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Satbayev University

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COPPER POLLUTION OF THE SNOW COVER IN ALMATY

Abstract. The natural environment of large cities is subject to strong anthropogenic pressure. Both the soil and the hydrosphere are exposed to pollution. At the same time, the atmosphere is one of the mechanisms means for the transfer pollutants that enter living organisms. The study of distribution routes, chemical reactions and interaction with the biosphere of released into nature substances and their compounds help to find means to minimize the negative impact to the environment. One of the ways to reduce costs is to find the best options for solving environmental problems. Such solutions are not possible without monitoring of pollutant emissions and environmental analytical control in particular. For the city of Almaty and the adjacent territory, for the first time in 2018-20, a research program on heavy metal pollution was carried out. This project made it possible to study the changes dynamics in soil and snow cover concentrations of the following elements: Copper (Cu), Zinc (Zn), Nickel (Ni), Lead (Pb), Cobalt (Co), and Cadmium (Cd). Along with the lithosphere, the water area of Kapshagay reservoir was studied. In addition, there was obtained the data on oxidizability, acidity, salinity and suspended solids. The dynamics of pollution by polychloryl biphenyl compounds has also been studied. The metals concentration was determined by the flame atomic absorption spectrometric method. The presence of these chemical elements in the lithosphere allowed assuming the presence natural sources of pollution against the background of anthropogenic factor exclusion. The lead content occupies a special position, since the presence of anthropogenic source is not excluded and requires further research and evaluation of the components of the incoming part of this chemical element balance. The article provides an analysis of the search for a source of copper pollution

of the snow cover in Almaty agglomeration territory. The source of copper emissions is assumed to be of natural origin. Based on the analysis of the wind regime, the location zones of sources of lithosphere pollution by copper are potentially determined. The study of the location of areas free from snow cover during the period of increasing copper concentration will allow determining more accurate location of zones producing the copper particles transfer.

Key words: Pollution, copper, snow cover, wind, heavy metals.

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АЛМАТЫ АГЛОМЕРАЦИЯСЫ ҚАР ЖАМЫЛҒЫСЫНЫҢ МЫСПЕН ЛАСТАНУЫ

Аннотация. Үлкен қалалардың табиғи ортасы антропогендік қысымға ұшырау ықтималдығы жоғары. Топырақ та, гидросфера да ластануға ұшырайды. Сонымен қатар, атмосфера, тірі организмдерге түсетін ластаушы заттарды тасымалдаушы механизмнің бірі болып табылады. Қоршаған ортаға тасталынатын заттар мен олардың қосылыстарының таралу жолдарын, химиялық реакцияларын және биосферамен әрекеттесуін зерттеу, қоршаған ортаға теріс әсерді азайту құралдарын табуға көмектеседі. Тасталымдарды азайту жолдарының бірі – қоршаған ортаны қорғау мәселелерін шешудің оңтайлы нұсқаларын іздеу. Мұндай шешімдер ластаушы заттардың шығарындыларын бақылаусыз және атап айтқанда, экологиялық сараптамасыз мүмкін емес. Алматы қаласы мен оған іргелес аумақтардың ауыр металдармен ластануы бойынша алғаш рет 2018-2020 жылдары ғылыми-зерттеу бағдарламасы жүргізілді. Бұл жоба топырақ пен қар жамылғысында келесі элементтердің: мыс (Cu), мырыш (Zn), никель (Ni), қорғасын (Pb), кобальт (Co), кадмий (Cd) концентрацияларының өзгеру динамикасын зерттеуге мүмкіндік берді. Литосферамен қатар Қапшағай су қоймасының акваториясы да зерттелді. Одан басқа, тотығу, қышқылдық, минерализация және қалқымалы заттар туралы мәліметтер алынды. Сонымен қатар, полихлорилбифенил қосылыстарымен ластану динамикасы зерттелді. Металдардың концентрациясы жалынды атомдық-абсорбциялық спектрометриялық әдісімен анықталды. Литосферада аталған химиялық элементтердің болуы антропогендік фактордан басқа табиғи ластану көздерінің болуын болжауға мүмкіндік берді. Мақалада

Алматы агломерациясының аумағындағы қар жамылғысының мыспен ластану көзін іздеуге талдау жасалған. Мыс тасталымдарының көзі табиғи болып саналады. Жел режимін талдау негізінде литосфераны мыспен ластау көздерінің орналасу аймақтары потенциалды түрде анықталады. Мыстың шоғырлануының жоғарылау кезеңінде қар жамылғысынан бос аумақтардың орналасуын зерттеу, ластаушы ретінде мыс бөлшектерінің тасымалдануын өндіретін аймақтардың орнын анықтауға мүмкіндік береді.

Түйінді сөздер: Ластану, мыс, қар жамылғысы, жел, ауыр металдар.

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ЗАГРЯЗНЕНИЕ МЕДЬЮ СНЕЖНОГО ПОКРОВА АЛМАТИНСКОЙ АГЛОМЕРАЦИИ

Аннотация. Природная среда крупных городов подвержена сильной антропогенной нагрузке. Загрязнениям подвергается как почва, так и гидросфера. При этом атмосфера является одним из средств механизма переноса загрязняющих веществ, попадающих в живые организмы. Изучение путей распространения, химические реакции и взаимодействие с биосферой выбрасываемых в природу веществ и их соединений помогают найти средства для минимизации негативного воздействие на окружающую среду. Одним из путей сокращения затрат является поиск оптимальных вариантов решения проблем охраны окружающей среды. Такие решения невозможны без мониторинга выбросов загрязняющих веществ и эколого-аналитического контроля, в частности. Для города Алматы и близлежащей территории впервые в 2018-20 гг., проведена программа исследований по загрязнению тяжёлыми металлами. Данный проект позволил изучить динамику изменений концентраций в почве и снежном покрове следующих элементов: медь (Cu), цинк (Zn), никель (Ni), свинец (Pb), кобальт (Co), кадмий (Cd). Наряду с литосферой была исследована акватория Капшагайского водохранилища. Кроме этого, получены данные по окисляемости, кислотности, минерализации и взвешенным веществам. Также изучена динамика загрязнений полихлорилбифенильными соединениями. Концентрация металлов определялась пламенным атомно-абсорбционным спектрометрическим методом. Присутствие указанных химических элементов в литосфере позволило предположить наличие

природных источников загрязнений на фоне исключения антропогенного фактора. В статье приводится анализ поиска источника загрязнений медью снежного покрова на территории Алматинской агломерации. Предполагается естественное происхождение источника выбросов меди. На основе анализа ветрового режима потенциально определены зоны нахождения источников загрязнения литосферы медью. Исследование расположения участков, свободных от снежного покрова в период роста концентрации меди, позволит определить более точное местоположение зон, продуцирующих перенос частиц меди как загрязняющего вещества.

Ключевые слова: загрязнение, медь, снежный покров, ветер, тяжелые металлы.

Introduction. In 2018-2020, in the laboratory of Hydrochemistry and Ecological Toxicology of the JSC "Institute of Geography and Water Security", for the first time (at least since the beginning of the 21st century) systematic research program was carried out on pollution by heavy metals and halogen-hydrocarbon compounds (polychlorinated biphenyls) of soil and snow cover of the territory of Almaty agglomeration.

Among the studied heavy metals in 2018-2020, the content in the soil and snow cover of the following elements was determined: Copper (Cu), Zinc (Zn), Nickel (Ni), Lead (Pb), Cobalt (Co), Cadmium (Cd). In addition to these pollutants, the content of suspended particles, oxidizability and acidity (pH) were also measured. The results of the conducted research can be used by environmental authorities to assess the condition of the environment and develop measures to reduce the negative impact to the territory not only within the area where people live, but also to wildlife areas that have both recreational potential and biodiversity conservation areas (Cherednichenko et. al., 2014; Madibekov et al., 2019; Madibekov et al., 2020; Amirgaliyev et al., 2022; Normatov et al., 2020).

Apart from the anthropogenic load to the natural environment, the natural region with a high content of one or more pollutants can serve as a source of pollution of the local area. The mechanism for the transfer of substances can be both: atmospheric air flows, precipitation, dissolution and removal of pollutants by groundwater as well as biological component of the chemical elements migration in the habitat of flora and fauna. In addition, there could be the natural mobility of chemicals, both individual elements and complex compounds, in the earth's crust (Cichała-Kamrowska et al., 2011; Felenberg et al., 1997).

This article considers Almaty agglomeration snow cover pollution by copper during the winter months of 2018 and 2019. The study object is the snow cover, which has a high sorption capacity and is the most informative in the study of technogenic atmospheric pollution (Reynolds et al., 2020; Vinogradov et al., 1967). Snow absorbs a significant part of the technogenesis products, accumulates them during the winter period and during the spring snowmelt, these substances enter the natural environment, mainly water and soil and polluting them. Consequently, the chemical analysis of snow will allow predicting the composition of future migrants in various natural objects of

urban landscapes, to determine the sources of pollution (Circular on target… et al., 2010). In addition, the period of snow cover is several months, which makes it possible to track the dynamics of pollution levels in a shorter period of time with a smaller degree of atmospheric turbulence. The periods between samplings at which there was a significant change in the pollutant concentration make it easier to localize in time and space the location of potential pollution source.

At the same time, the source of copper emissions is not known at first glance. Near the city of Almaty there are no copper smelters, no mining and processing facilities, and there are also no other industrial facilities that can serve as a source of copper emissions, both in pure form and in chemical compounds. Thus, we can assume the presence of natural pollution source, emissions from which can be carried by wind flows. Taking into account the presence of gray soils in the foothill zone of the Ile Alatau, the copper content in the soils of this altitudinal zone seems hardly probable, especially in the winter season (Kurmangaliyev et al., 1968:82; Durasov et al., 1981:152). Nevertheless, the transport of copper particles by wind is, in our opinion, the only mechanism for the transfer of this substance to the places of its accumulation, regardless of the pollution source nature.

The physiological activity of copper is associated mainly with its inclusion in the composition of the active centers of reductive-oxidative ferments. Insufficient copper content in soils adversely affects the synthesis of proteins, fats and vitamins and contributes to the infertility of plant organisms. Copper is involved in the process of photosynthesis and affects the absorption of nitrogen by plants. At the same time, excessive concentrations of copper have an adverse effect to the plant and animal organisms. The most effective method for assessing the degree of impact of technogenic load to the environment of cities and public health is the monitoring of atmospheric precipitation pollution (Felenberg et al., 1997:232; Vinogradov et al., 1967). It is these factors that are the main reasons for the study of copper pollution within the Almaty agglomeration.

Research methodology. Snow sampling for chemical analysis was carried out not only in the territory of Almaty city. Five zones were conventionally identified: mountainous territory; the territory of Almaty city; small towns and urban-type settlements; small settlements; coast of the Kapshagay reservoir. A total of 338 samples were taken during the project implementation period; 3525 physicochemical and toxicological measurements and analyzes were made.

Samples were taken at the time of maximum snow cover accumulation in the last ten days of January and first ten days of February 2018; in February 2019, and also in February 2020.

Heavy metals in the samples were determined by the flame atomic absorption spectrometric method with pretreatment of the samples on AA-7000 atomic absorption spectrophotometer from Shimadzu (Japan). That is atomic absorption spectrometer with a hollow cathode lamp for the respective metals to correct the coefficient of nonspecific absorption and with acetylene-air jet burner (Felenberg et al., 1997:232).

Sampling was carried out in an open flat area, 100 m away from local sources of

pollution during the period of maximum accumulation of moisture content in the snow along with measurements of snow density and moisture content in the snow measuring route. Snow samples were taken by the pit method for the entire thickness of the snow cover, with the exception of a 5 cm layer above the soil, with measurements of the sides and depth of the pit, depending on the snow cover. Sampling was carried out in sites with the area of 1 m^2 in plastic bags. The dimensions of the pit were measured in length and width to calculate the area of atmospheric precipitation. By sampling, the ingress of foreign substances was excluded, both at the time of sampling and during their storage and transportation to the laboratory. Due to the fact that the content of substances dissolved in sediments is small and is measured in milligrams or even fractions of a milligram per 1 dm^3 of water, strict observance of the conditions for sampling, storage and analysis of samples is required. The organization of transportation of samples ensured the minimum time between sampling and analysis of sediment samples.

The samples delivered to the laboratory were stored at – 5 – 15°C until they were processed. To melt the snow, the samples were placed overnight in pre-prepared containers. The settled samples were filtered through a paper filter with a white tape for further chemical and toxicological analysis.

The sampling results are shown in Table 1, which shows data about the concentrations of copper in the snow cover. The data presented in Table 1 characterize the spatial and temporal distribution of the copper content in the snow cover throughout the territory of the Almaty agglomeration.

Table 1. The content of copper in the snow cover of different zones of Almaty agglomeration for the three years of study.

Zone		Samples	Cu μg/dm^3		
№	Name		2018	2019	2020
1	Shymbulak Mountain Resort	1	0,0	2,6	25,9
		2	8,6	3,2	
		3	8,6	1,3	
2	Territory of Almaty city	1	3,6	4,9	26,1
		2	9,9	4,0	
		3	10,4	1,7	
3	Small towns, urban-type settlements	1	4,7	3,8	24,2
		2	11,1	3,2	
		3	9,9	2,0	
4	Small towns	1	5,3	2,5	23,4
		2	13,7	2,2	
		3	11,1	2,7	
5	Kapshagay reservoir and its coastal zone	1	5,0	3,7	24,6
		2	13,6	1,1	
		3	10,1	3,9	

As can be seen from Table 1, in 2018, in all five zones, in the period between the first and second surveys (sampling), there was a significant accumulation of copper in the snow cover. This was especially typical for Shymbulak Mountain Resort area,

small settlements and the coastal zone of Kapshagay reservoir. Small settlements are distributed throughout the territory of Almaty agglomeration and the average copper content characterizes in this case most of the territory. But, as it is illustrated below, to the east of Talgar town there was a zone with a high content of copper in snow cover. A year later, from survey to survey by zones, there was multidirectional dynamics of changes in the concentration of copper in the snow. In the mountainous area between the first and second surveys, there was an increase of the copper content in snow cover. At the same time, changes in the copper content in all zones, between surveys, did not exceed 3 μg/m^3. Data for 2020 is provided for comparison with previous years, and show the highest rates for the entire three-year study period.

Research results. According to the data provided in Table. 1, the increase of copper content in snow cover in the limits of the Mountainous area in 2018 is most clearly observed between the first (February 9) and second (February 24) surveys. The correctness of the data is confirmed by the results of the third survey, made on February 27. During the three-day period between the second and third surveys, there was no change in the concentration of copper in snow cover within the mountainous area. Good conditions for finding the source of pollution developed between the first and second surveys in 2018. These conditions include the following factors:

- Noticeable increase in copper concentration from 0.0 to 8.6 μg/dm^3.
- Short two-week period, from 9 to 24 February.
- Locality and remoteness from the industrial center territory, the location of which reduces the potential participation of the technogenic component of copper emissions into the environment.

Among the disadvantages, we can note: the singleness of the sampling site, lack of long-term observations, and regularity of the assumption of the existence of a mechanism for the transfer of copper particles by wind from the source to the sampling site.

A similar picture took place in 2019. At the same time, the increase in the concentration of copper in snow cover was not so significant, and amounted to 0.6 μg/dm3 between the first (January 22 - 26) and the second (February 04 - 08) surveys. The third survey, carried out at the end of February, revealed 2.5-times decrease of the copper content in snow cover compared to the previous survey. The conditions in 2019 will allow comparing the results of the search of the source zone from which come copper emissions registered in snow cover.

The soil cover in the considered area mainly forms ordinary grey soils and meadow-grey soils [9, 10]. At the same time, in the northwestern part of the coast of the Kapshagai reservoir, there are red earth soils, in which a high copper content could be presented. Naturally, such soils can serve as a potential source of copper near to the Kapshagai reservoir, when red earth sediments are released from snow cover.

It should be noted that measurements of wind direction and speed at weather stations are made at a height of 10 meters from the earth's surface. At the same time, the height of the transferred particles can differ significantly (in both directions) from the height at which wind measurements are taken. But, since the snow samples are taken from the surface of the earth, the representativeness of the available wind data has to be

considered with a certain degree of tolerance. Naturally, such a tolerance is limited by the scale of the roughness of the earth's surface (from fluctuations in the roughness of the ice crust to the heights of urban development, vegetation and relief), as well as turbulence in the atmosphere, where the particles of the precipitated substance moving and settle (Marsalek et al., 2014). A weak, but still fact, in defense of such a tolerance is the fact that the elevation difference from south to north in the zone of maximal depositing of pollutants exceeds a ten-meter mark.

The accumulation of copper in snow cover and the search of its sources require the analysis of the wind regime during the period of increasing copper content. For this reason, to the concentration distribution maps were added the diagrams of the prevailing wind directions at the meteorological stations "Shymbulak", "Kamenskoye Plateau" and "Esik town". These diagrams show the repeatability of the directions of the prevailing winds. Information about wind directions at the time of meteorological observations was taken from the site "Weather schedule rp5.kz" (Weather Schedule, 2022). For Shymbulak Mountain Resort, the constructed diagram indicates significant predominance of east and east-southeast winds during the period of increasing copper concentration in the snow cover in 2018. The data of the station "Kamenskoye Plateau" were taken to clarify the wind regime of the station "Shymbulak", as the closest observation location to the sampling point. As follows from Figure 1, according to the weather station "Kamenskoye Plateau", during the period under review in 2018, winds of the southern and southwestern directions prevailed.

The zone of maximum snow cover pollution in 2018 was located east of the Almaty city. The average distribution of copper content in snow cover does not reflect changes in the level of contamination between sampling periods. The distribution of levels of copper content characterizes the process of pollutant accumulation in snow cover. In the warm season, the main axis of the distribution of copper concentrations in the soil crosses the territory of Almaty city from the southwest to the northeast. By analyzing the wind regime that provides a certain level of snow cover pollution by copper in mountainous area, a sector of the potential location of the copper pollution source is singled out. It is located in the southeastern part of Almaty city on the eastern side of Ulken Almaty River in the mountainous area. The wind regime of the mountainous territory in 2018 had the main features also in 2019 during the period of increasing copper concentration in snow cover. That is confirmed by the similar data provided in Figure 2.

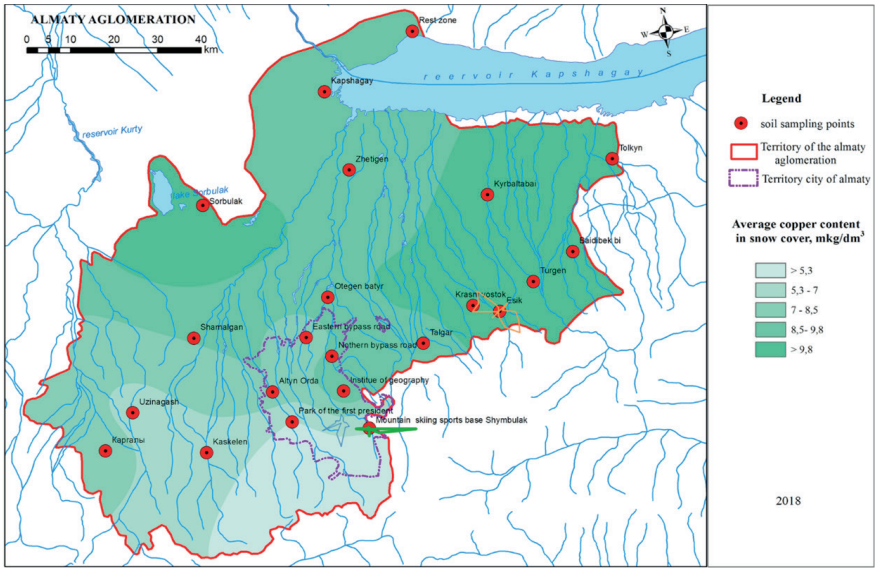

Figure 1. Average copper content in snow cover in 2018. Frequency diagrams of wind directions for the stations “Kamenskoye Plateau”, “Shymbulak” and “Esik” are also shown

The main area with a high content of copper in snow cover in 2019 was located in the territory of Almaty city. As can be seen from Figure 2, the axis of copper pollution concentrations in the city was located from southeast to northwest. According to the data presented in Table 1, in 2019, from survey to survey, there was a decrease in the concentration of copper in snow cover in the city. But in 2018 sampling showed an increase in copper content from the middle to the end of the winter period. In general, for the mountainous area in the limits of Almaty city, the distribution of the prevailing wind directions is characteristic within the range from east to south-west (90° - 225°). It is also worth paying attention to the zone of copper pollution between the towns of Talgar and Esik, where the wind of south and northwest direction took place. But this zone is not clearly expressed and was determined from year to year by seasons with a large spread in space. Copper concentrations in the lithosphere in this zone varied from 5 to 13.6 μg/dm^3 in 2018 and within the limits of 0.1-6.1 μg/dm^3 in 2019. Weakly expressed zone of copper pollution in the warm season appears in the west of the city limits. The source of this pollution may be located near the village of Izvestkovyi.

As can be seen from the figures, there is no direct relationship between the wind fields during the period of maximum change in the copper concentration in snow cover and the total accumulation of the pollutant. There could be several reasons for this: uncoordinated time moments of copper accumulation and periods of analysis of the wind field; difference between the level of wind measurement and the height of the pollutant transfer level; influence of atmospheric turbulence; incomplete understanding of the transport mechanism of the considered pollution element; possible influence of other factors (for example, the presence of obstacles for airflow, multiple deposition by particles moving), etc.

Studies conducted in 1987 by Kobzar and Tavrish (Kobzar et al., 1987:105) revealed an increased content (mg/dm^3) of zinc 700, copper 35 in atmospheric precipitation in the territory of Almaty. According to the research of M.S. Panin (Panin et al., 2011), in Almaty, the content of lead (Pb) in soils exceeds the sanitary standards by 2.9 times, and copper (Cu) by 4.4 times. In other words, a steady trend of high concentrations of copper, zinc and lead is continued for several decades.

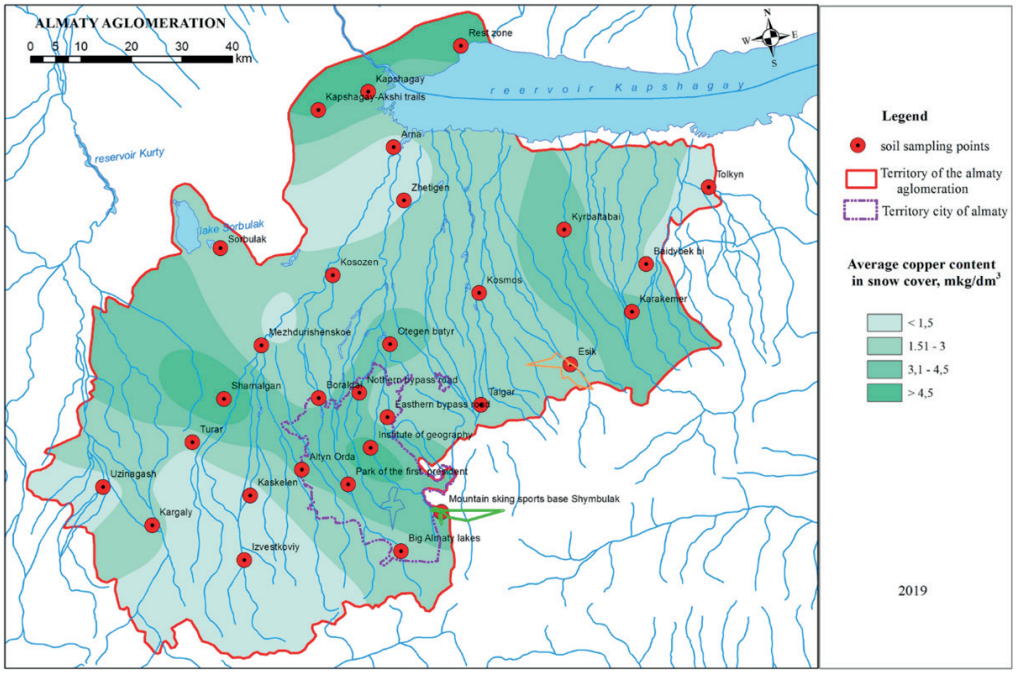

Figure 2. Average copper content in snow cover in 2019. Frequency diagrams of wind directions for the stations “Kamenskoye Plateau”, “Shymbulak” and “Esik” are also shown

Discussion. The existing dynamics of the copper content in snow cover leads to the conclusion that it is necessary to search the sources of these substances. In the case of lead, the source is more or less known - it is tetraethyl lead, a component of motor fuel. But it should be noted that additives containing lead are not used in motor fuel (Madibekov et al., 2011). An increased concentration of lead in the area of Shymbulak Mountain Resort may also indicate a natural source of this substance. Similar situation is observed in the area of Kaskelen town and to the north-west of Shamalgan village, as a result of neighborhood of the copper ore province, located to the north-north-west of Shamalgan village at a distance of up to 80 km, near to the area of Zhynkeldy River mouth. From this part of the region copper is transported towards the southern coast of the Sorbulak reservoir. The combination of high concentrations of copper and lead in the lithosphere, as well as the amplitude of concentration fluctuations over a short period of time, indicate the potential location of the source outside the city limits, which confirms its natural origin. Thus, lead is considered as the most characteristic substance, the entry

of which in the underlying surface is most typical for the anthropogenic sources. The increased content of copper in the area of recreation zone of Kapshagay reservoir may indicate another geological province. As evidenced by the red-brown soils which are characteristic for this area.

The listed places of the potential location of the zones-sources of copper pollution can also be localized and significantly refined using the analysis of satellite images. The allocation of areas of the territories of Almaty agglomeration free from snow cover, during the studied periods, can directly indicate the location of soils with a high copper content.

Apart from the copper content in snow cover, the presence of nickel and zinc in the snow cover and soil is also of interest (Barcan et al., 1996; Hubbard et al., 2007). The centers of maximum concentrations of both elements are located approximately in the same place - in the north-eastern part of Almaty city and partly in Talgar area. The presence of nickel can be considered as accompanying element in copper ores. Deposits of zinc-bearing ores often border with copper deposits (Itsikson et al., 1950). High concentration of zinc is also observed to the west of Almaty. A separate study also deserves the search for sources of cobalt and cadmium, since, by analogy, the version of their natural origin is not excluded. But for these two substances, the version of anthropogenic pollution should also not be excluded. In further studies, it is also necessary to assess the reasonability of judgments about the scale of emissions from technogenic sources that form the registered concentrations of these substances in the natural environment of Almaty agglomeration. In other words, the inventory of emissions within the limits of the city will help to determine the genesis of pollution sources and take environmental protection measures.

The content of lead in the lithosphere and atmosphere of the studied area also requires assessment of the scale of emissions from the burning fuel of vehicles. Otherwise, it is needed to determine a natural source of lead coming into the atmosphere.

Conclusion. The absence of obvious anthropogenic sources of copper pollution of the lithosphere within the limits of Almaty agglomeration leads to the need to search for natural sources. Such a search is indicated by the dynamics of copper concentration levels in snow cover. Taking into account the wind field in mountainous areas and distribution of soil types, we can identify the following potential location of the zones-sources of copper pollution: southern and south-eastern parts of the territory of Almaty, located in the limits of 90° - 225° from east to southwest direction and in the eastern bank of Ulken Almaty River in the mountainous zone. The

source of copper, near the Kapshagay reservoir, can be the red earth sediments during the melting of snow cover (in the cold half-year, taking into account the wind field). A weakly expressed zone of copper pollution in the warm season appears in the west of the city limits. The source of this pollution can be located in the area between the village Izvestkovyi and Kaskelen town. Another weakly expressed zone of copper pollution is located between the towns of Talgar and Esik.

The presence of nickel and zinc in the snow cover and soil can be considered as an accompanying element in copper ores. The centers of maximum concentrations of

both elements are located approximately in the same place - in the north-eastern part of Almaty city and partly in Talgar area. High concentration of zinc is also observed to the west of Almaty. And that is, despite the apparent absence of anthropogenic sources, also indicates the natural origin of these heavy metals in the soil and creates the need to search for sources of these substances.

The search for zones-sources of heavy metals entering the soil and snow cover can be carried out by analyzing satellite images covering periods of increasing concentrations of heavy metals in snow cover (Hubbard et al., 2007). The localization of areas free of snow cover, taking into account the wind field, may indicate the direct location of metal ore deposits that provide the observed level of pollution.

By the further assessment of the contribution of anthropogenic factor to the source of cadmium, cobalt, and lead entering the lithosphere, it is also required to search for natural sources of these substances (Forbes et al., 1976; Street et al., 1977). This may indicate sediments that include chemical compounds of the mentioned elements.

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