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Passive Sampling as a Low-Cost Method for Monitoring Air Pollutants in the Baikal Region (Eastern Siberia)

Olga I. Khuriganova *, Vladimir A. Obolkin, Liudmila P. Golobokova, Yuri S. Bukin and Tamara V. Khodzher

Limnological Institute Siberian Branch, Russian Academy of Sciences, 664033 Irkutsk, Russia

* Correspondence: Khuriganowa@mail.ru; Tel.: +7-39-5242-6502

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Abstract: The measured concentrations of inorganic pollutants, such as ozone (2015–2018), sulfur, and nitrogen oxides (2012–2018) at air monitoring sites in the south of Eastern Siberia were sampled, following the passive sampling method, and analyzed. The spatial inhomogeneity of atmospheric gas concentrations is presented. The ozone concentration is lower in urban areas than those in rural areas and the background level. However, the nitrogen and sulfur oxide concentrations are higher in the atmosphere over the city site. The seasonal dependence of the ozone concentration was determined using its maximum (March–April) and minimum (September–October) levels. The dynamics of the nitrogen and sulfur oxide concentrations indicate that they are at their highest in December–June and their lowest in July–August. To verify the validity of the pollutant concentration measurements sampled by passive sampling, we compared our results with those obtained following the automatic and filter pack methods. A linear regression analysis and a pairwise modification of Student's t test evaluated the concentrations of the air pollutant, sampled and measured using different methods, and they correlate well (r = 0.7–0.9). Full validation of the passive sampling method is not possible for some sites; therefore it is necessary to remove the remaining systematic errors in future work.

Keywords: Baikal Region; passive sampling; monitoring; statistical analysis; ozone; nitrogen oxides; sulfur dioxide

1. Introduction

Currently, great attention is being devoted to the quality of atmospheric air worldwide, which is mainly estimated according to the rate of trace gas pollutant concentrations. These trace gases include ozone (O_3) [1,2], nitrogen oxides (NO_x), and sulfur dioxide (SO_2) [3,4], and they adversely affect human health, particularly the respiratory system, as well as the Earth's flora [5]. Moreover, ozone is a greenhouse gas, and a quantitative increase in its concentration along with other greenhouse gases contributes to climate change.

Now, most attention is being devoted to studies in the Baikal Natural Territory (BNT), which is located in the south of Eastern Siberia, and includes Lake Baikal. Thanks to the large freshwater reservoir, the unique flora and fauna (60 per cent of the species are endemic) and the variety of the natural landscapes of the coastal area, Baikal is included in the United Nations Educational, Scientific and Cultural Organization (UNESCO) World Heritage List and the Acid Deposition Monitoring Network in East Asia (EANET) [6]. Therefore, it is vital that the water, air and surrounding area of Lake Baikal are protected.

Enterprises in the fuel-power engineering, chemistry and petrochemistry, steel, wood-processing and paper-making industries are predominant in the Baikal Region. Sulfur and nitrogen oxides are the main components of air pollution caused by these enterprises.

Increases in air emissions due to the operation of power-heating stations, production by industrial enterprises, and many other human activities [7,8], lead to adverse environmental conditions worldwide. Transport has become one of the main sources of air pollution by these gases in different parts of the world [9]. In the Baikal Region, the number of vehicles increased by over 80% from 2000 to 2014, and is still increasing by over 10,000 vehicles per year [10]. Owing to the increasing emissions into the atmosphere, it is vital that the gases in the atmosphere are monitored by different sampling and analyses methods.

The passive method for determining atmospheric air quality is a method used worldwide [11–14], particularly within international frameworks, such as the Acid Deposition Monitoring Network in East Asia (EANET) and the World Meteorological Organization (WMO). This method involves the accumulation of gases on an impregnated filter by occurred diffusion according to Fick's law [15,16]. The main advantages of this method are: Cheap sampling equipment, operation without the use of electricity, and the absence of stringent qualification requirements for the personnel installing the passive sampler equipment. Therefore, owing to these characteristics, this method is universal, and can estimate air conditions in places that are not easily reached, such as mountains, forests, aquatic areas and other locations.

Therefore, the purpose of this study is to evaluate the ability of the passive sampling method to sample trace atmospheric gases at the monitoring sites in the south of Eastern Siberia, which have different physio-geographical characteristics and anthropogenic impact rates. To evaluate the quality of the data obtained following the passive sampling method, we simultaneously followed the filter pack method and automatically analyzed the gases in situ. The obtained results may be useful for controlling urban air pollution at industrial enterprises and power plants that use new emission treatment technologies within the framework of gaseous emission treatment regulations.

This report summarizes the ozone, nitrogen and sulfur oxide concentrations measured following the passive sampling method. No substances, except for ozone, were previously measured at BNT by the passive method [17,18].

2. Experiments

We have conducted long-term studies of atmospheric air quality at three monitoring sites in the south of Eastern Siberia within the framework of the EANET Program since 2001. All of these sites meet the requirements for the background (Mondy), rural (Listvyanka), and urban (Irkutsk) conditions. Additional trace gas monitoring sites were set up on the west coast of Lake Baikal in June 2017 (Bugul'deyka). This site is semi-rural due to the types of sources, the volume of emissions in the region and its location in relation to the cities.

Site Mondy (51.40° N, 101.00° E) belongs to the network of background Russian sites, as it is located over 250–300 km away from the nearest industrial center, and does not contain any sources of air pollution. The site is located 2005 m above sea level, and is isolated by the Khamar-Daban and Eastern Sayan Mountains, with the highest peak reaching 3491 m (Mount Munku-Sardyk).

Site Bugul'deyka (52.32° N, 106.04° E) is located on the south-west coast of Lake Baikal. The Primorsky Mountains, with the highest peak located at 1205 m above sea level, and the southern side of Lake Baikal isolates the site from the main air flows. Atmospheric air at the site micro-circulates due to the terrain. The main sources of pollutants are local private-sector emissions, small coal stations and vehicles.

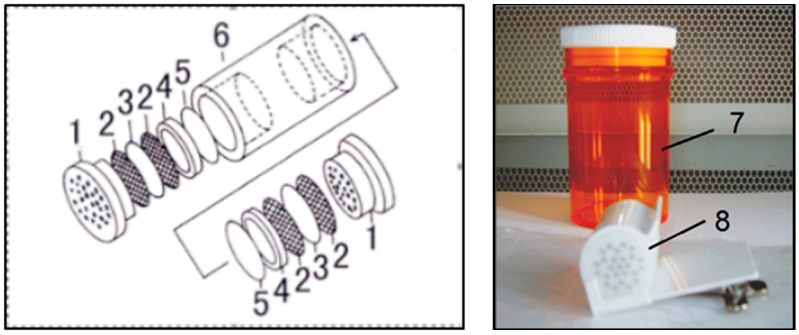
Site Listvyanka (51.51° N, 104.54° E) is located on the south-west coast of Lake Baikal, 60 km to the south-west of Irkutsk City. This site represents a rural area that is influenced by the industrial sources in the South Baikal Area [19]. The impact is both local and induced by certain meteorological conditions. During the past 10 years, Listvyanka has become renowned as a center of tourism, as it hosts numerous tourist hostels, and the number of vehicles within the region has increased.

Site Irkutsk (52.14° N; 104.15° E) is a large industrial city in Eastern Siberia, with a population of over 600,000 people. This city endures a wide variety of anthropogenic pressures. There are large

central heating and power plants, around one hundred small boiler-house plants, and numerous factories producing construction materials. There are developed road and railway networks, and one major airport within the city.

The concentrations of O_3, NO_x and SO_2 were measured at monitoring sites in South eastern Siberia following the passive sampling method. To verify the validity of the measurement results, we also applied the filter pack and automatic methods to measure the gases in the atmosphere.

At this work we used the Ogawa passive sampler [20,21] that consists of a plastic tube with holes on both ends. The caps on the inlets have 25 holes that allow for gas diffusion. Stainless-steel screens join an impregnated filter of approximately 14.5 mm in diameter and provide a shield against mechanical pollutants. Passive samplers accumulate pollutants into the body of an impregnated filter by chemical or physical absorption. The passive sampling method allows the estimation of the integral content of a specific gas over a certain period of time. The structure of a passive sampler is shown in Figure 1.



(**a**) (**b**)

Figure 1. Ogawa passive sampler components: 1—Inlet; 2—Stainless Steel Screens; 3—Collection Pad; 4—Ring; 5—Backing Tab; 6—Body; (**a**) [22]. 7—Plastic Sample Container; 8—Assembled Sampler (**b**).

We used the reagent shown in Table 1 to impregnate the filters. Sampler preparation and assembly were conducted in the laboratory. Depending on the site's status and the possibility of reaching them, filter exposure continued for two weeks to one month.

Table 1. Reagent, analyte and analytical method.

Gases	Absorption Reagent (a Volume Concentration)	Analyte; Analytical Method
SO_2	10% triethanolamine	SO_4^{2-}; Ion chromatography
O_3	Nitrite ion $NaNO_2 + K_2CO_3$	NO_3^-; Ion chromatography
NO_2	10% triethanolamine	NO_2^-; Ion chromatography
NO_x	10% triethanolamine + PTIO (2-phenyl-1-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl)	NO_2^-; Ion chromatography

After exposure, the sampler was placed into a plastic container that was then closed tightly with a lid and transported to the laboratory. In the laboratory, the filters with the samples were placed into 14-mL plastic test tubes, which were then placed into a freezer before analysis. According to the presented methodology [23], the filters with O_3 and SO_2 were extracted in 10 mL of deionized water, while the filters with NO_x and NO_2 were extracted in 8 mL of deionized water. Extraction occurred over one hour with periodical shaking.

The extracts were filtered using filters with 0.45-μm pores into the vials designed for an ICS-3000 ion chromatograph (Dionex, Sunnyvale, CA, USA), which measures the NO_3^-, NO_2^-, and SO_4^{2-} ions.

The gas concentrations were calculated according to the ions (Table 1) using the formulae shown in Table 2.

Table 2. Calculation of the gas concentrations in the surface atmosphere [23].

Gases	Formulas
SO_2 (ppb) = $\alpha_{SO2} \times W_{SO2}/t$	$\alpha_{SO2} = 39.4 \times (293/(273 + T))^{1.83}$
NO (ppb) = $\alpha_{NO} \times (W_{NOx} - W_{NO2})/t$	$\alpha_{NO} = 45.3 \times (-0.046 \times T + 219.94)/(-0.439 \times P \times RH + 208.16)$
NO_2 (ppb) = $\alpha_{NO2} \times W_{NO2}/t$	$\alpha_{NO2} = 77.2 \times (2.003 \times T + 89.41)/(0.637 \times P \times RH + 131.47)$
O_3 (ppb) = $\alpha_{O3} \times W_{O3}/t$	$\alpha_{O3} = 46.2 \times 102 \times (293/(273 + T))1.83/(9.94 \times \ln(t) - 6.53)$

W = average of collected amounts, (ng); α = coefficients (ppb × min/ng); T = average temperature during the measurement period (in °C); P = $(2 \times PN/(PT + PN))^{2/3}$; PN = water-vapor pressure at 20 °C (17.535 mmHg); PT = water-vapor pressure at the average temperature (mmHg); RH = Relative Humidity (%); t = exposure time (min).

To compare the measurement results sampled following the passive sampling method, we determined the sulfur dioxide content following the filter pack method (air pumping/forced method) according to [24], which involves sampling the air on four filters connected in series. Sulfur dioxide sorbed into the second polyamide filter PALL ULTIPOR and the third cellulose filter that was impregnated with potassium carbonate. The SO_2 content was calculated from the sum of the corresponding SO_4^{2-} ions, which is determined using the extracts of the second and third filters.

We also directly measured the concentrations of ozone, nitrogen and sulfur oxides. Ozone was measured using the Dylec Model 1007—AHJ optical ozonometer (Japan) with a temporal resolution of five minutes. The concentrations of nitrogen and sulfur oxides were measured using the R-310-A and SV-320-A analyzers developed by OPTEK, Russia. We simultaneously conducted the automatic registration of solar radiation intensity as one of basic photochemical ozone generation, atmosphere pressure, humidity and the wind speed and direction indices.

The quality of the analyses is verified by participating in international data quality control within the frameworks of the Acid Deposition Monitoring Network in East Asia [25], the World Meteorological Organization [26] and the European Monitoring and Evaluation Programme (EMEP) [27].

We evaluated the reliability of the differences between the alternative methods of studied atmospheric trace gases concentrations measurement using a pairwise modification of Student's t test.

The relationship between the gas concentrations obtained by different methods was evaluated by means of a linear regression analysis. The reliability of the linear regression model was determined using Fisher's F test. For the slope and intercept regression model coefficients, the 95% confidence intervals (CIs) were determined. In addition, for each regression model, the accuracy of the difference from the linear regression with slope = 1 and intercept = 0 was determined using the Fisher's F test—the reliability of the difference from the ideal case of the same readings of the compared methods. The analysis was performed using the car package [28] for the R programming language.

3. Results and Discussion

3.1. Measurement of Ozone Concentration

Many studies have been conducted on the concentration and dynamics of ozone in the atmosphere [29–31]. For a long time, it was believed that the main source of ozone in surface air was an intrusion from the overlying layers of the atmosphere. However, recently, it is found that photochemical generation involving NO_x under the action of solar radiation largely contributes to the tropospheric ozone budget [32–34], and serves as a secondary pollutant [35,36].

In this research, we analyzed the ozone concentration in the surface atmosphere sampled by passive sampling within a four-year observation period in the Baikal Region of the south of Eastern Siberia. Figure 2 shows that the seasonal dynamics of the ozone concentration can be traced at the Irkutsk, Listvyanka and Mondy sites, and is at its highest during spring (March–April) and at the lowest during autumn (September–October).

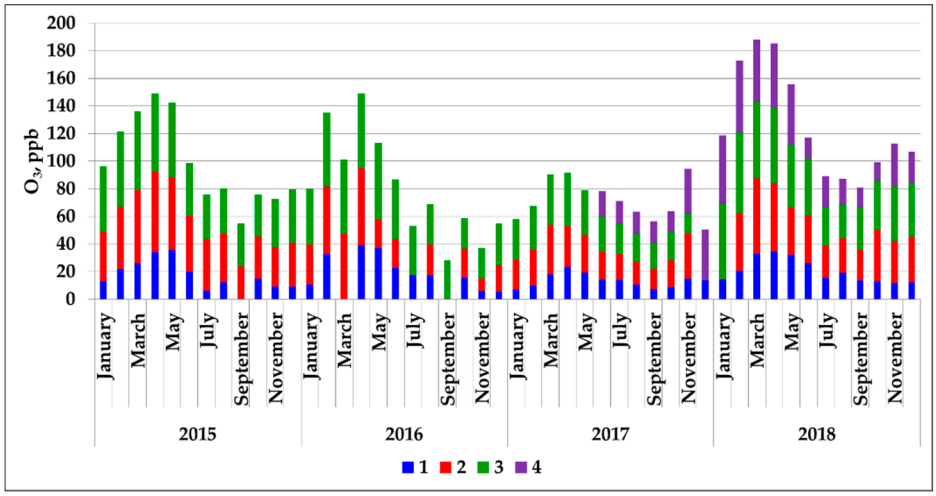


Figure 2. Inter-annual ozone concentration dynamics at the Irkutsk (1), Listvyanka (2), Mondy (3) and Bugul'deyka (4) monitoring sites sampled by the passive sampling method, 2015–2018.

For the first time, we present the ozone concentration data in the surface layer of the atmosphere at Bugul'deyka, on the west coast of Lake Baikal (Figure 2). The average monthly ozone concentration in Bugul'deyka is higher than that in Irkutsk and Listvyanka, but lower than that at the background site, Mondy. This is due to the absence of the major pollution sources in this area and the continuous purification of the atmosphere near the water body by fog, precipitation and dry deposition. In January–February (≈50 ± 12) ppb the maximum ozone concentration in the atmosphere of Bugul'deyka was observed, while the minimum was observed in September and October (≈14 ± 3) ppb.

The high ozone concentration in winter can be explained by terrain relief, as the village is located in the valley of a river, and is surrounded by mountain ranges that limit air movement over large areas on three sides. With the decrease in air temperature during the winter, the emissions from local boiler-house plants increases, and the generation of ozone is likely to increase.

According to Figure 2, at site Irkutsk during the spring maximum period, the ozone concentration reaches (≈45 ± 10) ppb, however, during the autumn minimum, this concentration falls to (≈10 ± 2) ppb. The main cause of the low ozone concentration under urban conditions may be the increased sink in the atmosphere, due to the oxidation of anthropogenic gases. As an example, Figure 3 presents a fragment of the joint automatic registration of the ozone and nitrogen dioxide concentrations at Irkutsk in April 2015.

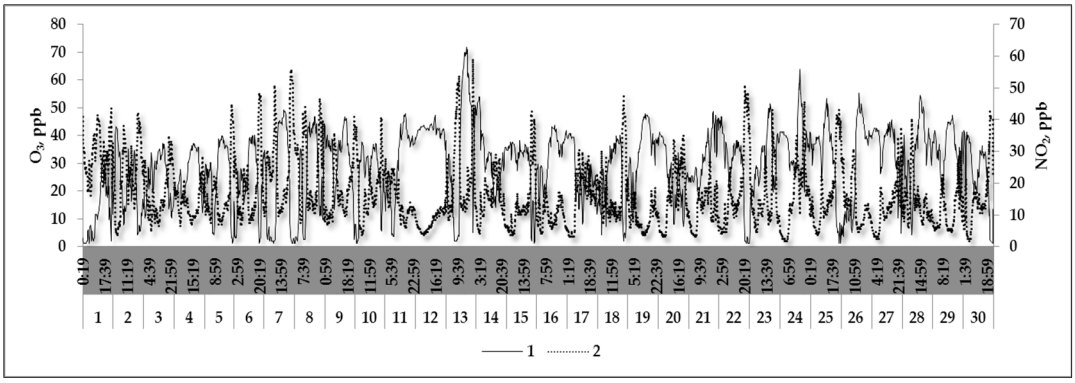


Figure 3. Variability of the hourly concentrations of ozone (1) and NO_2 (2) in Irkutsk during April 2015.

At sites Mondy and Listvyanka, a similar seasonal ozone concentration pattern is observed, with higher concentrations in the rural and background areas than those in the city. This is due to the remote location of the sites from the industrial centers of the region and the orographic features

of the terrain. In the cold season, episodic sharp drops in O_3 are observed in the surface atmosphere at site Listvyanka. The automatic registration of the ozone concentration recorded that, during the north-westerly transfer of polluted air masses from the industrial centers of the Baikal Region to Southern Baikal, the ozone concentrations in the atmosphere fell to zero, due to oxidation by pollutants, such as SO_2 and NO_x [18].

To confirm the validity of sampling by the passive method, we conducted a statistical analysis with the data obtained from the direct measurement of the ozone concentration at site Listvyanka (Figure 4a,b). The two methods exhibit good convergence with a high correlation coefficient ($r > 0.9$). At the background site Mondy, the link between the results obtained by passive and forced sampling methods in 2015–2016 is less strong, with a correlation coefficient of $r > 0.7$ (Figure 4c,d).

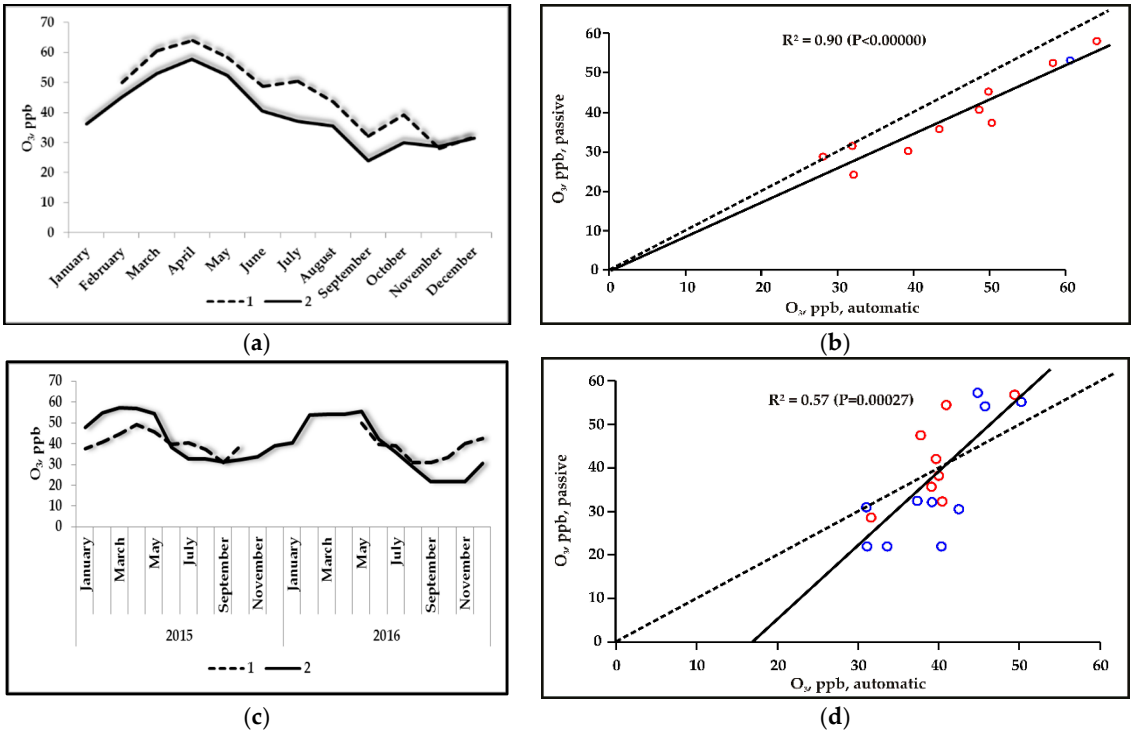


Figure 4. Comparative analysis of ozone concentrations sampled using the passive method and measured in the atmosphere at the Listvyanka (**a**,**b**) and Mondy sites (**c**,**d**). 1—Automatic method; 2—Passive method. In the figures (**b**,**d**), the red circles show the data obtained with a two-week exposure of the passive sampler, while the blue circles show the data obtained with the monthly exposure of the passive sampler. The solid line is a plot of the evaluated regression model, and the dotted line is the expected relationship with slope = 1 and intercept = 0. The value of the quality of the linear approximation R^2 and its statistical support P are shown in the figure.

Statistical analysis of the relationship between the values obtained by the passive and automatic methods for determining ozone in the atmosphere at the Listvyanka site (Figure 4b) shows that there is a strong linear relationship between these two methods ($R^2 = 0.9$ with $p < 0.00000$). The equation of the linear regression model is as follows: $O_{3passive} = (0.869 \pm 0.0955) \times O_{3automatic} + (-0.365 \pm 4.54)$. In the equation, the slope member, taking into account the error by value, is close to 1, and the intercept member is a small negative value. The resulting linear regression equation based on the Fisher test is significantly different from the equation with slope = 1 and intercept = 0 ($F = 17.43$, $p = 0.0008$).

This means that the reading of the passive method in Listvyanka, as a rule, is somewhat larger than the reading of the automatic method. The paired t test ($p = 0.00029$) confirms the reliability of the differences between the methods. Student statistics show that on average, the automatic method data was 6 ppb (95% confidence interval (CI) from 4 ppb to 9 ppb) more than the passive method data.

At the Mondy site, the relationship between the values of the passive and automatic method for determining ozone in the atmosphere (Figure 4d) shows that between these two methods there should be a reliable, not clearly expressed, linear relationship ($R^2 = 0.57$ with $p = 0.00027$). The equation of the linear regression model is as follows: $O_{3passive} = (1.7 \pm 0.3676) \times O_{3automatic} + (-28.893 \pm 14.7244)$. In the equation, the slope member differs significantly from 1, while the intercept member has a large negative value. Despite this fact, the resulting linear regression equation based on the Fisher test is not significantly different from the equation with slope = 1 and intercept = 0 ($F = 1.9577$, $p = 0.1736$). This means that the relationship between the passive and automatic data in Mondy, due to the large scatter of data, except for the obtained linear regression model, can also be effectively described by an equation with slope = 1 and intercept = 0. The paired t test shows that there are no significant differences between the readings of the automatic and passive methods ($p = 0.6339$). This result is consistent with the fact that the regression model with slope = 1 and intercept = 0 is applicable for the analysis. At this site, some measurements of the passive method were carried out with an exposure of two weeks, and part of the data with a monthly exposure. The graph shows that for the passive method with an exposure of two weeks, 5 out of 8 measurements lie above the regression line, and for the passive method with an exposure of one month, 7 out of 10 points lie below the regression line. Thus, different exposure times lead to different results of the passive method. Site Mondy is a clear mountain-top area, remote from the air pollution sources at a distance of 250–300 km. The ozone concentrations are high during the year, therefore an increase of the exposure time leads to a cumulative effect, and an underestimation of the ozone concentration compared to the automatic method. Perhaps, this explains the large scatter of the measurement results and the smaller R^2 value of the linear regression model and the large value of the intercept parameter.

Thus, based on the observed ozone concentration in the surface atmosphere by passive sampling and the comparison with other methods, the data used in the analysis of monthly and seasonal characteristics are well correlated. The disadvantage of the passive method is the inability to conduct analysis within daily ozone variations.

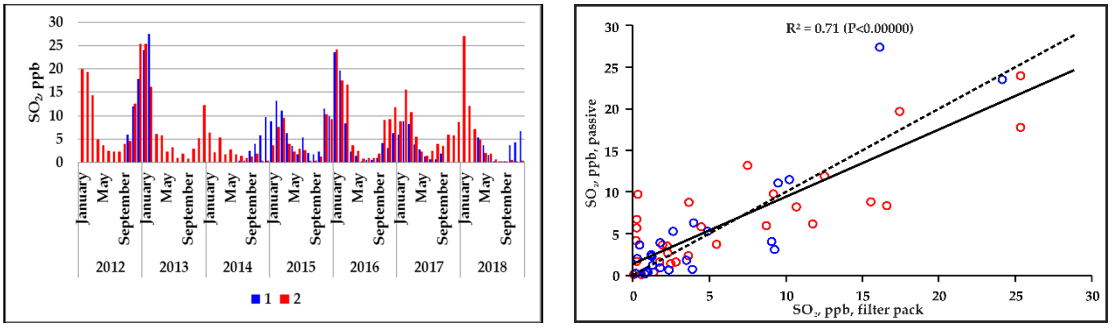
3.2. Sulfur and Nitrogen Oxides

Sulfur and nitrogen oxides in the atmosphere are both naturally occurring and originate from anthropogenic sources, which mainly include coal-fired power plants and vehicles in urban areas [37]. As atmospheric emissions from major coal-fired power plants enter the air at considerable heights (up to 200–300 m), their plumes can extend to tens or hundreds of kilometers in the direction of the air currents in the atmospheric boundary layer. In Siberia, forest fires, which have become more frequent in recent years due to climate change, significantly contribute to air pollution, including the gases studied here [38–40].

The monitoring of trace sulfur and nitrogen oxide gases, which are sampled and measured by different methods, is now vital for evaluating the state of the atmosphere in both cities and remote areas. Researchers in many countries have conducted long-term measurements of nitrogen and sulfur oxides [41–43]. In particular, the passive sampling method allows the state of the atmosphere in mountainous and forested areas, rural settlements and other places, to be assessed [44,45].

We are the first to obtain long-term data for the concentrations of SO_2 and NO_x that have been analyzed by passive sampling at atmospheric monitoring sites in the Baikal Region within the framework of the international EANET Program.

According to the seasonal dynamics of the SO_2 concentration, at the Irkutsk site the maximum concentration was observed during winter (≈20 ± 5) ppb, while the minimum was observed during the warm period (≈2.0 ± 0.5 ppb; Figure 5a).



(**a**) (**b**)

Figure 5. Seasonal variability of the sulfur dioxide concentration at the Irkutsk monitoring site, shown in (**a**); correlation of the concentrations obtained using the passive sampling and filter pack methods (**b**). 1—Passive method; 2—Filter pack method. The red circles on the graph show the data obtained during the two-week exposure of the passive sampler, and the blue circles show the data obtained during the monthly exposure of the passive sampler, while the solid line is the graph of the estimated regression model, and the dotted line is the expected relationship with slope = 1 and intercept = 0. The graphs show the quality value of the linear approximation R^2 and its statistical support P.

Statistical analysis of the relationship between the passive and filter pack values of the method for determining SO_2 in the atmosphere at the site in Irkutsk (Figure 5b) shows that between these two methods there is a pronounced linear relationship ($R^2 = 0.71$ with $p < 0.00000$). The equation of the linear regression model is as follows: $SO_{2passive} = (0.809 \pm 0.637) \times SO_{2filterpack} + (1.33 \pm 0.65)$. In the equation, the slope member is close to 1, the intercept member is slightly different from 0. Despite this fact, the linear regression equation based on the Fisher test is significantly different from the equation with slope = 1 and intercept = 0 ($F = 3.608$, $p = 0.034$). The paired t test shows that there are no significant differences between the readings of the passive and filter pack methods ($p = 0.65$). This pattern can be explained by the fact that in different ranges the concentrations of the passive and filter pack methods give different evaluations of the concentration of SO_2 in the atmosphere. At the concentrations of up to 7–8 ppb, the passive method gives slightly higher concentrations of SO_2, and at high concentrations, the filter pack method gives the increased readings.

Figure 6a shows the results of the automatic measurement of sulfur dioxide in Irkutsk from August 2014 to May 2015. When comparing the passive and automatic measurements of this gas, a high correlation coefficient was obtained ($r > 0.8$) (Figure 6b).

At the sampling point of Irkutsk, a mutual comparison of three methods for determining the concentration of SO_2 in the atmosphere was carried out: The automatic method, the passive method and the filter pack method (Figure 6). A comparison of the automatic and passive methods shows (Figure 6b) that there is a pronounced linear relationship between the SO_2 concentrations determined by these methods ($R^2 = 0.77$ with $p < 0.00433$). The relationship equation is as follows: $SO_{2passive} = (0.779 \pm 0.149) \times SO_{2automatic} + (-1.341 \pm 1.643)$. In the equation, the slope member is close to 1, the intercept member is slightly different from 0. The equation of linear regression based on the Fisher test is significantly different from the equation with slope = 1 and intercept = 0 ($F = 15.84$, $p = 0.0016$). The paired t test shows significant differences between the readings of the automatic and passive method ($p = 0.0057$). On average, the difference between the values of the automatic and passive methods is 3.4 ppb (95% confidence interval from 1.3 ppb to 5.5 ppb).

A comparison of the automatic method with the filter pack method (Figure 6c) shows a weak linear relationship ($R^2 = 0.61$ with $p < 0.0072$). The relationship equation is as follows: $SO_{2filterpack} = (0.52 \pm 0.147) \times SO_{2automatic} + (-2.22 \pm 1.62)$. In the equation, the slope member is significantly different from 1, and the intercept member is slightly different from 0. The linear regression equation in the Fisher test is significantly different from the equation with slope = 1 and intercept = 0 ($F = 62.43$, $p < 0.00000$). The paired t test shows significant differences between the readings of the automatic and filter pack methods ($p < 0.00000$).

The average difference between the values of the automatic and the filter pack methods is 7.0 ppb (95% confidence interval from 4.9 ppb to 9.1 ppb). Like the active method, the filter pack shows significantly lower SO_2 concentrations compared to the automatic method.

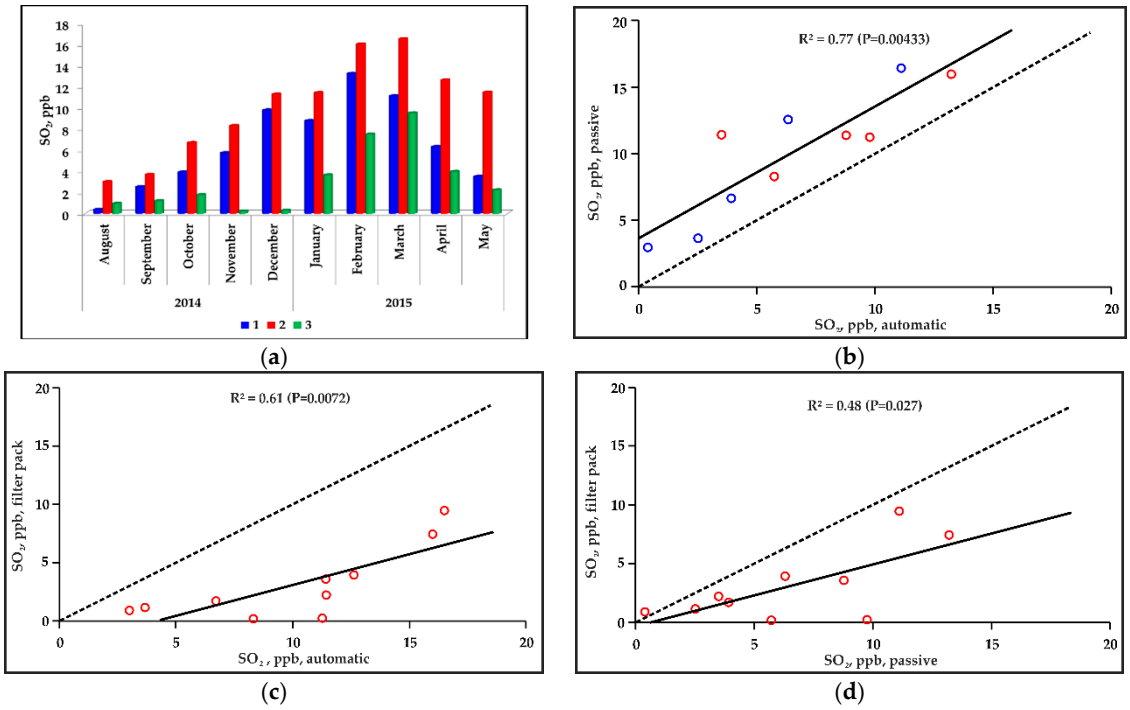


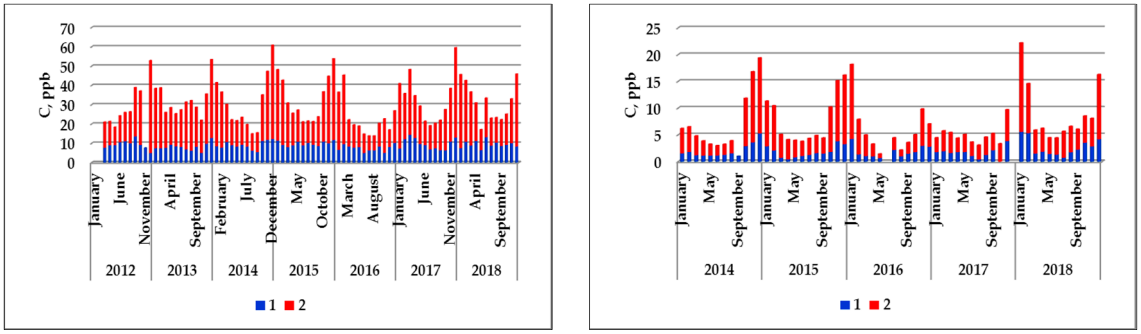
Figure 6. Sulfur dioxide concentration at the Irkutsk monitoring site in 2014–2015, shown in graph (**a**); correlation of the concentrations obtained using the automatic measurement and passive sampling methods shown in (**b**); concentration interconnection using the automatic measurement and samples selected by filter pack method (**c**); concentration interconnection using the passive measurement and samples selected by filter pack method (**d**). 1—Passive method; 2—Automatic method; 3—Filter pack method. In the figures (**b**–**d**), the red circles show the data obtained with a two-week exposure of the passive sampler, the blue circles (**b**) show the data obtained with the monthly exposure of the passive sampler. The solid line is a plot of the estimated regression model, the dotted line is the expected relationship with slope = 1 and intercept = 0. The figures show the value of the quality of the linear approximation R^2 and its statistical support P.

Between the data evaluated by the filter pack and the passive method, the linear relationship is reliable, but extremely weakly expressed (R^2 = 0.47 with p = 0.027). The relationship equation is as follows: $SO_{2filterpack} = (0.52 \pm 0.19) \times SO_{2passive} + (-0.30 \pm 1.47)$. In the equation, the slope member is significantly different from 1, the intercept member is slightly different from 0. The linear regression equation in the Fisher test is significantly different from the equation with slope = 1 and intercept = 0 (F = 12.99, p = 0.003). The paired t test shows that there are significant differences between the readings of the automatic and filter pack methods (p = 0.0057). The average difference between the values of the passive method and the filter pack is 3.4 ppb (95% confidence interval from 1.3 ppb to 5.5 ppb). It could be concluded that the filter pack method yields lower SO_2 concentrations compared to the passive method.

As a result of comparing the three methods for determining the concentration of SO_2 in the atmosphere: The automatic method, the passive method and the filter pack method (Figure 6), it is obvious that the filter pack method shows much lower SO_2 concentrations in November and December compared to the other two methods. It was possibly caused by any technical failure when using the filter pack method at the certain period (November–December, 2014).

Nitrogen oxides are components of the ozone cycle, as they influence the dynamics of the ozone layer and play a key role in the generation of photochemical "smog". Atmospheric pollution by nitrogen oxides influences both local and global environments. Here, we represent the nitrogen oxide (NO_x) measurements as the sum of the concentrations of NO and NO_2.

NO_x measurements commenced following the passive sampling method at the Irkutsk monitoring site in 2012 (Figure 7a) and at Listvyanka in 2014 (Figure 7b). We obtained a large number of pollutant concentration observations in the surface atmosphere in both urban and rural areas.



(**a**) (**b**)

Figure 7. Long-term nitrogen oxide dynamics at the Irkutsk (**a**) and Listvyanka (**b**) sites. 1—NO_2; 2—NO, obtained using the passive sampling method.

Figure 7 shows that the concentrations of nitrogen oxides in the surface layer of the atmosphere at the Irkutsk urban monitoring site are twice that at Listvyanka. This can be explained by the high number of anthropogenic pressures, such as vehicles in a city with a population that exceeds 600,000.

The nitrogen and sulfur oxide concentrations in urban and rural areas are also affected by seasonal and inter-annual variations depending on air temperature (Figure 8).

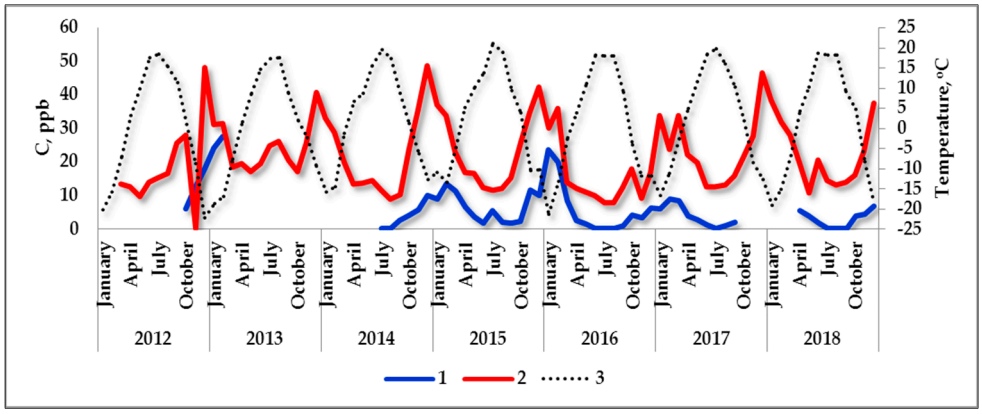


Figure 8. Seasonal and inter-annual variations in the concentrations of SO_2 (1) and NO_x (2) in the atmosphere of Irkutsk City according to air temperature (3).

During cold winters with low air temperatures (winter 2012–2013, 2015–2016), the SO_2 and NO_x concentrations in the surface atmosphere increased due to increases in the volume of the coal burned at the Irkutsk Heat and Power Plant.

4. Conclusions

Complex studies of trace gas pollutants have been conducted at three sites that have regularly monitored the atmosphere in the Baikal Region (south of Eastern Siberia) since 2010. The ozone, sulfur and nitrogen oxide concentrations in the surface atmosphere layer were studied following the passive method. In 2017, another rural site was established at the south coast of Baikal.

The passive sampling method was compared to the automatic and filter pack methods, and the O_3, NO_x and SO_2 measurements obtained with these different methods are well reproducible. The data obtained in ozone analysis and the sulfur and nitrogen oxide measurements obtained by these direct and passive methods are highly correlated.

Based on the results of the four-year O_3 studies, we have determined the annual seasonal dynamics in the surface atmosphere layer at the Irkutsk, Listvyanka and Mondy sites, with the maximum concentration reached in spring (March–April) and the minimum in autumn (September–October). At the Bugul'deyka site, high ozone concentrations were observed in the winter (January–February).

The average ozone concentration under urban conditions (Irkutsk) is significantly lower than that under rural (Listvyanka, Bugul'deyka) and background (Mondy) conditions. The short-term daily variations in the ozone concentration at site Listvyanka, measured automatically, depend upon both the photochemical generation of ozone under solar radiation during the day and partial destruction during the night, and on the sulfur and nitrogen oxide contents of anthropogenic emissions in the surface atmosphere layer. The seasonal dynamics of the SO_2 and NO_x concentrations in the atmosphere of Listvyanka and Irkutsk were tracked, and the concentrations were higher in winter, when the volume of fuel at burned thermal power plants increases, and were lower during warm periods. Site Mondy is still the background atmospheric measurement site within the Asian territory of Russia, where the sources and seasonal dynamics of gases under analysis are caused by natural processes.

Different statistical approaches have proven the passive sampling method efficiency: A pairwise modification of Student's t test; a linear regression model using Fisher's F test. During the study, the passive sampling method proves its capability for monitoring the overall behavior of the trace gas concentrations, but additional experimental work is needed to correct remaining systematic errors detected in some conditions.

The ease of use, operational efficiency, low cost of production and relatively high sensitivity are the main benefits of this method. Thus, we present this method as an optimal procedure for conducting long-term measurements in the remote, inaccessible areas of the Baikal Region.

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