Toxic elements (As, Se, Cd, Hg, Pb) and their mineral and technogenic formations in the snow cover in the vicinity of the industrial enterprises of Tomsk

A V Talovskaya\textsuperscript{1,2}, E A Filimonenko\textsuperscript{1}, N A Osipova\textsuperscript{1}, E E Lyapina\textsuperscript{1,2} and E G Yazikov\textsuperscript{1}

\textsuperscript{1}Tomsk Polytechnic University, Tomsk, Russia
\textsuperscript{2}Institute of Monitoring of Climatic and Ecological Systems, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia

E-mail: \textsuperscript{1}talovskaj@yandex.ru

Abstract. Snow samples were collected in four industrial areas of Tomsk where brickworks, factories for the production of reinforced concrete structures, machine repair industries and local boilers, petrochemical plant and thermal power station are located. Study of insoluble fraction of aerosols in snow and melted snow water was performed to determine the contents of the emissions from these facilities. The insoluble fraction of aerosols in snow is aerosol particles deposited on snow cover. As, Se, Cd, Hg, Pb concentration was analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Mineral modes of the elements were determined by scanning electron microscope. It was found the snow cover is mainly polluted by As – in the brickworks impact area, by Se – in the thermal power station impact area, and by Cd – in the impact area of densely located factories for the production of reinforced concrete structures, machine repair industries and local boilers. The research results show that the mineral modes of As are associated with arsenopyrite, of Pb – with galena in the insoluble fraction of aerosols in snow.

1. Introduction
Most toxic pollutants enter the atmosphere from anthropogenic sources such as motor vehicles, factories, power plants and others. While some emissions of metals are the result of natural processes (e.g. volcanic eruptions, dust storms, weathering of rocks, forest fires) there are emissions of anthropogenic origin (e.g. vehicles, factories, power stations). [1]. Industrial emissions of trace elements include nickel, chromium, lead, zinc, copper, mercury, arsenic and some others. Concentrations of these elements are above the natural level [2-5]. Also, presence of heavy metals is the cause of atmospheric solid particles toxicity [6, 7]. For example, the exposure to Ni, Cr, As, Cd may cause cancer diseases, lung damage and/or breathing problems. Heavy metals coming into soil and water from atmosphere destructively affect plant growth and yields [8]. The large cities with diversified industry are not characterized by presence of separate pollutants, but heavy metals associations in the environment, capable to produce a combined effect on the body. However, direct determination of their concentrations at the air is usually costly and labor consuming procedure. The atmospheric deposition is an important process removing aerosol particles and gases from the atmosphere. Snow is one of the main types of precipitations characteristic of middle and high latitudes areas in winter. At subzero temperatures the fallen snow gets accumulated on the ground forming a
snow blanket. Snow cover during formation and subsequent accumulation presents the chemical composition of the atmosphere [9, 10]. Snow plays an important role in the deposition of atmospheric contaminants [11]. Even at moderate snowfall a significant portion of elements precipitated from the atmosphere, because the snow is an effective absorber [12]. Snow cover is widely used as a reliable indicator of air pollution [13, 14]. Smaller particles should be given more attention to than larger ones because they have a high relative surface area, which facilitates the adsorption of pollutants [12]. Therefore, the snowpack serves as a reservoir for various pollutants such as heavy metals.

2. Materials and methods

2.1. Study area
Tomsk, with a population of 548 000 people, is located in the south-east of the West Siberian Plain (56°29'19", 84°57'08"). It is the administrative center of Tomsk region. The climate is continental with significant seasonal variation in the solar radiation. The wind regime is characterized by an average annual wind speed of 3.1 m/s. The highest wind speeds occur in winter months. The southern (33%) and south-west (15%) winds are predominant in Tomsk. The average annual temperature is negative, -0.5 °C. Annual rainfall is 450-590 mm. Average snow depth is 60-80 cm, snow lasts 178-180 days.

In Tomsk enterprises of petrochemical, energy, engineering, instrument-making, food processing, construction, pharmaceutical and other industries operate. In this paper we present data on trace elements concentrations (As, Se, Cd, Hg, Pb) in snow water and insoluble fraction of aerosols in snow in the vicinity of Tomsk’s enterprises. The soluble fraction of atmospheric aerosols accumulated during the winter in the snow attracts attention due to the fact that the biological effects of toxic dust are closely related to its solubility. Having entered the body highly soluble dust is dissolved in the mucus and other biological fluids (blood, lymph), in higher amounts and rapidly distribute throughout the body in dissolved form, exerting a toxic effect [15].

«Area I» that we have chosen in the central part of Tomsk is located in the area of wind mass transfer due to the prevailing wind directions dust emissions from the thermal power station by 100-meter height chimneys.

«Area II» is located in the northwestern part of Tomsk and includes the industrial area, where factories for the production of reinforced concrete structures, machine repair industries and local boilers are operated.

«Area III» is located in the eastern part of Tomsk by the north-east vector from the northern border of the brickworks industrial site.

«Area IV» is located in the north-east direction from the industrial area of one of the largest petrochemical plant in Russia, as well as near the gas power plant.

The background area was chosen at the landfill site observatory «Background» of Institute of Atmospheric Optics (Russian Academy of Sciences, Siberian Branch) (70 km south-west of Tomsk).

2.2. Sampling and preparation
Five snow samples were collected at each of the four studied areas of Tomsk in March 2013 and the distance between adjacent sampling points was 200 - 300 m. There were collected and researched 30 snow samples. Snow samples were collected at the points with undisturbed snow cover for all its depth, the mass of each sample was 15-18 kg. During collection the pit area from which the samples were measured and the time from the formation of a stable snow cover till snow sampling time were fixed.

Snow samples were melted at 20-22°C, and the snow water was filtered through a pre-weighed filter paper. The insoluble fraction of aerosols in snow on the filter were passed through a sieve with a mesh size of 1×1 mm and then weighed with the error of 0.01%. The samples of snow melted water and the insoluble fraction of aerosols were analyzed.
2.3. Analysis
The analysis was carried out in the laboratories of International Innovative Academic Center «Uranium Geology», Geocology and Geochemistry Department, Tomsk Polytechnic University, Russia. Hg concentration was performed by atomic-adsorption spectrometric method. The modes of element occurrence were determined using scanning electron microscope Hitachi S-3400N with an attachment for microanalysis Bruker XFlash 4010. As, Se, Cd, Pb concentration were studied by mass spectrometry method with inductively coupled plasma in Analytical Centre «Plasma» (Tomsk).

3. Results and discussion
Table 1 summarizes the results of analytic research of snow melted water and the insoluble fraction of aerosols in snow.

| Area | As | Se | Cd | Hg | Pb |
|------|----|----|----|----|----|
| insoluble fraction of aerosols in snow, mg kg⁻¹ |
| Background area | 10.0 | 12.2 | 0.30 | 0.08 | 76.7 |
| Iᵃ | 31.1 | 19.4 | 1.22 | 0.48 | 101.8 |
| IIᵇ | 10.7 | 7.5 | 1.11 | 0.33 | 70.1 |
| IIIᶜ | 12.4 | 8.8 | 0.67 | 0.11 | 34.4 |
| IVᵈ | 16.8 | 11.5 | 1.17 | 0.05 | 71.0 |
| Snow melted water, mcg l⁻³ |
| Background area | 0.38 | 0.10 | 0.03 | 0.003 | 1.04 |
| Iᵃ | 0.94 | 0.12 | 0.05 | 0.012 | 0.81 |
| IIᵇ | 0.49 | 2.72 | 0.04 | 0.005 | 0.20 |
| IIIᶜ | 2.83 | 0.24 | 0.04 | 0.015 | 0.46 |
| IVᵈ | 0.82 | 1.89 | 0.03 | 0.007 | 1.16 |

ᵃ the central part of city, the thermal power station impact area
ᵇ the northwestern part of city, the impact area of densely located factories for the production of reinforced concrete structures, machine repair industries and local boilers
ᶜ the eastern part of city, brickworks impact area
ᵈ petrochemical plant impact area

Elements concentrations were compared with the background concentration in order to detect abnormal concentrations.

It was observed that the Se concentration exceeds the background concentration in 27 and 19 times respectively in the snow melted water samples from II and IV area. That is more than other elements. The samples of I and III areas showed that Hg and As are characterized by the highest values above the background concentration.

Hg concentration exceeded the background concentration in 4-6 times in the samples from I and IV area. The concentration exceeded the background one in 3 times in the samples taken in the thermal power station impact area.

Cd concentration exceeded the background one in 2-4 times in the samples taken nearby industrial enterprises, but Se and Pb concentrations were not significantly higher than background values.

Results of electron microscopy scanning show that the mineral modes of As and Pb are associated with sulfides (arsenopyrite and galena) in the insoluble fraction of aerosols in snow (figure 1). The mineral particles size varies from 2 to 12 microns. We have found that Hg is present in the insoluble fraction of aerosols in snow in a physically adsorbed form.
The element composition of fly ashes from Tomsk thermal power station showed higher Hg and As concentrations. The thermal power station uses coals of Kuznetsk region which are of As-U-Ag-Be-Sn-Ge-Zr-Mo geochemical specialization [16].

According to literature data many chemical elements may be emitted during coal burning with the gas phase. Burning of fossil fuels is one of the man-made sources of As, Hg and Se in the urban atmosphere [17].

In addition, Se is one of the specific elements of petrochemical production emissions [13]. It also may form high concentrations of cement kiln dust [18]. It is known that in addition to plant emissions where Cd and its compounds are used in the production process this metal comes with dust emission of plants producing glass, ceramics (bricks) and other as well as along fuel combustion.

4. Conclusion
Therefore, the studies showed that the highest level of contamination with toxic elements was observed in vicinity of the thermal power station in Tomsk. At the same time the main polluting elements were detected in the petrochemical plant, brick and factories for the production of reinforced concrete structures impact areas. Mineral modes of As and Pb were identified in the insoluble fractions of aerosols in snow.

5. References
[1] Moreno T, Querol X, Alastuey A, Viana M, Salvador P, Campa A, Artinano B, Rosa J and Gibbons W 2006 Variations in atmospheric PM trace metal content in Spanish towns: Illustrating the chemical complexity of the inorganic urban aerosol cocktail Atmos. Environ. 40 6791-803
[2] Boyd R S 2004 Ecology of metal hyperaccumulation New Phytol. 162 563-67
[3] Krachler M, Mohl C, Emons H and Shotyk W 2003 Atmospheric deposition of V, Cr, and Ni since the Late Glacial: effects of climatic cycles, human impacts, and comparison with crustal abundances Environ. Sci. Technol. 37 2658-67

[4] Nriagu J O and Pacyna J M 1988 Quantitative assessment of worldwide contamination of air, water and soils by trace metals Nature 333 134-39

[5] Chen B, Stein A F, Maldonado P G, Campa A, Gonzalez-Castanedo Y, Castell N and Rosa J D 2013 Size distribution and concentrations of heavy metals in atmospheric aerosols originating from industrial emissions as predicted by the HYSPLIT model Atmos. Environ. 71 234-44

[6] Lighty J S, Veranth J M and Sarofim A F Combustion aerosols: factors governing their size and composition and implications to human health 2000 J. Air Waste Manage. 50 1565-618

[7] Seaton A, Tran L, Aitken R and Donaldson K 2010 Nanoparticles, human health hazard and regulation J. of the Royal Soc. Interf. 7 119-29

[8] Clemens S 2006 Toxic metal accumulation, responses to exposure and mechanisms of tolerance in plants Biochimie 88 1707-19

[9] Junge C E 1967 Determination of the acid content of aerosol particles Atmos. Environ. 5 165-75

[10] Osada K, Shido Y, Iid H and Kido M 2010 Deposition processes of ionic constituents to snow cover model Atmos. Environ. 44 347-53

[11] Kang J H, Choi S D, Park H, Baek S Y, Hong S and Chang Y S Atmospheric deposition of persistent organic pollutants to the East Rongbuk Glacier in the Himalayas Sci. Total Environ. 408 57-63

[12] Vasic M V, Mihailovic A, Kozmidis-Luburic U, Nemes T, Ninkov J, Zeremski-Skoric T and Antic B 2012 Metal contamination of short-term snow cover near urban crossroads: Correlation analysis of metal content and fine particles distribution Chemosphere 86 585-92

[13] Bosco M L, Varrica D and Dongarra G 2005 Case study: Inorganic pollutants associated with particulate matter from an area near a petrochemical plant Environ. Res. 99 18-30

[14] Hiromitsu S, Tanenori S and Kazuo S 1988 Heavy metal concentrations in urban snow as an indicator of air pollution Himalayas Sci. Total Environ. 77 163-74

[15] Espinosa A F, Rodriguez M T, Barragan de la Rosa F J and Sanchez J C 2002 A chemical speciation of trace metals for fine urban particles Atmos. Environ. 36 773-80

[16] Arbuzov S I, Volostnov A V, Rikhvanov L P, Mezhibor A M and Ilenok S S 2011 Geochemistry of radioactive elements (U, Th) in coal and peat of northern Asia (Siberia, Russian Far East, Kazakhstan, and Mongolia) Int. J. Coal Geol. 86 318-28

[17] Gaffney J S and Marley N A 2009 The impacts of combustion emissions on air quality and climate – From coal to biofuels and beyond Atmos. Environ. 43 23-36

[18] Kunal, Siddique R and Rajor A 2012 Use of cement kiln dust in cement concrete and its leachate characteristics Resour. Conserv. Recy. 61 59-68