Experimental Study And Numerical Analysis Of The Pollution In The Area Of Highway According To The Snow Cover Composistion

Vladimir F.Raputa, Vasili V.Kokovkin, Olga V. Shuvaeva, Sergei V.Morozov

Abstract—In present work the the quantitative regularities at the regional scale from the linear-type contamination source have been investigated. It has been shown with the use of snow cover as an indicator of long-term pollution in the vicinity of highway that the concentrations of aerosol constituents monotonically decreases with the distance from the contamination source. The application of mathematical model demonstrated a satisfactory agreement beetween calculated and experimentally observed data of contaminants distribution.

Keywords—aerosol transport, contaminants distribution

I. INTRODUCTION

Road transport is one of the major sources of air pollution in Novosibirsk [1]. The typical pollutants are nitrogen and sulfur oxides, heavy metals, as well as organic products of incomplete combustion of the fuel, such as polyaromatic hydrocarbons (PAHs) [1 - 4]. The dust emission arising from the road surface by moving vehicles consists of the substances that strew the way in winter period to prevent icing which includes sodium, calcium, magnesium, chloride, silicon, etc. In recent years much is being done to reduce the level of pollution from automobile emissions in Novosibirsk, but the effectiveness of interventions is often ambiguous and unpredictable. Thus, during the period 1998-1999 years the car park of the city was transferred to the use of unleaded gasoline. As a result a sufficient decrease in lead emissions was achieved bringing a positive impact on the environment. However at the same period a significant increase in PAHs emissions was registered, which apparently originated from the new types of anti-knock additives [3]. A considerable increase in the number of cars enhances a aggressive impact on the environmen, therefore the search for techniques to reduce emissions of pollutants inextricably linked with the need to monitor the state of the urban habitat. To assess the long-term pattern of contamination area in Siberia the snow cower may serve as a very suitable indicator. [3 - 6].

The goal of the present work is the study of spatial dynamics of pollution in the vicinity of major highways in Novosibirsk based on the study of the snow chemical composition of snow.

II. EXPERIMENT

The object of the study was the Soviet highway on the Left Bank of the Soviet District of Novosibirsk. The sampling was done at the end of the winter season 2007-2008 in the vicinity of motorway in the direction perpendicular to the predominant south-west winds [7]. The sampling rout is presented in Fig. 1:

on the windward side of the road the samples were taken at 8 locations on the leeward side - in 2 points according to the distances from the highway resented in Table. 1. The snow samples were taken using plastic tube 45 mm in diameter the entire depth of snow cover, the average value of the snow accumulation on the route under investigation corresponded to 116 kg/m².

Fig.1. The scheme of the snow cover sampling according to the wind direction.

Snow samples analysis

After fast melting the liquid samples were filtered through the filter with pore size 1 µm and than through membrane filter with a pore size of 0.45 µm. The filters with sediments were dried in air. Both in filtrates and sediments the major and trace elements were determined. For PAHs determination unfiltered probes were used: the analytes were previously extracted in methylene chloride, dried with anhydrous sodium sulfate, evaporated on a rotary evaporator to dry precipitate and dissolved in a small volume of acetone.

Analytical methods

Capillary electrophoresis (CE) with indirect photometric detection at 254 nm was applied for inorganic anions (chlorides, sulfates, nitrates, nitrites, fluorides and phosphates) determination in filtrates.

Flame atomic emission and atomic-absorption spectrometry (AES and AAS) were used for alkaline and alkaline earth metals (Ca, Mg, Na, K) determination.

Atomic-emission spectrometry with direct current plasma as a source of excitation (DCP-arc-AES) was used for the trace elements (Pb, Cu, Zn and others) determination.

Hyphenated method of capillary gas chromatography coupled with quadrupole mass spectrometric detector (GC-MS) was put on PAHs determination.

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Instrumentation.
The following equipment was applied:
- CE system Agilent 1600 (USA) with photodiode array;
- FAAS spectrometer Z 8000 Hitachi (Japan) with Zeeman correction;
- DCP-arc-AES spectrometer PGS-2 Carl Zeiss Jena (Germany) with spectra registration on photodiode array;
- GC-MS spectrometer Hewlett-Packard MSD (USA).

III. RESULTS AND DISCUSSION

The data obtained are summarized in Table 1, where the ions contents in dissolved part and essential trace elements concentrations as the sum of dissolved and particulate matter of the snow samples are given dependently on the distance from the highway.

Table 1. The content of macro- and microcomponents in snow cover samples.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>The distance m</th>
<th>Ion components, mM/L</th>
<th>Trace elements, µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Na⁺</td>
<td>K⁺</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>0.86</td>
<td>0.04</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>0.50</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>0.19</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0.16</td>
<td>0.01</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>0.14</td>
<td>0.04</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>0.10</td>
<td>0.008</td>
</tr>
<tr>
<td>7</td>
<td>110</td>
<td>0.05</td>
<td>0.007</td>
</tr>
<tr>
<td>8</td>
<td>150</td>
<td>0.04</td>
<td>0.005</td>
</tr>
<tr>
<td>9</td>
<td>-30*</td>
<td>0.04</td>
<td>0.006</td>
</tr>
<tr>
<td>10</td>
<td>-50*</td>
<td>0.02</td>
<td>0.003</td>
</tr>
</tbody>
</table>

* - leeward side of the road

It is seen that the concentration of all substances are decreased with increasing the distance from the anthropogenic source. The extent of deposition on the windward side of the road is much higher than on the leeward side, which is in agree with the frequency of wind directions in winter time [7]. For the main ionic constituents the strong correlation between the concentrations of sodium and chloride is noticed which confirms the origination sodium chloride is the main component of the mixture for winter padding the roads. Another component is, apparently, magnesium sulfate. The table also shows that with increasing the distance from the highway maintenance of all heavy metals decreases monotonically.

Comparing the spatial distribution of trace elements Cu, Zn and Pb in the area of the highway with the data obtained earlier, in 2001-2002 [3, 4] it should be noted that their concentrations in snow cover falls with distance from the highway in water soluble part and particulate matter as well [3]. Moreover, the decline in concentration was observed on both sides of the highway. For total trace element content in fine and vodorastvorennoy parts of the maximum concentration is shifted to windward of 50-60 m. Also note that the share ratio of trace elements in all three fractions for samples taken at a point distant 50 meters from the highway coincides with similar results obtained at 2001-2002.

The data on the content of 19 PAHs in snow samples is presented in Table 2. The most carcinogenic ones are bold. The total amount of carcinogenic PAHs is marked as ∑. The similar picture of monotonic decrease in concentration with the distance from the road is also visible for all PAHs.
Table 2. PAHs contents in snow cover samples versus the distance from the emitter

<table>
<thead>
<tr>
<th>№</th>
<th>PAH</th>
<th>Distance, m</th>
<th>Contents of PAHs, ng/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aacenaphthylene</td>
<td>105</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>Aceanaphthene</td>
<td>645</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Naphthalene</td>
<td>370</td>
<td>110</td>
</tr>
<tr>
<td>4</td>
<td>Fluorene</td>
<td>260</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>Phenanthrene</td>
<td>2300</td>
<td>120</td>
</tr>
<tr>
<td>6</td>
<td>Anthracene</td>
<td>80</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>Fluoranthene</td>
<td>770</td>
<td>120</td>
</tr>
<tr>
<td>8</td>
<td>Pyrene</td>
<td>657</td>
<td>120</td>
</tr>
<tr>
<td>9</td>
<td>Benzo(a)phenanthrene</td>
<td>120</td>
<td>78</td>
</tr>
<tr>
<td>10</td>
<td>Chrysene</td>
<td>560</td>
<td>175</td>
</tr>
<tr>
<td>11</td>
<td>Benzo(b)fluoranthene</td>
<td>240</td>
<td>78</td>
</tr>
<tr>
<td>12</td>
<td>Benzo(k)fluoranthene</td>
<td>150</td>
<td>81</td>
</tr>
<tr>
<td>13</td>
<td>Benzo(i)fluoranthene</td>
<td>41</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>Benz(e)pyrene</td>
<td>490</td>
<td>75</td>
</tr>
<tr>
<td>15</td>
<td>Benz(a)pyrene</td>
<td>160</td>
<td>49</td>
</tr>
<tr>
<td>16</td>
<td>Perelene</td>
<td>97</td>
<td>16</td>
</tr>
<tr>
<td>17</td>
<td>Dibenz(a,h)anthracene</td>
<td>95</td>
<td>12</td>
</tr>
<tr>
<td>18</td>
<td>Indeno(1, 2, 3 cd)pyrene</td>
<td>120</td>
<td>44</td>
</tr>
<tr>
<td>19</td>
<td>Benz(g,h,i)perelene</td>
<td>330</td>
<td>62</td>
</tr>
<tr>
<td>Σ</td>
<td>PAHs</td>
<td>7000</td>
<td>1730</td>
</tr>
<tr>
<td>Σ</td>
<td>carc. PAHs</td>
<td>1490</td>
<td>139</td>
</tr>
</tbody>
</table>

The model of estimation of polydisperse aerosol deposition

Preliminary analysis of the experimental results shows that the change in concentrations of major and minor components with distance from the highway is very significant. It allows to suggest the predominance of the large particles in aerosol deposition.

For a priori description of the matter of impurity distribution on the sedimentation rate \( W \) in the atmosphere we use the following two-parameter function [8, 9]:

\[
N(w) = \frac{a^{m+1}}{\Gamma(m+1)} w^m e^{-aw}, \quad m \geq -1, \quad a = \frac{m}{w_w},
\]  
(1)

where parameter \( w_w \) characterizes the sedimentation rate of prevailing fraction of impurity, \( M \) - a degree of uniformity of distribution of the particles in sedimentation rate, \( \Gamma(m) \) - Euler gamma function.

The starting point for the calculating of the field fallout for polydispersed particles from a point source is the ratio [8, 9]:

\[
p = \int_0^\infty w q_w N(w)dw,
\]
(2)

where \( q_w \) - the concentration field of monodisperse impurity with sedimentation rate \( w \).

In calculating the average concentration in the surface layer of the atmosphere the common meteorological conditions are of a great importance. These include so-called normal weather conditions, which used the power approximation of the wind speed and the vertical turbulent exchange coefficient [10]:

\[
u(z) = u_1 \left( \frac{z}{z_1} \right)^n, \quad K_z = k_1 \frac{z}{z_1},
\]
(3)

where \( u_1 \) and \( k_1 \) are \( u \) and \( K_z \) when \( z = z_1 \).

Using relations (3) and analytical solutions of the equation of turbulent diffusion for low-rise source in the concentration field \( q_w \) near the ground can be written as [9, 11]:

\[
q_w(x,y) = \frac{M c^\omega}{2(1+n)\pi k_0} \Gamma(1+\omega) x^{1.5+\omega} \exp\left( \frac{c - y^2}{4k_0x^2} \right)
\]
(4)

There axis \( X \) is oriented in the direction of the wind, the axis \( Y \) is directed in a transverse direction of the wind, - the
power source of impurity - parameter of the turbulent exchange in the direction of the axis, $M$ - the power source, $k_0$ - parameter of the turbulent exchange in the direction of the $y$ axis, $\omega = \frac{W}{k_1(1+n)}$.

Taking into account the relations (1) and (4) the expression (2) can be written as:

$$p(x,y) = \frac{M_p^{\eta_0}n!}{2(1+n)\pi x 4\eta_0^2} \exp\left(-\frac{c[x^2 + y^2]}{2\eta_0^2}\right) \frac{n!}{2^\eta_0} \frac{\Gamma(1+\eta_0)}{\Gamma(1+n+\eta_0)} \frac{c^{\eta_0}}{\Gamma(1+\eta_0)} x^\eta_0 d\omega,$$

$$= Q \frac{M_R^{\eta_0+2}}{2(1+n)\sqrt{\pi \eta_0} \Gamma(1+n+m)} R = a(1+n)k_1,$$

Then the concentration field produced by an infinite line source, is based on the superposition of fallout from the power source $H$ parameter of the turbulent exchange in the direction of the $\eta$ axis, $H = \theta_1 \cdot H \sin \beta$, $\beta$ - angle between the direction of the wind and the axle $X$.

The simplest form expression (7) acquires when the angle $\beta = \frac{\pi}{2}$. In this case, we obtain:

$$p_{mn}(x,y) = \int_{-\infty}^{\infty} p(x,\eta) d\eta,$$

where:

$$x = x_0 - \eta \sin \beta, y = y_0 - \eta \cos \beta, s_1 = \cos \beta + \sin \beta, s_2 = -\cos \beta + \sin \beta,$$

$$\eta_0$$ - control observation points.

Investigation of the properties of functions (8) shows that in the range $x \in (0,\infty)$ it reaches the maximum at a certain point $x_0$ increases monotonically when $x \in (0,\infty)$, and respectively decreases monotonically in the range values $x \in (x_0,\infty)$ and tends to zero at $x \to 0$, $x \to \infty$. Evaluation of the unknown parameters $\theta_1$, $\theta_2$, $\theta_3$ in relation (8) can be carried out by least squares method using the data from measurements of the density of impurity deposition in snow cover sampling points [12]. It should also be noted that value $C$ corresponds to the distance at which the maximum surface concentrations of light impurities is achieved [9].

**Numerical analysis of the results of experimental studies**

As has been mentioned a section of highway in the vicinity of which the snow cover sampling was done is oriented from the south-east to north-west. It allowed for the estimation of the fields of aerosol precipitation the simplified model (8), because the frequency of southern, south-west and west direction of winds during winter period is about 70% [7]. Accordingly the wind of north, north-eastern and eastern direction s constitute only 14% of that de bene esse allows to highlight the leeward and windward sides and determine the apportioning of aerosol particles removal of on both sides of the highway, as 5:1.

As an example, in Fig. 2a are shown the results of the field deposition of PAHs.

![Fig. 2. The measured and reconstructed by model (8) concentrations of PAHs (a) and benzo(a)pyrene (b) in snow cover samples. o - bearing and ● - control observation points.](image-url)

It is seen, that the results of the numerical reconstruction of the concentration field are quite consistent with the measurements at the control points. The estimates of parameters $\theta_1$, $\theta_2$ directly related to the characteristics of the dispersion composition of the samples were used to restore a field of concentration of benzo(a)pyrene (Fig. 2b). In this case, the model (8) was used for the evaluation the only $\theta_1$ parameter and for its determination the reference point located at 20 m from the road was used.

Thus, in frames of present investigation with the use of snow cover as an indicator of long-term pollution in the vicinity of highway it has been established that the concentrations of inorganic cations (K, Na, Ca Mg, Pb, Cu and Zn) and anions (Cl, SO$_4$)$^2$–, NO$_3$)$^-$ as well as organic ingredients (19 PAHs) monotonically decreases with the distance from the contamination source. Based on analytical relationships (1) and (4) a mathematical model was developed to assess the fields of a single and long-term pollution areas. The application of proposed model showed its satisfactory agreement with experimentally observed contaminants distribution. To reconstruct the fields of aerosol deposition a relatively small number of control of observation points were used . Taking into account the polydispersity of the impurities it is possible to interpret the results of experimental studies in a large range of the distances within a unified model. It should be noted the high levels of PAHs in snow cover both near and far away from the highway, indicates a significant air pollution by fine components. In respect that vehicle emission pays the dominant influence on the environment of the city the theoretical and applied research need to further expand on this problem with the greater involvement of instrumental methods for monitoring the current air pollution and developing of the effective interventions to reduce the adverse effects.
REFERENCES

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