1 pg·m^{-3} (indoors) and 0.7 pg·m^{-3} to 2.3 pg·m^{-3} (outdoors). A different situation occurred in Gliwice, where higher 24-h concentrations of Hg_p were observed in the laboratory than outdoors for the most of the measurement period. In Gliwice, the mean indoor Hg_p concentrations were twice as high (6.1 pg·m^{-3}) as the outdoor values (3.0 pg·m^{-3}). The range of the 24-h Hg_p concentrations was 2.4 pg·m^{-3} to 27.4 pg·m^{-3} in the laboratory and 1.1 pg·m^{-3} to 6.1 pg·m^{-3} in the atmospheric air. The Mann–Whitney and Wilcoxon tests confirmed a statistical significance of the differences between the mean values of indoor and outdoor Hg_p concentrations only in Gliwice ($\alpha_{\text{assump.}} = 0.05$, $p_{comp.} < 0.0002$).

The I/O ratios of the 24-h concentrations of Hg_p in both cities are presented in Figure 3. In Warsaw, half of the 24-h I/O values yielded a result slightly lower than 1. In Gliwice, the ratio was high (only in three cases was it less than 1) and the maximum and mean I/O values there were 9.1 and 2.3, respectively. In Warsaw, the highest I/O value slightly exceeded 3, while the mean ratio was 1.1.

The 24-h indoor and outdoor concentrations of Hg_p were significantly correlated in Warsaw; the 24-h indoor concentrations of Hg_p were also correlated with the PM_1 concentrations inside the teaching room (Table 2). The Mann–Whitney and Wilcoxon tests confirmed that the mean values of indoor and outdoor Hg_p concentrations in Warsaw were equal ($\alpha_{\text{assump.}} = 0.05$, $p_{comp.} < 0.93$). Therefore, it can be concluded that in Warsaw, the infiltration of Hg_p from atmospheric air must have had an expected and obvious impact on the indoor Hg_p concentrations. In Gliwice, however the situation was different. There were no significant indoor and outdoor correlations between 24-h Hg_p concentrations; the 24-h concentrations of indoor Hg_p were not significantly correlated with 24-h PM_1 concentrations.

The authors believe that the indoor PM_1 in Gliwice was enriched with gaseous Hg. The outdoor Hg_p concentrations were twice as low as the indoor Hg_p concentrations, so the PM_1 particles that were transported into the room were not very rich in Hg. On the other hand, when the observations were carried out, the laboratory in Gliwice was not as often aired as the teaching room in Warsaw, therefore the concentrations of gaseous Hg could be maintained at a higher level longer than in the teaching room. Although the concentrations of gaseous Hg in both rooms, measured periodically, varied significantly, their higher values (10 to 20 ng·m^{-3}) were more frequently observed in Gliwice. Considering that in urban areas ambient concentrations of gaseous Hg usually remain below 2 or 3 ng·m^{-3} [32,58,59], the valued measured at the rooms were high, which indicates their possible correlation with the Hg_p levels. It seems that much higher concentrations of indoor PM_1 were observed in Gliwice, and the differences in the meteorological conditions present at both sites over the measurement period were the reason that the PM_1 particles inside the laboratory room in Gliwice adsorbed gaseous Hg much more effectively than in the case of the Warsaw teaching room. However, a categorical confirmation of these conclusions will only be possible when parallel continuous measurements of gaseous Hg and Hg_p in both rooms are carried out.

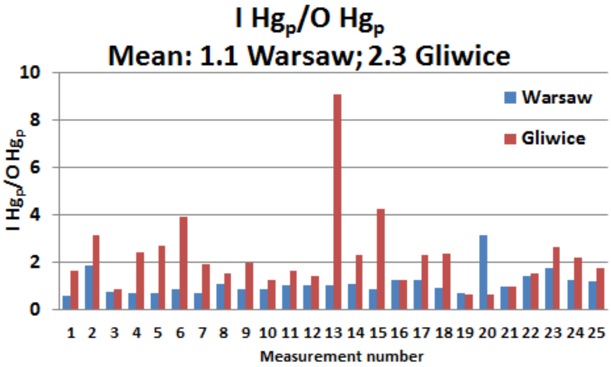

Figure 3. Ratio of the 24-h indoor (I) and outdoor (O) Hg_p concentrations in Gliwice and Warsaw.

In any case, the fact that the PM_1 particles infiltrated from the outside were enriched with mercury inside both rooms is also supported by the analysis of Hg_p content in the PM_1 (Table 1; Figure 4). Although during the measurement period the average indoor and outdoor concentration of Hg_p in Warsaw was equal, the average Hg_p content in PM_1 (ppm) was twice as high indoors as outdoors. Such a twofold increase in Hg_p in the indoor PM_1 as compared with the Hg_p content in the outdoor PM_1 also occurred in Gliwice. In both cities, the differences (indoor–outdoor) were statistically significant (Mann–Whitney and Wilcoxon tests; $\alpha_{\text{assump.}} = 0.05$, $p_{comp.} < 0.0001$). The average ratio of the 24-h Hg_p content in the indoor/outdoor PM_1 was twice as high in Gliwice as in Warsaw, amounting to approximately 3 and 1.5, respectively (Figure 4).

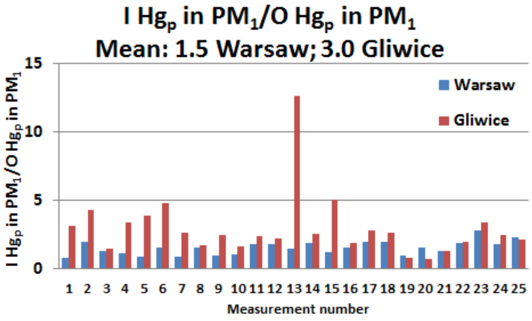

Figure 4. Ratio of the 24-h indoor (I) and outdoor (O) Hg_p contents of PM_1 in Gliwice and Warsaw.

These observations lead to the conclusion that the indoor air pollution, even if there are no additional sources of fine PM and PM-bound Hg, might pose a greater threat to the health of people staying inside such a room, than hazards caused by external air pollution. The conditions inside rooms of buildings, such as teaching rooms, i.e., a constant temperature, slight air movements and limited air exchange, can favour the sorption of air gaseous components on the surfaces of PM particles. This process might be especially effective on a well-developed surface area of fine PM particles.

Certainly, the effectiveness of this phenomenon depends on the chemical composition of the PM particles. In Poland, fine atmospheric particles are richer in elemental carbon (large surface area) and inorganic salts (e.g., NaCl and KCl with strong sorption properties) in winter than in summer [46]. Therefore, it can be suspected that during the winter, the phenomenon described in the presented paper may have a great impact on the level of the pollution of indoor air with Hg_p.

4. Conclusions

In Warsaw and Gliwice, the PM_1 concentration inside the teaching room during the summer was mainly influenced by the intensity of the atmospheric PM_1 infiltration. Therefore, the PM_1 reaching the indoor premises had the same composition and properties as the atmospheric PM_1. On the other hand, gaseous Hg could have been more strongly absorbed on the indoor PM particles than in the atmospheric air. One of the reasons for such a phenomenon is the occurrence of much higher concentrations of gaseous Hg indoors than outdoors. This is why, inside the rooms, toxic properties of PM_1 can be more harmful than the properties of the atmospheric PM_1. The enrichment of indoor PM_1 particles with mercury suggests that in the case of such PM components as Hg the influence of the polluted atmospheric air on the indoor air quality was more evident than in the case of PM_1.

Taking into account the length of time when students and academic staff stayed inside the rooms, despite generally identified low levels of mercury concentration outside of the buildings and intensive efforts on straining the presence of any significant mercury sources inside the examined premises, during the last couple of years the mercury exposure has been found to be a real threat and must be properly dealt with. It is worth emphasizing that the aforementioned conclusions pertain to the mercury associated with very fine PM particles, and therefore, to the ones which can easily be transferred into the lungs and other parts of the human body together with the adsorbed compounds.

Acknowledgments: The work was financed within two projects of the National Science Centre (No. DEC-2013/09/N/ST10/04224 and No. 2012/07/D/ST10/02895). This research was supported by The Faculty of Civil and Environmental Engineering basic (statutory) research projects.

Author Contributions: The study was completed with cooperation between all authors.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Lin, C.C.; Peng, C.K. Characterization of indoor PM_{10}, $PM_{2.5}$, and ultrafine particles in elementary school classrooms: A review. *Environ. Eng. Sci.* **2010**, *27*, 915–922. [CrossRef]
2. Morawska, L.; Afshari, A.; Bae, G.N.; Buonanno, G.; Chao, C.Y.H.; Hänninen, O.; Hofmann, W.; Isaxon, C.; Jayaratne, E.R.; Salthammer, T.; et al. Indoor aerosols: From personal exposure to risk assessment. *Indoor Air* **2013**, *23*, 462–487. [CrossRef] [PubMed]
3. Alves, C.; Duarte, M.; Ferreira, M.; Alves, A.; Almeida, A.; Cunha, Â. Air quality in a school with dampness and mould problems. *Air Qua. Atmos. Health* **2016**, *9*, 107–115. [CrossRef]
4. Wangchuk, T.; He, C.; Dudzinska, M.R.; Morawska, L. Seasonal variations of outdoor air pollution and factors driving them in the school environment in rural Bhutan. *Atmos. Environ.* **2015**, *113*, 151–158. [CrossRef]
5. Romagnoli, P.; Balducci, C.; Perilli, M.; Vichi, F.; Imperiali, A.; Cecinato, A. Indoor air quality at life and work environments in Rome, Italy. *Environ. Sci. Pollut. Res.* **2016**, *23*, 3503–3516. [CrossRef] [PubMed]
6. Dumała, S.M.; Dudzińska, M.R. Microbiological indoor air quality in Polish schools. *Rocz. Ochr. Sr.* **2013**, *15*, 231–244.
7. Polednik, B. Particulate matter and student exposure in school classrooms in Lublin, Poland. *Environ. Res.* **2013**, *120*, 134–139. [CrossRef] [PubMed]
8. Polednik, B. Variations in particle concentrations and indoor air parameters in classrooms in the heating and summer season. *Arch. Environ. Prot.* **2013**, *39*, 15–28. [CrossRef]
9. Zwoździak, A.; Sówka, I.; Fortuna, M. Influence of PM_1, $PM_{2.5}$, PM_{10} Concentrations in indoor school environment on spirometric parameters in schoolchildren. *Rocz. Ochr. Sr.* **2013**, *15*, 2022–2038.

10. Zwoździak, A.; Sówka, I.; Krupińska, B.; Zwoździak, J.; Nych, A. Infiltration or indoor sources as determinants of the elemental composition of particulate matter inside a school in Wroclaw, Poland? *Build. Environ.* **2013**, *66*, 173–180. [CrossRef]
11. Mainka, A.; Zajusz-Zubek, E.; Kaczmarek, K. $PM_{2.5}$ in urban and rural nursery schools in Upper Silesia, Poland: Trace elements analysis. *Int. J. Environ. Res. Public Health* **2015**, *12*, 7990–8008. [CrossRef] [PubMed]
12. Mainka, A.; Zajusz-Zubek, E. Indoor air quality in urban and rural preschools in Upper Silesia, Poland: Particulate matter and carbon dioxide. *Int. J. Environ. Res. Public Health* **2015**, *12*, 7697–7711. [CrossRef] [PubMed]
13. Brągoszewska, E.; Mainka, A.; Pastuszka, J.S. Bacterial aerosols in an urban nursery school in Gliwice, Poland: A case study. *Aerobiologia* **2015**. [CrossRef]
14. Pastuszka, J.S.; Paw, U.K.T.; Kabała-Dzik, A.; Kohyama, N.; Sokal, J.A. Respirable airborne fibers in the home environment in Upper Silesia, Poland, compared with Davis, California. *J. Aerosol Sci.* **2000**, *31*, 484–485. [CrossRef]
15. Colbeck, I.; Nasir, Z.A.; Ali, Z. Characteristics of indoor/outdoor particulate pollution in urban and rural residential environment of Pakistan. *Indoor Air* **2010**, *20*, 40–51. [CrossRef] [PubMed]
16. Wichmann, J.; Lind, T.; Nilsson, M.A.M.; Bellander, T. $PM_{2.5}$, soot and NO_2 indoor–outdoor relationships at homes, pre-schools and schools in Stockholm, Sweden. *Atmos. Environ.* **2010**, *44*, 4536–4544. [CrossRef]
17. Worobiec, A.; Samek, L.; Krata, A.; Van Meel, K.; Krupinska, B.; Stefaniak, E.A.; Karaszkiewicz, P.; Grieken, R.V; Van Grieken, R. Transport and deposition of airborne pollutants in exhibition areas located in historical buildings–study in Wawel Castle Museum in Cracow, Poland. *J. Cult. Herit.* **2010**, *11*, 354–359. [CrossRef]
18. Hänninen, O.; Hoek, G.; Mallone, S.; Chellini, E.; Katsouyanni, K.; Gariazzo, C.; Cattani, G.; Marconi, A.; Molnar, P.; Bellander, T.; et al. Seasonal patterns of outdoor PM infiltration into indoor environments: Review and meta-analysis of available studies from different climatological zones in Europe. *Air Qual. Atmos. Health* **2011**, *4*, 221–233.
19. Goyal, R.; Kumar, P. Indoor–outdoor concentrations of particulate matter in nine microenvironments of a mix-use commercial building in megacity Delhi. *Air Qual. Atmos. Health* **2013**, *6*, 747–757. [CrossRef]
20. Che, W.W.; Frey, H.C.; Lau, A.K. Comparison of sources of variability in school age children exposure to ambient $PM_{2.5}$. *Environ. Sci. Technol.* **2015**, *49*, 1511–1520. [CrossRef] [PubMed]
21. Othman, M.; Latif, M.T.; Mohamed, A.F. The PM_{10} compositions, sources and health risks assessment in mechanically ventilated office buildings in an urban environment. *Air Qual. Atmos. Health* **2016**, *9*, 597–612. [CrossRef]
22. Rogula-Kopiec, P.; Pastuszka, J.S.; Rogula-Kozłowska, W.; Majewski, G. Particulate matter in indoor spaces: Known facts and the knowledge gaps. *Ann. Warsaw Univ. Life Sci. – SGGW, Land Reclam.* **2015**, *47*, 43–54. [CrossRef]
23. Pastuszka, J.S.; Paw, U.K.T.; Lis, D.O.; Wlazło, A.; Ulfig, K. Bacterial and fungal aerosol in indoor environment in Upper Silesia, Poland. *Atmos. Environ.* **2000**, *34*, 3833–3842. [CrossRef]
24. Lippman, M. *Environmental Toxicants: Human Exposures and Their Health Effects*; John Wiley & Sons: New York, NY, USA, 2009.
25. Spellman, F.R. *The Science of Air Concepts and Applications*; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2009.
26. Rogula-Kopiec, P.; Rogula-Kozłowska, W.; Kozielska, B.; Sówka, I. PAH concentrations inside a wood processing plant and the indoor effects of outdoor industrial emissions. *Pol. J. Environ. Stud.* **2015**, *24*, 11–17. [CrossRef]
27. Rogula-Kopiec, P.; Pastuszka, J.S.; Rogula-Kozłowska, W.; Czechowski, P.O.; Majewski, G. Suspended dust in office and laboratory-the effects of selected factors on the concentrations and the respirable fractions content. In *Air Protection in Theory and Practice*; Konieczyński, J., Ed.; Instytut Podstaw Inżynierii Środowiska Polskiej Akademii Nauk: Zabrze, Poland, 2014; pp. 231–242.
28. Mainka, A.; Brągoszewska, E.; Kozielska, B.; Pastuszka, J.S.; Zajusz-Zubek, E. Indoor air quality in urban nursery schools in Gliwice, Poland: Analysis of the case study. *Atmos. Pollut. Res.* **2015**, *6*, 1098–1104. [CrossRef]
29. Lindberg, S.E.; Stratton, W.J. Atmospheric mercury speciation: Concentrations and behavior of reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* **1998**, *32*, 49–57. [CrossRef]

30. Pyta, H.; Rosik-Dulewska, C.; Czaplicka, M. Speciation of ambient mercury in the Upper Silesia region, Poland. *Water Air Soil Soil. Pollut.* **2009**, *197*, 233–240. [CrossRef]
31. Hladikova, V.; Petrik, J.; Jursa, S.; Ursinyova, M.; Koèan, J. Atmospheric mercury levels in the Slovak Republic. *Chemosphere* **2001**, *45*, 801–806. [CrossRef]
32. Pyta, H. *Ambient air pollution by mercury species at the urban station in Zabrze, Southern Poland*; EDP Sciences: Roma, Italy, 2013.
33. Schleicher, N.J.; Schäfer, J.; Blanc, G.; Chen, Y.; Chai, F.; Cen, K.; Norra, S. Atmospheric particulate mercury in the megacity Beijing: Spatio-temporal variations and source apportionment. *Atmos. Environ.* **2015**, *109*, 251–261. [CrossRef]
34. Pirrone, N.; Cinnirella, S.; Feng, X.; Finkelman, R.B.; Friedli, H.R.; Leaner, J.; Telmer, K. Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmos. Chem. Phys.* **2010**, *10*, 5951–5964. [CrossRef]
35. Siudek, P.; Frankowski, M.; Siepak, J. Atmospheric particulate mercury at the urban and forest sites in central Poland. *Environ. Sci. Pollut. Res.* **2016**, *23*, 2341–2352. [CrossRef] [PubMed]
36. Bełdowska, M.; Saniewska, D.; Falkowska, L.; Lewandowska, A. Mercury in particulate matter over Polish zone of the southern Baltic Sea. *Atmos. Environ.* **2012**, *46*, 397–404. [CrossRef]
37. Forlano, L.; Hedgecock, I.M.; Pirrone, N. Elemental gas phase atmospheric mercury as it interacts with the ambient aerosol and its subsequent speciation and deposition. *Sci. Total Environ.* **2000**, *259*, 211–222. [CrossRef]
38. Malcolm, E.G.; Keeler, G.J. Evidence for a sampling artifact for particulate-phase mercury in the marine atmosphere. *Atmos. Environ.* **2007**, *41*, 3352–3359. [CrossRef]
39. Xiu, G.L.; Jin, Q.; Hang, D.; Shi, S.; Huang, X.; Zghang, W.; Bao, L.; Gao, P.; Chen, B. Characterization of size fractionated particulate mercury in Shanghai ambient air. *Atmos. Environ.* **2005**, *39*, 419–427. [CrossRef]
40. Tchounwou, P.B.; Ayensu, W.K.; Ninashvili, N.; Sutton, D. Review: Environmental exposure to mercury and its toxicopathologic implications for public health. *Environ. Toxicol.* **2003**, *18*, 149–175. [CrossRef] [PubMed]
41. Clarkson, T.W. The three modern faces of mercury. *Environ. Health Perspect.* **2002**, *110*, 11–23. [CrossRef] [PubMed]
42. Harrison, R.M.; Yin, J. Particulate matter in the atmosphere: Which particle properties are important for its effects on health? *Sci. Total Environ.* **2000**, *249*, 85–101. [CrossRef]
43. Englert, N. Fine particles and human health—A review of epidemiological studies. *Toxicol. Lett.* **2004**, *149*, 235–242. [CrossRef] [PubMed]
44. Pastuszka, J.S.; Wawroś, A.; Talik, E.; Paw, U.K.T. Optical and chemical characteristics of the atmospheric aerosol in four towns in southern Poland. *Sci. Total. Environ.* **2003**, *309*, 237–251. [CrossRef]
45. Pastuszka, J.S.; Rogula-Kozłowska, W.; Zajusz-Zubek, E. Characterization of PM_{10} and $PM_{2.5}$ and associated heavy metals at the crossroads and urban background site in Zabrze, Upper Silesia, Poland, during the smog episodes. *Environ. Monit. Assess.* **2010**, *168*, 613–627. [CrossRef] [PubMed]
46. Rogula-Kozłowska, W.; Klejnowski, K.; Rogula-Kopiec, P.; Ośródka, L.; Krajny, E.; Błaszczak, B.; Mathews, B. Spatial and seasonal variability of the mass concentration and chemical composition of $PM_{2.5}$ in Poland. *Air Qual. Atmos. Health* **2014**, *7*, 41–58. [CrossRef] [PubMed]
47. Rogula-Kozłowska, W.; Majewski, G.; Czechowski, P.O. The size distribution and origin of elements bound to ambient particles: A case study of a Polish urban area. *Environ. Monit. Assess.* **2015**, *187*, 1–16. [CrossRef] [PubMed]
48. Majewski, G.; Rogula-Kozłowska, W. The elemental composition and origin of fine ambient particles in the largest Polish conurbation: First results from the short-term winter campaign. *Theor. Appl. Climatol.* **2016**, *125*, 79–92. [CrossRef]
49. Majewski, G.; Rogula-Kozłowska, W.; Czechowski, P.O.; Badyda, A.; Brandyk, A. The impact of selected parameters on visibility: First results from a long-term campaign in Warsaw, Poland. *Atmosphere* **2015**, *6*, 1154–1174. [CrossRef]
50. Badyda, A.J.; Dabrowiecki, P.; Lubinski, W.; Czechowski, P.O.; Majewski, G. Exposure to traffic-related air pollutants as a risk of airway obstruction. *Adv. Exp. Med. Biol.* **2013**, *755*, 35–45. [PubMed]
51. Pyta, H.; Rogula-Kozłowska, W. Determination of mercury in size-segregated ambient particulate matter using CVAAS. *Microchem. J.* **2016**, *124*, 76–81. [CrossRef]

52. Rogula-Kozłowska, W.; Klejnowski, K. Submicrometer aerosol in rural and urban backgrounds in southern Poland: Primary and secondary components of PM_1. *Bull. Environ. Contam. Tox.* **2013**, *90*, 103–109. [CrossRef] [PubMed]
53. Kozielska, B.; Rogula-Kozłowska, W.; Klejnowski, K. Seasonal variations in health hazards from polycyclic aromatic hydrocarbons bound to submicrometer particles at three characteristic sites in the heavily polluted Polish region. *Atmosphere* **2014**, *6*, 1–20. [CrossRef]
54. Seinfeld, J.H.; Pandis, S.N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; John Wiley & Sons: New York, NY, USA, 2006.
55. Huang, H.; Cao, J.J.; Lee, S.C.; Zou, C.W.; Chen, X.G.; Fan, S.J. Spatial variation and relationship of indoor/outdoor $PM_{2.5}$ at residential homes in Guangzhou city, China. *Aerosol Air Qual. Res.* **2007**, *7*, 518–580.
56. Cao, J.J.; Huang, H.; Lee, S.C.; Chow, J.C.; Zou, C.W.; Ho, K.F.; Watson, J.G. Indoor/outdoor relationships for organic and elemental carbon in $PM_{2.5}$ at residential homes in Guangzhou, China. *Aerosol Air Qual. Res.* **2012**, *12*, 902–910. [CrossRef]
57. Rozbicka, K.; Majewski, G.; Rozbicki, T. Seasonal variation of air pollution in Warsaw conurbation. *Meteorol. Z.* **2014**, *23*, 175–179.
58. Majewski, G.; Czechowski, P.O.; Badyda, A.J.; Rogula-Kozłowska, W. The estimation of total gaseous mercury concentration (TGM) using exploratory and stochastic methods. *Pol. J. Environ. Stud.* **2013**, *22*, 759–771.
59. Majewski, G.; Czechowski, P.O.; Badyda, A.; Kleniewska, M.; Brandyk, A. Ocena stężenia całkowitej rtęci gazowej (TGM) na terenie stacji tła regionalnego Granica-KPN (województwo mazowieckie, Polska) w latach 2010–2011. *Rocz. Ochr. Środ.* **2013**, *15*, 1302–1317.