RESEARCH PAPER

MONITORING FOR ELEMENTAL COMPOSITION OF PARTICULATE MATTER DEPOSITED IN SNOW COVER AROUND COAL-FIRED THERMAL POWER PLANT (KARAGANDA, CENTRAL KAZAKHSTAN)

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ABSTRACT. Studies on thermal power plant areas with respect to chemical composition of particulate matter deposited in snow cover are limited. This study aims to monitor (2014–2022) particulate load and trace elements associated with the particulate matter distributed around (0.5-4.5 km) the coal-fired thermal power plant in Karaganda. In this study, snow cover was used as an effective scavenger of atmospheric pollutants. Using instrumental neutron activation analysis and atomic absorption spectrometry, the content of 26 elements and Hg, respectively, was determined in the particulate phase of snow. The results showed that particulate load varied from 26 to 1751, with mean of 427 and a background of 47 mg m^{-2} d^{-1}. Anthropogenic impact caused a significant increase in content of U, Hg, Ta, Zn, Na, Cr, Co, Sr, Rb, Cs, Sc, Ca, Fe, Nd, Ba (2–30 times) in the samples compared to the background. Metal-bearing phases of Zn, Ba, As, U-Ta-Nb were detected through scanning electron microscope. The highest levels of particulate load (169–1032 mg m^{-2} d^{-1}) and element contents in the samples were localized up to 0.7 km from the thermal power plant. The changes of particulate load and element composition of snow deposits during the monitoring period were connected with temperature, modernization of dust-collecting equipment, composition of coal and fly ash, long-range transport of emissions from other industries. The element content and metal-bearing phases in the particulate phase of snow can be used as markers for identifying emission sources from coal combustion.

KEYWORDS: urban snow pollution; rare elements; heavy metals; metal-bearing phases; atmospheric deposition; coal combustion

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INTRODUCTION

Atmospheric pollution is largely associated with the development of thermal power, about 38–40 % of the world's energy demand is met by coal-fired power plants (International… 2023). Despite the various benefits it suggests, the operation of a thermal power plant can contribute to environmental pollution. Coal contains various trace elements, including heavy metals, rare-earth elements and radioactive elements (Arbuzov and Ershov 2007; Córdoba et al. 2012; Dai et al. 2012; Ambade 2014; Finkelman et al. 2018; Arbuzov et al. 2019; Hou et al. 2023). Consequently, coal combustion is considered as one of the main sources of anthropogenic inputs of trace elements in the atmosphere (Carpi 1997; Zereini et al. 2005; Jayasekhe 2009; Finkelman et al. 2018; Zhao et al. 2018). Many of the trace elements in the suspended particulate matter create serious environmental problems due to their toxicity (Schwarze 2006). Particulate matter which result from combustion processes is a potential contributor to human health (Nemmar et al. 2002).

It is important for environmental monitoring purposes to identify trace element contents in the particulate matter emitted by coal-fired thermal power plant and to assess their distribution at long distances from the source.

Snow cover as a natural environment is widely used by many researchers to study pollutants and identify sources of anthropogenic air pollution. Most studies have focused on the concentration of chemical and ionic components in the snow cover in urbanized and background areas, for example, in Russia

(Kasimov et al. 2012; Ianchenko et al. 2016; Grebenshchikova et al. 2017; Eremina and Vasil'chuk 2019; Pozhitkov et al. 2020; Vlasov et al. 2020; Krickov et al. 2022), Republic of Kazakhstan (Temirzhanova et al. 2021), Lithuania (Krastinytė et al. 2012; Baltrėnaitė et al. 2014; Taraškevičius et al. 2018), Slovenia (Gaberšek and Gosar 2020). However, studies for areas of thermal power plants with respect to the element composition of particulate matter deposited in the snow cover (particulate phase of snow) are limited. For example, the anthropogenic impact of the Novosibirsk thermal power plant (Russia) was connected with high concentrations of Sn, As, Ge, Sb, Nb, U, Th in the particulate phase of snow (Bortnikova et al. 2009; Raputa et al. 2020; Artamonova 2020). In Irkutsk (Russia) some elements (Si, Fe, Mg, Mn) were identified as dominant elements in the vicinity of the thermal power plant (Filimonova et al. 2015). In Ulaanbaatar (Mongolia), the main source of As, Cd, Cu, Mo, Ni, Pb, Sr, V, W in the snow cover were emissions from a thermal power plant (Sorokina et al. 2013). In the particulate phase of snow collected in the vicinity of Pavlodar thermal power plant (Republic of Kazakhstan) heavy metals (Hg, Bi, Sr, Ni, V) were identified as dominant elements (Panin and Azhaev 2006). However, the content of a wider range of trace elements, including rare-earth and radioactive elements, in the particulate matter deposited in the snow cover and their transport on the different distances in the vicinity of coal-fired thermal power plants were insufficiently studied.

A large thermal power plant located in the Central Kazakhstan (Karaganda city) was chosen as an object for the investigation, because high-ash coal is combusted there, which can lead to an increase in anthropogenic emissions of particulate matter into the urbanized area. Additionally, anthropogenic particles generated in the industrial locations transport to the nearby residential areas of the city based upon the meteorological factors.

The investigations of the snow cover and soil were carried out within industrial areas of Karaganda city and its fellow town in the period of 1991–1993 (Kalmykov and Malikova 2017). This study showed that the particulate load varied from 1500 to 4300 mg m^{-2} d^{-1} and exceeded the background value (60 mg m^{-2} d^{-1}) 25–75 times at the distance of 1 to 3 km from the thermal power plant. It was identified the high content of Se, P, Hg, Mo in the solid airborne particles deposited in the snow cover around the thermal power plant. It was also determined that soil in this area was polluted by some heavy metals and metalloids (Pb, Zn, Cd, Hg, Se, Cr, Cu, Mo, Sb, Mn, Bi, P).

Some authors (Arbuzov et al. 2014; 2016; 2019; Amangeldykyzy et al. 2021) showed that coal of Central Kazakhstan, which is used in the studied thermal power plant, include high contents of some elements (e.g. Sc, Cr, Co, Zn, Sr, Ba, Ce, Nd, Rb, Th, U). These elements could be emitted into the air during high temperature combustion and then deposited on the snow cover around the plant.

The deposition rates of particulate matter and the environmentally relevant chemicals on the snow cover were insufficiently studied during the last 30 years around the thermal power plant located in Karaganda city. Additionally, there are still some gaps with respect to quantification of rare elements, including rare-earth and radioactive elements, in the particulate phase of snow cover within areas impacted by the thermal power plant.

The aim of this study is to monitor (2014–2022) particulate load and trace elements associated with particulate matter distributed within 0.5–4.5 km of the coal-fired thermal power plant in Karaganda using snow cover. Consequently, the main objectives of this study were: (a) to determine the level of particulate load; (b) to analyze 27 elements, including metals and metalloids (As, Hg, Cr, Sr, Ba, Co, Zn, Sb), rare-earth (La, Ce, Eu, Lu, Yb, Sm, Tb, Nd), radioactive elements (U, Th), Cs, Hf, Rb, Sc, Ta, Ca, Na, Fe, Br associated with the particulate phase of snow; (c) to identify metal-bearing phases of dominant elements in the particulate phase of snow; (d) to study the spatial and temporal changes of particulate load and elemental composition of particulate phase of snow considering some meteorological parameters and stages of modernization of dust-collecting equipment at the thermal power plant.

MATERIALS AND METHODS

Study area

The study area is the vicinity of the coal-fired thermal power plant. It is located in the city of Karaganda, Central Kazakhstan, with a population of 502 964 (data for 2022). Karaganda is one of the largest industrial, economic, scientific and cultural centers of the Republic of Kazakhstan. The city is located in the steppe landscape. Karaganda has a humid continental climate with harsh and long winters.

Blizzards and snowstorms are not uncommon in the winter season, with temperatures ranging from -15.1 to -34.7°C (open source: weather in the city of Karaganda). Snow cover usually covers the ground from mid-October to the end of February. During the monitoring period, snow cover averaged 38 cm in 2014–2017, 24 and 28 cm in 2021 and 2022, respectively. Southwestern (36%), southern (19%), and eastern (19%) winds prevail in the study area during the winter season (open source: weather in the city of Karaganda).

The thermal power plant has been in operation since 1977 and is located in the northern part of Karaganda, in 1.5 km from the residential areas of the city (Fig. 1).

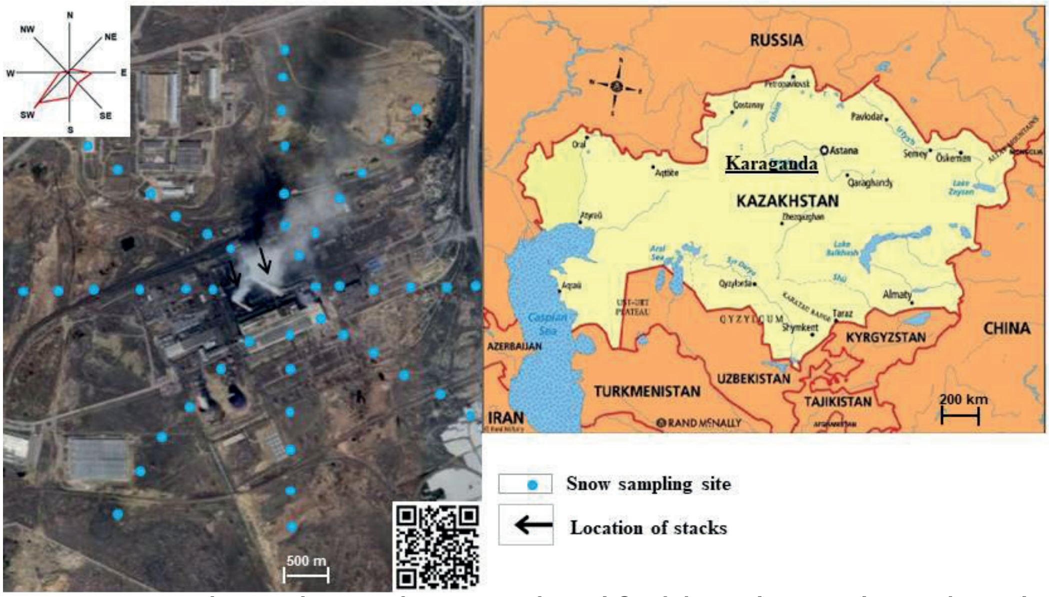

Fig. 1. Study area showing the Karaganda coal-fired thermal power plant and sampling sites (source: Google Earth, Republic of Kazakhstan, modified)

The heating season is from October 15 to April 15. The power plant operates on the high-ash coal from the Ekibastuz basin (Republic of Kazakhstan) and fuel oil. This thermal power plant uses 25x10^5 tons of coal and 35 tons of fuel oil per year. The thermal power plant generates an energy capacity of 670 MW and a heat capacity of 1174 Gcal/hour. The pollutants, including particulate matter, discharged through two tall stacks (180 and 270 m) (open source: Karaganda thermal power plant).

Sampling and sample preparation

The collection and analysis of snow cover samples in the vicinity of the thermal power plant were carried out from 2014 to 2017, from 2020 to 2021. Sampling and sample preparation were carried out according to Russian State Standard for air pollution control and several studies (Saet et al 1990; Kasimov et al. 2012; Baltrėnaitė et al. 2014; Filimonova et al., 2015; Grebenshchikova et al. 2017; Taraškevičius et al. 2018; Artamonova 2020; Ianchenko and Kotova 2022).

The samples were collected in seven directions from the thermal power plant (northeast, northwest, north, east, south, southeast and southwest) at a distance of 0.5; 0.7; 1.6; 2.2; 3.2 and 4.5 km from the stacks. Additionally, for the selection of monitoring sites locations following factors were considered: 1) prevailing wind direction; 2) extension of emissions depending on stack heights; 3) flat terrain; 4) accessibility of the sampling sites; and 5) distance from roads and other emission sources. The background area was chosen at a distance of 55–80 km from Karaganda to be sufficiently distant from the city to avoid its polluting influence.

Snow sampling was carried out in the period from 2014 to 2022. Every year snow samples were taken at once in the period from the end of January to the beginning of February, during the maximum thickness of the snow cover and before the period of snow melting. In total, 101 samples were collected during the monitoring period, each weighing approximately 15 kg.

At each monitoring site, a pit was made along the vertical profile from the top of the snow cover to 5 cm above the land in order to avoid contact with the soil. This sampling approach allowed us to obtain representative data on the accumulation of particulate matter in the snowpack over the winter season. Snow samples were taken with a plastic shovel, then stored and transported in polyethylene bags. Snow samples were melted at room temperature, then the snow water was filtered ("Blue Line" filter type) to obtain the particulate phase of snow, which was then sieved (1 mm sieve) and weighed in the laboratories. The filtration of snow-melted water was also conducted to separate particulate metals from dissolved metals in the samples. Therefore, the content of the elements was determined in the particulate phase of snow.

Laboratory analysis

Chemical and mineralogical analyses the particulate phase of snow samples were performed in the laboratories of the Uranium Geology International Centre and research nuclear reactor in Tomsk Polytechnic University (Russia). The analyses were conducted using replicates, method blanks and standard reference materials in order to maintain the standard quality.

It was used the instrumental neutron-activation analysis (INAA) and atomic absorption spectrometry (AAS) for analytical investigations of the particulate phase of snow samples collected in the vicinity of the thermal power plant and background area. These methods do not need for special sample preparation and have a low detection limit of elements which are shown in Appendix A.

Method of INAA was used to measure content of some heavy metals and metalloids (As, Cr, Sr, Ba, Co, Zn, Sb), rare-earth (La, Ce, Eu, Lu, Yb, Sm, Tb, Nd), radioactive elements (U, Th), Cs, Hf, Rb, Sc, Ta, Ca, Na, Fe, Br in the samples. These laboratory measurements were carried out on the unique scientific IRT-T equipment (nuclear geochemical laboratory, accreditation certificate № RA.RU.21АБ27 from 08.04.2015). The weight of 100 mg sample was used for measure of element content. When applying INAA the digestion of the samples was not necessary (Witkowska et al. 2005). The samples were irradiated with reactor neutrons for 3 to 18 hours followed by cooling from 7 days to 3 weeks (Sudyko 2016). The gamma-ray activate was measured with Ge-detector (GX3518, Canberra Inc.). The quality of INAA was controlled using a certified standard for particulate phases (Baikal silt BIL-1 GSO 7126-94). INAA is effective used for determination of element composition in different natural objects (Witkowska et al. 2005; Mezhibor et al. 2009; Soktoev et al. 2014; Sudyko 2016; Arbuzov et al. 2019; Farkhutdinov et al. 2021).

Content of mercury in the samples was measured by AAS with pyrolytic volatilization using an atomic absorption spectrometer RA-915+ with pyrolyzer PYRO-915 (Lumex, Russia) and software package RA915R. In samples, Hg compounds were atomized at 850°C in a cuvette connected with an open absorption cell. Three replicate measurements were performed for each sample, weighted 150 mg. From these replicates average content of Hg in each sample were calculated. The relative measurement error is within 20–28%. A standard soil sample (SDPS-3) with a mercury concentration of 290±58 ng/g was used as a standard reference material. A number of papers have been published in which the mercury content in snow samples was determined using atomic absorption spectrometry (Filimonenko et al. 2014; Grebenshchikova et al. 2017; Gustaytis et al. 2018; Talovskaya et al. 2019).

The mineralogical composition of the samples was determined by X-ray diffraction (XRD) analysis on a D2 PHASER powder diffractometer (Bruker, Germany) with Cu-Kα radiation (30 kV and 10 mÅ). The diffractometer was monitored by means of a computer, using software package DIFFRACplus v.15.0. The samples (1 g each) were compressed and placed on plastic sample holder for XRD analysis. XRD patterns were recorded over a 2θ interval of 3–70°, at a rate of 3° (2θ)/min and a sampling distance of 0.02° (2θ). The mineral phases and its content (in %) in the samples was identified using Diffrac. Eva V3.2 software, based on the calibration curves obtained from different standard samples of known mineral composition. The detection limit for mineral content was 1% in the samples (Talovskaya et al. 2018). The precision of the diffractometer was controlled before and after the experiments, using the Si standard.

The mineral and anthropogenic particles abundance in the samples were studied using binocular microscope (Leica ZN 4Dr). On this microscope we first determined the percentage content of each particle type, then the percentage of the group of mineral and anthropogenic particles, so that the content of all identified particles in total was 100 %.

Some published research applying the scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) to identify and characterize solid metal-bearing phases in the snow deposits (Golokhvast and Shvedova 2014; Miler and Gosar 2015; Gustaytis et al. 2018; Shevchenko et al. 2020). The samples of particulate phase of snow were analyzed by SEM-EDS in the laboratories of Karaganda State Technical University, Republic of Kazakhstan. Scanning electron microscope (Tescanr Orsayr Holdingr, Czech) coupled with an Oxford INCA EDS system was used to study the morphology and chemical composition of some individual particles in the samples. Samples were mounted on double-sided carbon type with the surface area of 25 mm^2 and sputter coated with a thin layer of carbon for conductivity. The SEM-EDS analysis was carried out in a high vacuum, at 20 kV accelerating voltage, magnifications of 3.00 kx and 15 mm working distance. The INCA Energy software was used to identified element content in some individual particles. It is based on semi-quantitative analysis with 5-15% relative accuracy depending on identified element.

Data analysis

STATISTICA 8.0 was used to calculate the mean values±SE (standard error of mean), median, Spearman correlation coefficients and their significance as well as to perform cluster analysis (Ward's method of amalgamation with 1-r distance), revealing the differences between groups using Mann–Whitney U and test Kruskal-Wallis non-parametric test when comparing more than two groups. The differences were considered significant at p = ≤ 0.01 at the 0.05 level. Nonparametric tests were used, because Lilliefors and Kolmogorov-Smirnov tests had shown that the variables do not correspond to normal distribution.

Following indexes were calculated to assess particulates pollution in accordance with research studies by some authors (Saet et al. 1990; Kasimov et al. 2012; Baltrėnaitė et al. 2014; Filimonova et al. 2015; Taraškevičius et al. 2018; Vlasov et al. 2020). The calculations of *particulate load* (P_n, mg m^{-2} d^{-1}) were made using Equation 1:

$$P_n = \frac{P_o}{S \times t} \quad (1)$$

where P_o is the mass of the particulate phase (mg); S is the square of the snow pit (m^2); t is the time representing the stable snow cover formation duration up to sampling day (d).

The concentration coefficient (K_c) representing the level of element enrichment in the particulate phase of snow in relation to the background content was determined using Equation 2:

$$K_c = \frac{C_i}{C_b} \quad (2)$$

where C_i is the element content in the particulate phase of snow (mg/kg); C_b is the background element content in the particulate phase of snow (mg/kg).

It can be stated that, if K_c values are higher than 1.5, element could be of anthropogenic origin (Saet et al. 1990).

The total levels of contaminants from a particular group of elements or the general contamination levels were expressed by the *total pollution of snow cover* (Z_c), calculated according to the Equation 3:

$$Z_c = \sum K_c - (n-1) \quad (3)$$

where K_c is concentration coefficients for elements with $K_c \geq 1.5$, n is the number of elements, having $K_c \geq 1.5$.
Classification of pollution level based on the particulate load and total pollution of snow cover are shown in Table 1.

RESULTS

Particulate load and mineral composition of particulate phase of snow

Particulate load in the vicinity of the thermal power plant between 2014 and 2022 ranged from 26 to 1751 mg m^{-2} d^{-1}, with a background of 47 mg m^{-2} d^{-1}. During the monitoring period, the mean of particulate load was 427 mg m^{-2} d^{-1}, which corresponds to moderately hazardous and highly hazardous level of pollution.

The spatial and temporary changes of particulate load both in was revealed during the six-year monitoring period.

In the period from 2014 to 2022, there was a statistically significant (p ≤ 0.001) decreasing of particulate load from 1.5 to 5 times (Fig. 2a). A sharp decrease in particulate load has been identified since 2015. In subsequent years (2016–2021), no significant changes in particulate load were observed. It was observed the changes in particulate load from hazardous pollution level and dangerous risk level in 2014 to moderately hazardous and highly hazardous levels in 2015–2017. In 2021 and 2022, allowable pollution level and non-dangerous risk level were identified.

Table 1. Pollution level based on the particulate load (P_n) and total pollution of snow cover (Z_c) (Saet et al. 1990; Kasimov et al. 2012; Baltrėnaitė et al. 2014)

Pollution level	Risk level	P_n, mg m^{-2} d^{-1}	Z_c
Allowable	Non-dangerous	≤250	≤64
Moderately hazardous	Highly hazardous	250-450	64-128
Hazardous	Dangerous	450-850	128-256
Highly hazardous	Very dangerous	≥850	≥256

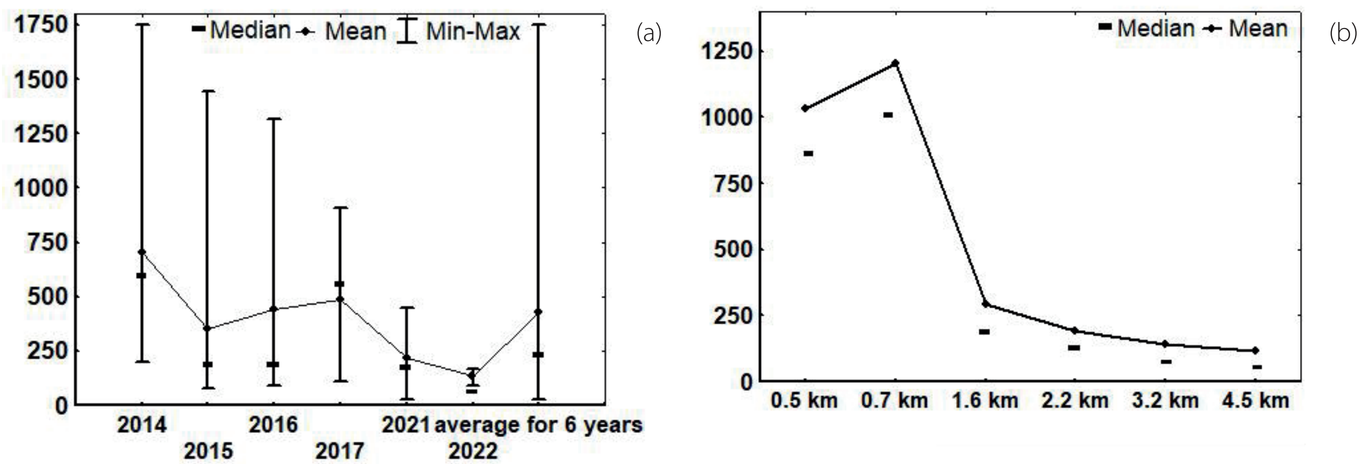

Fig. 2. Particulate load (mg m^{-2} d^{-1}) around the coal-fired thermal power plant: a) dynamics from 2014 to 2022 (according to the non-parametric Kruskal-Wallis test p-value is less 0.001 at the 0.05 level); b) distribution in the north-east direction (mean for 2014–2022)

Particulate load was decreased with distance from the thermal power plant in the northeastern direction of the main mass transport of pollutants (Fig. 2b). Over a six-year monitoring period, the highest level of particulate load was observed at a distance of up to 0.7 km (169–1032 mg m^{-2} d^{-1}), and within 1.6–4.5 km the particulate load was decreased on average from 1.5 to 4 times (118–276 mg m^{-2} d^{-1}).

It was determined the content of mineral (6–13%) and anthropogenic (87–94%) particles in the particulate phase of snow. Mineral particles include such minerals as quartz (3–6%) and feldspars (2–5%). Anthropogenic particles include soot and coal dust (18–20%), slag and ash (20–22%), Fe-rich (21–25%) and Al-Si-rich spherules (23–25%). It was also identified plant residues (1–2%). The content of the identified particles in the samples did not change significantly during the monitoring period.

According to X-ray diffraction data, the content of mineral phases was 73.5%, and the amorphous phase was 26.5%. Mullite (21.9%) was identified as the predominant mineral phase, which associated with Al-Si-rich spherules. The content of quartz (14.2%), albite (12.1%), kaolinite (12.7%), and chlorite (15.2%) was detected by XRD on a smaller proportion in the samples.

Elemental composition of particulate phase of snow

Average content of the elements in the particulate phase of snow around studied plant for the monitoring period and in the background area are given in Table 2. Geochemical peculiarities of the samples were connected with the high content of U, Hg, Ta, Zn, Na, Cr, Co, Sr, Rb, Cs, Sc, Ca, Fe, Nd, Ba relatively to background (Fig. 3). Results shown that the content of elements in the samples exceeded the background from 1.5 to 30 times during period of 2014–2022 (Table 3).

During the monitoring period, high concentrations of U (K_c=3...24), Hg (K_c=8.8...29), Ta (K_c=1.6...14), Zn (K_c=1.5...6.6), Na (K_c = 1.9...3.4) were observed relative to the background in the particulate phase of snow. Another elements (Cr, Co, Sr, Rb, Cs, Sc, Ca, Fe, Nd, Ba) were less concentrated in the samples (K_c=1.5...3). The content of Th, Br, Sb, As and some lanthanides was determined at the background level (K_c≤1.5) in the particulate phase of snow. Content of elements exceeding the background by more than 2 times indicate local anthropogenic sources of element origin.

Table 2. Mean element contents in the particulate phase of snow around coal-fired thermal power plant (2014–2022) and in background area (mg/kg)

Element	Mean±SE	Background content*	Element	Mean±SE	Background content*
Na, %	0.6±0.05	0.2	Cs	2.3±0.3	1.1
Ca, %	2.6±0.2	1.3	La	20.8±0.8	19.9
Fe, %	2.7±0.1	1.7	Hf	4.3±0.1	4.4
Hg	0.45±0.1	0.03	Ce	50.3±2.8	47.5
As	7.5±0.4	8.6	Nd	22.6±2.0	15.9
Zn	235±40.3	86.4	Ta	2.1±0.9	0.3
Sb	3.4±0.4	3.4	Sm	5.1±0.3	4.5
Co	17.1±1.4	9.6	Eu	1.2±0.05	1.0
Cr	74.2±10.7	34.5	Tb	0.8±0.05	0.6
Ba	595±25.3	467	Yb	2.7±0.1	2.7
Sr	263±19.6	85.1	Lu	0.5±0.03	0.4
Sc	23.2±7.4	11.1	Th	4.5±0.2	4.3
Br	8.8±0.8	9.3	U	8.3±3.5	0.7
Rb	30.5±3.3	13.1			

* - background levels of elements in the samples are the authors' data

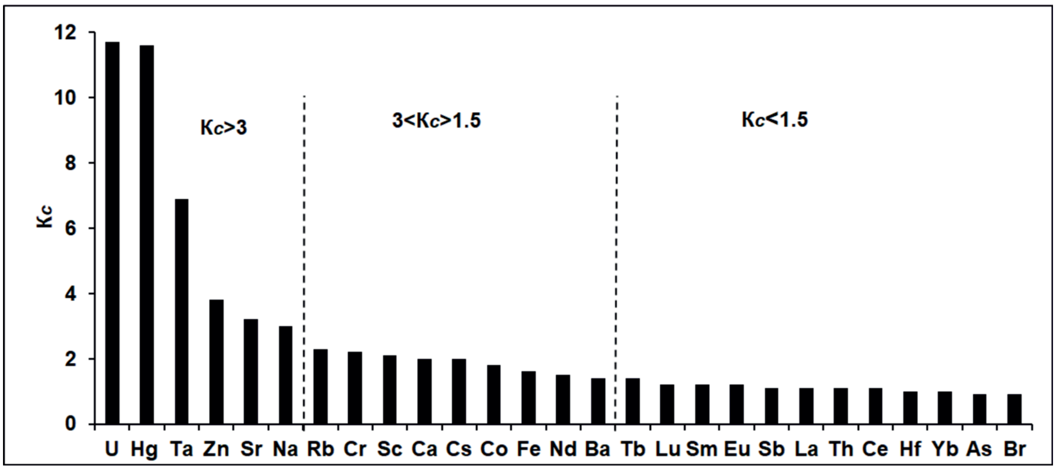

Fig. 3. Accumulation of elements in the particulate phase of snow relative to the background around the coal-fired thermal power plant (mean for 2014–2022, Z_c=68)

During the monitoring period, the total pollution of snow cover changed from moderately hazardous pollution level and highly hazardous risk level in 2014-2016 to allowable pollution level and non-dangerous risk level in 2021-2022 (Table 3).

Cluster analysis was identified 7 significant geochemical associations of elements (Fig. 4) in the particulate phase of snow in the vicinity of the thermal power plant during the monitoring period: 1) Tb-Sm-Eu-Ce-La (r~0.69...0.96), 2) Lu-Yb-Hf-Br (r~0.65...0.88), 3) U-Ta-Nd-Ba (r~0.82...0.99), 4) Cr-Co-Zn-Sb-As (r~0.78...0.89), 5) Sr-Ca (r~0.48), 6) Rb-Hg (r~0.41), 7) Fe-Na (r~0.77).

During the monitoring period (2014–2022), significant correlations of U-Ta-Nd (r~0.71...0.88), Sm-Ce-La-Hf (r~0, 65...0.88), Cr-Co (r~0.77...0.95) were remained in the particulate phase of snow.

The identified geochemical associations could indicate the common sources of the elements in the snow cover and the modes of their occurrence in the particulate phase of snow. It was identified the metal-bearing phases of U, Ba, As, and Zn in the particulate phase of snow using the scanning electron microscope. Additionally, it was determined U-Ta-Nb-bearing phases with Ti, Fe, Ca impurities (average size: 42 µm) (Fig. 5a). Particles (size: 2.0-2.3 µm) consisting of S, Ba and As were assumed as mixture of As sulphides and Ba sulphate (Fig. 5b). Particles (size: 9.8 µm) containing S and Zn were assigned to be Zn sulphides. Particles of Zn sulphides were also found in the particulate phase of snow in the vicinity of thermal power plants in the south of the Western Siberia (Talovskaya et al. 2018).

The temporal changes of the element contents in the samples was shown in Table 3 as the concentration coefficients. During the monitoring period, it was determined that from 2015 to 2022 there was a statistically significant ($p \leq 0.01$) decrease in the content of Na (0.7...0.4 mg/kg), Fe (2.9...2.1 mg/kg), Zn (318...86.4 mg/kg) Sb (3.9...2.9 mg/kg), Co (21.2...11.3 mg/kg), Cr (105...42 mg/kg), Sc (38.2...12.2 mg/kg), Cs (2.9...1.6 mg/kg) in the particulate phase of snow. Uneven statistically significant distribution ($p \leq 0.001$) of Hg, U, Ta, Nd, Rb, As content was determined in samples collected in different years during the monitoring period. In the samples no significant change ($p \geq 0.1$) in the content of Ca, Ba, Sr, Th and lanthanides over the years was revealed, which may indicate constant sources of element emissions into the environment.

Table 3. Changes of element concentration coefficients (K_c) in the particulate phase of snow and total pollution of snow cover (Z_c) around the coal-fired thermal power plant (2014–2022)

Period of monitoring	K_c				Z_c
	>10	3–10	1.5–3	≤1.5	
2014	Hg_{17}	$Sc_{3.5}Na_{3.5}$ $Ca_{3.5}Zn_{4}$	Ta_2Co_2 Cs_3Sr_3 $U_3Cr_3Rb_3$	Fe, As, Sb, Ba, Br, La, Hf, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Th	71
2015	$Ta_{14}U_{25}$	$Na_3Sr_3Hg_6$	$Co_2Cr_2Cs_2$ $Nd_2Rb_2Ca_2Zn_2$	Fe, As, Sb, Ba, Sc, Br, La, Hf, Ce, Sm, Eu, Tb, Yb, Lu, Th	77
2016	Hg_{29}	$Cs_3Rb_3U_3$ $Sr_{3,4}Na_{3,5}$	$Ca_{1.6}Zn_{1.6}Nd_{1.6}$ $Ta_{1.6}Tb_{1.6}$ $Fe_2Cr_2Co_2$	As, Sb, Ba, Sc, Br, La, Hf, Ce, Sm, Eu, Yb, Lu, Th	75
2021	$U_{10}Hg_{24}$	Sr_4Ta_6	$Fe_{1.6}Lu_{1.7}$ $Zn_2Na_2Ca_{2.5}$	As, Sb, Co, Cr, Ba, Sc, Br, Rb, Cs, La, Hf, Ce, Nd, Sm, Eu, Yb, Th	56
2022	$Ta_{13}U_{21}Hg_{24}$	–	$Lu_2Na_2Ca_2Sr_{2.5}$	Fe, As, Zn, Sb, Co, Cr, Ba, Sc, Br, Rb, Cs, La, Hf, Ce, Nd, Sm, Eu, Tb, Yb, Th	62

* subscripts correspond to the average value of K_c

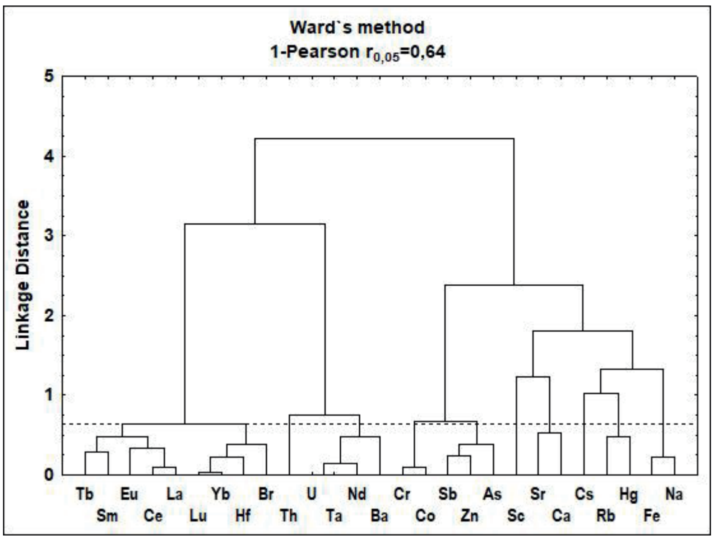

Fig. 4. Clusters of related elements in the particulate phase of snow around the coal-fired thermal power plant (2014–2022, n=39)

It was determined that the element contents in the samples collected in 2021–2022 were significant lower in comparison with the results for the period of 2014–2016.

In the period of 2021–2022, it was revealed the statistically reliable 2–6 times increasing of Ce, Ta and U content in the particulate phase of snow in comparison with the data for the period of 2014–2016. This was due to the different distribution of elements with distance to the northeast from the thermal power plant (0.5–4.5 km) during the monitoring period. In 2021-2022 a peak of Ce, Ta, and U content in samples collected at a distance of 1.6 km was determined.

During the monitoring period (2014–2022), it was revealed the significant decrease of Hg, Br, La, Hf, Eu, Cs, Tb, Yb, U content in the samples collected in the northeastern direction at a distance of 0.5 to 4.5 km from the thermal power plant. In addition, the maximum content of these elements were determined in the samples collected at distances of up to 1.6 km. The content of Th, Lu, Nd, Ba in the samples did not change significantly with distance from the thermal power plant. As content in the samples was increased at a distance of 0.5 to 4.5 km, which was explained by volatility of this element. It was observed peak of Zn, Co, Cr, Ca content in the samples taken at a distance of 4.5 km from the thermal power plant. As an example, Fig. 6 shows the distribution of Co, Cr, Hg, La, Ce, Rb, Nd, Sc, Th, U content in the particulate phase of snow in the north-east direction from the plant.

DISCUSSION

During the observation period around the thermal power plant in Karaganda, the decrease in particulate load and the contents of elements in the samples was due to various factors. Firstly, dust-collecting equipment were reconstructed with fly ash collection efficiency of 96.5–99.5% at the thermal power plant in 2014-2016. In addition, in 2016, a new power unit with an electrostatic precipitator was installed with fly ash collection efficiency of 99.75%, which made it possible to reduce the inputs of dust and gas emissions (open source: Ensuring reliable and high-quality energy supply).

Secondly, the identified changes over monitoring period could be connected with the meteorological parameters and the depth of the snow cover. The average values of these parameters over the years are shown in the tables in the Appendix B. The impact of these factors was observed in 2021 and 2022, when particulate load (219 and 135 mg m^{-2} d^{-1}, respectively), the element contents in the samples and snow cover depth (24 and 28 cm, respectively; open source: weather in the city of Karaganda) were the lowest during the monitoring period. Consequently, 2021 and 2022 were sparsely snowy, which could affect the ratio of the processes of "dry" and "wet" deposition of pollutants from the atmosphere. It was determined the significant positive correlation (r~0.55...0.66) between particulate load and temperature in the winter seasons. Additionally, between 2014 and 2017, the average temperature during the winter season was -15.6ºC, in 2021–2022 the temperature was 10.5ºC (open source: weather in the city of Karaganda). This could have an impact on the consumption of coal burning at the plant, as a consequence, on the level of particulate load during these periods.

The highest level of particulate load, that was observed at a distance of up to 0.7 km from the stacks of the thermal power plant, on the one hand, was due to the close location of the open coal warehouse, where the coal was unloaded, crushed and transported on conveyors to the boiler house bunkers. On the other hand, an additional factor could be the processes of scavenging the emitted fine particles by ice pellets formed when water vapor freeze in the smoke plume of the thermal power plant. This effect was investigated and confirmed for the coal-fired thermal power plant in Kyzyl (Russia) (Belyaev et al. 1997). Due to this phenomenon, most of the particulate emissions in the winter could be deposited nearby to the thermal power plant.

Previous studies on snow cover pollution in Karaganda (1991–1993) showed that particulate load within a radius of 1–3 km from the thermal power plant was on average 2500 mg m^{-2} d^{-1} (Kalmykov and Malikova 2017). It can be seen that over a 30-year period (from 1991–1993 to 2014–2022) particulate load was decreased into six times in the impacted area of the thermal power plant. Additionally, the average particulate load in the vicinity of Karaganda thermal power plant (427 mg m^{-2} d^{-1}) was slightly higher than in the vicinity of Pavlodar thermal power plant located in Kazakhstan (338 mg m^{-2} d^{-1} (Panin and Azhaev 2006)); in two-three times higher than in the vicinity of some thermal power plants located in cities of Western Siberia

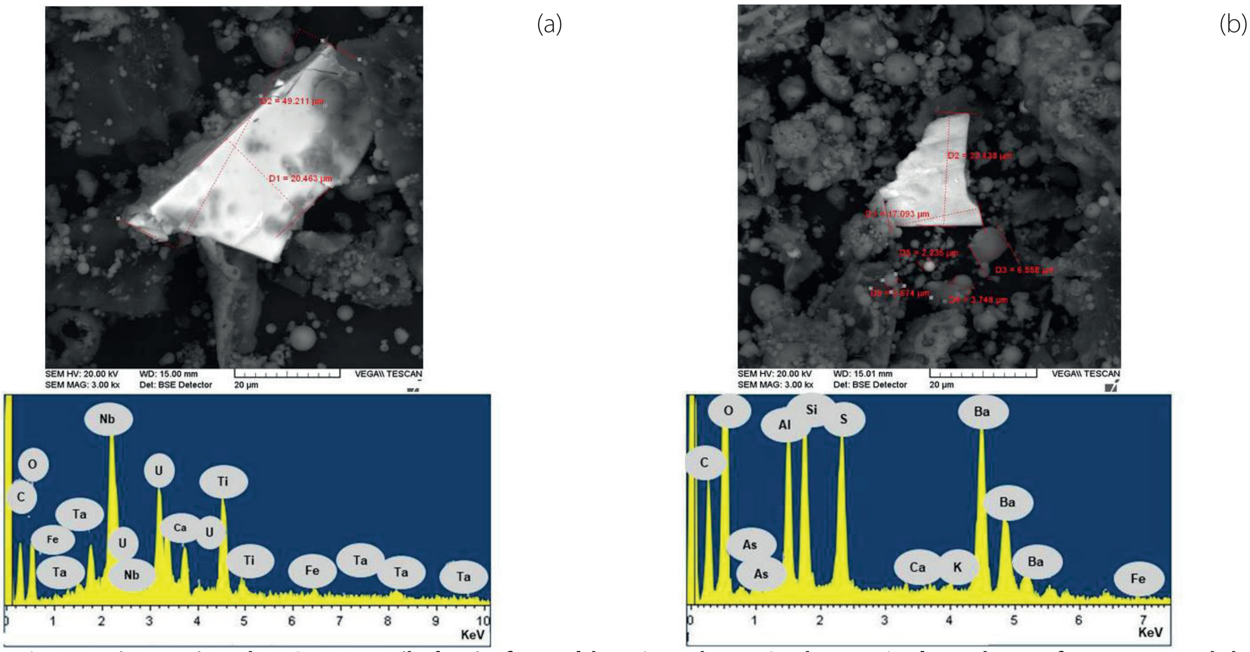

Fig. 5. SEM images (on top) and EDS spectra (below) of metal-bearing phases in the particulate phase of snow around the coal-fired thermal power plant: a) U-Ta-Nb-bearing phases with Ti, Fe, Ca impurities; b) mixture of sulphides of As and sulphate of Ba

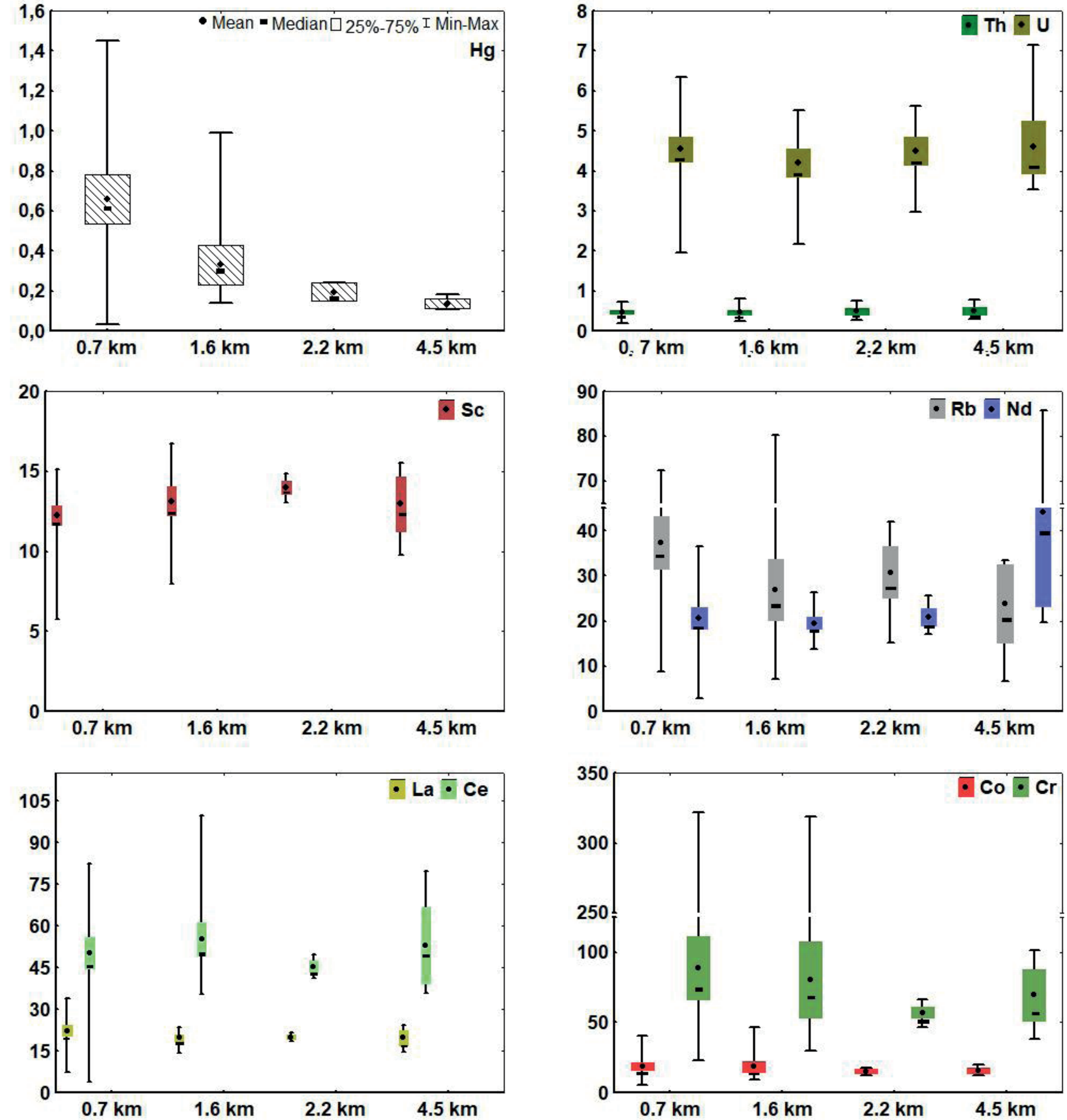

Fig. 6. The distribution of element content (mg/kg) in the particulate phase of snow in the north-east direction from the coal-fired thermal power plant (average for 2014–2022)

(201–555 mg m^{-2} d^{-1} (Talovskaya et al. 2019); 143 mg m^{-2} d^{-1} (Artamonova 2020)).

The content of the identified mineral phases and spherules in the particulate phase of snow could be related to the composition of fly ash. Earlier we determined that Al-Si-rich spherules and Fe-rich spherules with sizes of 0.2–41.7 µm in the particulate phase of snow correspond in their morphology to the same spherules with sizes of 1.5-126 µm in fly ash (Adil'bayeva et al. 2017). Some studies (e.g. Goodarzi 2006; Magiera et al. 2011; Zyryanov et al. 2011) also show that fly ash is characterized by the content of the spherules. Valeev D. and co-authors (2019) showed that Ekibastuz coal fly ash consists mainly of quartz, mullite and magnetite. Consequently, spherules and mineral phases contained in the fly ash might be released into the air and then deposited in the snow cover.

The changes of some element contents in the particulate phase of snow with distance from the thermal power plant could be related to the impact of local anthropogenic sources, on the one hand, and the particle sizes that transport these elements in the air, on the other hand.

The identified peak of Ce, Ta, and U content in samples collected at a distance of 1.6 km could be associated with the impact of the local anthropogenic sources, which began to actively operate since 2017 at a distance of more than 2 km from the thermal power plant. The identified peak of Zn, Co, Cr, Ca content in the samples collected at a distance of 4.5 km was probably associated with the long-range transport of emissions from industries located in the city of Karaganda and its fellow town. In the industrial and coal combustion processes, fine particles can be formed and released into the atmosphere (Dai et al. 2012; Lanzerstorfer 2018; Czech et al. 2020). Wu J. and coauthors (2022) showed that Fe- and Ti-containing particles (>100 nm) were dominated in the metal-containing emissions of thermal power plants. The most volatile-toxic elements (Sb, As, Hg) were contained mainly in submicron fraction (<0.05

microns) or vapor-gas phase of aerosol (Lanzerstorfer 2018; Czech et al. 2022). Ba, Sr, Zn, Rb, Cr, Co, Th, U condense on fine particles (<1 μm), which are not retained by electrostatic precipitators, escaping its and then emit into the air (Krylov 2017; Lanzerstorfer 2018). Therefore, large particles might be deposited nearby to the plant; otherwise fine particles could be transported far from the source. As a result, anthropogenic geochemical areas could be formed at different distances from the industries and thermal power plants.

Identified geochemical peculiarities of the particulate phase of snow in the vicinity of the thermal power plant, on the one hand, was associated with the impact of the emission sources of the plant, on the other hand, with the long-range transport of emissions from other industries and transport of the city, and its fellow cities. Some studies were shown that the possible source of some heavy metals in the air could be exhaust and non-exhaust vehicle emissions (Golokhvast et al. 2015; Vlasov et al. 2020).

In the research (Kalmykov and Malikova 2017) performed in 1991–1993 in the vicinity of Karaganda thermal power plant, in the particulate phase of snow high Hg content were determined due to the impact of coal combustion. It was also identified that Zn, Hg, Cr, Sb content was exceeded the background in soil. It was suggested that the emissions of the elements into the air was related due to the complex impact of the thermal power plant and the diffuse pollution.

The identified geochemical peculiarities (high levels of some rare-earth elements, Sc, U, Hg, Ba, Sr) of the particulate phase of snow in the vicinity of the thermal power plant was probably due to the composition of the used coal and fly ash. We determined that the content of Na, As, Sc, Br, Cs, Th and lanthanides in dust from electrostatic precipitators was in 2–17 times higher than their content in fly ash. Additionally, the content of Zn and U in the fly ash was 2–3 times higher than in the dust from the electrostatic precipitators. These facts might also indicate the sources of elements in particulate matter emitted into the air.

Coal ash was more enriched with trace elements compared to coal (Arbuzov and Ershov 2007). Levels of elements in the fly ash of the same coal at different thermal power plants could vary significantly. Some published researches were identified the high concentrations of rare elements (rare-earth, Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce) in the coal of Central Kazakhstan (Arbuzov et al. 2014; 2016; Amangeldykyzy et al. 2021). In addition, Arbuzov S.I. and coauthors (2014; 2019) showed that coal basins of Kazakhstan were significantly enriched in siderophile group of elements (Fe, Co, Cr), rare-earth elements (Sc, lanthanides), Ba, Sr, U, Th. Moreover, coals of Ekibastuz basin (Kazakhstan) contained very high Hg concentration (Kalmykov and Malikova 2017). Micromineral modes of rare-earth elements, Hf, Sc, Ta, Ba, native and intermetallic compounds were found in coals (Arbuzov et al. 2019; Amangeldykyzy et al. 2021). These elements could be emitted into the air during coal combustion.

CONCLUSIONS

The results of long-term snow cover monitoring (2014–2022) made it possible to study the spatial and temporal changes of particulate load and element contents in particulate matter deposited in snow cover in the vicinity of the coal-fired thermal power plant.

During the six-year monitoring period, U, Hg, Ta, Zn, Na, Cr, Co, Sr, Rb, Cs, Sc, Ca, Fe, Nd, Ba were the main pollutants around the coal-fired thermal power plant. The content of these elements in the particulate phase of snow and particulate load were 2–30 times higher than the background. Metal-bearing phases of Ba, As, U-Ta-Nb, anthropogenic particles (coal particles, slag, ash) and mullite were found in the particulate phase of snow, reflecting the impact of the thermal power plant.

This study demonstrated a decrease in particulate load and content of some elements (Na, Fe, Zn, Sb, Co, Cr, Sc, Cs) in the particulate phase of snow from 2015 to 2022. Comparison of the results obtained for 2014–2016 with data from 2021–2022 showed significantly high content of U, Ce, Ta in the samples collected in the last two years of monitoring. It was determined that the content of Ca, Ba, Sr, Th and some lanthanides in the particulate phase of snow did not change from year to year.

The results showed moderately hazardous and hazardous levels of particulate pollution in 2014–2017, which changed to allowable level in 2021–2022.

The revealed variability of particulate load and elemental composition of the samples were connected, on the one hand, with modernization of dust-collecting equipment from 2015 at the thermal power plant to reduce emissions into the air. On the other hand, it was found the correlation between particulate load and temperature in the winter seasons.

Particulate load and content of Hg, Br, La, Hf, Eu, Cs, Tb, Yb, U in the particulate phase of snow were determined to decrease with distance of 0.5-4.5 km from the thermal power plant in the northeast direction. We found significantly high particulate load and element contents in the samples collected at distances up to 0.7 km. This could be connected, on the one hand, with the impact of open coal warehouse located close to the monitoring sites. On the other hand, the processes of scavenging of fine solids by ice pellets in the stacks of the plant could contribute to the deposition of emissions at close distances.

The peculiarities of the element composition of the particulate phase of snow were caused by the composition of fly ash, the emitted dust, and the geochemical specificity of coals used at the thermal power plant. During the monitoring period, identified peaks in the content of some elements in samples were probably associated with the long-range transport of emissions from industries of the city and its fellow town.

The identified trace elements (e.g. rare-earth, Sc, U, Hg, Ba, Sr) in the particulate phase of snow could be used as markers of pollution from coal combustion in the urban atmosphere.

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Appendix A.

Table 1. The instrumental neutron activation analysis detection limit of 27 elements (Soktoev et al. 2014) and atomic absorption spectrometry detection limit of Hg (Talovskaya et al. 2019) in particulate phases

Element	Detection limit, mg/kg	Element	Detection limit, mg/kg
Na	10	Ta	0.01
Ca	300	Sc	0.02
Fe	100	Tb	0.005
As	0.3	Sm	0.01
Co	0.1	Eu	0.004
Cr	0.2	La	0.01
Sb	0.05	Ce	0.06
Ba	10	Yb	0.009
Zn	10	Nd	1.0
Br	0.3	Lu	0.001
Rb	0.5	U	0.06
Cs	0.01	Th	0.01
Sr	100	Au	0.005
Hf	0.009	Hg	0.005

Appendix B.

Table 1. The average values of snow cover depth in Karaganda in the winter season of 2014–2022

Snow cover depth, cm	Year					
	2014	2015	2016	2017	2021	2022
Annual	34	38	36	38	24	28
December	27	29	28	28	25	26
January	41	48	44	51	32	35
February	35	36	34	36	16	23

Open source: https://ldas.gsfc.nasa.gov/data

Table 2. The average values of temperature in Karaganda in the winter season of 2014–2022

Temperature, (oC)	Year					
	2014	2015	2016	2017	2021	2022
Annual	-16,8	-15,1	-14,8	-14,4	-10,2	-10,5
December	-15,7	-14,4	-14,1	-13,8	-10,1	-10,0
January	-19,9	-18,2	-17,2	-16,7	-12,3	-12,2
February	-14,5	-13,1	-11,6	-12,3	-9,1	-9,8

Open source: https://www.kazhydromet.kz/