

Heavy Metals in the Air and Snow Cover of Ulan Bator

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Abstract—Field observations have been used to characterize air pollution in Ulan Bator by heavy metals during the 2008/2009 heating season. The degree of technogenicity of emissions and their main sources are determined. The diurnal and seasonal dynamics of atmospheric pollution are considered. It is found that many pollutants exceed maximum permissible concentrations (MPC). The most dangerous components in the urban atmosphere include Pb (up to 26 mean daily maximum permissible concentrations (MPCmd) and airborne particles (up to 21 MPCmd). The study revealed very high levels of total air pollution, especially in the center of the city (air pollution index (API) > 50). Soluble forms of heavy metals as contained in the snow are characterized by a maximally high degree of pollution hazard for the urban environment, with a low degree corresponding to solid-phase depositions. Snow cover pollution decreases as follows: yurt districts > industrial zone > multi-storey districts.

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INTRODUCTION

Assessments of the air quality situation in cities are usually limited to determining the amount of gaseous components and the various dust fractions. Heavy metals and metalloids (HM) that are supplied in large amounts to the air environment as a result of anthropogenic activity are less well studied. This is accounted for by the characteristics of atmospheric monitoring networks that are not specifically designed for automated measurements of HM concentrations, and by the complexity and high cost connected with determination of the trace element composition of aerosols. HM content levels in the air are most commonly roughly estimated by indirect methods using the relationships between amounts of HM supplied to the atmospheric air and their deposited amounts recorded in the snow cover [1].

Ulan Bator is grouped with five cities of the world with the most heavily polluted atmosphere [2, 3]. The main contribution to pollution is made by local brown coals used in heating, which are distinguished by elevated contents of many HM, a long-lasting heating season (about 140 days), and by the city's location in the intermontane depression, which promotes polluted air stagnation. The unfavorable ecological situation is

compounded by the existence of extensive yurt districts in the city, because the yurts are heated by means of primitive stoves producing elevated amounts of brown coal combustion products [3–5]. As a result, this brings a real threat to human health, with an ever increasing incidence rate of lung cancer and cardiovascular and respiratory diseases. In 10% of cases, the polluted air is the chief cause for mortality [6]; therefore, investigations into HM content levels in the city's atmosphere are of particular current importance. The air of Ulan Bator is mainly monitored for concentrations of gaseous pollutants: NO_x, SO₂ and CO, synthetic organic substances, and the various dust fractions [3–10]. Pb contents are also examined in [3, 8, 10], and the macrocomponents of atmospheric dust (Al, Si, S, Ca, and Fe) are analyzed in [9].

The goal of this paper is to assess the air pollution by HM during a winter season when the city experiences the most severe technogenic pressure. The study is based on HM concentration measurements in atmospheric aerosols and in the snow cover of Ulan Bator for the winter 2008/2009. More specifically, the objectives were: 1) to determine the main atmospheric pollution sources and the composition of emissions; 2) to study the diurnal and seasonal dynamics of HM content levels

in the air in different districts of the city; 3) to compare the measured concentrations with existing sanitary norms, and 4) to make a differentiated (with respect to the functional zones) assessment of atmotecnogenic pollution of snow.

OBJECT FOR STUDY AND POLLUTION SOURCES

Ulan Bator is situated in a latitudinally extended intermontane depression drained by the Tuul river. The anticyclonic weather regime in the wintertime and the accompanying frequent temperature inversions promote accumulation of pollutants in atmospheric ground-level layers, and smog formation [3–5, 11, 12].

Currently the population of Ulan Bator is 1.11 million against the country's total population size of 2.74 million [13]. The number of urban inhabitants is increasing from year to year, especially because of the expansion of the yurt districts, with half the population of the capital city living there [3, 10, 13]. The city has about 160 thousand yurts and private houses, each of which consumes, on the average, 5 t of coal and 3 m³ of fuel wood per year for heating and cooking purposes [3]. In addition to private stoves, a significant contribution to atmospheric pollution comes from the fuel and energy complex represented by three thermoelectric plants (TEP) where about 5 mil. t of coal are burned every year, as well as by boilers consuming about 400 thou t of coal [8].

The TEP are all located in the industrial zone, while the boiler houses are concentrated in the multi-storey districts. Heating of the city uses brown coals from the Nalaikh, Baganuur and Chuluut deposits which are enriched (with respect to percent abundances of lithosphere) to extents by factors of several tens larger than Pb, As and Mo and several times larger than Cu, Sr, Cd and Ni, and, in comparison with the other brown coals, they are enriched with Pb, Cu, Ni, W and Mo [14]. An additional contribution to atmospheric pollution is made by the construction, woodwork and timber, light and food industries.

The motor transport, currently accounting for about 107 thousand automobiles, i.e. nearly 60% of Mongolia's transport vehicles, is the source of urban air pollution by Pb, Zn, Cd, Cu, Fe and V [13–15]. The discharges of exhaust gases from transportation facilities constitute 68% of the Pb emissions, because Mongolia has used leaded gasoline to date [3, 10]. The unfavorable ecological situation is compounded by constant traffic jams; the most congested sections of the roads deal with about 60 thousand vehicles per day [3].

Atmospheric pollution from different sources differs markedly in different seasons. In spring and autumn, the principal agents are wind erosion of soils, and burning of fuel wood; winters see a dramatic increase in the proportion of pollutants from coal burning. Atmospheric pollution in the summertime is lower because of seasonal storm rainfalls. Discharges

of exhaust gases from motor-vehicle transport are supplied to the atmosphere throughout the entire year in about the same amounts [9, 16].

MATERIALS AND METHODS

Field investigations were made in December – early March 2008/2009 by the Joint Integrated Russian-Mongolian Biological Expedition (Russian acronym: SRMKBE) of the Russian Academy of Sciences and the Mongolian Academy of Sciences. Samples of air aerosols and snow cover were collected. The city was divided into five functional zones differing by the type of utilization and by the specialization of pollution sources (Fig. 1). Observations of the state of the atmosphere were carried out at six points located within the boundaries of the multi-storey (points A-C) and yurt (D-F) zones. Using aspirators PU-3E and PU-4E, installed at the height of 1 m from the ground surface, the air was circulated through analytical aerosol filters AFA for 40 min at the rate of 10 L/min. A total of 132 aerosol samples were obtained.

Because of the windy snow-deficient winters, the snow cover occurs mainly on northern slopes [7, 11]. The snow was sampled to its entire depth by means of the sampling tube with a cross-sectional area of 20 cm², and 10 samples were taken at each of the 21 points (see Fig. 1), including three background points 10 km to the west of the city. The snow samples were melt at room temperature, and the solid and liquid phases were separated by filtration through ashless paper filters with the pores 2 μm in diameter. Discrimination phase analysis provided information on contents of mobile water-soluble forms of HM and forms associated with mineral and organomineral carriers [1].

The filters were used to determine the amount of airborne particles (AP) (hazard class III), and total HM contents by the ICP-MS method with Perkin Elmer Elan-6100 mass spectrometer in the Research Institute of Mineral Resources. We considered the chemical elements of hazard class I (Be, Cr, Cd and Pb), II (Mn, Fe, Ni, Cu, As and Co), III (Zn, Mo, Sn, Sb, W and Bi) and IV (V) as well as the elements that are not assigned to the hazard classes but govern the geochemical specific character of Ti, Sr, Th and U emissions [17, 18].

The degree of technogenicity of air aerosols and airborne snow water was estimated by using the coefficient of aerosol concentration $Ka = A/K$, where A is the concentration of an element in air aerosols, and K is percent abundance of this element in the granite layer of the earth's continental crust [19, 20]. The enrichment of the urban snow with HM was determined by calculating the concentration coefficient Kc relative to background values. Total pollution of the snow cover was characterized by the coefficient $Zc = \sum Kc - (n - 1)$, where n is the number of elements with $Kc > 1.0$ [15]. The values of Zc correspond to the territory's pollution hazard levels: low, not hazardous (< 32); medium, moderately hazardous (32–64); high, hazardous (64–128); very high, very hazardous

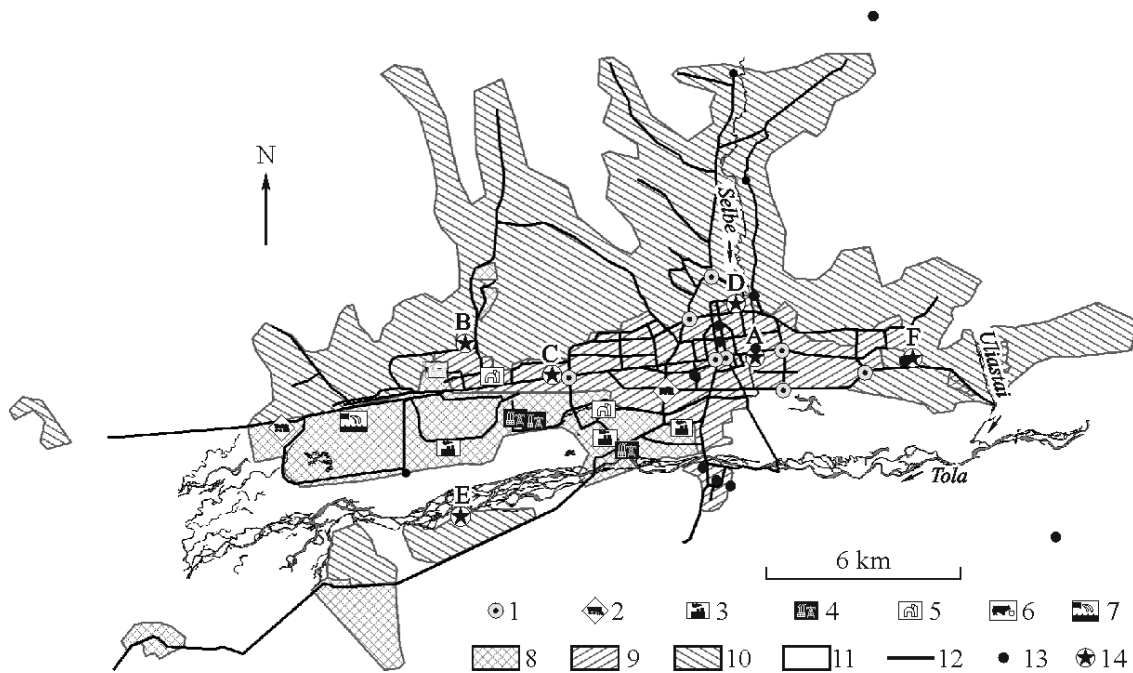


Fig. 1. Pollution sources, functional zoning of Ulan-Bator and sampling points.

Transport objects: (1) large circular crossroads, (2) railway station building. Industrial installations: (3) TEP, (4) construction, (5) textile, (6) food, (7) pollution control facilities. Functional zones: (8) industrial, (9) multi-storey district, (10) yurt district, (11) recreation, (12) transport. (13) snow cover sampling points; (14) point of observation of atmospheric air conditions: (A) Institute of Geography, Mongolian Academy of Sciences, (B) Tolgoit, (C) 1st microdistrict, (D) Chingeltei, (E) Yaarmak, (F) Joint Russian-Mongolian Integral Biological Expedition Base.

(128–256), and maximally high, exceptionally hazardous (> 256).

Sanitary assessments used the (developed in Russia) maximum permissible maximum-single (MPSms) and mean daily concentrations (MPCmd) of pollutants in the atmospheric air of settlements [17]. The degree of air pollution was determined from HM contained in it and expressed by fractions of MPC. The HM summation effect was estimated by using an integral atmospheric pollution index (API) as calculated by the formula: $API = \sum(C_i/MPC_i) \cdot K_i$, where C_i – is the mean daily concentration of the i -th substance in the air, MPC_i is its MPCmd, and K_i is a coefficient for converting air pollution by the i -th substance to pollution by SO_2 . The values of K_i are 1.5; 1.3; 1.0, and 0.85, respectively, for hazard classes I, II, III and IV. Depending on the API values, the air pollution level was determined as low ($API < 5$), elevated (5–7), high (7–14) or very high (> 14) [18]. The atmospheric pollution indices as developed by European and American scientists have not been used in the present case, because they are intended for contents of oxides and AP in the air and disregard HM contents [21].

A statistical processing of data involved calculating selective average C_{av} , standard deviations, variation coefficients C_v , and fluctuation amplitudes of element contents using the Microsoft Excel and Statistica 7.0 software packages. Paragenetic associations of elements with common regions of accumulation and removal

were identified by using cluster analysis (the *Single Linkage* algorithm), and the similarity in the behavior of elements was estimated by the correlation coefficient r . Interpolation of HM concentrations at the stage of mapping was done by the method of inverse distance weighting in the ArcGIS 10.0 software package.

ASSESSING THE POLLUTANTS EMISSIONS TO THE ATMOSPHERE

Chemical Composition of Atmospheric Dust

Dust contained in the atmospheric ground-level layer of Ulan Bator is dominated, as regards fraction of total mass, by Sr and Fe whose concentrations range from $n \cdot 10$ to $n \cdot 100 \mu\text{g}/\text{m}^3$ (Table 1). Pb, Mn, Ti, Cr, Cu, Ni and Zn form a group with concentrations from $n \cdot 0.1$ to $n \mu\text{g}/\text{m}^3$. Fe and Ti have high percent abundances; together with Mn, Cr and, partly, with Zn they enter the atmosphere with terrigenous dust [9]. Elements of high technophilia (Pb, Cr and Zn) are intensely discharged in the process of the economic activities. [22]. The content of Co, As, Mo, Be, Sb, Sn, W, V, Th and U varies from $n \cdot 0.001$ to $n \cdot 0.01 \mu\text{g}/\text{m}^3$; the smallest fraction of total mass corresponds to Cd and Bi. Many of these HM refer to the elements of geochemical specialization of brown coals used in the city for heating purposes [14].

Mean daily samples of atmospheric dust and airborne snow are enriched with chalcophile and siderophile elements which are supplied to the atmosphere

Table 1. Daily mean concentrations of heavy metals in airborne dust ($\mu\text{g}/\text{m}^3$) at six observation points, Ulan Bator

Date of observation	Hazard class																Not assigned to hazard classes				
	I				II				III				IV				Sr	Th	Ti	U	
	Be	Cr	Pb	Cd	As	Co	Cu	Fe	Mn	Ni	Bi	Mo	Sd	Sn	W	Zn					V
15.12.08	$3 \cdot 10^{-2}$	2.9	7.7	$15 \cdot 10^{-3}$	0.040	0.02	2.4	31	0.8	2.1	$2.6 \cdot 10^{-3}$	0.07	0.100	0.338	0.021	2.1	0.004	50	0.049	2.1	0.064
28–29.01.09	$2 \cdot 10^{-2}$	2.8	4.0	$11 \cdot 10^{-3}$	0.777	0.02	1.9	95	9.5	2.6	$4.9 \cdot 10^{-3}$	0.11	0.067	0.162	0.031	3.4	0.050	82	0.028	11	0.083
6–7.02.09	$2 \cdot 10^{-2}$	2.5	3.0	$44 \cdot 10^{-3}$	0.717	0.06	1.8	126	11	2.6	$4.2 \cdot 10^{-3}$	0.09	0.067	0.075	0.050	3.8	0.131	93	0.034	15	0.095
4–5.03.09	$2 \cdot 10^{-2}$	2.0	3.9	$16 \cdot 10^{-3}$	0.023	0.01	1.5	99	9.4	2.3	$3.4 \cdot 10^{-3}$	0.08	0.056	0.069	0.050	2.9	0.078	79	0.024	12	0.076
20–21.01.09	$1 \cdot 10^{-3}$	0.8	0.9	$0.3 \cdot 10^{-3}$	0.002	0.02	0.6	29	0.9	1.3	$0.2 \cdot 10^{-3}$	0.11	0.004	0.078	0.018	0.7	0.023	0.5	0.005	1.3	0.002
7–8.02.09	$2 \cdot 10^{-3}$	0.5	2.8	$2.2 \cdot 10^{-3}$	0.002	0.03	0.5	30	1.2	0.7	$0.6 \cdot 10^{-3}$	0.07	0.005	0.034	0.012	0.5	0.019	0.3	0.006	1.3	0.003
6–8.03.09	$3 \cdot 10^{-3}$	0.8	0.1	$0.1 \cdot 10^{-3}$	0.002	0.05	0.5	36	2.0	1.0	$0.1 \cdot 10^{-3}$	0.06	0.003	0.024	0.019	0.6	0.016	0.5	0.007	2.1	0.003
31.01 – 1.02.09	$1 \cdot 10^{-3}$	0.6	1.8	$0.3 \cdot 10^{-3}$	0.007	0.02	0.4	21	0.5	0.7	$0.2 \cdot 10^{-3}$	0.04	0.002	0.009	0.008	0.6	0.007	0.5	0.002	0.9	0.002
8–9.02.09	$1 \cdot 10^{-3}$	0.5	3.8	$3.0 \cdot 10^{-3}$	0.012	0.01	0.5	20	0.5	0.9	$0.3 \cdot 10^{-3}$	0.03	0.001	0.018	0.009	0.8	0.000	0.4	0.003	1.2	0.002
3–4.02.09	$2 \cdot 10^{-3}$	0.6	0.2	$0.3 \cdot 10^{-3}$	0.012	0.02	0.3	23	0.6	0.9	$0.2 \cdot 10^{-3}$	0.03	0.001	0.005	0.010	0.5	0.031	0.5	0.004	1.2	0.003
9–10.02.09	$1 \cdot 10^{-3}$	0.7	1.5	$0.8 \cdot 10^{-3}$	0.009	0.03	0.4	26	0.6	0.7	$0.1 \cdot 10^{-3}$	0.03	0.001	0.006	0.010	0.5	0.033	0.4	0.005	1.3	0.002
14.12.08	$3 \cdot 10^{-3}$	0.8	0.9	$2.5 \cdot 10^{-3}$	0.035	0.03	0.5	34	0.7	1.0	$0.9 \cdot 10^{-3}$	0.04	0.008	0.034	0.015	1.5	0.059	0.5	0.006	2.3	0.005
30–31.01.09	$3 \cdot 10^{-3}$	0.5	2.8	$2.0 \cdot 10^{-3}$	0.010	0.03	0.5	37	1.1	1.0	$0.5 \cdot 10^{-3}$	0.04	0.003	0.018	0.014	0.7	0.047	0.7	0.008	4.5	0.003
4–5.02.09	$3 \cdot 10^{-3}$	0.7	0.6	$0.3 \cdot 10^{-3}$	0.022	0.03	0.5	48	1.4	0.8	$0.2 \cdot 10^{-3}$	0.03	0.003	0.005	0.013	0.4	0.063	0.8	0.011	3.4	0.005
11–12.02.09	$3 \cdot 10^{-3}$	0.5	1.3	$0.3 \cdot 10^{-3}$	0.010	0.02	7.0	36	0.9	0.8	$0.2 \cdot 10^{-3}$	0.05	0.003	0.007	0.020	6.3	0.044	0.7	0.008	2.1	0.004

p. A – Institute of Geography (center of the city, multi-storey district)

p. B – Tolgoit district (west, multi-storey district)

p. C – 1st microdistrict (west, multi-storey district)

p. D – Chingeltei district (center, yurt district)

p. E – Yaarmak district (south-west, yurt district)

p. F – SRMKBE base (east, yurt district)

mainly together with industrial emissions and exhaust gases from transport vehicles: Sb, Pb, Bi, Zn, Cd, Mo, Sn, As and W (Table 2). Compared to the granite layer of the earth's crust, the concentration of these elements in atmospheric depositions is higher by factors of several tens and hundreds. Lithophile elements (Ti, V, Be, Th, Mn, U, Cr and W) and Fe accumulate weakly in aerosols, which is consistent with global tendencies for enrichment of atmospheric aerosols with HM [15, 20].

Comparison of HM concentrations in the air with standard concentrations showed that the most unfavorable situation has emerged in the center of the city where the concentrations of many pollutants exceed MPCmd (see Table 1, p. A): Pb (by factors of 10–26); Mn (by a factor of up to 11); Be and Fe (by a factor of 2–3); Ni (by a factor of 2–2.5); Cu and Cr (by a factor of 1–2), and Zn (by a factor of up to 1). AP content in the air is also extremely high throughout the entire winter period, varying from 6.5 to 21 MPCmd (Fig. 2,

a). The eastern part of the city is less polluted (see Table 1, p. E) where the standards of mean daily content of elements are exceeded for Pb (by a factor of 3–9.5), Cu (up to 7), Zn (up to 2), Mn (up to 1.5) and Ni (1),

Table 2. Accumulation rate of chemical elements in atmospheric depositions and in airborne snow water on the territory of Ulan Bator

Aerosol concentration coefficient K_a	Atmospheric depositions	Airborne snow water
$n \cdot 0.1 - n \cdot 1$	Ti, V, Co	–
$n \cdot 1 - n \cdot 10$	Mn, Fe, Th, Be, U	Mn, Fe, Th, Ti, V, Cr, Co, Ni, Cu, Sr
$n \cdot 10 - n \cdot 100$	Zn, Mo, Cd, Sn, As, Sr, Cu, Bi, Ni, Cr, W	Zn, Mo, Cd, Sn, As, U, Pb, Be
$n \cdot 100 - n \cdot 1000$	Sb, Pb	Sb, W, Bi

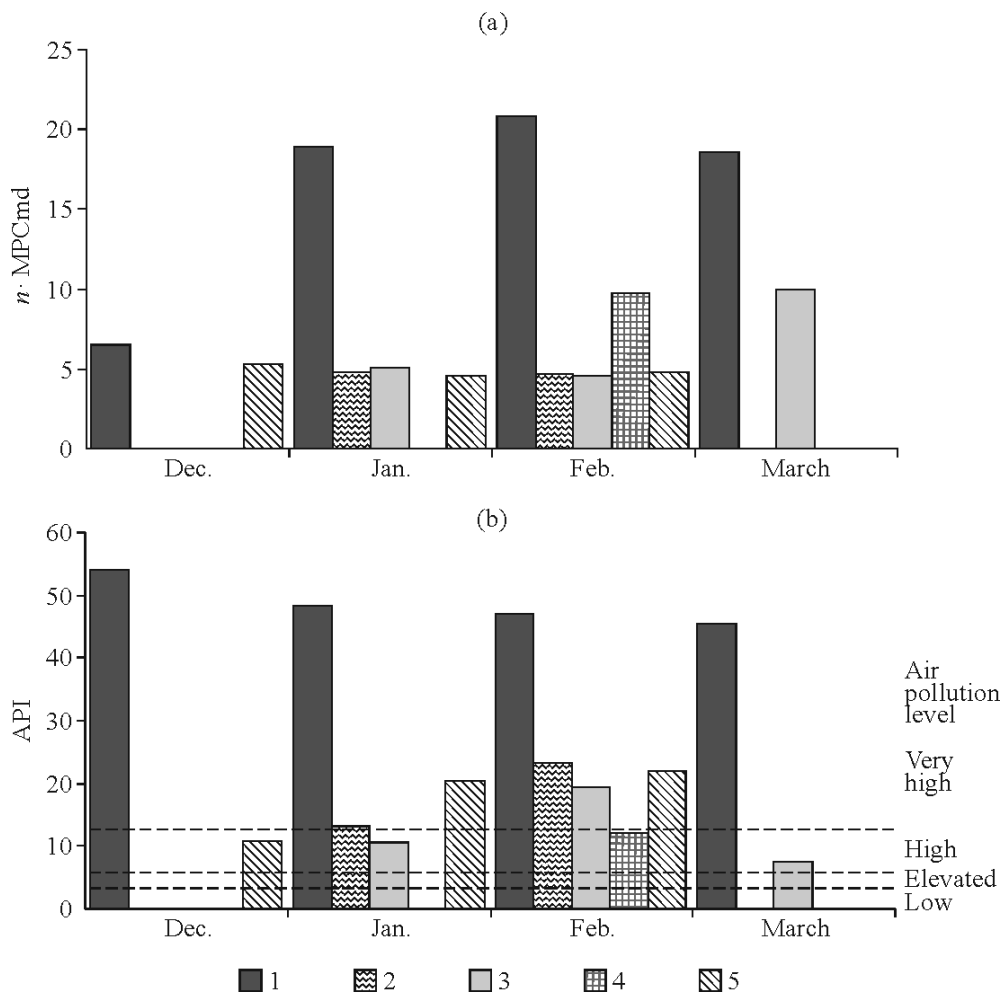


Fig. 2. Mean daily concentrations (in fractions of MPCmd) of airborne particles in the atmospheric air of Ulan Bator (a), and air pollution indices for the atmosphere of Ulan Bator (b) in December 2008 – March 2009.

(1) center of the city, multi-storey district (A), (2) center of the city, yurt district (D), (3) western part of the city, multi-storey district (B, C), (4) southwestern part of the city, yurt district (E), (5) eastern part of the city, yurt district (F). (A–F) for observation points, see Fig. 1 and Table 1.

while the AP in the air fluctuated between 4.5 and 5.3 MPCdm. Within the multi-storey district in the western part of the city (see Table 1, pp. B and C), the air showed elevated contents of Pb (3–9 MPCdm), Mn (up to 2) and Ni (up to 1.2). The yurt districts showed an excess of the standard for Pb: by a factor of 6–12 in the central part of the city, and of up to 5 in the southwestern part (see Table 1, pp. D and E, respectively). The entire area showed high AP contents, i.e. from 4.5 to 10 MPCdm in different months, which is in agreement with data from [4] for the winter seasons 1989/1990, 1990/1991 and 1992/1993 when their amounts were 1.65 mg/m³ (15 MPCdm).

Characteristics of Diurnal Behavior and Seasonal Dynamics of Air Pollution

The observations of the diurnal behavior of atmospheric air conditions were made in the central part of the city, in the vicinities to the Institute of Geography, Mongolian Academy of Sciences. Compared to December 2008, during January–March 2009 the content of Mn in the atmosphere increased 10–12 times, Ti – 7, Fe – 3–5, and Sr, Zn and Ni 1.5–2 times, whereas the Pb content decreased by a factor of 1.5–2. The concentrations of the other chemical elements changed little during the winter period.

For Mn, Cu, Pb and AP the MPCms were established [17], which makes it possible to assess their hazard to human health (Fig. 3). Cu contents in the atmosphere were at a relatively safe level, with the standards being exceeded only in January when a single emission of Cu was 3.5 µg/m³ (1.2 MPCms). The content of Mn in January–March was increasing during the daytime hours to 10.0–13.5 µg/m³ (1–1.4 MPCms). Only

rarely did the Pb concentrations only drop below 2 µg/m³ (2 MPCms), and they even reached 12 µg/m³ (12 MPCms).

AP content in the atmosphere during December–January did not exceed standard levels, whereas during February–March it increased considerably to reach 0.5 mg/m³ (1 MPCms). During the winter period, on the average, the AP content was 1.3 MPCms, which is responsible for the high incidence rates of chronic diseases [7]. The main sources of minor AP are provided by transport (abrasion of road pavement surface), and by the large-scale atmospheric transfer. The plots of diurnal behavior clearly show concentration peaks around 9–11 and 20–23 hours. Such peaks were also recorded when monitoring the Ulan Bator atmosphere in the winter season 2009/2010 [6, 7].

Thus the atmospheric air during the winter time was the least polluted in December 2008, pollution increased toward the beginning of February of the following year, and was dropping gradually toward March. Such a seasonal behavior of atmospheric pollution may be attributed to the fact that January and the beginning of February constitute the coldest time in the year, with a short duration of sunshine, the steady-state temperature inversion, and the maximum intensity of operation of the fuel and energy complex [11, 12]. The persistence of this tendency can only be corroborated through many years of monitoring.

In the summertime, the most severe atmospheric pollution was observed along the motor roads (Pb, Zn, V, Cd and Mo) and in the industrial zone (Mo, Cd and Zn). The As, Cd, Zn, Cu and Cr elements are normally concentrated near their sources, whereas Pb and V can be transported in the air to distances of several kilometers [16].

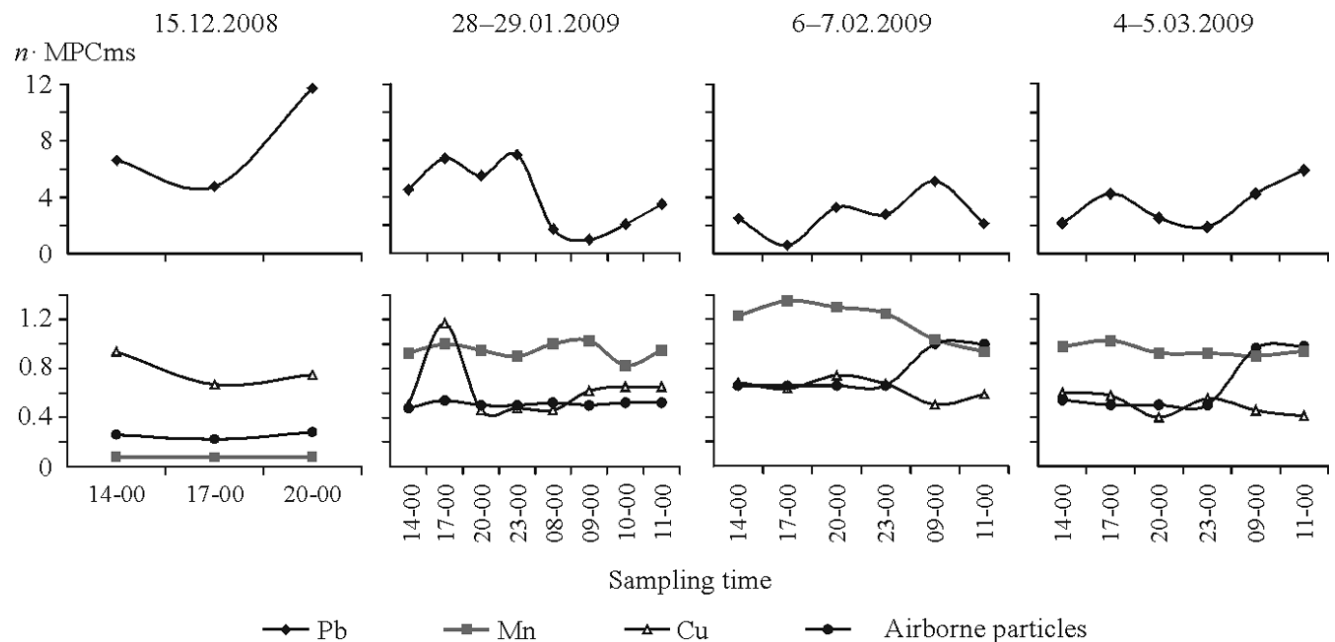


Fig. 3. Diurnal variation in Pb, Mn, Cu and dust contents (in fractions of MPCms) in the air of the central part of the city in December 2008 – March 2009.

*Assessing the Air Pollution Hazard
During a Winter Season*

Diurnal and seasonal variability of HM content levels in the atmosphere is governed by many factors. Analysis of the diurnal behavior of pollutants concentrations reveals numerous large single emissions of Pb, Mn and AP which give rise to and exacerbate respiratory diseases. The estimated mean daily concentrations point to a low quality of the atmospheric air which everywhere includes Pb, Mn, Cu, Ni, Zn and AP in amounts bringing the threat to human health, which leads to a reduction in human longevity [2, 5]. Pb brings the most serious threat; its content exceeds the permissible standards several tens of times throughout the entire winter period.

The highest total pollution by HM with extremely low API was recorded in the center of the city (see Fig. 2, b), which is accounted for by the characteristics of topography (the bottom of the depression, and the gentle feet of the slopes), and by heavy traffic. At points with lower elevations (see Fig. 1 and 2, b, item D), the API value is twice as large. Judging from the API values, air pollution is decreasing outward from the center of the city. In the center, the pollution level is very high throughout the entire heating season, while in the other districts of the city it is high or elevated. Overall, the state of the atmospheric air during the winter period is estimated as unsatisfactory and even dangerous to human health.

The atmospheric conditions in the city can be considerably improved via switchover to the more effective and environment-friendly types of fuels. In the first place, it is necessary to exclude the application of leaded gasoline, and actively introduce advanced technology in the field of coal gasification and water-coal fuels. In the yurt districts, stoves of the latest

modification with lower fuel requirements and smaller emissions.

ASSESSING DEPOSITIONS OF POLLUTANTS
ON SNOW COVER

HM Content in Snow Cover

The amount of airborne particulate matter and the chemical composition of snow provide information regarding the emissions of pollutants, i.e. their deposition on the snow cover over the course of a cold period. The largest amount of airborne particulate matter was recorded in the snow of the yurt districts of Ulan Bator ($Kc = 24$). In multi-storey districts and in the industrial zone, Kc is 8.3 and 8.6, respectively. In the solid phase of snow, the average content of trace elements produces the series $Al > Ca > Fe > K > Na > Mg > S > T i > P > Mn$, in which the sequence of elements is similar to the Clarke (percent abundance) series, which indicates a significant contribution from terrigenous dust. In the dissolved phase, the first positions in the series of the trace elements $Ca > S > K > Na > Mg > P > Mn > Fe > Al > Ti$ are occupied by technogenic elements, otherwise it corresponds to the series of water migration [23]. The supply of large amounts of Ca and S in the two forms is due to the emissions from heating sources [24].

Accumulation of HM in comparison with the background is reflected by the series in Table 3. The high coefficients Kc point to a multiple increase in the supply of anthropogenic aerosols to the atmosphere which are then deposited on the snow cover. Increased HM contents are recorded even in background samples of snow water and airborne particulate matter (Table 4), because the pollution plume along the river valley extends over several kilometers from the city. The

Table 3. Series of HM accumulation in airborne and dissolved snow water fractions for Ulan Bator

Territory	Airborne fraction	Dissolved fraction
City as a whole	$Sr_{3.1}$ $Mo_{2.9}W_{2.7}As_{2.5}U_{2.5}Zn_{2.5}$ $Ni_{2.4}Be_{2.3}Co_{2.2}Sb_{2.1}Th_{2.1}Mn_{2.0}V_{2.0}Cr_{2.0}$	$Mo_{121}Be_{99}Sn_{99}$ $U_{41}Ni_{33}As_{33}Sr_{30}W_{27}$ $Sb_{17}Co_{14}$
Industrial zone	$Zn_{4.6}W_{4.2}$ $U_{3.8}As_{3.6}V_{3.0}Th_{3.0}$ $Co_{2.9}Fe_{2.9}Cr_{2.7}Ti_{2.6}$ $Pb_{2.3}Cu_{2.3}Bi_{2.2}$	As_{52} Ni_{41} $Co_{18}Mn_{11}$ $Zn_{6.4}Fe_{4.6}Bi_{2.8}Th_{2.8}$
Yurt districts	$Mo_{6.6}Sr_{4.5}$ $Ni_{3.6}Be_{3.3}As_{3.2}$ $Mn_{2.9}Co_{2.8}Cr_{2.5}Sb_{2.5}$ $V_{2.3}Pb_{2.2}Zn_{2.1}Cu_{2.0}$	$Mo_{278}Be_{165}Sn_{165}$ $U_{69}W_{47}Sr_{46}$ $Ni_{38}As_{36}Sb_{21}Co_{17}$ $V_{7.2}Cd_{5.7}Cu_{3.8}Zn_{3.6}Pb_{3.0}Ti_{2.3}$
Multi-storey districts	Elements do not accumulate	$Be_{84}Sn_{84}$ $Ni_{25}U_{21}As_{20}Mo_{17}Sb_{16}$ $W_{9.5}Co_{8.9}Mn_{5.6}Fe_{4.8}Zn_{4.1}$ $Bi_{3.8}Th_{3.6}Pb_{3.4}Cu_{2.9}$

Note. Subscripts – values of Kc ; bold type corresponds to HM accumulating within one functional zone in both fraction.

largest accumulation is characteristic for W, Th, U, Be, Mo, As, Sr, Sn, and Sb, which are supplied together with emissions from heat power industries and concentrate in the ash emissions from TEP [14].

The city is witnessing an increase of HM content in the dissolved snow fraction capable of actively migrating in landscapes. Compared to solid-phase depositions, the mass of HM in the liquid phase is far smaller, but their anomalies are distinguished by a very high contrast [4, 24], which brings a potential threat to the urban environment.

In the snow cover, contents of pollutants vary with functional zones (see Tables 3 and 4), i.e. they are determined by the location, specialization and capacity of pollution sources. HM accumulate most intensely in yurt districts, and especially high concentrations correspond to Mo, Be and Sn emissions from coal burning. In multi-storey districts, elements accumulate weakly. As time elapses, the snow cover HM pollution level in the central part of the city is increasing [4].

All functional zones and fractions distinctly show a paragenetic association: Ti-Mn-Th-Fe-Ni-V (with $r = 0.91-1.0$, with a minimally significant $r_{min} = 0.81$), which includes elements supplied in significant amounts together with terrigenous dust (see Table 2). The dissolved fraction generates the Be-Sn association ($r = 1.0$ at $r_{min} = 0.81$), and the airborne fraction produces W-U ($r = 0.99$) and Cd-Sn ($r = 1.0$). The possible reason behind the production of these associations is that Be and Sn deposit largely with fine dust, whereas W, U, Cd and Sn deposit with coarse dust. In some functional zones, the composition of associations is determined by the characteristics of the chemical composition of emissions: the Bi-Co association ($r = 0.99$ at $r_{min} = 0.95$) for both fractions corresponds to the industrial zone, while Zn-Pb and V-Sr ($r = 0.97-1.0$ at $r_{min} = 0.81$) deposit in the yurt districts.

Many paragenetic associations of HM in the city's snow cover, and the coefficients Kc reflect the chemical composition of ash emissions from coal burning. On industrial installations of TEP with high combustion temperatures, the specific elements include As, Bi, Zn, Th, Fe, Co, Cr, and Cu. Air emissions from yurt stoves contain Be, Cd, Mo, Sb, Sr, and V. The differences in the emission composition at different combustion temperatures are due to the two types of sources of coal combustion products: TEP or stoves in yurts whose emissions are about identical as regards the amounts ($11.6-12.3 \mu\text{g}/\text{m}^3$) but differ by absorbed HM [9].

Assessing Total Pollution of Snow Cover

Nowadays, the summary index Zc of airborne snow water pollution for the city averages 30, which corresponds to a low pollution level (see Table 4 and Fig. 4, a). On the contrary, the dissolved fraction is characterized by a very high degree of pollution with $Zc = 559$ (see Table 4 and Fig. 4, b).

The yurt districts experience the highest technogenic pressure, where the airborne fraction of snow water

shows an average pollution level ($Zc = 41$) which reaches in local anomalies a very high level (191). The dissolved fraction exhibited the highest pollution level: Zc averages 853, increasing to 2360. The main source of HM comes from stove heating emissions. Because of the low combustion temperature, and the low height of the chimneys, large amounts of dust and small pieces of coal containing a broad spectrum of HM deposit within living rooms and on the territory surrounding the yurts.

The industrial zone showed an average pollution level of airborne snow fraction ($Zc = 42$), and a high level (as high as 111) at some points. The dissolved snow fraction exhibited the highest pollution level (averaging $Zc = 547$, peaking at 696). In the multi-storey districts, the pollution level of the airborne snow fraction is low in general ($Zc = 6$), whereas it is the highest (313) for the dissolved fraction.

In the early 1990s, the pollution level of Ulan Bator was estimated as relatively weak, and the Zc values of the solid phase of snow in the central part of the city varied from 20 to 30, increasing to 40 in the valley of the Selbe river [4]. Thus the contrast of the HM anomalies in the snow cover has increased considerably during the last two decades.

A particular snow cover pollution hazard for Ulan Bator implies that coal combustion productions, with their amounts increasing from year to year, are with reactive pollutants to an extent several hundred times larger than the natural background. Dissolved forms of HM bring the contamination threat to groundwater and surface waters and, hence, to human health.

The schematic maps for the spatial distribution of Zc (see Fig. 4) confirm the exceptionally dangerous snow cover pollution with dissolved forms of HM in the yurt districts, and in the western part of the industrial zone. Solid phase depositions on the city's territory are characterized largely by a weak level of pollution, against the background of which there occur moderately and strongly contrasting anomalies in the western part of the industrial zone, and in the yurta district in the eastern part.

CONCLUSIONS

1. The main sources supplying HM to the atmosphere are terrigenous dust (Be, Cr, Mn, Th, Ti, U, V, and W), industries and transport (As, Bi, Cd, Cr, Cu, Mo, Pb, Sb, Sn, W, and Zn), and thermal power industries (As, Cd, Cu, Mo, Ni, Pb, Sr, V, and W), whose contribution increases many times during the wintertime. Specialization of emissions differs according to where coals are burned: on industrial installations TEP (As, Bi, Zn, Th, Fe, Co, Cr, and Cu) or in yurta stoves (Be, Cd, Mo, Sb, Sr, and V).

2. Particularly hazardous in the air of Ulan Bator are Pb and AP whose high concentrations (as high as 26 and 21 MPCmd, respectively) were revealed across the entire territory of the city. MPC were also found to be exceeded for Mn, Cu, Be, Fe, Ni, Zn, and Cr. The

Table 4. Trace element concentrations in suspended and dissolved fractions of snow water for the city of Ulan Bator

Parameter	Be	Cr	Pb	Cd	As	Co	Cu	Fe	Mn	Ni	Bi	Mo	Sd	Sn	W	Zn	V	Sr	Th	Ti	U
Suspended fraction																					
Background territories ($n = 3$)																					
C_{av} , mg/kg	27	615	704	12	24	144	722	$32 \cdot 10^4$	9222	339	5	82	31	58	103	2282	692	2628	79	30	38
C_v , %	27	3.9	44	56	15	3.2	12	4.7	36	13	5.3	78	16	16	38	25	3.4	29	11	4.2	38
City as a whole ($n = 17, Zc = 30$)																					
C_{av} , mg/kg	61	1233	1	14	62	310	1201	$61 \cdot 10^4$	18524	826	9	242	66	87	281	5627	1391	8225	166	54	96
C_v , %	142	88	108	120	123	115	116	108	158	161	97	246	73	88	124	132	107	161	133	106	141
Industrial zone ($n = 4, Zc = 42$)																					
C_{av} , mg/kg	76	1672	1	15	89	421	1662	$93 \cdot 10^4$	24050	988	11	132	67	104	429	10	2085	11035	236	79	145
C_v , %	79	87	90	91	67	84	108	98	97	99	79	84	66	93	83	133	95	97	96	97	87
Yurt districts ($n = 6, Zc = 41$)																					
C_{av} , mg/kg	87	1505	1	19	79	397	1434	$70 \cdot 10^4$	26798	1232	10	539	77	100	323	4840	1621	11852	221	65	121
C_v , %	160	92	138	141	151	135	134	120	173	175	131	181	97	109	161	110	119	176	748	116	173
Multi-storey districts ($n = 7, Zc = 6$)																					
C_{av} , mg/kg	30	750	916	9	32	172	737	$35 \cdot 10^4$	8275	385	6	49	56	66	161	3469	798	3511	79	31	47
C_v , %	20	8.3	44	25	25	15	24	13	17	13	20	19	28	17	29	26	15	18	42	17	24
Dissolved fraction																					
Background territories ($n = 3$)																					
C_{av} , mg/kg	0.001	2.0	0.37	0.07	1.0	0.31	7.8	54	54	0.25	0.004	0.40	0.21	0.01	0.5	14	3.0	42	0.02	1.2	0.07
C_v , %	0.0	0.0	60	150	78	62	58	90	55	0.0	0.0	0.0	22	0.0	108	25	0.0	61	3.1	116	73
City as a whole ($n = 17, Zc = 559$)																					
C_{av} , mg/kg	0.99	3.3	1.2	0.2	32	4.3	23	262	383	8.3	0.011	48	3.5	0.99	14	64	9.9	1283	0.05	2.0	2.7
C_v , %	150	83	86	158	107	114	78	72	110	117	118	210	80	149	202	136	171	137	90	140	218
Industrial zone ($n = 4, Zc = 547$)																					
C_{av} , mg/kg	0.26	3.0	1.07	0.10	50	5.51	16	250	588	10.3	0.011	27	2.73	0.26	15	92	4.5	1375	0.05	1.2	2.3
C_v , %	109	39	50	84	122	151	92	78	132	161	107	87	60	109	64	166	39	79	27	90	79
Yurt districts ($n = 6, Zc = 853$)																					
C_{av} , mg/kg	1.65	3.8	1.11	0.42	34	5.36	30	272	346	9.6	0.007	111	4.31	1.65	25	52	21.7	1964	0.04	2.8	4.5
C_v , %	107	93	89	113	86	89	82	45	86	85	80	142	86	107	195	124	119	142	70	95	221
Multi-storey districts ($n = 7, Zc = 313$)																					
C_{av} , mg/kg	1.65	3.8	1.11	0.42	34	5.36	30	272	346	9.6	0.007	111	4.31	1.65	25	52	21.7	1964	0.04	2.8	4.5
C_v , %	107	93	89	113	86	89	82	45	86	85	80	142	86	107	195	124	119	142	70	95	221

Note. n – number of samples.

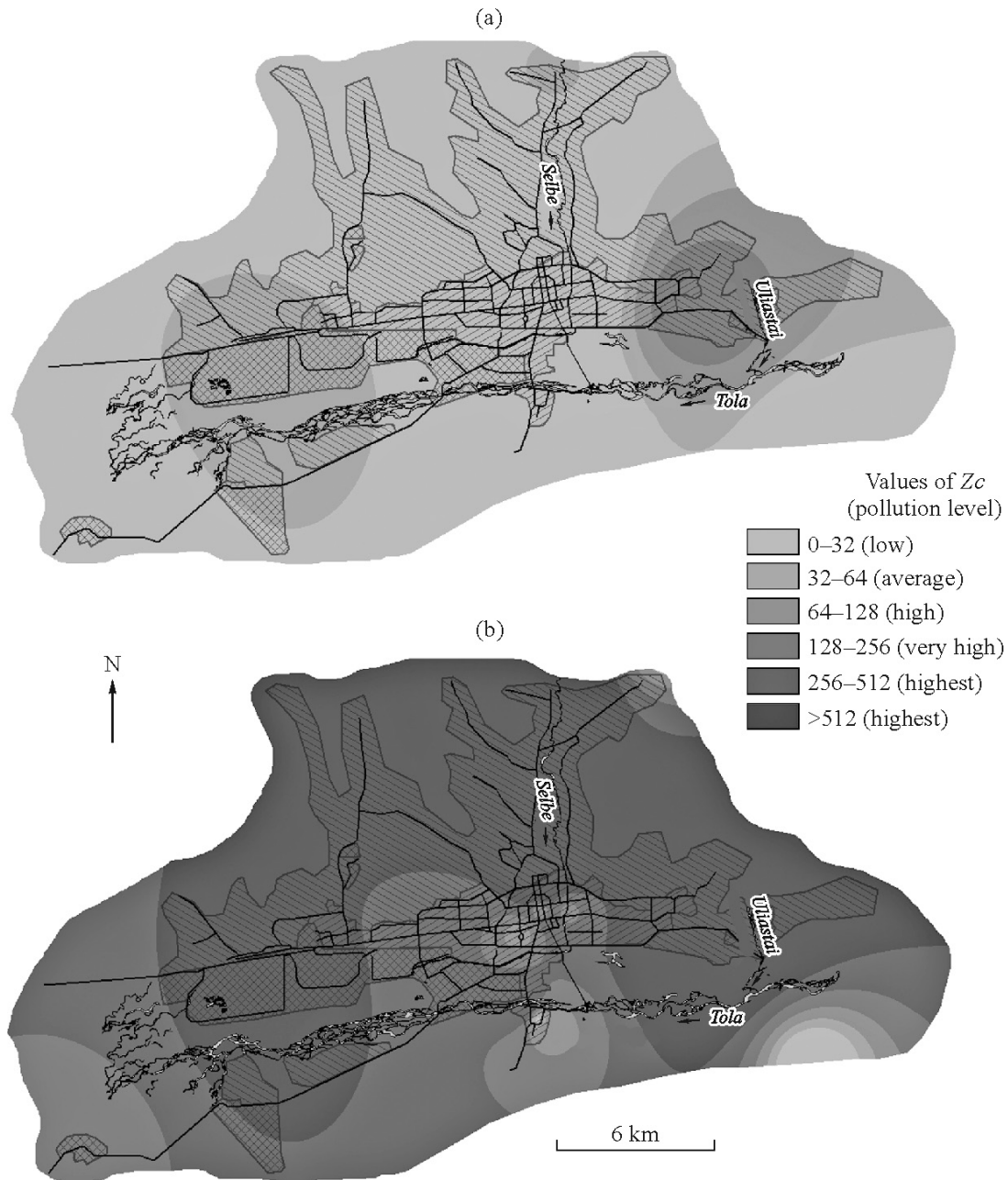


Fig. 4. Total contamination of airborne (a) and dissolved (b) snow water fractions with heavy metals according to the Z_c index. For conventional notation of the functional zones, see Fig. 1.

snow cover accumulates Mo, Be, Sn, Sr, U, As, W, and Ni, for which in the greater part of the city K_c in the dissolved and airborne snow fractions exceeds 30 and 2.5, respectively.

3. Maximum air pollution ($API > 50$) was recorded in the central part of Ulan Bator, which is accounted for by the descending air currents down the slopes of the hollow, and by its stagnation at the bottom in the case of anticyclonic weather regime. HM content in the air was decreasing outward from the center, yet it remained high and elevated ($API > 5$). At the end of winter, HM generated moderately and strongly

contrasting polyelement anomalies in the snow cover in the center and in the eastern part of the city as well as in the western part of the industrial zone. The yurt districts ($Z_c = 41$ in the airborne snow fraction, and 853 in the dissolved fraction), and the industrial zone were experiencing the strongest technogenic impact during a winter season.

4. The two last decades saw an increase in depositions of atmospheric HM, leading to an expansion of the areas covered by their anomalies in the snow cover. During a winter season, content levels of HM in aerosols were increasing between December and early February,

decreasing gradually toward March 2009. During a 24-hour-long time interval, HM emissions were peaking in the morning (9–11) and late-evening (20–23) hours.

5. A central objective of further atmospheric research for Ulan-Bator is to determine the chemical composition of aerosols of different sizes and HM migrating predominantly in the gaseous sphere. This would offer a means of forecasting the transport range of pollutants, their lifetime in the atmosphere, and their effects on the population. Another important goal is also to include air emissions of nuclides from burning brown coals on the list of pollutants to be monitored.

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