

Identification of aerosol sources based on the relationship of individual concentrations of anthropogenic pollutants

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The problem of identification is very actual, because its solution makes it possible to determine the contribution of different sources – the institution, the city, the country – to the air pollution at a given point. The paper describes the formalized approach that, on the basis of experimental data, allows the determination of the contribution of different sources to the pollution of snow cover of a point-receptor. The solution technique is based on the minimization of discrepancies between measured and calculated data. Methods of mathematical programming (the Lagrange multiplier method, the affine scaling method) were used. Polycyclic aromatic hydrocarbons (PAH) are considered as the most effective tracers. The distribution of reference PAH concentrations simplifies considerably the problem and allows the least squares method to be used.

Introduction

As far as we know, the identification implies a search for certain functional dependences between the emissions and precipitation of some components

$$Qx = M. \quad (1)$$

Different formulations of this problem are possible:

- the determination of contributions coming from an individual source to the composition of precipitation at a certain point (M),
- the investigation of regularities in the dispersal of contaminants (x),
- the refinement of inventory compilation of local sources (Q).

One of the most promising methods of identification of the sources is the experimental analysis of precipitation, at which the contributions of sources are revealed from the relationship of concentrations of a given set of compounds. For this purpose, detailed data are needed on the chemical

composition of emissions of all potential sources. Industrial emissions of enterprises of different branches of industry and motor transport differ in their composition. Besides, in many cases the composition of pollutants varies quite widely, depending on the technology used in the framework of one or another branch. It has been known that the peculiarities of coal burning regimes result in a considerable difference in chemical composition of gas emissions and light ashes.¹ The methods of analysis of snow samples enable one to determine a great number of elements and compounds,² in particular, 12 individual polycyclic aromatic hydrocarbons (PAH). The relationships of PAH concentrations in the industrial emissions of different power production facilities as well as of motor transport can easily be distinguished^{3,4} (Table 1).

The results of chemical analysis of snow samples, collected at a considerable quantity and at the representative points allow us to determine sources on the city scales. Since in a big industrial center there are traditionally several hundreds of stationary sources, their identification is complicated to be realized only by the method of expert assessments.

Table 1. The PAH concentration normalized by benzo(a)pyrene in emissions of different sources (Refs. 3 and 4)

Source	Phenanthrene (Ph)	Anthracene (A)	Fluoranthene (Fl)	Pyrene (P)	Benzo(a)-anthracene (BA)	Chrysene (Ch)	Benzo(b)-fluoranthene (BFL-b)	Benzo(k)-fluoranthene (BFL-k)	Benzo(g,h,i)perylene (BPL)	Indeno(1,2,3-c,d)pyrene (IP)
Boiler rooms, coal	9	1.3	5.3	8.5	1	0.6	0.7	1	0.3	0.45
Boiler rooms, black oil	6.6	1	1.2	3.3	5.8	10.8	3.1	4.8	1.0	1.2
Stoves, coal	4.1	1.2	3.8	4.8	0.7	0.9	0.7	0.5	0.3	0.4
Stoves, firewood	3.3	0.48	1.9	2.2	0.6	1.6	1.1	0.9	0.6	0.9
Carburetor engine	0.0	0.0	43	7	4.2	10	4.4	4.5	5.5	0.0
Diesel engine	36	0.8	23	23	2.5	1.3	0.0	1	1.2	0.0
IrkAZ–SUAL	4.6	0.8	8.0	8.4	0.9	2.5	3.4	0.9	0.8	0.3

A formalized approach is necessary, which would allow one to construct, based on the experimental data, a model of distribution of contaminants over the territory of a city with the account of the balance relationships for each component.

Possible statements of the identification problem

It is assumed that at a certain given territory there are n emission sources; in this case (X_j, Y_j) are the coordinates of the j th source, for example, a boiler room ($j = 1, \dots, n$). Each of the boiler rooms emits to the air basin the m number of main components Q_{ij} (kg/h), ($i = 1, \dots, m$). We can derive the balance equations based on the mass of emissions, i.e., the amount (mass, $\text{kg}/\text{m}^2 \cdot h$) of a given component at a given point $M_i(X_k, Y_k)$ is equal to the sum of emissions multiplied by the weighting factors for all the sources of this component (with the account of the arrival due to long-distance transfer), except for the case that this component is carried out beyond the limits of the observed territory:

$$M_i(X_k, Y_k) = \sum_{j=1}^n x_{jk} Q_{ij} - \sum_{j=1}^n P_j Q_{ij} + P_i' Q_i', \quad (2)$$

where x_{jk} is a certain coefficient ($1/\text{m}^2$) depending, in particular, on the mutual location of the j th source and k th receptor, the peculiarities of scattering relief of the locality and so on, P_j is the fraction of the j th source emission leaving the territory due to the long-distance transfer, $P_i' Q_i'$ is the inflow of the i th component to a receptor point due to the long-distance transfer.

Because both in calculating emissions and in making chemical analyses to determine the quantity of precipitated components, the errors of methods, instruments, and so on affect the values of the quantities obtained, the determination of an error is being made as follows

$$\delta_{ik} = M_i(X_k, Y_k) - \sum_{j=1}^n Q_{ij} x_{jk} + \sum_{j=1}^n Q_{ij} P_j.$$

It is assumed that the samples are taken at r points. The sum of error squares in all the observation points

$$\sum_{k=1}^r \delta_{ik}^2 = \left(\sum_{k=1}^r [M_i(X_k, Y_k) - \sum_{j=1}^n x_{jk} Q_{ij} + \sum_{j=1}^n Q_{ij} P_j] \right)^2$$

must be minimized. Thus, we have the problem for absolute extremum. Taking into account the peculiarities related to the convexity of the constructed distribution function, we can assume that the solution of the problem (2) can be sought using the rule of the Lagrangian multipliers. In this case the limitations of the type of inequalities are not needed. Based on data of long-term observations of chemical composition of atmospheric precipitation (AP) in the Lake Baikal region it is known that in the industrial centers of the region the local pollution by main components is

by orders of magnitude higher than in the surrounding background regions,⁵ therefore in the first approximation the arrival of pollutants due to long-distance transfer can be neglected.

First, the components of the vector \mathbf{x} were chosen as unknown values. It was assumed that if we set the function of impurity distribution from each source using one or another model of its dispersal, the problem reduces to the estimate of model validity. Then we select the minimum of sum of squares of differences between the calculated and experimental data as the estimate characteristics:

$$\sum_{i=1}^m \sum_{j=1}^n (x_{jk} - p_{jk})^2, \quad (3)$$

where p_{jk} denotes the weighting factors determining the fraction of the source emission Q_{ij} , which falls at a point M_{ik} (by analogy with the method of least squares). The balance (1) impose the limitations.

This formulation of the problem is, first of all, characterized by the simplicity of solution. After calculating the partial derivatives $L(x, \lambda)$ of the Lagrangian function by components of the Kuhn–Tucker vector (x, λ) we obtain a set of linear equations with a square matrix of coefficients.

With the large number of chemical tracers available, whose ratio is constant within the emission from the sources of some definite type, another formulation of the problem is possible, which was previously noted. As we have already mentioned, the PAH emission spectrum (the combination of relative concentrations normalized by benzo(a)pyrene) is known and different for motor transport, boiler rooms, house stoves and some technological processes. The distribution of PAH relative concentrations, obtained for snow cover at a point, can be reconstructed using the combination of spectra characteristic of different types of emissions. In this case the problem is simplified essentially as compared with Eqs. (1)–(3), because, turning to relative concentrations, we do not need using any hypothesis describing the transfer of pollutants. The contribution of different sources is determined statistically by the method of least squares for the multidimensional problem.

It should be stressed that in abandoning the use of the theory and information about the spatial distribution of sources, points of emission, etc., we essentially increase the uncertainty of the problem and limit its information base. At the same time, with such an approach the errors are excluded, which inevitably are a necessary accompaniment of any hydrodynamic models. Therefore, such a statement of the problem has significant advantages but for its realization it is necessary to have an extended and reliable database on the emission composition.

For the problem being considered the following matrix equation is used

$$\mathbf{Q}\mathbf{Q}^T \mathbf{x} = \mathbf{Q}\mathbf{M}, \quad (4)$$

where \mathbf{Q} is the matrix of relative content of individual PAH (or other tracers) in the industrial

emissions of different sources, \mathbf{M} is the vector of relative content of indicators in a snow sample. The vector \mathbf{x} contains the required weighting factors (contributions) of different types of sources to the pollution of snow cover at a given point. The problem is solved analytically

$$\mathbf{x} = (\mathbf{Q}\mathbf{Q}^T)^{-1}\mathbf{Q}\mathbf{M}.$$

Results of approbation

To identify the emission sources in Irkutsk, Shelekhov, Slyudyanka, and also in the settlement of Bayandai, the results of chemical analysis of snow cover samples were used. The samples were collected during 1996, 1997, 1999, as well as in 2002 and 2004.

The statement of the problem in the form of Eqs. (1) to (3) was tested for the pollution sources of the city of Slyudyanka. At present there are 18 boiler rooms functioning in the city. To solve this problem, it is worth combining in pairs 4 small emission sources located several meters apart. Thus, 16 sources

were considered. Snow samples were taken at 8 points (in the center and in the outskirts of the city) during two years. From all the compounds, which concentrations were determined in chemical analysis of snow samples, sulfates and calcium ions were chosen for identification. To determine p , we used the inverse dependence on the distance between the emission source Q_{ij} and k th point of sampling (l_{jk}), as well as the source stack height h_j :

$$p_{jk} = \frac{1}{(l_{jk}h_j)} \cdot 1000. \tag{5}$$

Upon solving the set of equation (1) and (3) the fractions of the contributions from each boiler room at every point of sampling were obtained. As a criterion of reliability and consistency of the derived solution the nonnegative character of derived coefficients was used. It turned out that for a correct statement of the problem it is necessary to introduce fictitiously the negative emission source simulating the long-distance transfer (carrying the pollutants out of the city). Some results of the analysis are shown in Fig. 1.

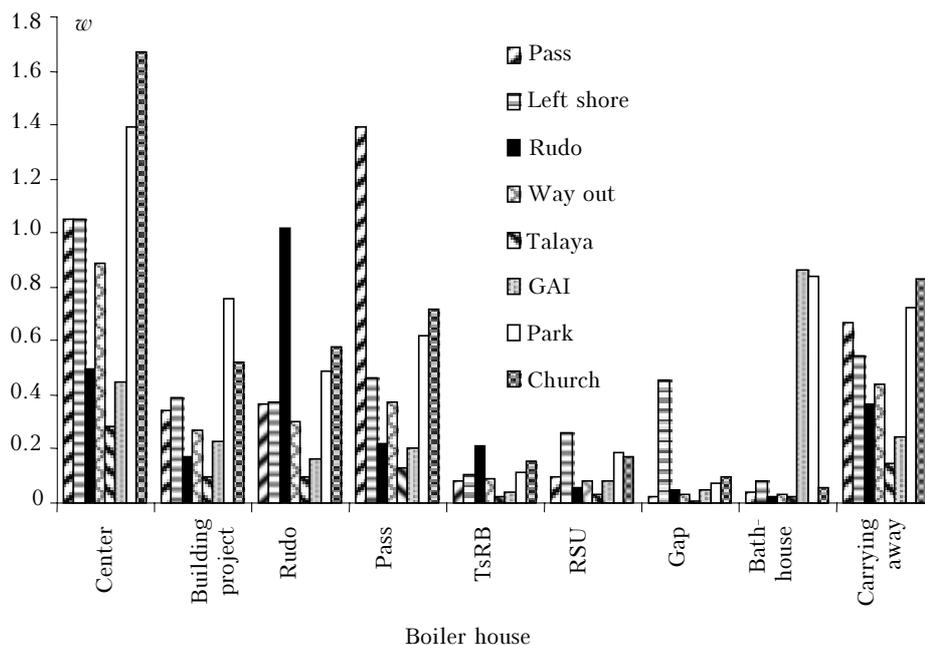


Fig. 1. Weighting factors ($w = x_{jk}$), characterizing the effect of emissions of separate boiler rooms (Center, Building project, Rudo, Pass, TsRB, RSU, Gap, Bath-house) on the points-receptors (Mountain pass, Left shore, Rudo, Way out, Talaya, GAI, Park, Church).

Table 2. Contributions of sources of different types to the pollution at a receptor point, %

Receptor	Sources						IrkAZ
	Carburetor engines	Diesel engines	Stoves, firewood	Stoves, coal	Boiler room, black oil	Boiler room, coal	
Point on the path							
Irkutsk–Slyudyanka	9.5	2.8	87.7	–	–	–	–
Slyudyanka	5.7	7.9	22.8	–	–	63.6	–
Shelekhov	–	3.6	33.5	–	–	–	62.9
Bayandai	–	4.0	76.5	11.2	–	8.3	–

The mean module of the difference between p and x was 0.04 (the relative error is 15%). It should be noted that it has been just in Slyudyanka that the criterion (5) better shows the regularities of pollutant precipitation than more complicated models of the dispersal, because separate parts of the city are isolated from each other by the Khamar–Daban mountain ridge spurs. Accordingly, for precipitations, averaged over a large period of time (4–5 months), the distance from the source to the receptor point is more important than the direction of main transfer and other peculiarities of the emission dispersal (Fig. 2).

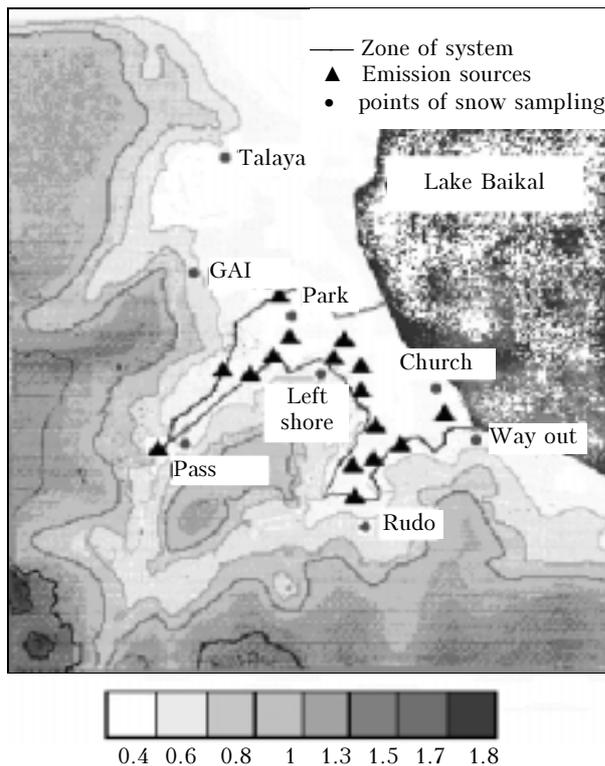


Fig. 2. The situation of emission sources and sampling points in the city of Slyudyanka. (Altitude above sea level, in km. Baltic system).

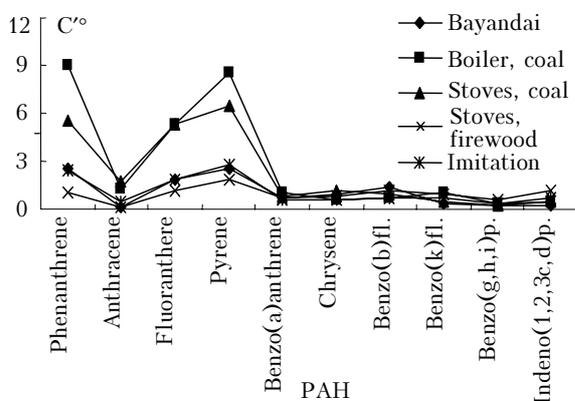


Fig. 3. Normalized (to benzo(a)pyrene) PAH concentrations in the emissions and snow cover near the settlement Bayandai.

In solving the second problem, formalized in the form of the matrix equation (4), we used as chemical tracers 12 polycyclic aromatic hydrocarbons (PAH). Only the first results have been obtained, which allow one to look forward to the prospects for further development of the approach (Table 2, Fig. 3). The analysis was made not for different parts of the city but for populated areas and points on the path, because in this case the sources are best determined and the methods can be tested quite simply.

Out-to-one correspondence between real emissions and obtained contributions is hard to reveal, because, first, the volume of motor transport emissions is unknown, and, second, in those receptor points located outside the cities and for which it is better to identify local sources of emissions, the long-distance transfer effect increases.

Conclusion

It has been apparent from the above-mentioned studies that a combined approach is necessary, which makes it possible to simultaneously take into account both the concentrations of individual PAH and the results of ion analysis. From the preceding paper¹ it is known that the concentration of sulfur-containing compounds allows one to identify stationary sources because in the motor transport emissions the content of sulfur-containing compounds is small. Thus, SO₂ specific emissions for the carburetor engines are 20 times smaller than the emissions of nitric oxides.⁶

Later on, for testing the technique it is quite pertinent to use the experimental methods such as the addition of certain chemical tracers when burning coal in boiler rooms with the goal of observing their dispersal.

Among the PAH considered the most important ones should be distinguished and used as chemical tracers in determining sources with the account of the regularities of the dispersal (Eqs. (1) to (3)). In this case it is necessary to refine the criterion (5) by both using experiments and models of the dispersal. The joint use of statistical and deterministic approaches would allow us to obtain most reliable results.

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