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Results of AAS Measurements of Atmospheric Trace Metals Deposition in Snow Cover in Lower Kama Urban Agglomeration.

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ABSTRACT

The study of pollutant level of snow cover of the explored territory required establishment of more than 80 sample plots within the territory of several hundreds square kilometers including industrial area of Naberezhnye Chelny (steam power plants, JSC KAMAZ plants, etc.), which are exposed to intense human impact of the area of agroindustrial complex of the Tukai district, the part of "Lower Kama" national park area, and the territory of the city of Naberezhnye Chelny as well. Within the framework of the study snow sampling was carried out within these sample plots, its main features and contaminators' weight content were defined. Moreover, the results of long-term observations over snow cover state of the territory of the Naberezhnye Chelny (Lower Kama) urban agglomeration that allow - taking into account synoptic conditions by the end of cold period - forecasting the beginning of intense snow melting and planning snow-measuring measures and sampling correspondingly. To assess impact on environment, accumulated with snow and soil cover of pollutants, their inflow per unit area and per explored territory was estimated. Obtained results allowed to asses the snow cover contamination level by several complex indicators. The snow cover contamination level based on this data should be recognized as quite considerable: median value of contamination total index K_p^5 is 15,1 that allow us to relate this territory to heavily polluted. Whereby partial coefficients of contamination with cooper and zinc, and manganese iron and nickel to a somewhat less degree, make a major contribution to this index.

Keywords: Lower Kama agglomeration, snow cover, heavy metals, background contents, anthropogenic impacts.

CORRESPONDING AUTHOR

INTRODUCTION

Naberezhnye Chelny and Tukai municipal district of the Republic of Tatarstan comprise the Naberezhnye Chelny urban agglomeration. Due to the high concentration of industrial plants within this territory over a number of years Naberezhnye Chelny has been included in the eligible list of cities with highest level of atmospheric air pollution published by Federal Service for Hydrometeorology and Environmental Monitoring of Russia [1]. Various pollutant sources impact on the top of the ground is reflected by the state of snow cover acting as an effective natural tablet accumulator of atmogenic pollutants.

In the territories characterized by the presence of stable snow cover during a long period of time, this cover acts as an essential object of ecological monitoring [14,16, 5].

MATERIALS AND TECHNIQUES

A generally accepted major feature of snow or soil cover is its cumulative contamination index Z_C (see for example [4], which is defined according to the equation:

$$Z_c = \sum_1^n K_c - (n-1) = 1 + \sum_1^n \frac{C_i - C_b}{C_b},$$

(1)

where $K_C = C_i/C_b$ — concentration ratio, i.d. index of pollutants content increase ratio at the sampling point C_i over its content at the background segment C_b; n — the number of substances sampled.

It is assumed if Z_C ranges within $32 - 64$, snow cover contamination level is low, if it ranges within $64 - 128$ — average, $128 - 256$ — high, more than 256 — very high [7].

In many cases, particularly when assessing snow cover contamination level, pollution coefficients K_p are used, which are ratio of pollutant content in substance sampled to prohibitive amount established by authorized bodies. Chemicals maximum permissible concentrations (MPC) in snow water are not rated in Russia, therefore they are often compared to MPC in water objects of household water use and cultural and general water use or in water of water objects used for fishery purposes [11, 17].

Since all water basins of the Republic of Tatarstan are related to water basins of commercial fishing importance, in this work snow cover contamination was assessed relatively MPC $_{fw}$.

In order to avoid ambiguity related to space and temporal variability of snow cover, as an indicator characterizing average air pollution level within the explored territory over a period of examination is usually taken (see for example [13]) not pollutant concentration in snow, but their mass ingressing per unit area over a period of snow cover formation to sampling:

$$\pi = C \cdot w,$$

(2)

where π — pollutant ingress per unit area, kg/km^2; C — it concentration in melt water, mg/dm^3, w — moisture content at the point of sampling, mm.

Considering pollutants ingress from atmosphere approximately equal in the course of a year, it's possible to calculate their mass per unit area per year:

$$I = \pi \cdot \frac{365}{\Delta \tau_{dep}},$$

(3)

where I — annual pollutant ingress per unit area, t/(year·km^2), τ_{dep} — time of stable snow cover occurrence until sampling time.

Thus, pollution coefficients can be recounted according to the formula

$$K_{p,i} = \frac{\pi_i}{MPD_i},$$ (4)

whereby, maximum permissible deposition (maximum permissible deposition, MPD) is equal to

$$MPD_i = MPC_{fw,i} \cdot \bar{w},$$ (5)

where $MPC_{fw,i}$ — maximum permissible concentration of i-th pollutant for water of commercial fishing importance, $\bar{w}$ — average moisture content in the explored territory.

Whereas integral assessment is conducted [15] by total pollution indexes for five priority pollutants:

$$K_p^5 = \sum_{i=1}^{5} K_{p,i}.$$ (6)

In accordance with total pollution index the gradation of territories from very clean ($K_p^5 < 0,5$) to extremely contaminated ($K_p^5 > 16$) is carried out.

Relation between chemicals in snow cover differs from that in Earth crust. There is a group of elements, primarily, Al, Mn, Si called lithophylous, in relation to which concentration of other elements in the Earth's crust changes relatively slightly. Snow is characterized by enrichment with a number of elements in relation to lithophylous ones. Due to natural processes, enrichment may occur from several times to several orders of magnitude. Anthropogenic pollution can significantly increase snow enrichment with separate elements. Enrichment factor (Li et al., 2011) is

$$EF_i = \frac{(C_i/C_l)_{snow}}{(C_i/C_l)_{crust}}$$ (7)

where C_i и C_l — concentration of explored and lithophylic elements correspondingly; indexes *snow* and *crust* relate to snow and lithosphere.
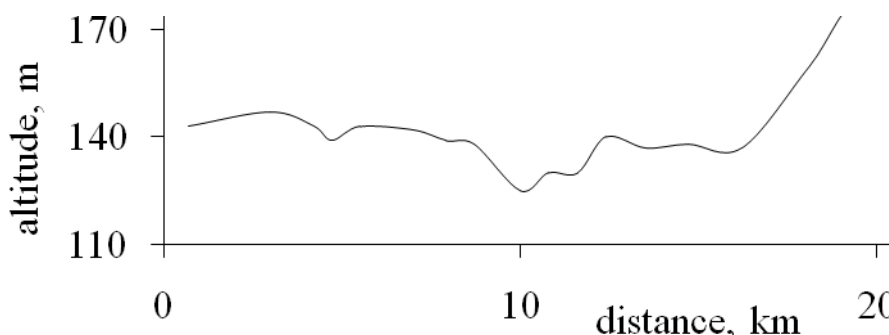
EXPERIMENTAL PART

Figure 1: Relief profile north eastward from the industrial site relative coordinates (Mavrin et al., 2005).

The Republic of Tatarstan is located in the east of East European Plain in the middle course of the Volga river and lower course of the Kama river. Climate is moderately continental, snow period duration - 5 – 5,5 months (from mid November to beginning of April). Average temperature of January is -14°C, of July + 19°C. Average annual precipitation is 460 – 520 mm [12].

Relief can be briefly characterized as a rolling plain with maximum elevation changes of more than 60 m. Relief profile north eastward from the relative origin of industrial site coordinates is shown in Fig. 1.

Explored territory includes a part of industrial site with unauthorized landfills, a part of sanitary protection zone, roads, forest plantations, gardens, farmlands, meadow lands, half grown forests, and ravines. Annual average wind rose is not too contrast. In the winter northerly and north-westerly winds prevail. With due account for rose wind, industrial site (steam power plants, factories of machine-building and petroleum complex) and roads location, and minor rivers geography, 80 sample plots were laid in the city of Naberezhnye Chelny, around the factories of JSC KAMAZ, in the territory of Tukai district and in the national park "Lower Kama" according to Fig. 2. During 2004 – 2013 360 samples of snow cover were taken.
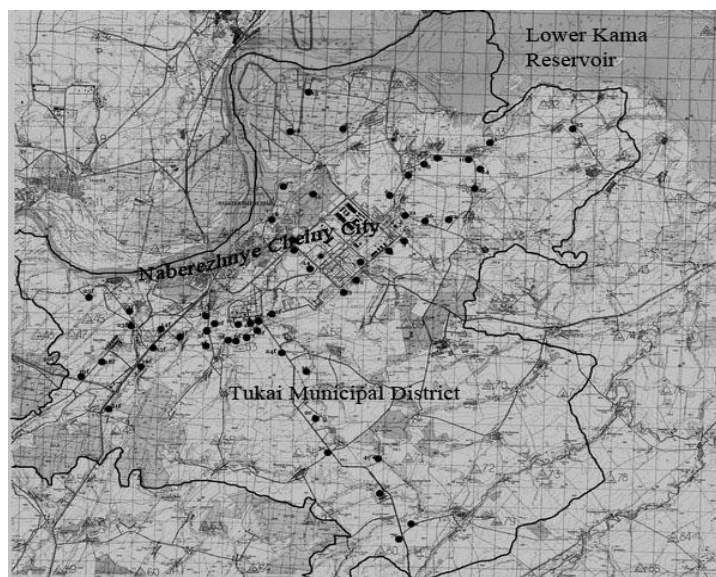

Figure 2: Sample plots location in the territory of Tukai district and the city of Naberezhnye Chelny.

Sampling date was selected to the effect that snow cover was of maximum thickness on the one hand, and intense spring snow melting didn't begin on the other hand. Since the beginning of intense snow melting during observation period fell on the period from March, 20 to April, 8 [3] sampling was usually carried out about March, 15. At that point, average occurence time τ_{dep} used in the formula (3) was 109 days.

When sampling snow a polyethylene sampler 1 m long and with a diameter of 110 mm was used. Each composite sample consisted of four individual samples was taken from a square with area of 4 м^2. Each snow core was cut to full depth of snow cover.

Primary sample treatment for water-soluble compounds finding included snow melting, settling during 34 hours, sample residue discharge into bottles, measuring total volume of melt water and filtrating. Heavy metals finding (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in melt water was carried out by a method of atomic absorption spectrometry with electrothermal atomization on the spectrometer KVANT-Z.ETA [10].

RESULTS

During winter periods since winter 2003/2004 in the laboratory ALTSI Science Research Sector snow cover sampling, its main properties characterization and quantitative chemical analysis have been carried out. Sampling was carried out not long before the beginning of intense snow melting to the effect that period length since stable snow cover formation was maximum.
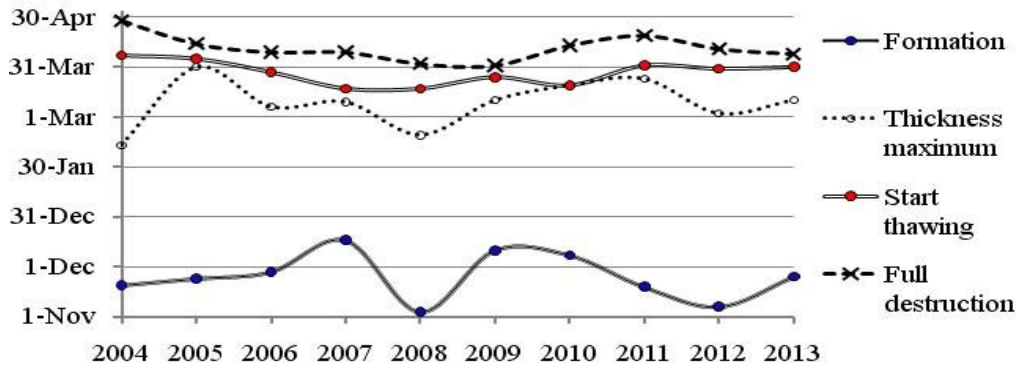
Figure 3: Changes of snow cover term formation and destruction in 2004-2013

Interval from the time of snow cover maximum thickness achievement to snow melting beginning can be extremely short, therefore it's very important to choose the right moment of representative samples taking. Over a period of observations (Fig. 3) snow cover within the examined territory was started destroying about March, 27. Thus, it makes sense to select sampling time about March, 15.

Snow cover within the territory under study (Table 1) is characterized by both quite considerable temporary and spatial variability due to variability of weather conditions from year to year and non-equivalence of sample plots in the context of snow accumulation conditions as well.

Table 1: Snow cover basic parameters.

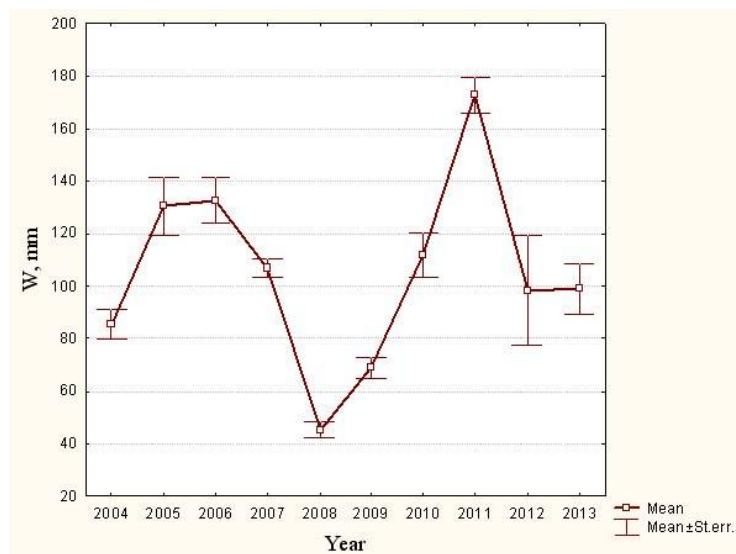|	Parameter	Thickness, cm	Bulk density, g/cm^3	Moisture content, mm
Quartiles	Q_0 (min)	12	0.099	23
	Q_1	31	0.208	75
	Q_2 (median)	44	0.241	100
	Q_3	56	0.279	134
	Q_4 (max)	90	0.469	274
Q_3-Q_1		24	0.071	59
Range excluding emissions and end points		12 – 90	0.102 – 0.384	23 – 222

Figure 4: Temporary variability of snow cover moisture content within the explored territory.

Average moisture content amount over a period of observations is shown in Figure 4. This parameter range is quite considerable, there's no noticeable tendency towards its increase or decrease.

Annual average and average long-term heavy-metal concentration values in snow cover in comparison with maximum allowable concentration in water of water objects used for fishery purposes is shown in Table 2.

Table 2: Heavy metals concentration in melt water of snow cover.

Year	Average concentration, mcg/l							
	Cu	Cd	Pb	Mn	Zn	Fe	Cr	Ni
2003-2004	7.90	1.10	4.60	55.00		117.50	3.80	19.30
2004-2005	6.70	0.30	1.90	17.00	698.00	219.70	2.10	73.60
2005-2006	3.80	0.10	2.40	13.80	11.80	46.50	3.00	4.70
2006-2007	7.10	1.00	2.80	5.10	9.30	69.30	6.00	1.90
2007-2008	29.80	0.20	1.80	41.20	200.70		1.60	21.00
2008-2009	5.70	0.10	0.70	17.50	40.10	42.90	1.10	8.70
2009-2010	10.50	0.20	3.70	5.90	105.20	66.00	1.10	11.90
2012-2013	87.00	0.30	2.70	14.10	130.20	292.90	2.70	
average long-term	19.81	0.41	2.58	21.20	170.76	122.11	2.68	20.16
$MPC_{fw,i}$	1.00	5.00	6.00	10.00	10.00	100.00	20.00	10.00
$C_{crust,i}$, mg/kg [a]	55	0.1	14	900	70		100	20

a) elements' clarke in the Earth's crust [6]

Data on annual ingress of chemical substances rated per unit area of the explored territory over a period of observations is shown in Table 3.

Table 3: Quantity of heavy metals ingressing from snow cover into the explored territory.

Element	Ingress quartile, kg/km^2					Q_3-Q_1	Range emissions and end points	MPD, kg/km^2
	Q_0 (minimum)	Q_1	Q_2 (median)	Q_3	Q_4 (maximum)			
Cu	30	225	586	1621	$2,37 \cdot 10^5$	1396	30 – 3716	100
Cd	0,98	5,25	10,59	26,3	3336	21,1	0,98 – 57,9	500
Pb	4	76	174	391	$3,64 \cdot 10^4$	316	4 – 865	600
Mn	40	327	952	2241	$4,90 \cdot 10^4$	1914	40 – 5111	1000
Zn	132	844	2717	$1,10 \cdot 10^4$	$2,69 \cdot 10^6$	$1,02 \cdot 10^4$	132 – $2,63 \cdot 10^4$	1000
Fe	365	2572	5835	$1,26 \cdot 10^4$	$1,63 \cdot 10^6$	$1,00 \cdot 10^4$	365 – $2,76 \cdot 10^4$	10000
Cr	1,1	66	118	280	7908	214	1,1 – 601	2000
Ni	43	156	417	1237	$4,56 \cdot 10^4$	1081	43 – 2858	1000

According to the test chart "probability – probability", made in the program Statiatica 6.0, (Fig. 5) moisture content distribution in sampling points is of lognormal nature. To calculate maximum permissible ingress of pollutant according to the formula (5) it's reasonable to use not arithmetic average, but median value of moisture content, that is 100 mm.
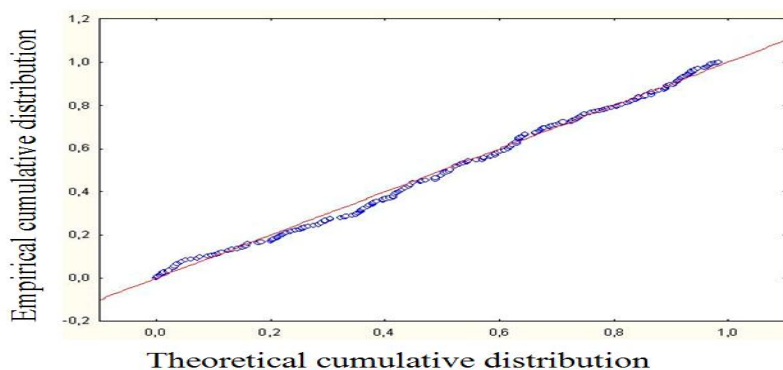
Figure 5: Test chart "probability – probability" for lognormal distribution of moisture content *w* on snow cover samples.

Analyzing results of heavy metals ingresses into the explored territory (Table 3) it's possible to notice that they are variable to a much greater extent than physical parameters of snow cover: they change from sufficiently low values to very high ones, which exceed maximum permissible values in a few orders. For some metals even median (local background) ingresses of these pollutants exceed MPD. Thus, there are little points not polluted with copper, and exceeding of MPD with zinc is observed in almost three-quarter of all points. In the full assessment of contamination level by total index of contamination K_p^5, 60 % of samples are assessed as heavily or extremely polluted and only 29 % as clean ones.

The presence of large amount of extremely polluted points within the explored territory makes the nature of contamination indexes distribution far from normal: only value of $\log(\log(K_p^5))$ is properly distributed.

Total index Z_c computation using median content of heavy metals as local background ones gives more favourable assessment of contamination level: only 8% of samples shows high or very high level of contamination, and 82% - low level. Apparently, local background contents of pollutants are of little use to apply this index adequately, and it's necessary to turn to the global background levels corresponding to heavy metals content in the snow cover of territories, which are not exposed to intense anthropogenic impact, for example, such as provided in the record on pollution of snow cover of Alaskan natural sanctuary "Cape Krusenstern" [2].

Enrichment factors calculated in relation to lithophylic element Mn are very much different for various heavy metals: for chrome EF is about 1, for lead, cooper, and nickel — from several units to several tens, and for zinc and cadmium it exceeds 100, and is more than 1000 in certain years.

FINDINGS

The results of long-term observations over snow cover state of the territory of the Naberezhnye Chelny (Lower Kama) urban agglomeration allow drawing conclusions regarding intensity of anthropogenic impact, main pollutants' priority, and the nature of their distribution. The snow cover contamination level based on this data should be recognized as quite considerable: median value of contamination total index K_p^5 is 15,1 that allow us to relate this territory to heavily polluted. Whereby partial coefficients of contamination with cooper and zinc, and manganese iron and nickel to a somewhat less degree, make a major contribution to this index. The alternative total index of pollution Z_c requires for its calculation information on pollutants' content in the object under study. Assumption of possible using of local background values was not proved out, since median level of pollution with some heavy metals, especially copper and zinc, exceeds established maximum permissible level even discounting extremely polluted points.

CONCLUSION

Snow accumulation within the explored territory is uneven and changes from year to year that makes pollution level assessment based on pollutants' mass concentration in snow cover melt water unreasonable.

Under these conditions it is more adequate to use pollutant's mass ingressing from snow cover per unit area of underlying surface when calculating pollution indexes.

ACKNOWLEGEMENT

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