

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Anomalous Manifestations of River Cl⁻ Runoff In The North Of The East European Plain.

D. N. Khayrullina*, and A. A. Kurzhanova.

Kazan Federal University, Kremlevskaya, 18, Kazan, 420008, Russia.

ABSTRACT

The article assesses the abnormal manifestations of runoff concerning one of the most active aquatic migrants - chloride ion - from the basin geosystems of East European Plain north. The methodology used in this study is based on the evaluation of annual value deviations runoff of chloride ions from the standard. Thus, the annual values of the ion runoff in the range of 0-15% and 85-100% provision were referred to abnormal performances, for which anomaly ratio (AR) was calculated. It was revealed that the runoff of chloride ions has the greatest anomaly and variability in the basin geosystems of middle taiga subzone (CA = 24.2%) of high plains (CA = 28.0%), composed of mixed, easily soluble chemo- and organogenic sediments (CA = 25.4%) due to the greater development and cavernous porosity of these river basins, predetermining their openness to the outside (atmogenic, anthropogenic) factors. The smallest abnormality and variability is typical for the river basins of lowlands (CA = 20.8%), composed of weakly permeable loamy rocks (CA = 18.6%) due to the prevalence of a surface runoff over an underground drain - one of the key sources (along with anthropogenic one) of analyte ions.

Keywords: anomaly, basin, the runoff of chloride ions, river flow, the East European Plain

**Corresponding author*

INTRODUCTION

Due to the absence of a biochemical barrier and a high migration ability of chloride ions the abnormal manifestations of their runoff (along with SO_4^{2-} and Na^+K^+) are the indicator of an anthropogenic impact, as they quickly reflect an emerged anthropogenic load, its intensity and scale, as well as a possible shift of geochemical balance in the basin ecosystems [1-3].

The aim of this work is the evaluation of the abnormal manifestations concerning the runoff of chloride ions in a variety of natural and anthropogenic conditions of the East European Plain north.

Modern regional research in the field of anthropogenic transformation is one of the main factors of ion runoff abnormal manifestations, associated primarily with N.P. Torsuev, V.A. Belonogov and V.A. Fedorova works [2-5]. As for the study of ion runoff abnormal manifestations, it should be noted here that the majority of current research is related to the consideration of spatial hydrogeochemical anomalies of groundwater. These anomalies have a natural [6], and a anthropogenic origin [6-10]. The genesis of abnormal manifestations, in its turn, is related to the study of element concentration seasonal variations in a river flow, which are also conditioned, as a rule, by groundwater flow variations [11, 12]. A number of works is devoted to the detailed assessment of development factors, the origin of groundwater chemical composition and hydro-geochemical anomalies [13-15].

METHODS

The methods of anomaly isolation may be divided into two groups:

I. The isolation of anomalies in a time aspect (at an observation point):

I.1. The isolation of anomalies according to series maximum or minimum values.

I.2. The isolation anomalies according to mean-square deviation from standard:

- Deviation of values by $\pm 3 \delta$ from standard, large anomalies are presented by values exceeding δ , and extremals presented by more than 2δ ,
- The analysis of probability curves (the probabilities) concerning the occurrence of values.
- The analysis of value position in the general row of observations (the ratio of maximum (minimum) value to the norm).
- The analysis of relative and absolute indicators using the data of maximum value provision.

II. The isolation of anomalies in a space (evaluation of anomaly area coverage):

II.1. The consideration of anomaly manifestation area (e.g., regional anomaly covers more than 50% of the studied area).

II.2. The consideration of area and the amplitude of anomaly manifestation, which gives a more accurate picture about the regional and local anomalies [16-18].

The approaches to the separation of extreme manifestations of anomalies were also differentiated. Extremal conditions included:

1. The phenomena which exceed the cumulative effect of normal processes (in geology).
2. The processes of maximum and minimum intensity in time (in geomorphology) [16].

The evaluation of abnormal manifestations concerning chloride ions runoff is based on the data of 47 hydrological stations of the Northern Territorial Administration for Hydrometeorology and Environmental Monitoring of Russian Federation, located in the north of the East European Plain (Fig. 1).



Fig. 1. Schematic map of meteorological stations and hydrological posts location in the north of the East European Plain

The value of Cl⁻ runoff was calculated according to the methodology proposed by V.A. Belonogov according to the formula (1) [2, 3]. Since the river basin area varies widely, then the Cl⁻ runoff value is calculated (kg/km²):

$$W_{Cl^-} = \frac{\sum_{i=1}^n (Q_i \cdot C_i)}{\sum_{i=1}^n Q_i} \cdot a \cdot W_{water} \cdot 10^3 \quad (1)[2, 3]$$

where C_i and Q_i – the concentration of ions (mg/l) and water consumption (m³/sec) as of the selection date state;

W_{water} – water flow volume per year (km³);

n – number of samples per year;

S – river basin area, km²;

a – correction factor, defined as the ratio of long-term average observation period of water flow to the drain for a particular year.

Abnormal manifestations of chloride ion runoff were estimated according to the method proposed by G.R. Safina [16]. The method is based on the evaluation of chloride ions runoff annual values deviation from the standard. Thus, the annual values of the ion runoff from 0 to 15% of the supply were classified as positive anomalies, 85 - 100% were classified as negative anomalies [16]. The values of the ion runoff from 50 to 85% of the supply correspond to the period of relative "hydrochemical background".

We estimated the amount of positive ion runoff anomalies, since the latter are the main contributors to the total ion runoff as in the case of suspended sediment runoff estimation [16].

Abnormality ratio was calculated using the formula (2):

$$CA = \frac{x_i \cdot 100\%}{\sum_{i=1}^n x_i} \quad (2),$$

where x_i – the runoff of analyzed ions in this year, kg/km²,
 n – number of observation years [16].

The software packages «Statistica 7» and «Statgraphics Plus» were used for time series handling.

The selection of analyzed hydrological stations was conditioned by the following circumstances:

1. An observation period should be at least 14 years to isolate the abnormal values of ion runoff [16].
2. In order to identify the natural zoning of chloride ion runoff anomalous manifestations, the location of the river basins should be in different natural zones and subzones, such as tundra and taiga (northern, middle and southern taiga).
3. In order to determine the effect of river water content (the volume of river basin) it is necessary to separate rivers by the area of their basins: small - up to 5000 km², average - 5000 - 25000 km², large - more than 25000 km².
4. In order to detect the impact of relief on the chloride ion runoff anomalies the river basins were divided into altitude groups: up to 150 m - lowlands, from 150 to 200 m - uplands, 200 m - high plains.
5. The analysis of pools with different composition of rocks and their constituents, mixed hemoorganogenic sedimentary, sedimentary undivided, sands, clay loams and clays (Table 1) [5, 16, 19].

Table 1: Distribution of river basins by category

Category name	The number of hydrological stations	Category name	The number of hydrological stations
Landscaping area		Geological structure	
Tundra	1	Clay loams	10
Northern taiga	6	Sedimentary undivided	13
Middle taiga	34	Sands, pebbles	12
Southern taiga	6	Mixed, chemo- and organogenic sedimentary rocks	11
Altitude category		Basin area	
< 150 m	26	Small	27
150 – 200 m	17	Average	10
>200 m	4	Large	9

RESULTS

This article described the natural and anthropogenic conditions which influence the anomaly and the variability of Cl⁻ runoff: zone factor, river basin area, the height of relief and geological structure (Figure 2-4).

Natural zoning. Analyzed river basins are located in areas such landscaping zones as tundra and taiga (northern, middle and southern one).

According to calculations, a sharp differentiation of positive abnormal manifestations of ion runoff for different zones of the studied area is not marked and varies in the range of 19.7-24.2% (Fig. 2).

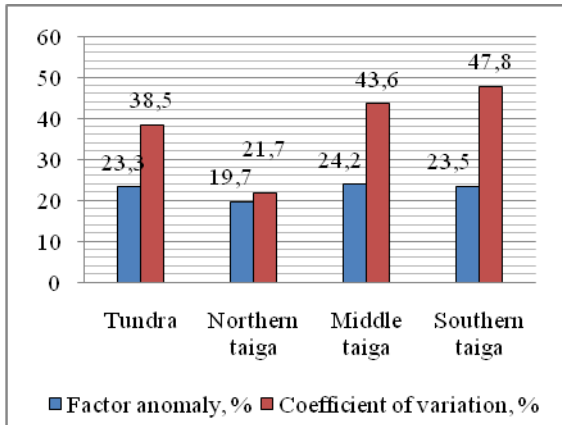


Fig. 2: Change of CA and C_v of Cl^- runoff in different natural zones and subzones in the north of the East European Plain

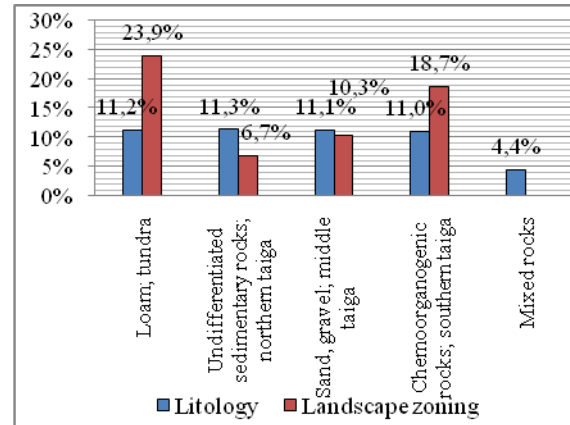


Fig. 3: C_v change of Cl^- runoff in different natural zones and subzones and depending on the composition of rocks during hydrochemical background in the north of the East European Plain

However, the greatest values of CA = 24.2% are recorded within the middle taiga subzone. An indirect indication of anomaly presence is the coefficient of variation (C_v): the highest unevenness, reflected in the variation coefficient is observed for southern taiga ($C_v = 47.8%$) at CA= 23.3% [16, 20-21]. On the contrary northern taiga is characterized by the lowest values of CA (19.7%). Besides, for the middle taiga C_v is maintained at the level of 43.6% (at the standard of less than 33%), two times less (21.7%) for the northern taiga subzone (Fig. 2).

This pattern may be conditioned mainly by different forest areas in the basins - one of the main factors determining the uniformity of water flow, sediments and dissolved substances [16]. Thus, the northern taiga is less studied and has the largest forest area, which determines the low rates of C_v and K (Fig. 2).

For tundra zone CA= 23.3% (Fig. 2).

As for the variability of ion runoff unevenness during the period of "hydrochemical background", the highest values are observed within the treeless tundra zone ($C_v = 23.9%$), the lowest values are observed for northern taiga subzone ($C_v = 6.7%$) (Fig. 3).

Relief height. The analyzed river basins are referred to three altitude groups: lowlands (150 m), elevated plains (150 - 200 m) and high plains (200 m) (Fig. 4).

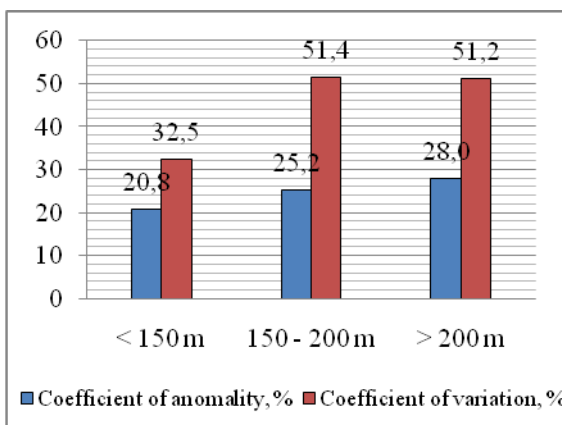


Fig. 4: The variability of CA and C_v of Cl^- runoff according to altitude groups of various basins in the north of the East European Plain

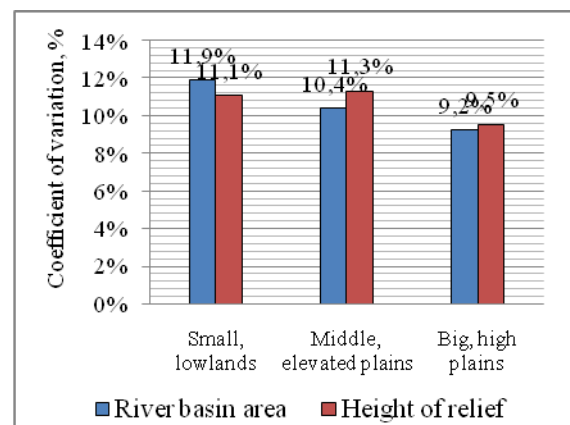


Fig. 5: The change of C_v of Cl^- runoff depending on the river basin area and the height of the relief during hydrochemical background in the north of the East European Plain

According to estimations CA varies from 20.8 to 28% for the analyzed categories. The highest CA is observed for high plains, making 28% ($C_v = 51.2\%$), which indicates, apparently, their greater exposure to the outside (anthropogenic) influence, since they are comparatively better drained and therefore are better developed economically.

Besides, the lithology of the river basins, located on the elevation marks, is presented by more ancient carbonate and sulfate karst rocks [22-23]. Precipitation, accumulating industrial emissions, CO_2 and a lowered pH value, penetrate freely in fractured rocks and are subjected even more to the leaching of rocks. Thus, the underground feeding value and, consequently, salinity are increased [22]. Possibly it determines relatively high CA values.

It is known that lowlands are composed mainly of sand rocks (of alluvial and lake origin) with the predominance of accumulative processes over denudation ones. In this case, the mineralization of rivers flowing within lowlands is reduced. The smallest CA = 20.8% ($C_v = 32.5\%$) is observed for lowlands.

Elevated plains, in its turn, have CA = 25.2%, C_v is a maximum one and makes 51.4%.

The situation is different for the period of "hydrochemical background". The unevenness of ion runoff is the lowest one for high plains ($C_v = 9.5\%$), indicating, apparently, the "leveling" effect of karst rocks and underground river supply for ion runoff (Fig. 5).

Lithological factor. CA for this category ranges from 18.6 to 25.4%, C_v ranges from 23.3 to 51.2%. The basins composed of mixed, chemo- and organogenic sediments represented, as is well known, by highly soluble sulfate and haloid salts which increase the salinity of rivers draining them, the highest values of CA = 25.4% are recorded (C_v is the maximum one here and is equal to 51.2%) (Fig. 6) [24].

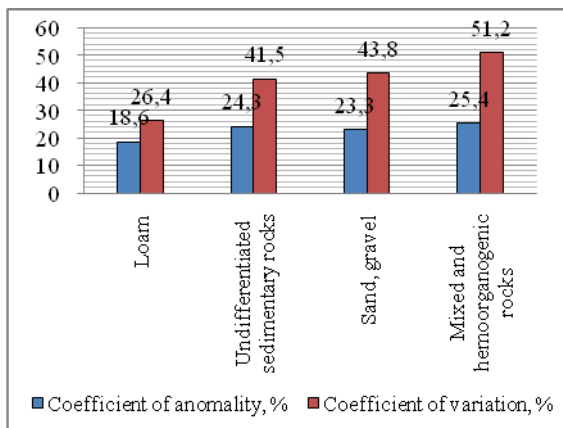


Fig. 6: Variability of CA and C_v of Cl^- runoff depending on the composition of rocks in the north of the East European Plain

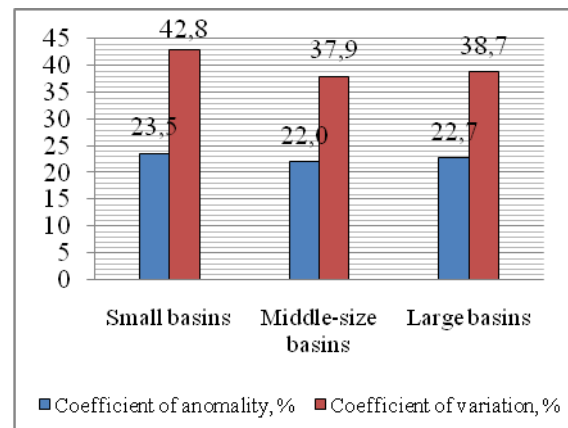


Fig. 7: Variability of CA and C_v of Cl^- runoff depending on the area of the river basin in the north of the East European Plain

Interestingly, the smallest unevenness ($C_v = 4.4-11.0\%$) (Fig. 3) is recorded during the period of hydrochemical background for this category of rocks.

Undifferentiated sedimentary rocks indicate a slightly smaller, but still a significant CA = 24.3% ($C_v = 41.5\%$). CA is below and equal to 23.3% ($C_v = 43.8\%$) (Fig. 6) for the basins composed of sand and loam rocks. This is conditioned by the fact that indigenous marine whole sediments have a relatively higher content of relatively soluble compounds by age compared with later sandy deposits formed predominantly by inert SiO_2 .

The rivers, draining poorly permeable clay deposits, have the smallest CA = 18.6% (C_v does not exceed norm and is equal to 26.4%). This is conditioned by the fact that in the basins composed of low permeable rocks, surface runoff is much more than an underground drain (the main component of analyzed ion income) which makes an impact on CA value [22].

Basin area. Anomaly factor for basin geosystems of different size changes a little (22-23.5%), as well as the variation coefficient (37.9-42.8%), indicating that the small dependence of anomalous manifestations and the unevenness of the ion runoff from this feature.

For the period of "hydrochemical background" the maximum unevenness is fixed for small river basins, which also indicates the influence of karst rock composition ($C_v = 11.9\%$) (Fig. 4). The smallest unevenness is observed within the large river basins draining predominantly unconsolidated sand deposits ($C_v = 9.2\%$), (Fig. 4).

SUMMARY

The performed analysis allows to make the following conclusions:

- 1) the highest values of the studied parameters are related to the basin geosystems located within the middle taiga subzone (CA = 24.2%) on the high plains (CA = 28.0%), composed of mixed, easily soluble chemo- and organogenic sediments (CA = 25.4%) due to the greater development and karst formation of these river basins, predetermining their openness to the outside (atmogenic and anthropogenic) factors;
- 2) lowlands are characterized by the lowest values (CA = 20.8%), composed by low permeability loamy rocks (CA = 18.6%) due to the prevalence of surface runoff over underground one - one of the key (along with anthropogenic one) sources of analyzed ions.

ACKNOWLEDGEMENTS

The author thanks the associate professor of landscape ecology department at K(P)FU A.V. Gusarov for the provision of extensive consultations on the manuscript drafts.

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

REFERENCES

- [1] Posohov E.V., 1977. The formation of the hydrosphere chloride waters. *Gidrometeoizdat*: 248.
- [2] Belonogov V.A., Galimzyanova Z.R., Torsuev N.P., Fedorova V.A. Human evolution and the transformation of ion runoff in ECHR taiga zone // *News of Russian geographical society*. - 1999. - V. 131, Issue 3. - pp. 61 - 67.
- [3] Belonogov V.A., N.P. Torsuev, V.A. Fedorova, 2001. Continuous monitoring and probabilistic and statistical analysis as the most objective approach to the problem of standards surface water quality. *Water management in Russia: problems, technology, management*, vol. 3, 4: 311.
- [4] Torsuev N.P., 2007. Spatial and temporal organization of karst systems. *Homeland*: 180.
- [5] Denmukhametov R.R., Sharifullin A.N., 2015. The structure of the chemical denudation and the methods of its determination. *Mediterranean Journal of Social Sciences*, vol. 6, № 1: 247-251.
- [6] Chudaeva V.A., O.V. Chudaev, 2011. The features of rare earth elements accumulation and operation in the surface waters of the Far East within the conditions of natural and anthropogenic anomalies. *Geochemistry*, №5: 523-549.
- [7] Zinyukov Yu.M., 2011. Innovative methodological approaches of hydrogeochemical monitoring conduct in the areas of intensive technogenesis. *Bulletin of VSU, Ser. Geology*, №2: 194-203.
- [8] Kopylov I.S. The formation of trace element composition and hydro-geochemical anomalous zones in the groundwaters Kama Ural Region. *Bulletin of Perm Univ. Ser. Geology*, Issue 3 (24): 30-47.
- [9] Kramchaninov N.N., A.N. Petin, 2012. Underground water regime of mining areas of the Kursk magnetic anomaly Belgorod region and their qualitative composition. *Geology, geography and global energy*, №2 (45): 233-240.
- [10] Ken W.F. Howard, Paul J. Beck, 1993. Hydrogeochemical implications of groundwater contamination by road de-icing chemicals. *Journal of Contaminant Hydrology*, Vol. 12, Issue 3: 245-268.
- [11] Yakovlev P.I., 2008. The main issues of water research concerning the identification of deep groundwater discharge foci into rivers, surface waters, erosion cuts by remote and hydrological methods. *Potable water*, №5: 22-29.

- [12] Carleton R. Bern, Melanie L. Clark, Travis S. Schmidt, Jo Ann M. Holloway, Robert R. McDougal, 2015. Soil disturbance as a driver of increased stream salinity in a semiarid watershed undergoing energy development. *Journal of Hydrology*, Vol. 524: 123-136.
- [13] Lyakhovich V.V., Plaksenko A.N., Ipat'eva I.S., Bocharov V.L., Vishnevsky A.A., 1988. Accessory minerals in Archean komatiites of the Kursk magnetic anomaly. *Reprints of the Academy of Sciences of the USSR. Earth Science Sections*, vol. 300, № 3: pp. 133-136.
- [14] Kuznetsov V.A., 2001. Self-cleaning of river valley landscapes from the radioactive contamination. *Lithosphere*, №1 (14): 13-21.
- [15] Ivanov G.N., 2014. Dynamics of water ecosystem pollution by heavy metals in Lake Seliger. *Proceedings of Instorfa scientific journal*, №9 (62). Tver: TvGTU: 16-24.
- [16] Safina G.R., 2015. Anomalous Manifestation of Erosion and Suspended Sediment Yield in the East of Russian Plain. *Research journal of pharmaceutical biological and chemical sciences*, 6 (4): p. 2103
- [17] Gumbel E.J., 1958. *Statistics of extreme N. Y.*, Columbia UP. XX: 375.
- [18] Starkel L., 1976. The modeling of extreme (catastrophic) meteorological events in the contemporaneous evolution of slopes. *Geomorph. and climate*. Wiley and Sons: 175-179.
- [19] Dedkov A.P., Mozzherin V.I., 1996. Erosion and sediment yield on the earth, vol. 236: pp. 29-33.
- [20] Sorokina E.P., 1983. Mapping of technogenic anomalies for the geochemical evaluation of urbanized areas. *The issues of geography. Landscape-geochemical zoning and environmental protection*, Coll. 120: 55-67..
- [21] Hajrullina D.N., G.R. Safina, 2010. Opportunities of use mechanical denudation's electronic data base for studying time variability of weighed deposits' drain. *Journal of Ecology and Industrial Safety*, 2: 6-12.
- [22] Filenko R.A., 1974. *Hydrological zoning of the North of the European Part of the USSR*. Publishing House of Leningrad University Press: 223.
- [23] Khayrullina D.N., 2014. About correlation analysis of atmospheric precipitation chemical compound in the North of the Russian plain. 14th international multidisciplinary scientific GeoConference SGEM: pp. 267-272.
- [24] Kurbanova S.G., Denmukhametov R.R., Sharifullin A.N., 2014. Assessment of speed concerning the recent floodplain alluvium accumulation in basin of minor rivers of the east of the Russian plain. *Life Science Journal*, vol. 11, № 11: 480-483.
- [25] Khayrullina D.N., Fedorova V.A., 2014 Sodium balance structure within the elementary geosystems (by the example of basin of the Elva river in the Komi republic), *Advances in Environmental Biology*, vol. 8, № 4: 1015-1020.