

Identification of emissions from heat and power plants based on data of chemical analysis of precipitation

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Received December 25, 2001

The data on emissions from stationary heat and power plants are compared with the data of analysis of snow chemical composition. Use of thermodynamic models in interpreting data of snow sampling is discussed. Possible ways for solution of related problems and areas for further research are analyzed.

Introduction

As known, among all industries, heat and power production contributes most significantly to atmospheric pollution, and for some cities of Eastern Siberia this contribution makes up to 70% and even more.^{1,2} Concentration of the benzapilene in all Siberian cities in winter exceed the maximum permissible concentration (MPC) by 6 to 10 times (24 times in Chita).³ This is connected with conditions unfavorable for diffusion and large number of small boiler houses. Thus, emissions of the energy industry are one of the main sources of both primary and secondary aerosols in cities of Eastern Siberia.

Analysis of peculiarities in emissions from different objects of energy industry

The heat sources most thoroughly studied from the ecological point of view are heat and power plants and high-power boiler houses equipped with either oil/gas or coal-burning furnaces,⁴ which are characterized by stationary burning conditions. At the same time, a lot of low-power fuel-bed boilers with periodic load of solid fuel are in use. These boilers are characterized by the cyclic burning mode.

It is just the peculiarities of coal burning conditions that lead to significantly different composition of volatile soot: volatile soot in emissions of large boiler houses and heat and power plants consists mostly of inorganic compounds with only small amount of unburnt carbon, while particles emitted by small boilers and furnaces are covered by soot with high content of benzapilene and other polyaromatic hydrocarbons (PAH) and therefore they are biologically active. Large heat and power plants are characterized by sulfation of the mineral part of fuel, which consists in binding of sulfur oxides by compounds of Ca and other metals contained in solid soot particles, and the increase in the mass of solid emissions due to sulfation can reach 2.5% (Refs. 5 and 6). At coal burning in small boilers and furnaces, almost all sulfur contained in fuel is emitted into the atmosphere in the form of SO₂ (Ref. 4).

Computational methods for estimating emissions

Up to date the basic information for evaluation of the effect of heat sources on the environment consists of specific ecological indices: emissions of some or other substance per unit fuel burnt or unit energy produced. However, it should be noted that known techniques for estimation of ecological characteristics of low-power heat sources were developed based on the experience of using boilers and furnaces on the European part of Russia for burning coal mined there (Donetsk, Moscow, Ural, Vorkuta coals).⁷ Nobody proved that these techniques are valid for coal burning on the territory of Eastern Siberia in small boilers of specific design.^{4,5}

A drawback of this analysis is also the uncertain component composition of the mineral part of emitted particles, which, as was mentioned above, varies significantly depending on the burning conditions. For individual cases it can be determined experimentally, however it turns out rather laborious to obtain average indices that are needed for analysis of heat supply systems. It should be noted that now there are no reliable methods for description of heterophase transformations of the mineral part of coal in the burning zone and in the gas channel of power systems. In this connection, it seems promising to use the data on accumulation of mineral components in snow during the heating period to check the values of total and specific emissions.

General approach to reconstruction of data on emissions

To make use of the results of chemical analysis of precipitations in order to identify the data on the emission sources, it is needed:

- to select a “reference” component, whose content in a sample correlates well with the deposition (flow to the surface);
- to reveal relationships between the content of the reference component in a sample and other

components of interest with the allowance for sample accumulation period.

The PAH, chlorinated hydrocarbons (for example, dioxins), heavy metals, and ion composition of precipitations (cations and anions) can be used as indicator substances for identification.

In some papers,⁸ the snow cover is considered as a sort of sediment consisting of snow and ice crystals, water, water vapor, and air. The chemical composition of snow cover is determined not only by atmospheric pollution of snow through dry and wet deposition of anthropogenic and natural pollutants, but also by snow interaction with soil air and the soil-vegetation cover as a whole.

The dynamics of chemical elements and compounds is not thoroughly studied yet. In Ref. 8 it was noted that conditions in autumn are favorable for substance migration from soil to snow. At snow cover cooling, the content of soluble salts decreases because of the decreasing amount of a fluid-like phase, which supposedly exists on the surface of snow crystals. As this occurs, a part of the substance is emitted as an insoluble sediment. In spring the amount of soluble salts increases again, and in the snow melting period it is naturally scavenged.

The snow sampling data were compared with the results of analysis of fresh snow. The fall-out for the winter period estimated from analysis of snow cover turns out to be lower than the estimates obtained for fresh snow (samples were taken after every snowfall) for the same period. For example, for sulfates it was about 28%.

Thus, the main complicating factors are:

- chemical reactions in snow and at snowfall, as well as migration of chemical elements in the snow cover;
- superposition of the effects of individual different-type sources on the snow composition at a sampling point.

Numerical models used for identification

To compare the snow sampling data with the data on emissions and to estimate the effect of different sources on snow pollution at some point, it is needed to use a numerical model of pollutant dispersal. In this paper the problem is formulated on the scale of a city, and mean concentrations for a rather long period (from November till March) are needed. Thus, if the fall-out is thought proportional to the concentration (it is a widely used approximation in transport models), then at the first stage a stationary local model is sufficient for calculations. For example, a model based on a Gaussian plume can be used; this model has gained a wide recognition in environmental organizations of the European Union and the USA (version ISC3).

Besides, to estimate the fall-out of sulfur-containing substances at the urban territory, we used a regional Lagrange model we have earlier developed. Its application allowed us to find:

- the ratio between the processes of dry and wet deposition, as well as the influence of the accepted dry deposition rates on its integral value;
- the actual position of plumes generated by groups of sources at different wind direction and their relation to conditional city boundaries used in this paper.

As to the exchange reactions and phase transitions, in which a part of the emitted substance is likely lost, those can be described numerically by use of thermodynamic models.⁹ At successive formulation of the problems on seeking the equilibrium states of a system containing air and water vapor, as well as different gaseous pollutants, ice, and solution of electrolytes (Table 1), we can trace the transformation of mineral compounds from emission to melting.

Table 1. Example of calculation of atmosphere and precipitation composition at $T = 253$ K and $P = 1$ atm

Substance	Gibbs energy (G), J/mol	State, mol/kg	
		initial	equilibrium
1	2	3	4
<i>Gas phase</i>			
N ₂	–48564	26.7	26.7
O ₂	–51997	7.17	7.17
CO ₂	–447698	$1.19 \cdot 10^{-2}$	$1.19 \cdot 10^{-2}$
H ₂ O	–289678	$6.99 \cdot 10^{-2}$	$3.39 \cdot 10^{-2}$
O ₃	81224	$1.42 \cdot 10^{-6}$	0.0
NO ₂	–26676	$3.50 \cdot 10^{-8}$	$1.46 \cdot 10^{-13}$
NO	37849	$6.05 \cdot 10^{-12}$	0.0
HNO ₃	–201594	0.0	$1.95 \cdot 10^{-12}$
HNO ₂	–142869	$7.87 \cdot 10^{-13}$	$4.17 \cdot 10^{-14}$
SO ₂	–359719	$3.49 \cdot 10^{-7}$	$2.48 \cdot 10^{-11}$
<i>Solid phase (snow)</i>			
C:H ₂ O	–304207	1.05	1.09
C:CaCO ₃	–1230090	$6.99 \cdot 10^{-7}$	$4.96 \cdot 10^{-7}$
C:NaCl	–429696	$8.74 \cdot 10^{-8}$	$4.38 \cdot 10^{-13}$
C: KCl	–457562	$8.74 \cdot 10^{-8}$	$2.60 \cdot 10^{-13}$
C: CaSO ₄	–1461916	0.0	$1.48 \cdot 10^{-7}$

Table 1 (continued)

1	2	3	4
<i>Liquid phase</i>			
H ₂ O	–303833	$3.49 \cdot 10^{-4}$	$5.61 \cdot 10^{-6}$
K ⁺ · NO ₃ [–]	–520700	$3.49 \cdot 10^{-14}$	$2.16 \cdot 10^{-8}$
Ca ²⁺ · 2NO ₃ [–]	–1016041	$3.49 \cdot 10^{-14}$	$6.98 \cdot 10^{-9}$
H ⁺ · HCO ₃ [–]	–709762	$3.49 \cdot 10^{-14}$	$3.98 \cdot 10^{-9}$
K ⁺ · HCO ₃ [–]	–992622	$3.49 \cdot 10^{-14}$	$3.90 \cdot 10^{-9}$
Ca ²⁺ · 2HCO ₃ [–]	–1959885	$3.49 \cdot 10^{-14}$	$5.99 \cdot 10^{-9}$
Na ⁺ · HCO ₃ [–]	–970455	$3.49 \cdot 10^{-14}$	$5.00 \cdot 10^{-9}$
2K ⁺ · SO ₄ ^{2–}	–1466319	$3.49 \cdot 10^{-14}$	$3.74 \cdot 10^{-9}$
Ca ²⁺ · SO ₄ ^{2–}	–1440960	$3.49 \cdot 10^{-14}$	$1.85 \cdot 10^{-8}$
2Na ⁺ · SO ₄ ^{2–}	–1421986	$3.49 \cdot 10^{-14}$	$4.97 \cdot 10^{-9}$
K ⁺ · Cl [–]	–458440	$3.49 \cdot 10^{-14}$	$5.44 \cdot 10^{-8}$
Ca ²⁺ · 2Cl [–]	–891521	$3.49 \cdot 10^{-14}$	$2.39 \cdot 10^{-8}$
Na ⁺ · Cl [–]	–436273	$3.49 \cdot 10^{-14}$	$7.24 \cdot 10^{-8}$
System mass, kg		0.0286	0.0286
Gibbs energy of the system G _{sys} , J		–58705.2	–58706.6

Estimation of sulfur balance for Irkutsk

An attempt to identify emission sources from the results of snow sampling was undertaken using the city of Irkutsk as a case study. Irkutsk is an administrative center of Irkutsk Region with more than 600 000 population. The part of emissions from energy industry makes up to 86% of total emissions and 99% of sulfur dioxide emissions.⁶ The city territory includes 236 operating industrial and municipal boiler houses and one large heat and power plant. Furnace heating is typical for some districts.

Snow sampling and ion analysis of snow samples are carried out at the city territory every year late in winter. The concentrations of anions SO₄^{2–}, NO₃[–], HCO₃[–], Cl[–] and cations Ca²⁺, Na⁺, K⁺, Mg²⁺, NH₄⁺ in snow samples are determined. Usually no more than 10 samples were collected in different parts of the city, and this allowed the pollution of precipitation in Irkutsk to be estimated as compared with that in other, in particular, background, sites. However, for detailed study of the structure of city pollution and identification of pollution sources, the number of samples was increased in recent two years. In March of 2000 36 samples were collected at 19 points in Irkutsk and 3 samples were taken from city suburbs, while in 2001 70 samples were taken at 38 points.

Sulfate ion was taken as a reference compound, because sulfuric compounds in Irkutsk are contained only in emissions of the energy industry. The comparison of the configuration of experimental and calculated sulfate pollution fields shows a good agreement between them. Thus, the experimental data confirm the conclusions drawn earlier based on calculations: pollution of air and surface in Irkutsk with sulfur compounds is determined by low-power boilers, because the maximum concentrations and fall-out of sulfuric compounds are observed just on the territories with high concentration

of low-power boilers.¹⁰ The sulfate concentrations near the heat and power plant and large boiler houses, as well as in the areas of furnace heating are low.

One of the main tasks of this work was compilation of the sulfur balance for Irkutsk. The calculated total emission of sulfur oxides by all boilers in Irkutsk for the period from November 1 until March 1 was found to be 12545.28 t.

Table 2 gives the variability range for the calculated characteristics that is determined by some constants. To refine the calculated characteristics, specific meteorological information is needed.

Table 2. Deposition of sulfuric compounds in Irkutsk

Characteristic	Calculated fall-out		Measurements		
	Minimum	Maximum	2001		
			2000	19	38
			points	points	points
Mean, t/km ²	0.23	1.3	0.21	0.43	0.53
Maximum, t/km ²	0.44	2.5	0.57	1.15	1.83
Integral, t	57.2	340	73.9	152	186.2

It should be explained that the fifth column of Table 2 gives the results for 2001 obtained from the data for only those points, at which samples were collected in 2000, and the data given in the last column were obtained with the use of all samples collected in 2001. Thus, it is obvious that the results of 2000 were somewhat underestimated because of the insufficient number of sampling points.

The excess of calculated values over the measured ones is likely caused by overestimation of calculated emissions, as well as the sulfate dynamics in the snow cover (according to our estimates, up to 30% of loss) and, possibly, by sulfate loss with filtered-out particles.

In 2001 the winter in Irkutsk was abnormally long (the snow cover was established in early October, that

is, two weeks earlier than usually) and cold. Boiler houses in January obviously operated with the maximum power, because the mean temperature was close to the minimum one. Therefore, the fall-out as a whole turned out to be twice as large as in the previous year.

The increase of the number of sampling points allowed us to find more accurately the zones of maximum fall-out in the central part of the city. The mean concentration increased by 20% as compared with the estimate obtained using only those points, at which snow samples were taken in the previous year.

However, in the northwestern industrial part of the city (Leninskii district) the doubling of the number of points from 6 to 12 changed neither the pollution field configuration nor the mean concentration of sulfates. The field of sulfate pollution there is rather even, and therefore 6 points were quite representative.

Conclusion

The first attempt to identify emissions of the energy industry from the data on chemical composition of the snow cover was very interesting, though not unambiguously successful. The configuration of the fields of snow pollution with sulfates coincides with the calculated one and thus confirms the conclusions obtained from numerical simulation. However, in the absolute value, the calculated fall-out exceeds the measured one at least twice. Analysis of possible causes for this discrepancy has led to formulation of some new problems concerning both new experiments, analysis of their results, and improvement of the methods of numerical simulation.

Such a formulation of the problem obviously imposes high requirements on the accuracy of information on the emissions, including a comprehensive inventory of the sources. In the presence of more than two hundreds of heat sources, it is practically impossible to estimate the operation of each of them. Therefore, for checking up the technique, it is worth carrying out such investigations in a small town or village located rather far from large industrial centers.

At the same time, as a reference compound, sulfates work well for identification of emissions from the energy industry as a whole, unlike, say, the role in different city districts in comparison with, for example, motorcar exhausts. For identification of emissions from objects of the energy industry, it is desirable to use PAH as indicator substances.

Besides, it was found that chemical reactions and, possibly, migration of the studied compounds proceed in snow in spite of the low temperature.

Thus, the problem was formulated as thermodynamic simulation of processes in the snow cover under different freezing and melting conditions both in nature and in the sampling process. Chemical analysis of the composition of large particles that are filtered out is obviously needed.

More accurate initial data and analysis of snow samples collected in a small town, as well as further study of processes proceeding in the snow cover and use of PAH as a reference compound will allow development of the reliable technique for identification of emissions from the energy industry.

Acknowledgments

This work was partly supported by the Russian Foundation for Basic Research, Project No. 01–02–16643.

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