

MINISTRY OF EDUCATION AND SCIENCE OF
THE RUSSIAN FEDERATION
“NATIONAL RESEARCH TOMSK POLYTECHNIC UNIVERSITY”

A.V. Talovskaya

**PROFESSIONAL ENGLISH
ATMOSPHERIC AEROSOLS IN ENVIRONMENT**

LECTURE NOTES

for master students teaching according to master program
“Ecology and nature management”, “Ecological environmental problems”

Tomsk polytechnic university
2014

THEME 1. PRINCIPAL CONCEPT OF AEROSOL STUDY

The atmospheric aerosol is defined as an assembly (сбор) of liquid and solid particles suspended in a gaseous medium, usually air, long enough to enable (делать возможным) observation and measurement.

Aerosols are tiny particles suspended in the air with sizes ranges from around 100 мкм to a few nm.

Major biogeochemical processes are visualized by aerosols. It is fog, fume, smoke, fires, smog. You know, the concentration of aerosol smog due to photochemical reaction with exhaust gases in industrial center is comparable with the consequences of dust storms. You can visualize aerosols like mists, hazers as well as during dust storms, volcano eruption and anthropogenic pollution.

The study of aerosol is interesting for a number of reasons.

Aerosols play very important roles in atmospheric processes, environmental quality, and biochemical cycles of trace elements and compounds. Depending upon aerosol size, type, and location, it can either cool the surface, or warm it.

Aerosols affect the radiative energy budget on both the regional and global scales. The role of aerosols in climate forcing is a critical factor in assessment and prediction of climate changes. Aerosol forcing has two major components, direct and indirect. Direct effects of aerosols are the influence of the aerosols on the planet's radiation balance by the scattering of solar radiation, which result in the cooling of the Earth's surface.

Aerosol can help clouds to form, or they can inhibit cloud formation. Aerosols are believed to have indirect effect on climate by changing the properties and amount of clouds. The aerosol cycles are closely connected with the hydrological processes in the atmosphere due to a substantial interaction between aerosols and clouds. Aerosols interact with cloud droplets, ice crystals, and gases. Aerosols strongly affect the microphysical processes in clouds. Changing aerosols in the atmosphere can change the frequency of cloud occurrence, cloud thickness and

rainfall amounts. That is why clouds do not scatter light well and allow much of the Sun light to pass through and reach the surface.

Anthropogenic emissions leading to atmospheric aerosols have increased dramatically over the past century. There are also concerns about the effects of aerosol on human health.

As you can see aerosols in the atmosphere arise from natural sources, and from anthropogenic activities.

Two major aerosol types may be distinguished: primary and secondary. *Primary aerosols* are directly emitted into the atmosphere from the Earth's surface, mainly from open water and soil areas, biological sources, and anthropogenic processes. *Secondary aerosols* are formed by physical and chemical processes within the atmosphere. They can be generated in the atmosphere by gas-to-particle conversions (after chemical conversion in the atmosphere, which generally involves gases, pre-existing aerosols and water vapor).

Aerosols occur naturally, originated from *анимация dust wind-driven to the atmosphere*. Dust aerosols are especially connected with dust storms in deserts. An important feature of dust aerosol is its long range transport in the atmosphere. *Клип про бурю*.

Deserts, and first of all, the Sahara, are one of the most powerful sources of dust aerosol input to the atmosphere. It's known the Saharan dust transport across the Atlantic Ocean and reach North America. It was observed Saharan dust over Europe as well.

Increasing the aerosol concentration in Siberia near Baikal Lake was responded with the episodic dust storms in the deserts of Mongolia and Kazakhstan.

Next type of natural aerosols is originated from *sea spray evaporation*.

Sea-salt aerosol originates from the oceanic surface due to wave breaking phenomena.

Volcanic aerosols originate due to emissions of primary particles and gases (e.g., gaseous sulfur) by volcanic activity.

Most of the particles ejected from volcanoes (dust and ash) are water-insoluble mineral particles, silicates, and metallic oxides, which remain mostly in the troposphere. Millions of tons of sulfur dioxide gas from a major volcanic eruption can reach the stratosphere. After converting to sulfuric acid droplets, these aerosols reflect energy coming from the sun.

As you can see, with eruptive emissions the cloud of volcanic matter rises to a very high altitude and deposits much later in different places. For instance, the Krakatau cloud was up to 60 km and deposited after three years. Another example, El Chichon cloud was up 37 km and observed in Italy and Japan six months later and caused a temperature decrease in the northern hemisphere by half a degree during three years.

Next types of natural aerosols is originated from forest and grassland fires and living vegetation, so called biological aerosols. For example one of the main sources of atmospheric aerosols in Siberia is forest fires. Biomass burning and emissions of organic gases by vegetation are one of the sources of carbon aerosol.

Biological material is present in the atmosphere in the form of pollens, fungal spores, bacteria, viruses, insects, fragments of plants and animals, etc. Bioaerosols can occupy up to 30% of the total atmospheric aerosol volume at a given location.

Some the particles enter atmosphere from the space (cosmic aerosol). It is from 1 to 5 million ton per year.

The highest aerosol concentrations are usually found in urban areas.

Anthropogenic sources are those determined by human activity – industrial wastes from chimneys, toxic exhaust from cars, fires, explosions, soil erosion in agriculture, fossil fuel combustion, and open mining.

Industry dust category includes aerosols from transportation (e.g. road dust etc.), coal combustion (fly ash etc.), cement manufacturing, metallurgical industries, and waste incineration. For example, the street sample contains minerals and dried leaves, glass, glass fibers, paper fibers, cement dust, coal dust, soot, and burned wood.

Elemental carbon, also called black carbon, graphitic carbon, or soot, is emitted directly into the atmosphere, predominantly from combustion processes.

It shows data of global balance of aerosol sources in 1980-s. Let's analyze it. Sea-salt and dust aerosols are the dominate types of the natural aerosols. Anthropogenic aerosols contribute about 10% of the total aerosol loading in our atmosphere.

As was already mentioned, photochemical and chemical reactions in the atmosphere are responsible for the fine aerosol fraction, the so-called *secondary aerosols*. Some of proposed reactions are given. It generally involves gases, pre-existing aerosols and water vapor. Some mechanisms like coagulation, nucleation and condensation involve in the producing secondary aerosols.

This aerosol is composed of mostly sulfates and nitrates. Also various organic substances can make a large contribution in the total aerosol mass. In particular, sulfa oxide is oxidized to sulfuric acid and the rate of conversion is influenced by the presence of heavy metal ions (e.g., Fe, Mn, V). Sulfate aerosol leads generally to cooling of a climate system.

Urban aerosols are mixtures of primary particulate emissions from industries, transportation, power generation, and natural sources and secondary material formed by gas-to-particle conversion mechanisms.

Particulate matter pollution is nowadays one of the problems of most concern in great cities not only because of the adverse health effects but also for the reduced visibility; on a global scale effects on the radiative balance are also of great importance. That is why, air quality standards for PM with diameter 10 and 2,5 mass concentration was added in the European Directive (Directive 1999/30/EC). Atmospheric PM is a complex mixture of elemental and organic carbon, ammonium, nitrates, sulfates, mineral dust, trace elements, and water.

Numerous trace elements are found in particulate matter. Trace element emissions arise from a large number of different source types in urban areas. As you can see, metals contribute considerably to the anthropogenic sources. For

example, motor vehicles burning leaded fuel, electric arc steel furnaces and secondary lead smelters contribute to atmospheric lead and zinc concentrations.

Radioactivity aerosols arise from both nature sources such as the decay products of radon gas, or they can be cosmogenic, such as beryllium-7. The exposure of miners of uranium and other ores and minerals to radon and its aerosol-borne decay products is of major significance.

When nuclear explosions began the radioactive artificial (искусственные) aerosols were emitted in the atmosphere. These aerosols are formed from the detonation of nuclear weapons, the testing of nuclear weapons and from nuclear reactor accidents. Several tens of seconds after an explosion, these aerosols contain about 100 different radioactive isotopes. Of these, ^{90}Sr , ^{137}Cs , ^{14}C , and ^{131}I (iodine) are considered the most toxic.

An important characteristic of aerosols is their size distribution. The size of the particles strongly affects particle behavior and live time in the atmosphere as well as deposition in the human respiratory tract.

Atmospheric aerosols consist of particles ranging in size from a few tens of angstroms (Å) to several hundred micrometers.

Particles smaller than 0,1 micrometers in diameter are called “*ultra fine*”. Particles from 0.1 to 1 micrometers in diameter are generally referred to as “*fine*” and those larger than 1 micrometers diameter as “*coarse* (крупный).”

Fine particles can often be divided roughly into two modes (форма): the *nuclei mode* and the *accumulation mode*. Fine particles tend to be produced either directly from combustion sources, or by gas to particle conversion involving reaction products of sulfates, nitrates, ammonium and organics.

The *coarse* mode is formed by mechanical processes and usually consists of man-made and natural dust particles.

Sometimes fine and coarse modes are divided at 2.5 micrometers in diameter.

Aerosol size map is shown on the slide. It is based on data from MODIS on NASA’s Terra satellite from 2005 to 2008.

On the map green areas show distribution of large particles. Its natural aerosol particles, such as dust and sea salt. Red areas show where aerosols consisted mostly of small particles emitted from forestry fire and burning fossil fuels. Yellow areas show plumes with an even mix of small and large particles. Gray shows where the sensor did not collect data. High aerosol amounts are linked to different process in different places and times of year.

Now I want to show you fine particles distribution in the atmosphere of Tomsk city in different seasons. As you can see the aerosol concentration is higher in winter and autumn. It is connected with the increasing of fuel combustion processing in cold period.

You know, stratospheric aerosols are originated mostly by meteoritic dust and volcanic aerosols. The stratospheric lifetime of coarse particles (dust and ash) is only about 1–2 months due to removal by settling. Particles are presented mostly by ultrafine modes. It is distributed over a period of 2 years.

You know, tropospheric aerosols are originated by natural and anthropogenic sources. But, a significant fraction of the tropospheric aerosol is anthropogenic in origin. Residence times of particles in the troposphere vary only from a few days to a few weeks. It is distributed in upper troposphere a period of 1-4 months, lower troposphere a period of 6-10 days.

Because wet and dry deposition lead to relatively short residence times in the troposphere. They are two removed particles mechanisms from the atmosphere.

Today scientists use remote sensing and ground-based instruments to study and monitor aerosols properties. They supplement (дополнять) each other databases.

The primary exposure pathways for toxins and pathogens include (see Figure):

- gastrointestinal tract (ingestion прием внутрь),
- respiratory tract (inhalation), and
- skin (percutaneous чрезкожный absorption).

If inhaled, some aerosols can be harmful to people's health.

More recent studies indicate that fine particles (PM 2.5 μm in diameter) are more likely associated with adverse (вредный) health effects than other fractions.

This figure shows the fractionation of particles sizes that occurs (попадать) with progressive depth in the system.

The largest inhaled particles (5 micron m to somewhat greater than 10 micron m) are deposited in the mucous linings (слизистая оболочка) of the nasopharyngeal (носоглоточный) tract. Progressively smaller particle sizes are deposited in successively deeper portions of the respiratory tract.

The aerosols can cause the respiratory diseases such as chronic lung illness - asthma, bronchitis, cancers of lungs and etc.

THEME 2. METHODS OF AEROSOL STUDY

There is the World Meteorological Organization (WMO). It is a specialized agency of the United Nations. It studies the state and behavior of the Earth's atmosphere, its interaction with the oceans, the climate it produces and the resulting distribution of water resources.

This network consists of Global Atmosphere Watch measurement stations. The **Global Atmosphere Watch (GAW)** programme of WMO is a partnership involving 80 countries, which provides reliable scientific data and information on the chemical composition of the atmosphere, its natural and anthropogenic change, and helps to improve the understanding of interactions between the atmosphere, the oceans and the biosphere.

GAW focal areas are ozone, ultraviolet, aerosols, selected reactive gases, and precipitation chemistry. It is measured on Global, Regional and Contributing stations. As for aerosols their microphysical, optical, and chemical properties are measured.

Obtained data of atmospheric aerosol properties are transferred in the World Data Centre for Aerosols. You can have a look at these data on-line.

As far as you can see, remote sensing instruments include satellite, aircraft and lidar. It makes it possible to study cloud and aerosol properties. Lidar instruments complement satellites.

The different networks of ground-based stations are indicated by the dot colour on the map. For example, European Aerosol Research Lidar Network (EARLINET, red dots) provides observation in European countries. The Asian Dust Network (violet dots) is an international virtual community designed originally to track outbreaks of dust from China, Mongolia and Russia. *Анимация*. The Siberian Lidar station is located in Tomsk city.

There is agreement between France National research center and Russian research Institutes (Institute of atmosphere optics in Tomsk) about creation of European research community “Yak-aerosib” to study of carbon cycle and ozone,

and aerosol concentrations over Eurasia. There more the project provide perspective for understanding how Siberian forests effect on the carbon cycle.

Networks of ground-based instruments include Global, Regional and Contributing stations.

Portable Gas analyzers are used to determine gas concentration. Aspiration absorption is one of the most frequently used ways of air sampling. Instruments are called *aspirators*. Both sorbents (for gaseous phase) and filters (for aerosols) are used for air sampling.

Recently natural environments accumulating aerosols have been widely used in the environmental monitoring. In this case snow cover as a natural plane table – accumulator shows real value of dry and wet atmospheric falls in cold season. Low temperatures provide conservation of chemical compounds occupied with snow during whole winter season. Studying of snow cover chemical composition allows to find out the special areas of pollution and to calculate real landscape pollution during the period with stable snow cover.

So, you should understand for the reason that particles being in the air have mainly anthropogenic origin therefore chemical composition show its anthropogenic pollution and also anthropogenic pollution of atmosphere.

In contrast to another natural environment snow is homogeneous and it is formed under similar conditions. In snow the information about pollutants is accumulated with two ways:

1. While snow falling occurs the particles are captured by atmospheric dust i.e. atmospheric scavenging occurs.

2. Dry precipitation, i.e. gravitational dust precipitation in snowless period of time.

When snow forming and falling as a result of dry and wet scavenging, concentration contaminant in snow is in 2–3 orders higher than in atmospheric air.

Works dealing with snow sampling and analysis of snow pollution by different substances are usually called *snow geochemical investigations* or in brief

– *snow survey*. *Atmogeochemical investigating method* has been intended for study of background dust load and peculiarities in substantial composition of regional dust-aerosol fall-outs (Weiss, Herron, 1978; Drake, Moote, 1980). Sampling and analysis of snow are carried out according to GOST 17.1.5.05–85, atmosphere pollution monitoring manual (РД 52.04.186–89), methodological recommendations given in works of Vasilenko V.N. and et al. (Василенко и др., 1995), Nazarov I.M. and et al. (Назаров и др., 1978), methodological recommendations (Методические..., 1982).

Possibility of using snow cover as an indirect indicator of atmospheric state in the conditions of large-size urban zone with a number of contamination sources has been proved by experiments carried out by Institute of mineralogy, geochemistry and crystal chemistry of rare elements in cooperation with Institute of petrography on the territory of a large city (Методические ..., 1982). A specific of the Siberian region is the deposition of dust-aerosol on the snow cover that lasts here for several months. Thus, a snow cover testing was made at territory of Western Siberia (Язиков, Рихванов, 1996; Шатилов, 2001; Язиков, 2001 and et al.).

Starting from 1980 contamination monitoring of snow cover operates on the base of snow survey of Statecomhydromet, dust and its components fallout data is obtained at former USSR territory (Василенко, Назаров, 1985). *Stationary networks* of Statecomhydromet regional subdivisions are situated at Russia territory evenly both at background parts in the distance from anthropogenic sources and at contaminated territory not far from cities and industrial zones. On the base of generalized data dealt with stationary snow networks maps are made and the direction and capacity of contaminant transportation are determined at territory of Russia. For example, at Siberia territory the snow cover and aerosols composition are carried out with a help of snow survey more than in 500 observation sites.

Snow sampling analysis from stationary network sites is carried out in line with two programs, which differ from one another by components in testing snow samples (table 1). The first program is carried out in labs of all stations, the second one – approximately at 50 % all stations.

Table 1

Components in analyzing snow samples (PД 52.04.186-89)

Name of monitoring program	Analyzing components in snow samples
The first program	1) suspended substances content (i.e. dust); 2) acidity (<i>pH</i>) and electroconductivity; 3) content of basic water soluble compounds – sulphates, nitrates, ammonium and chlorides
The second program	1) suspended substances content (i.e. dust); 2) acidity (<i>pH</i>) and electroconductivity; 3) content of water soluble compounds – sulphates, nitrates, ammonium, chlorides, potassium, sodium, magnesium, calcium; 4) content of heavy metals and surface active agents; 5) for certain regions – content of number of specific for region compounds

The survey at the temporal expeditionary network is usually carried out at *industrial cities territory* to determine the atmospheric air pollution structure or in *the neighbor of contaminant emission source* to determine impact zones and to carry out contaminant activity monitoring.

Sampling is carried out taking into account relief characteristics and their expositions relative the direction of main wind, and also at the parts of anthropogenic gas-dust emission. When snow sampling is labored because of meteorological conditions the dust-aerosol fallout is carried out using plane table. In whole it is recommended to combine sampling places with sites of basic investigations.

The sites of snowgeochemical expeditionary network are located evenly on observable territory with density which is enough for solving problem.

For snow survey in cities subject to assigned task approaching rectangular network the size of 1×1 km, 500×500 m or 250×250 m is used. Sampling density must provide revealing of the most important pollution focus. In big cities sampling density is recommended 1-5 samples per 1 sq. km. It is used for revealing pollution focuses, dealt with industrial zones or independent large enterprises. To recognize the most polluted territories the sampling density becomes more close 25-30 samples per 1 sq. km.

Scale of snowgeochemical surveying on cities should be 1:50 000, on industrial enterprise territory – 1:25 000, on mining deposit territory – 1:5000.

There are two stages to determine snow cover contamination at the networks:

- 1) sampling at sites of stationary network;
- 2) sampling preparation and chemical analysis.

Snow sampling and preparation

Subjected to monitoring goals snow is sampled layer-by-layer or weekly, monthly. Snow sampling is carried out at the end of February or the beginning of March before the intensive period of snow melting.

Snow sampling is done by snow sorter or from holes (pit method).

Snow is usually sampled with standard arrangement for snow collection (it is a tube section 70 cm long with toothed bottom edge for slotting of thin crust of ice over snow, it has centimeter scale outside to measure snow cover height). Snow sample consists of some snow cores taken with arrangement for snow collection snow cover whole depth.

Quantity of snow cores in sample is determined on the basis of production conditions of melt water volume. It should be no less 2-3 liters in one sample. If snow cover height is 35 cm quantity of snow cores in sample is 6, and if snow cover height is 80 cm quantity of snow cores in sample is 4. Samples are placed in plastic bags and delivered in chemical laboratory.

Snow sampling is carried out by pit method for the whole thickness of snow cover, except for 5 cm layer over soil, measuring sides and depth of the pit. Firstly pit the size of 30·30 cm is put, then snow is sampled with a help of a porcelain dish or a plastic scoop in the plastic bag full. During sampling pit can be widen to fill whole plastic bag. After sampling the plastic bag with snow is tied with string with label in which is indicated a sample number. Then the pit sides and depths are measured. Sample weight is – 15–20 kg. Sampling site, sampling date, sampling depth and sampling size are logged.

Sample preparation starts with snow melting at room temperature, and then includes the following actions: filtration, drying, dressing and weighing (fig. 1).

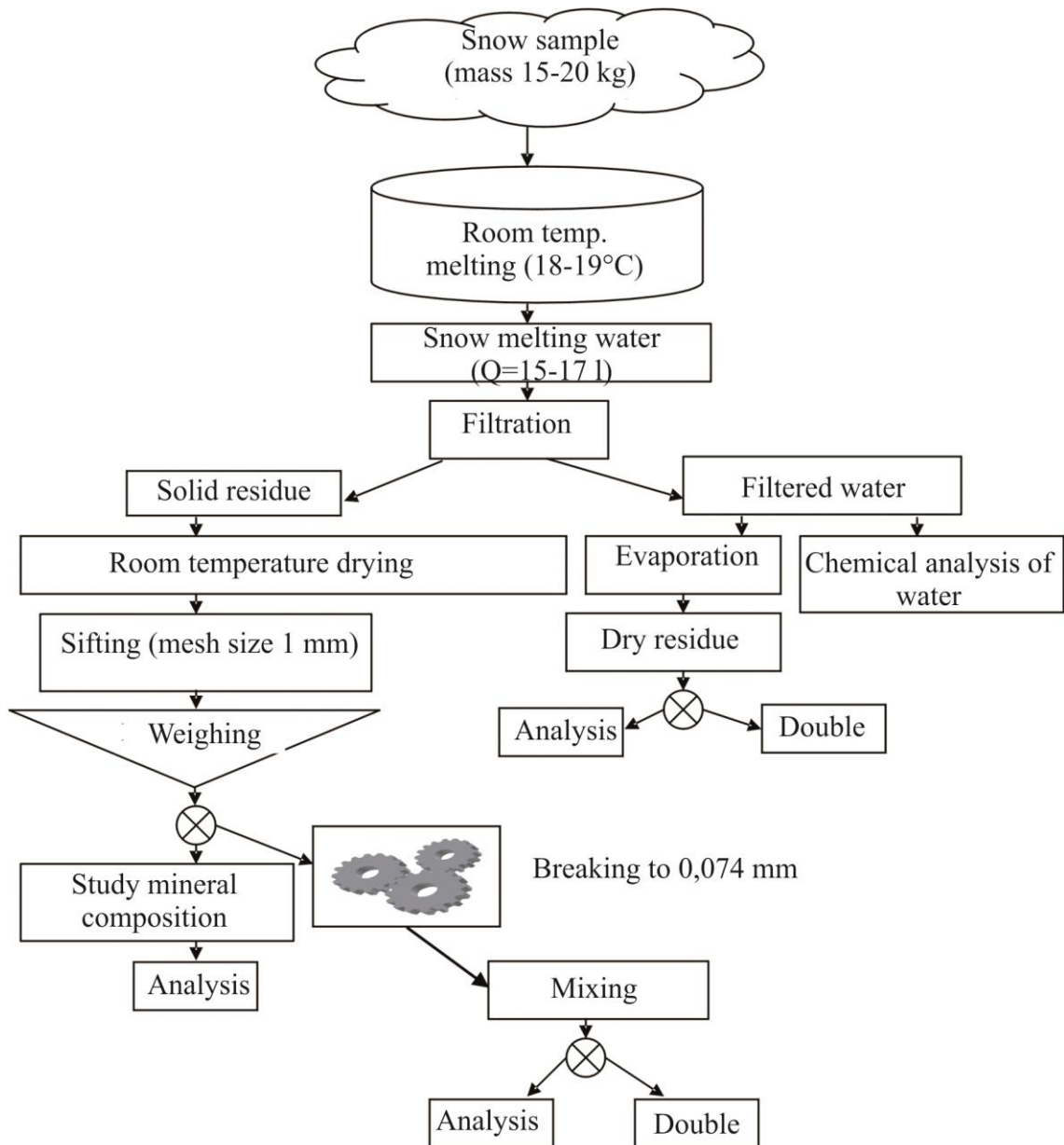


Fig. 1. Scheme of snow preparation

Melting water is filtered, in the process of which the insoluble phase on ash-free filter and melting water are produced. Insoluble phase is isolated by means of ash-free filter and dried out. Dried samples are dressed through the bolt with the size of mesh 1 mm to remove the impurities and are weighed. The difference in the filter mass before and after filtration shows the dust mass in samples.

Snow sample preparation involves separate analysis of snow melting water obtained by melting, and the insoluble fraction of the aerosols in snow.

Procedure of geochemical data processing

Characteristics of contaminant fallout on territory are determined by results of snowgeochemical survey at field network. Maps with special distribution of contaminant (dealing with an every testing component) and maps connected with integral contaminant index are made.

On the base of obtained information the geochemical characteristics are calculated. Characteristics calculations are calculated according methodic recommendations (Методические, 1982).

The following factors are calculated by the snow sampling results.

Weight of dust in snow sample allows for determination of **dust load** (P_n) in terms of mg/m² per day or kg/km² per day which correlates with each other. Dust load is a quantity of solid particles which are settled in a unit of time on a unit of square. Dust load is calculated by the formula (1):

$$P_n = P_o / S \times t \quad (1)$$

P_n – dust load, mg/m² per day (kg/km² per day); P_o – weight of the snow solid residue, mg (kg); S – square of the pit, m² (km²); t – number of days from snow-up day (the day when snow falls out and does not melt) to sampling day.

Dust load is characterized by the following contamination level and morbidity level:

- less than 250 mg/m² per day – low contamination level; safety morbidity level;
- 250–450 mg/m² per day – middle contamination level; mildly unsafe morbidity level; increase in bronchial asthma and conjunctivitis;
- 450–850 mg/m² per day – high contamination level; unsafe morbidity level; increase in respiratory and sense organs morbidity;
- more than 850 mg/m² per day – very high contamination level; immensely unsafe morbidity level; increase in morbidity more than 2 times.

According to snow geochemical survey on the territory of Tomsk in 2008 the dust load value changed from 16 mg/m² per day to 303 mg/m² per day whereas average value was 63 mg/m² per day (fig. 4). The comparison of standards (Геохимия ..., 1990) the dust load value on the territory of Tomsk changes from low contamination level to middle one.

The most contrast parts of average daily dust inflow per snow cover are situated on the territory of northeastern part of Tomsk where there are main plants of building industry and also they are situated on territory of central part of Tomsk where there is power station.

Concentration coefficient is shown the anomalous of element concentration relatively the background value. It is calculated by the formula (2):

$$KK = C / C_b, \quad (2)$$

KK –concentration coefficient; *C* – element concentration, mg/kg; *C_b* – background value of element concentration or geochemical the noosphere clarke, mg/kg.

According to concentration coefficient the geochemical row of element association from the highest value to the lowest value are constructed. If the concentration coefficient is more than 3 it means the local sources have emitted dust with elements. In contract to that if the concentration coefficient is less than 3 dust with elements is related to diffuse pollution. The concentration coefficient helps to determine the dominant elements for dust aerosols which come from different plants.

The concentration coefficient with respect to the background value gives the geochemical characteristic of the studied aerosols in impact areas of several plants in Tomsk (table 2).

Table 2

A number of geochemical elements ranges from the highest value to the lowest one

Impact area	Concentration coefficient			
	More than 10	10...5	5...3	3...1
Construction plants	Tb16.2–U16.1– Yb15.2–As12.7– La11.5	Sm9.9–Ta9.7– Na7.9–Ce6.9– Ba6.4–Lu5.9	Hf3.5–Th3.1	Sc1.8–Fe1.5– Ca1.5–Hg1.2

reinforced concrete plants	U22–As16.8–Tb13.1–Yb12.5–La12.1	Ta9.6–Sm9.1–Ba7.5–Ce6.7–Na5.1	Lu4.6–Hg3.9–Sr3.8–Ca3.1–Sb3.1–Th3	Hf2.6–Co1.9–Fe1.5
Power station	U21.2–Tb13.9–As13.8–Yb13–La11.6	Ta9.5–Sm9.3–Ba7.4–Ce6	Lu4.7–Sr4–Hg3.5–Na3.4–Th3	Sb2.1–Hf1.9–Co1.8–Ca1.7–Fe1.6–Br1.5
Petrochemical plant	U26.2–Tb16.6–Yb16.2–La15.3–Ta13–Sm11.3	As9.7–Ba8.5–Ce8.3–Lu5.9–Hg5.1	Th4.7–Na4.1–Hf3.3–Br3	Sr2.1–Fe1.9–Sb1.6–Cs1.4
Tomsk	U13,8–Tb11,5	Yb9,5–La9–Ba8,6–Ta8,1–As7,6–Sm7,6–Ce5,2	Na4,5–Ag4,3–Br4,2–Lu4,1–Hg4,2–Sb3	Th2,3–Hf2,1–Sr1,8–Ca1,5–Fe1,4–Co1,3–Sc1,2–Eu1,1–Cs1–Cr0,9–Rb0,8–Au0,3

We can find out the plant which is responsible for the higher concentration of some elements in dust aerosols. For example, U, Tb, Yb, La, Ba, Ta, As, Sb, Ce, Na, Ag, Br, Lu, Sb, Hg are the dominant elements in dust aerosols of Tomsk. Tb, As, Na, are the dominant elements in dust aerosols of construction plants.

Factor of pollutant (element) load on the environment is calculated by the snow sampling results. The factor is defined as a pollutant mass falling on a unit of square in a unit of time. Total pollutant mass (P_n , dust burden) and element concentrations (C) in the snow solid residue are used to calculate the factor. Based on that the following factors are calculated.

1. Total load producing by the chemical element emissions in the environment (or average daily fallout of metals on the city territory) is calculated by the formula (3):

$$P_{total} = C \times P_n, \text{ mg/km}^2 \text{ per day.} \quad (3)$$

2. Coefficient of relative increase in total elements load is calculated by the formula (4):

$$K_p = P_{total} / P_b, \quad (4)$$

P_b – background value of total element load. It is calculated by the formula (5):

$$P_b = C_b \times P_{nb}, \quad (5)$$

P_{nb} – background value of dust load, it is 10 kg/km² per day for the non chernozem zone of Russia.

As the anthropogenic abnormalities usually comprise many elements, total pollution factor (Z_c) and factor of total element load (Z_p) are calculated. It characterizes the impact of the group of elements. The factors are calculated by the formula (6–7):

$$Z_c = \sum K_k - (n-1); \quad (6)$$

$$Z_p = \sum K_p - (n-1), \quad (7)$$

n – a number of elements having K_k and K_p values more than 1.

There is the following gradation for values of total pollution factor:

- less than 64 – low contamination level; safety morbidity level; lower change of children's health;
- 64–128 – middle contamination level; mildly unsafe morbidity level; increase in total morbidity;
- 128–256 – high contamination level; unsafe morbidity level; increase in total morbidity and number of illness children;
- more than 256 – very high contamination level; immensely unsafe morbidity level; very high level of morbidity, there are many children with chronic diseases and abnormalities in physical abilities.

For example, total pollution factor value ranges from 64 to 128 in Tomsk. It refers to the middle contamination level.

Mineral and anthropogenic particles in the insoluble fraction of aerosols in snow

In addition the material constitution of snow solid residue investigating can be carried out. Modern mineralogical methods of investigation (such as electron microscopy, spectrum microanalysis with laser sampling, panning analysis, X-ray analysis, thermal analysis, impulse cathodic luminescence) are used to study material constitution of snow solid residue.

Mineral and anthropogenic particles can be determined with a help of modern methods according to patent № 2229737 on October, 17, 2002. (Yazikov E.G., Shatilov A. Yu., Talovskaya A.V. The method of determination of snow cover

pollution with anthropogenic components). It allows determine areas of anthropogenic particles high concentration and their source.

Microscopic examination of samples is carries out by the binocular stereoscopic microscope. Detailed study of microparticles makes possible to characterize particles with determination of color, luster, hardness, transpa-rency, form, and size of particles, characteristic of surface, degree of roundness and oxidization.

In the samples one determines the percentage of all types of mineral, biogenic and anthropogenic particles by the method of comparison with standard circles of S.A. Vakhromeev template (Вахромеев, 1956) in such a way that content of all particles would make 100 % (fig. 2).

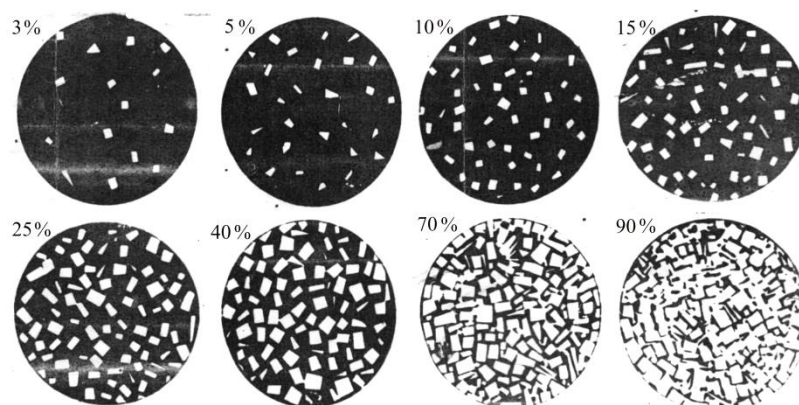


Fig. 2. Comparative method of determination (from S.A. Vakhromeev)

The essence of this method consists in comparison of amount of particles in the sample observed under microscope in some field of view with standard circles, on the black background of which there is a number of white figures. When compared it is not difficult to find the closest in composition standard and in this way state the percentage of each type of particles in the sample.

On the basis of the data one can determine the content and relationship of minerals, biogenic particles, and anthropogenic formations.

This section is made on basis of mineral composition studying of snow solid residue on urban territories of the south of the West Siberia (Шатилов, 2001; Язиков, 2003; 2004; 2006; Таловская, 2008).

According to results of investigation there were mineral and anthropogenic particles in snow solid residue samples.

Mineral and biogenic particles.

1. Transparent colourless particles, gravel and non-gravel present microparticles of quartz structure of the top soil layer. Sizes of particles are from 28 μm to 1 mm. Under electron beam quartz has got high intensity of fluorescence and blue colour.

2. Brown-orange or yellow, semitransparent, partially gravel particles present microparticles of quartz bank sand covered with iron hydroxide and manganese hydroxide. Sizes of particles are from 28 μm to 1 mm.

3. The microparticles of dendro-vegetational origin. Sizes of particles are from 0,1 mm to 0,6 mm.

4. Gravel particles of reddish colour – feldspars. Sizes of particles are from 20 to 500 μm . Under electron beam feldspar has got high intensity of fluorescence and pink colour.

5. Clay particles, mainly kaolin. Sizes of particles are 15 μm .

6. Mica flakes of different colour and tints: colourless, green and golden. Sizes of particles are from 50 to 750 μm .

7. Particles of amphiboles, the special feature of them is rectangular cleavage. Sizes of particles are from 3 to 5 μm .

8. Semigravel particles of carbonate, milky colour. Sizes of particles are from 30 to 550 μm . Under electron beam carbonate has got high intensity of fluorescence and violent yellow colour.

Presence of mineral particles in investigated samples is confirmed by X-ray phase analysis. By way of analysis the quartz, carbonate, feldspar, hematite (goethite) and also clay minerals (illite-montmorillonite, hydrobiotite and trace chlorite) were identified in samples against the background of X-ray phase analysis.

Mineral part of coals burnt in boiler rooms generally consists of aluminosilicates, carbonates and iron sulfides.

According to X-ray structure analysis this fact explains that in samples of snow solid residue there is presence of amorphous quartz (glass phase), cristobalite and mullite forming at high-temperature processes of the combustion chamber of boiler rooms. Iron oxides can pass to environment both with emissions of fuel-energy complex and metal-working plants. Erosion of banks, emissions of building industry plants, anti-ground surface icing actions and also long-range air-mass transport from Central Asia are the natural minerals source.

Electrical power engineering (27 %), nonferrous metallurgy (22,5 %) and ferrous metallurgy (15,8 %), petroleum production (9%) and oil refining (5,1 %), enterprises for oil extraction and refinement (15,5 %), transport (13,1 %), coal industry, gas industry, mechanical engineering and also enterprises for extraction and manufacture of building materials are the basic sources of anthropogenic atmospheric pollution connected with human activity (Экологический, 2002).

The following types of *anthropogenic particles* were found out in examined samples:

1. Light-grey and white microspherules with vitreous luster and hollow inside (fig. 3). Sizes of particles are from 14 μm to 280 μm .



Fig. 3. Microspherules of silica-alumina composition (binocular, magnification 50^x)

There are two hypotheses of silica-alumina hollow microspherules (SAHM) – anthropogenic hypothesis and cosmic hypothesis. Anthropogenic hypothesis was proved by way of example ash of pulverized coal firing (Кизильштейн, 1987; 2002). These silica-alumina hollow microspherules are one

of the components of ash loss of heat coal-fired power stations. According to results it was discovered that SAHM consist of mullite and sillimanite. In addition the chemical analysis showed that they are mainly enriched by Al_2O_3 and Fe_2O_3 ,

CaO, SO₃ a little. Cosmic hypothesis was examined by the way of example nizhnepermiskikh saline deposits.

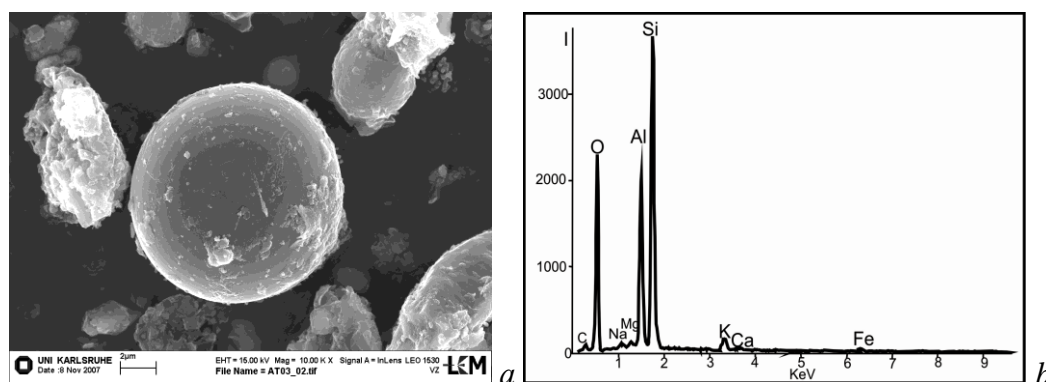
Several spherical fritted formations of silicate and mixed composition were found in nizhnepermisky age mine salt washed out the surface of salt deposit (Ivanov, 1968).

The investigations of snow solid residue of Tomsk district Tomsk oblast' showed that these white microspherules consist of mullite (Языков, 2006).

Abundance of these particles in snow solid residue shows that they are emissions of heat boiler rooms and electric power stations using coal in their process technology.

Two types of microspherules distinguished by their morphology were revealed according to results of detailed electron microscopic investigations.

Smooth spherules are formed at high-temperature process and they are emitted into atmosphere. They mainly include Al and Si in their composition; they are often called “combustion spheres” (Аэрозоли ..., 2006) (fig. 4).



*Fig. 4. Smooth Al-Si- microspherules (0,5...12 μm):
a) under an electron microscope (magnification 10^{Kx}); b) energo-dispersive spectrum*

They can transport by air mass for long distances. They were discovered in the Arctic aerosols by scientists (Sheredan, 1985; Аэрозоли ..., 2006). Diameter of these spherules changed from 0,5 to 12 μm. They are enriched by Al, Si, K and other macroelements.

Presence of microspherules consisting of mullite mainly (as the spectrum of elements is in line with the spectrum of mullite) is characteristic of snow solid residue (Reed, 2005). Diameter of microspherules changed from 1 to 2 μm.

According to results of X-ray structural analysis there is mullite in samples of snow solid residue.

Porous particles of fly ashes containing Al and Si mainly were found in samples. The size of them was from 5 to 45 μm . Spectrum of the chemical element content in these particles is analogous to the spectrum of smooth spherules (fig. 2.2.13). Porous particles of fly ashes pass to atmosphere with emissions of heat electric power stations (Аэрозоли..., 2006).

2. Black microspherules with metallic luster (metallic microspherules) (fig. 5). Magnetic properties are representative of these particles. Sizes of particles are from 14 to 420 μm .

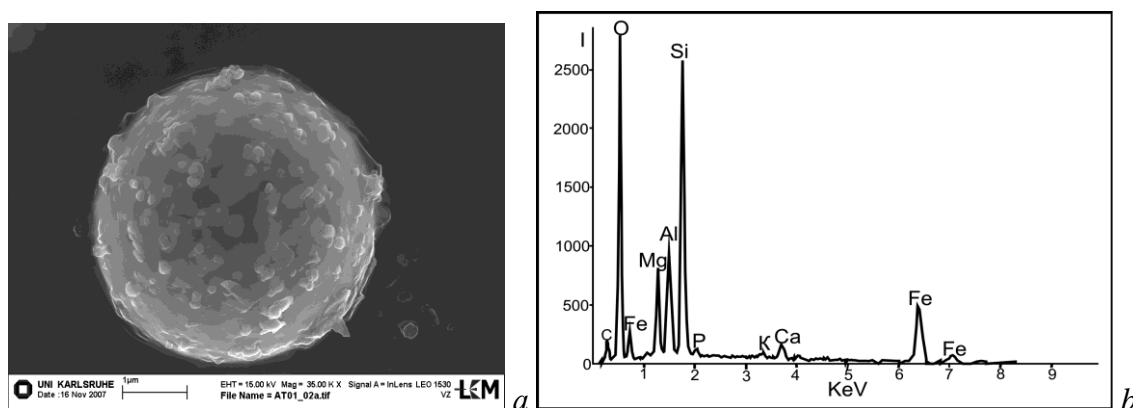
For the first time these spherical particles were discovered by Murray in the late 19-th century (Murray, 1876). Firstly they were found in bottom silt of the Pacific Ocean and later they were found in different natural formations: in Antarctic ice (Schmidt, 1963; Виленский, 1972), bottom ocean silts (Hunter et al., 1960; Parkin et al., 1968), atmospheric dust (Виленский, 1966), saline deposits (Match, 1966; Иванов et al., 1969), peat (Выпадение..., 1975; Бояркина et al., 1976). Under conditions of sedimentation the composition of particles allows to suggest at the very beginning of the investigation that they are cosmic particles. However, later similar spherules were discovered in great numbers in volcanic outburst (Hodge et al., 1964) and industrial emissions (Hoppe et al., 1954; Кощенко..., 1973; Буштуева, 1976). They appear also to be formed by huge blast (Keidl, 1969) and because of other types of human activity.

Microbeads containing magnetite, maghemite and hematite were discovered in fly ash of pulverized coal firing at thermal power station (Кизильштейн et al., 1991).

Carried out detailed investigations of single metal microspherules isolated from samples of snow solid residue situated on the mechanical engineering and metal working area and where the casting houses are operating show that they are

waste of their production and they present magnesioferrite (ЯЗИКОВ et al., 2003; ЯЗИКОВ, 2006).

Abundance of metal microspherules in samples of snow solid residue shows that they are anthropogenic. According to results of detailed investigations of these particles with a help of laser microspectral analysis it was discovered that Fe, Ti, Au, Ca are prevalent in their composition. Based on the results of detailed electron microscopic investigations 3 types of microspherules were discovered. They contained Fe, Mn and Mg oxides, differed their morphology and had the size from 2 to 20 μm .



*Fig 5. Microspherules containing Fe and Mg oxides (2...6 μm):
a) under an electron microscope (magnification 35 K^{\times}); b) energo-dispersive spectrum*

Metalworking plants and emissions of fuel-and-energy company are the source of these particles entry on the territory of Tomsk and its suburb.

Owing to characteristics of atmospheric mass circulation these particles precipitate on the area of villages located out of Tomsk. According to the results of X-ray structural analysis the content of minerals of Fe oxide was detected in samples of snow solid residue. This entitles us to suppose that these minerals present in these microspherules.

3. Non-transparent black flatten form particles are particles of soot and coal (fig. 6). They are typical emissions of heat boiler rooms when burning rubbish. They mainly contain carbon. They have electromagnetic properties. Sizes of particles change from 4 to 40 μm . They present in all samples.

4. Black or brown with submetallic luster formless particles are particles of slag and ash (fig. 7).

According to results of electron microscopy the porous structure or shapeless mass are typical of these particles. These particles contain Al, Si, Ca, Na, Fe etc. Sizes of these particles are from parts per hundred to 720 μm . Particles of slag pass to environment as a result of emissions of heat boiler rooms using coal.

According to results of the investigation of shapeless brown particles with a help of laser microspectral analysis it was discovered that content of Fe, Ti, Cu, Al mainly present in them. These particles present slag containing mostly Fe oxides.

5. Particles of woodwork. They present sawdust and their sizes are from 140 μm to 1 mm (fig. 8).

6. Particles of crushed brick. Their sizes are from 0,2 to 0,6 μm (fig. 9). These particles prevail in samples of sanitary-protection zones of brick production plants.

7. Fibrous particles. Their sizes are from 1 to 2 mm.

8. Saccharide particles covered with white thin coat. Their size ranges from 50 to 100 μm .

9. Brown microspherules with glassy luster. Their size ranges from parts per hundred to tenth μm .

10. Black conchoidal particles of duff dust. They are widely distributed in snow samples of the coalmining area. Particles get snow cover both from surface coal mines and enriching factories. According to data of the laser microspectral analysis in the composition of particles there are C, Fe, Ca having weak electromagnetic properties. Their size changes from 28 μm to 1 mm.

11. Brown shapeless small metal particles. According to data of the laser microspectral analysis these particles contain Mn, Mg, Al, Ti, Cu, Ca, Cd. Magnetic properties are typical of them. Grey iron foundry is a basic source. They are in samples of mechanical engineering and metal working areas. Size of particles is from 14 to 520 μm .

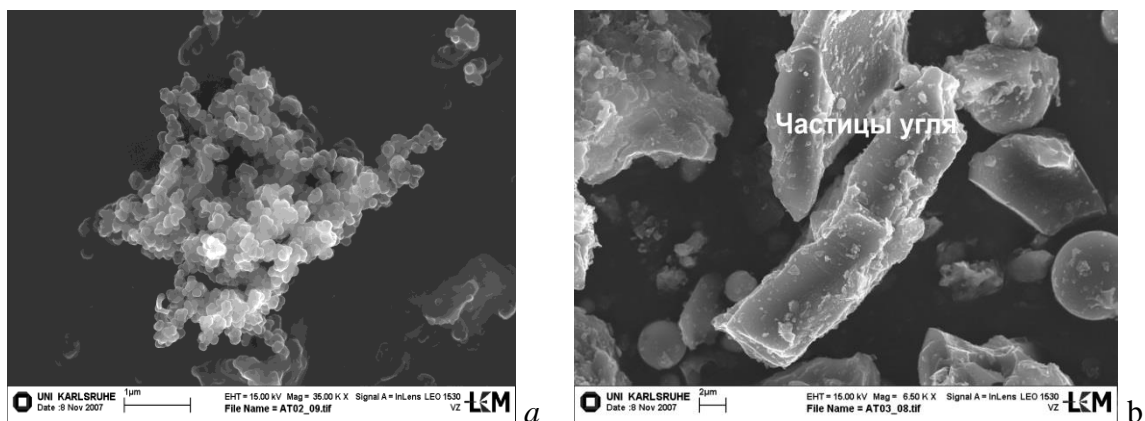


Fig. 6. Particles of soot and coal (4...40 μm):

a) particles of soot under an electron microscope (magnification 35 K^{\times}); b) particles of coal under electron microscope (magnification 6,5 K^{\times});

12. Orange angular particles present particles for plastic manufacturing. They have weak electromagnetic properties. Size of particles changes from 14 to 280 μm . These particles present in samples of snow solid residue of Tomsk OJSC “Sibelectromotor” area.

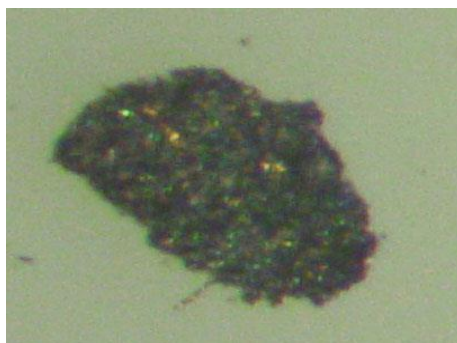


Fig. 7. Particles of slag (14...720 μm): a) under binocular microscope (magnification 50 $^{\times}$); b) particles of slag under an electron microscope (magnification 1 K^{\times} , resolution 20 μm); c) energodispersible spectrum



Fig. 8. Woodwork particles (from 140 μm to 1mm) (binocular, magnification 50 $^{\times}$)

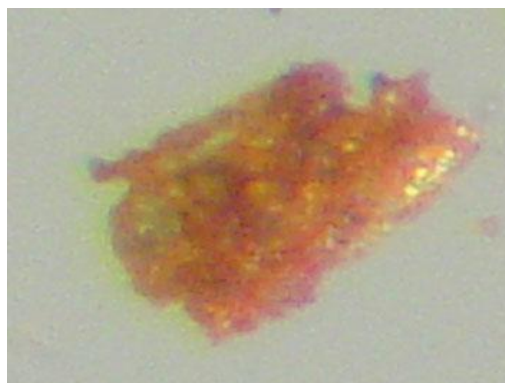


Fig. 9. Crushed brick (0,2...0,6 μm) (binocular, magnification 50 $^{\times}$)

13. Grey semiangular silicate spherules. They have weak electromagnetic properties. According to laser microspectral analysis these particles contain Si, Fe, Mn, Mg, Al, Ca, Cd in their composition. These particles are typical of emissions of iron foundry. Size of particles changes from 14 to 520 μm .

In baseline regions the natural constituent of dust aerosol fallings in snow cover is upon the average 70 % for Vasyuganskoe swamp though the anthropogenic component represents microparticles of soot (90 %). Jet fires of oil fields in the Ob high-water bed are the most probable source of soot. Whereas samples took 70 km away from SW of Tomsk on the territory of wildlife reserve "Tomsky" have 80 % (natural) to 20% (anthropogenic) ratio and also specific mineral composition.

Natural origin microparticles are base of aerosol fallings in oil-and-gas producing area with low urbanization at lower course of the river Ob' on the territory of towns such as Strezhevoy, Megion and Kedrovyy. The source of anthropogenic origin particles (soot, metal and non-metal microspherules) is probably a private sector, small industrial enterprises and also numerous jet fires of oil fields.

Particles of dust prevail in samples of coal mining area of Kuzbas (at upper river of the Tom') where the town Mezhdurechensk is situated. It is connected with activity of the numerous surface coal mines situated around the town. Under the microscope these samples are black and look like dust.

Particles of bearing strata prevail in samples of snow cover solid residue in ore mining area of Khakasiya (at upper stream of the Vershina Tei) where the similarly-named settlement of mineworkers is situated and where iron ore deposit excavate. It is connected with mining firing in open cast mine and its dump pit.

The composition of aerosol fallings depend on specific character of industrial production and their local sources of pollution. Thus, microparticles of metallurgical slag and metal-working prevail in snow samples of solid residue on

the territory of mechanical engineering and metal-working area (OJSC “Rubtsovsky plant, Altaysky region).

The similar composition of snow solid residue is on the territory of OJSC “Sibelectromotor”(Tomsk) where particles of metallurgical slag, waste of sandy jet metal-working and production of plastic prevail.

The portion of anthropogenic and natural origin particles in snow solid residue on the territory of Tomsk changes from 10 to 40 % and from 60 to 90 % appropriately. The high level of anthropogenic environmental load on the territory of Tomsk is due to different industrial plants (fig. 10).

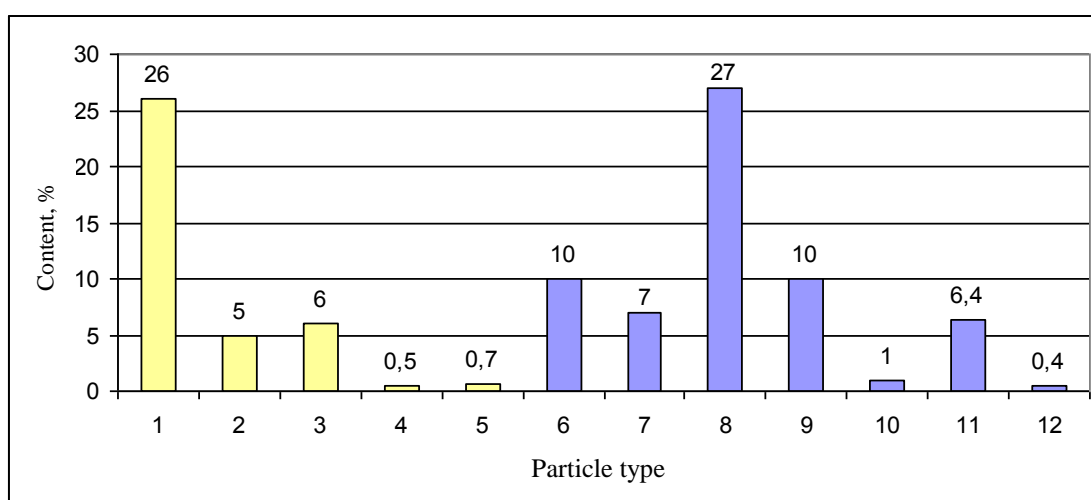


Fig. 10. Mineral composition of snow solid residue on the territory of Tomsk:
Natural mineral components (1–5): 1 – transparent colourless particles, non-gravel (quartz); 2 – quartz grains with films and inclusions of iron hydroxides; 3 – wood-vegetable origin particles; 4 –reddish-brown particles (feldspar); 5 – particles of mica.
Anthropogenic components (6–12): 6 – aluminosilicate microspherules (mullite); 7 – metal microspherules (magnesioferrite); 8 – particles of soot and coal; 9 – particles of slag and ash; 10 – fibrous particles; 11 – crushed brick; 12 – particles of paint

The natural component of dust and aerosols in winter is mainly presented by particles of quartz and plant residues (10...40 %) coming in consequence of the river Tom’ wind erosion and due to sanding roads when it is ice-slick. The principal part of anthropogenic material is particles of soot and coal (20...50 %), slag and ash (15...25 %), aluminosilicate microspherules (5...15 %) passing in environment mainly with emissions of fuel-energy complex.

The high content of slag, soot and coal particles (25...30 %) is accounted for by uptown in impact area of Tomsk GRES-2 and also in the area of private sector – in the northern part of Tomsk.

Thus, mineral composition of dust aerosol fallings on the urbanized territories with diversified anthropogenic load is differed by proportion of natural and anthropogenic origin particles and also it is determined by specificity of local pollution sources.

Reference

1. Bernabe´ J.M., Carretero M.I., Gala´ E. Mineralogy and origin of atmospheric particles in the industrial area of Huelva (SW Spain) // *Atmospheric Environment*. 39. 2005. Pp. 6777–6789.
2. Bryan R. Bzdek, M. Ross Pennington, Murray V. Johnston. Single particle chemical analysis of ambient ultrafine aerosol: A review // *Journal of Aerosol Science*. – 52. 2012. Pp. 109–120.
3. Calvo A.I., Alves C., Castro A., Pont V., Vicente A.M., Fraile R. Research on aerosol sources and chemical composition: Past, current and emerging issues // *Atmospheric Research*. 120–121. 2013. Pp. 1–28.
4. Calvo A.I., Alves C., Castro A., Pont V., Vicente A.M., Fraile R., 2013. Research on aerosol sources and chemical composition: Past, current and emerging issues. *Atmospheric Research* 120–121, 1–28
5. Katyal Timy. *Environmental Pollution* / T. Katyal, P. M. Satake, R. Kumar. – India : Anmol Publications PVT.LTD, 2001. – 302 p.
6. Kondratyev K.Ya., Ivlev L.S., Krapivin V.F., Vatotsos C.A. *Atmospheric aerosol properties: formation, processes and impacts* – Springer, 2006.
7. Levin Z., Cotton W.R. et. All. *Aerosol pollution: impacts on precipitation* – Springer, 2009.
8. Lollar Barbara Sherwood. *Environmental Geochemistry*. Vol. 9: *Treatise on Geochemistry* / B. S. Lollar. – Amsterdam : Elsevier, 2005. – 630 p.
9. Plakhov A.M. *Environmental Safety and Health: Textbook* / A.M. Plakhov, A.G. Dashkovsky, V.D. Fedosova. – Tomsk : TPU Press, 2000. – 119 p.
10. Some aspects of ecological problems: textbook/ N.V. Baranovskaya, I.A. Matveenko, R.M. Danilenko, A.V. Talovskaya. – Tomsk: TPU pub.eddition, 2009. – 110p.
11. Yazikov E.G., Talovskaya A.V., Nadeina L.V. *Geoecological environmental monitoring: coursebook*. – Tomsk: TPU Publishing House, 2013. – 131 p.

Периодические издания:

1. *Journal aerosol science*
2. *Atmospheric environment*
3. *Water, air, and soil pollution*
4. *Environmental monitoring and Assessment*
5. *Atmospheric Research*