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Integrated Assessment of Groundwater Contamination in the Pre-Volga Region (Russia) and Identification of Potential Health Risks to the Public

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ABSTRACT

Contamination of drinking groundwater with toxic trace elements poses a threat to public health. The present study analyzed samples of various groundwaters from the Pre-Volga Region, Russia. The groundwaters studied in the Pre-Volga Region are classified into four hydro- chemical facies based on the proportion of cations and anions: (I) gypsum waters, (II) mirabilite waters, (III) waters altered by ion exchange, and (IV) fresh infiltration waters. Gypsum groundwaters exhibit relatively high concentrations of Al, Mn, Sr, Co, Cr and Fe, mirabilite waters contain elevated levels of Ni, Pb and As, sodic waters have high concentration levels of Cu and Fe, and hydrogen carbonate waters are enriched in Zn, Ba and V. Most samples of gypsum and mirabilite waters exhibit high salinity, rendering them inappropriate for human consumption. Pollution index of groundwater (PIG), trace metal evaluation index (TMEI), contamination index (CI), trace metal pollution index (TMPI), trace metal toxicity index (TMTI), non-carcinogenic health risk (HI) and carcinogenic health risk (CR) were used to assess the level of pollution in the study area. The calculation of indices indicates that due to natural and anthropogenic pollution, the groundwater of the Pre-Volga Region is primarily contaminated with high levels of $SO4^{2-}$, TDS, Fe, Mn, Al, Ni, and As to a greater extent, and lesser concentrations of Ba, Pb, and Co. The study's findings will furnish valuable insights into crafting comprehensive strategies for safeguarding the quality of subterranean potable water in the Pre-Volga Region.

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INTRODUCTION

Groundwater is a crucial resource and frequently deemed to be a safer alternative to surface water sources because of the natural filtration process of contaminants through the soil layer (Wang et al., 2020). However, cases of groundwater contamination from both natural and anthropogenic sources have been reported in studies (Venkatramanan et al., 2014; He & Wu, 2019). The contamination of drinking groundwater with trace metals is now a major environmental concern (Sankhla & Kumar 2019; Singha et al., 2020). The study of trace metals is of wide interest due to their hazards as pollutants, including their longevity in the atmosphere, ability to accumulate in the human body through bioaccumulation, and toxicity and carcinogenicity even at low concentrations (Jacob et al., 2018; Ali et al., 2019). Natural processes of pollution include soil erosion, weathering and dissolution of rocks and soils, ion exchange, contact with products of volcanic activity and others (Ciner et al., 2020; Wang et

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al., 2021). Anthropogenic sources of trace metals include landfills and effluents from mining, industrial, agricultural and domestic wastes, population growth is affected (Dahiya, 2022; Ahirvar et al., 2023).

Trace metals can be present in the food chain, exposing humans to their potential harmful effects (Mitra et al., 2022). Certain trace metals (Fe, Cu, Co, and Mn), are essential for the human metabolic system when consumed in small amounts. However, ingestion of such metals in quantities above the permitted dose can lead to symptoms of poisoning, and long-term ingestion of metals above the permitted concentration can cause various diseases (Setia et al., 2020). Other metals (Cr, Cd, Pb and As) cause serious health effects even at lower concentrations (Pandit et al., 2020; Sahoo & Sahu 2022).

There is no universal method of calculating contamination levels to assess metal contamination of groundwater. Estimation of total metals is insufficient to determine groundwater contamination levels (Wei et al., 2019; Kumar et al., 2020). Thus, numerous techniques for computing water quality indices have been broadly employed to comprehensively evaluate multiple hazards from heavy metals in groundwater (Saleh et al., 2019; Singha et al., 2020). As every index has its specific focus, a combination of multiple indices has been used in most research studies to establish the overall pollution status (Yakovlev et al., 2021; Ahirvar et al., 2023).

The formation of groundwater's chemical composition in the Pre-Volga Region situated in the middle reaches of the Volga River (European part of Russia) is influenced by various geological, economic, and physiographic factors. All pollution sources in the Pre-Volga Region have been identified, including industrial, mining, transport, municipal, agricultural, and energy sources (Nuriev, 2002). However, the most significant sources of pollution in the Pre-Volga Region are related to agriculture, including cattle farming, pig farming, poultry complexes, agricultural aviation loading sites, machine-tractor workshops and stations, sewage disposal pipelines, and the use of fertilizers and pesticides (Nuriev, 2002). Previously collected data in the Pre-Volga Region indicate that the concentrations of certain trace metals exceed the maximum permitted concentration (MAC) multiple times within the vicinity of pollution sources (Nuriev, 2002).

Given the crucial role of groundwater in providing household and drinking water in the Pre-Volga Region, and the numerous potential sources of water contamination with trace elements, assessing groundwater quality in the Pre-Volga Region is an urgent task. The theoretical analysis of the research problem allowed us to formulate the hypothesis that the groundwater of the Pre-Volga region is significantly polluted and that, in addition to the geological factor, anthropogenic activities have an impact on the quality of these groundwaters. In this regard, the purposes of this research are to comprehensively assess the extent of groundwater contamination in the Pre-Volga Region and to identify potential risks to public health. This is the first time that generally accepted indices have been used to assess the quality of drinking groundwater in the Pre-Volga Region. This study is unique in both the sampling location and the comprehensive approach used to establish the properties and identify the level of metal contamination in drinking groundwater. The study results will inform the development of integrated measures for managing drinking groundwater quality in the Pre-Volga Region.

MATERIAL & METHODS

Study area

Groundwater sampling was carried out in August 2022 within the Pre-Volga Region (figure 1). In total, 41 groundwater samples were collected from wells ranging in depth from 38 to 161m. Most groundwater samples were obtained from long-term operating wells that provide water to residential areas, livestock farms and other agricultural industries. Occasionally, samples were collected from shallow wells and springs. Over 90% of groundwater samples are representative of the Permian carbonate-terrigenous and sulphate-carbonate aquifer complexes (53% and 22%,

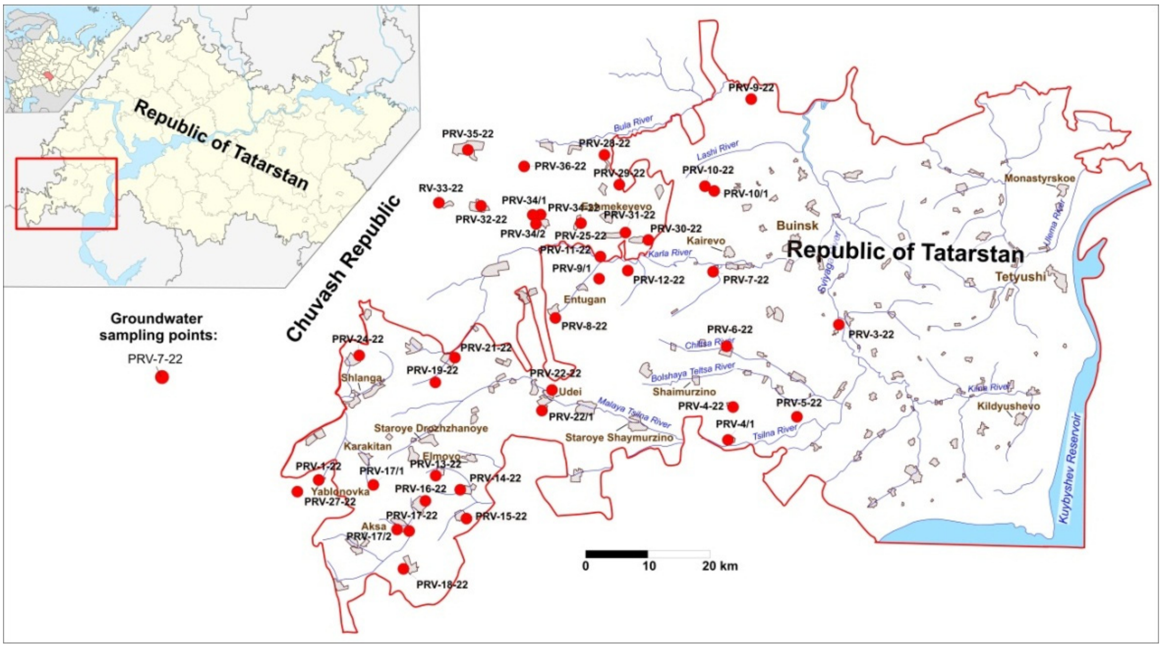

Fig. 1. Map of groundwater sampling in the Pre-Volga Region

respectively). The remaining samples belong to overlying hydrogeological units of Mesozoic age. The area of the Pre-Volga Region in the Russian Federation is situated in the eastern part of the East European Platform. Specifically, it occupies the right bank of the Volga River near the Kuibyshev Reservoir, including the southeastern part of Tatarstan, southern Chuvashia, and northern Ulyanovsk Oblast. The study area is located in the territory of the Tokmovsky arch and the Kazan-Kirovsky trough, where the sedimentary type of rocks is widespread, containing mainly ziolitic rocks, carbonate rocks, argillaceous rocks, siltstones, sand-gravel mixtures, sands, gypsum and others. At depth, in the crystalline basement, igneous and metamorphic rocks are developed (Burov et al., 2003). In terms of hydrogeology, the research area is situated within the Pre-Volga Region of the Volga-Sursky artesian basin. Most of the water supply wells, up to 180 m in depth, are situated in rocks comprising of Permian sediments. Genetically, these sediments constitute continental lagoonal and shelf marine formations that are characterized by interbedded mudstones, siltstones and sandstones (Physical..., 2019). The primary source of domestic drinking water supply in the Republic of Tatarstan is groundwater obtained from the Tatar and Kazan stages of the Upper Permian, with additional supply originating from the Mesozoic aquifer complexes located in the south-west region (Nuriev, 2002).

Sample collection

Water sampling was performed using polymer tubes. Samples were passed through a 0.45 µm membrane filter and acidified using high-purity HNO_3 until pH dropped below 2.

Analysis of physical and chemical parameters of water and trace metals

Physico-chemical parameters (pH, Eh, total dissolved solids (TDS) and temperature), were directly determined at the time of sampling. The pH and Eh were measured using a replaceable electrode, and TDS and temperature were measured with a MARK-603/1 conductometer (VZOR, Russia). The redox potential value was re-evaluated under standard circumstances. The main anions (HCO_3^-, SO_4^{2-}, and Cl^-) and cations (Ca^{2+}, Mg^{2+}, and Na^+) were identified by ion chromatography on an LC-20 Prominence liquid chromatograph (Shimadzu, Japan). Metals

(Al, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, As, Fe, Ba, Sr, and V) in water were analyzed using a ShimadzuAA-7000 atomic absorption spectrometer. Quality assurance for each parameter was provided by three parallel samples to determine a mean, as well as through timely calibration of the measuring instruments.

Pollution indices

The PIG index (pollution index of groundwater) assesses how pH, salinity, and ion content parameters impact on water quality and human health. The PIG determined through a series of steps (Rao, 2012; Ahirvar et al., 2023). Initially, the relative weight (R_w) of each parameter is established on a 1 to 5 scale. The R_w value is contingent upon the separate impacts of parameters on water quality and human health (Rao, 2012). The weighting parameter W_p, which assigns a weight to each water quality characteristic, is obtained from Eq. (1):

$$W_p = \frac{R_w}{\sum R_w} \tag{1}$$

The status of concentration (S_c) of water quality measure is calculated using Eq. (2):

$$S_c = \frac{C}{D_s} \tag{2}$$

where C is the observed concentration of the individual parameter, D_s is the individual water quality standard. The PIG index is calculated using Eqs. (3 and 4):

$$O_w = W_p \times S_c \tag{3}$$

$$PIG = \sum O_w \tag{4}$$

where O_w is the overall water quality. The waters are classified as follows: PIG < 1.0 is insignificant pollution, 1.0 < PIG <1.5 is low pollution, 1.5 < PIG < 2.0 is moderate pollution, 2.0 < PIG < 2.5 is high pollution, and PIG > 2.5 is very high pollution (Rao, 2012).

The TMEI index (trace metal evaluation index) was calculated using the Eq. (5):

$$TMEI = \sum_{i=1}^{n} \frac{TM_{Conc}}{TM_{MPC}} \tag{5}$$

where TM_{Conc} and TM_{MPC} represent the monitored concentration and the maximum permitted concentration for a specific trace metal, respectively (Zakir et al., 2020). It is assumed that <0.3 is very pure, 0.3 - 1.0 is pure, 1.0 - 2.0 is slightly affected, 2.0 - 4.0 is moderately affected, 4.0 - 6.0 is strongly affected, > 6.0 is seriously affected (Haque et al., 2019).

The CI (contamination index) values were estimated as per the Eq. (6):

$$CI = \sum C_{Fi} = \sum \frac{C_{Oi}}{C_{Si}} - 1 \tag{6}$$

where C_{Fi} is the factor of pollution, C_{Oi} is the measured concentration of ith metal, C_{Si} is the maximum permissible concentration of ith metal. The CI is calculated by summing the contamination factors of individual metals exceeding C_{Si}. Groundwater CI are classified into three levels of pollution: CI < 1 for low, 1–3 for moderate, and > 3 for high pollution. The critical value for CI is 3 for household consumption (Singha et al., 2020).

The TMPI index (trace metal pollution index) is given by Eq. (7) and calculated using Eq. (8) and Eq. (9):

$$TMPI = \frac{\sum_{i=1}^{n}\left(Q_i \times W_i\right)}{\sum_{i=1}^{n} W_i} \quad (7)$$

$$Q_i = \frac{C_i}{S_i} \times 100 \quad (8)$$

$$W_i = \frac{k}{S_i} \quad (9)$$

where Q_i represents the sub-index of the ith trace metal parameter, W_i is the unit weight of the ith metal reflecting its relative importance, n specifies the number of metals, C_i refers to the concentration of the ith trace metal in µg/L, S_i denotes the highest permissible standard concentration of the ith metal, and k represents a proportionality constant. The researchers adopted a value of k = 1 following the approach of Wanda et al. (2012). The highest standard permissible concentration for drinking-water quality is sourced from Table 1 of the World Health Organization (WHO) guidelines (WHO, 2017). The critical TMPI value for drinking water is 100, as per Ahirvar et al. (2023). Though a modified scale is often used: when the TMPI is less than 15, the pollution level is considered low, when it ranges between 15 and 30 it is medium, and when it exceeds 30, it is high (Prasad & Bose, 2001).

Index TMTI (trace metal toxicity index) was calculated using the Eq. (10):

$$HMTL = \sum_{i=1}^{n} C_i \times HIS_i \quad (10)$$

Table 1. Values of trace metal parameters for calculating water pollution indices.

Element	C_i, µg/L	HIS_i	K_p	RfD_{ing}	RfD_{derm}	SF, mg/L
Al	200	685	$1 \cdot 10^{-3}$	1.3	0.07	-
Cr	50	895	$2 \cdot 10^{-3}$	3	0.08	0.5
Mn	500	797	$1 \cdot 10^{-3}$	24	0.96	-
Co	100	1011	$4 \cdot 10^{-4}$	0.3	0.06	-
Ni	20	993	$2 \cdot 10^{-4}$	20	0.8	1.7
Cu	2000	805	$1 \cdot 10^{-3}$	40	8	-
Zn	3000	913	$6 \cdot 10^{-4}$	300	60	-
Cd	3	1318	$1 \cdot 10^{-3}$	0.5	0.03	15
Ba	1300	800	$1 \cdot 10^{-3}$	70	14	-
Pb	10	1531	$1 \cdot 10^{-4}$	1.4	0.42	0.0085
V	-	648	$1 \cdot 10^{-3}$	1	0.01	-
As	10	1676	$1 \cdot 10^{-3}$	0.3	0.12	1.5
Sr	-	0	$1 \cdot 10^{-3}$	600	120	-
Fe	300	0	$1 \cdot 10^{-3}$	700	140	-

where C_i represents the concentration of metals in water (mg/kg), HIS_i is the total hazard score assigned to the metal based on the Toxicological Profiles of the Priority List of Hazardous Substances prepared by the Agency for Toxic Substances and Disease Registry (Table 1) (Zakir et al., 2020). The subsequent water classifications according to TMTI values: low toxicity ranges from 0-100, moderate toxicity ranges from 100-300, high toxicity ranges from 300-500, very high toxicity ranges from 500-1000, and toxicity above 1000 is deemed extremely high (Yakovlev et al., 2021).

HI index (non-carcinogenic health risk) was evaluated using a multi-step procedure based on the risk appraisal methodology advised by the United States Environmental Protection Agency (USEPA, 2004; Kumar et al., 2019). The initial step incorporates Eqs. 11 and 12:

$$ADD_{ing} = \frac{C_i \times IR \times EF \times ED}{BW \times AT} \quad (11)$$

$$ADD_{derm} = \frac{C_i \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \quad (12)$$

where ADD_{ing} (µg/kg·day) and ADD_{derm} (µg/kg·day) are the average daily doses through ingestion and dermal absorption of water, respectively (Kumar et al., 2019). In equations (11) and (12) C_i is the concentration of the TMs (µg/L), IR is the ingestion rate (2.0 L/day), EF represents exposure frequency (350 days), ED is exposure duration (30 years), BW indicates body weight (70 kg), AT is the average time (10950 days), SA represents exposed skin area (18000 cm^2), Kp is the skin adherence factor (Table 1), ET represents exposure time (0.58 h/day), CF is the conversion factor (0.001).

The non-carcinogenic risks were determined by applying the hazard quotient (HQ) which calculated by Eq. (13):

$$HQ_{ing/derm} = \frac{ADD_{ing/derm}}{RfD_{ing/derm}} \quad (13)$$

where RfD_{ing} и RfD_{derm} are the ingestion and dermal reference doses (µg/kg·day), respectively (Table 1) (Kumar et al., 2019), HQ_{ing} and HQ_{derm} are the hazard quotient through ingestion and dermal absorption, respectively.

The hazard index (HI) represents the overall potential non-carcinogenic health risks arising from various trace metals found in water. Calculation of the HI was performed using Eqs. (14 and 15) as described by Zakir et al. (2020).

$$HI_{ing/derm} = \sum_{i=0}^{n} HQ_{ing/derm} \quad (14)$$

$$HI = HI_{ing} + HI_{derm} \quad (15)$$

The threshold level is 1.0, indicating potential non-carcinogenic health hazards for the nearby community when HI value exceeds 1.0 (Mohammadi et al., 2019).

The CR (cancer risk) was calculated for exposure to a carcinogens (Cr, Ni, Cd, As, Pb) using the following Eq. (16 and 17):

$$CR_{ing/derm} = ADD_{ing/derm} \times SF \tag{16}$$

$$CR = CR_{ing} + CR_{derm} \tag{17}$$

where, *SF* is the slope factor (mg/kg·day Table 1) (USEPA, 2004; Kumar et al., 2019). The values of SF for the carcinogens were introduced from the California Office of Environmental Health Hazard Assessment (OEHHA, 2020). The acceptable range for CR is 1.0×10^{-6} to 1.0×10^{-4}, and values of CR > 10^{-4} imply a significant human cancer risk (Mohammadi et al., 2019).

Statistical analysis

Statistical analysis of data and creation of multiple graphs were conducted with OriginPro 9.9.0.225, Release 2022 (OriginLab Corporation, USA). Water quality maps were generated utilizing 'Surfer 13' software.

RESULTS AND DISCUSSION

Hydrochemistry and physico-chemical parameters of groundwater

When using the Piper diagram to identify groundwater types and hydrochemical facies, it was observed that the majority of groundwaters consist of blends of calcium and sodium waters according to cation composition, with a small input from the magnesium component (figure 2). Based on their anionic composition, the investigated groundwaters predominantly belong to hydrocarbonate and sulphate types. The sulphate groundwater (consisting of gypsum and mirabilite) in the study area exhibits a hydrochemical appearance due to the widespread presence of evaporites which dissolve in the water (Nuriev, 2010). It has been observed that hydrocarbonate magnesium-calcium groundwater holds significant importance for the Pre-

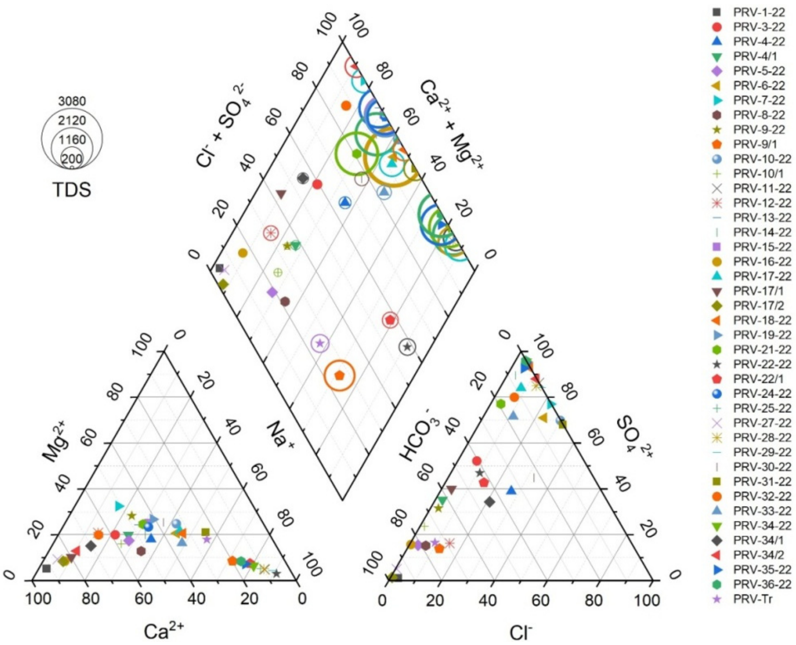

Fig. 2. Distribution of the ionic composition of the groundwater of the Pre-Volga Region on the Piper diagram (the size of the icons corresponds to the mineralization)

Table 2. Physicochemical properties and ion content in the Pre-Volga Region groundwater.

Water type	Hydrochemical facies	Value	T, °C	pH	TDS, mg/l	Eh, mV	Ion content in water, mg/l					
							HCO^{3-}	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+
Deep circulation waters	Gypsum waters (I)	min	8.2	6.93	503	132	0.0	100	21.2	58.1	28.2	32.5
		max	15.3	8.20	3088	354	286	1785	521	415	226	450
		mean	12.5	7.51	1468	208	60.2	876	106	218	109	183
	Mirabilite waters (II)	min	10.7	7.53	506	95	0.0	111	8.5	14.2	7.1	49.4
		max	15.1	8.55	2398	236	770	1743	267	111	98.0	439
		mean	12.3	7.99	1481	284	141	817	115	66.7	35.6	321
Waters changed through ion exchange influence	Sodic waters (III)	min	8.0	7.51	651	-	140	125	70.4	65.1	42.2	84.6
		max	10.6	7.80	950	113	562	160	110	107	47.0	150
		mean	9.3	7.66	800	-	351	143	90	86	44.6	117
Infiltration freshwater	Hydrocarbonate waters (IV)	min	6.2	7.06	208	234	90.1	1.4	0.5	67.2	6.0	3.6
		max	13.8	7.84	788	389	305	72.1	66.4	216	70.0	56.5
		mean	11.2	7.39	362	306	161	37.8	11.7	96.4	22.4	25.8

Volga Region (Nuriev, 2002). Table 2 displays the main ion concentrations in the facies. The Piper diagram reveals that 18 samples fall under hydrochemical facies I (gypsum waters, Ca^+–SO_4^{2-}) and 11 samples are located closer to the zone of facies II (mirabilite waters, Na^+–SO_4^{2-}). Considering that a majority of the samples from facies I and II exhibit salinity levels greater than 1000 mg/l, it is reasonable to assume the presence of deep groundwater circulation. Two samples are classified as facies III (sodic waters, Na+-HCO_3^-) and likely reflect water formation through cation exchange of calcium for sodium during filtration through the terrigenous component of the section. The final 10 specimens belong to facies IV (Ca^{2+}–Na^+–Mg^{2+}–HCO_3^-), signifying shallow circulating hydrocarbonate fresh water. For comparison, the majority of samples collected from groundwater in the Chelyabinsk Region are calcium (1.1 - 239.2 mg/l) and hydrocarbonation (33.6 - 674.7 mg/l) waters (Nokhrin & Davydova, 2020). In the Varaha river basin of India, the levels of Ca^{2+} (35 to 75 mg/l) and SO_4^{2-} (23 to 170 mg/l) in the groundwater are lower than those found in Pre-Volga waters, the levels of Na^+ (159 to 883 mg/l), HCO_3^- (400 to 970 mg/l), and Cl^- (140 to 1470 mg/l) are higher than the values discovered in the present study, and Mg^{2+} concentrations (30 to 115 mg/l) remain relatively similar (Rao, 2012). It is noteworthy that the use of pesticides leads to contamination of groundwater in the Pre-Volga Region with Ca^{2+}, Mg^{2+}, K^+, Na^+, NH^{4+}, NO^{3-}, SO_4^{2-}, HCO_3^-, and PO_4^{3-} (Nuriev, 2002).

The values of the physico-chemical parameters of the groundwater facies of the Pre-Volga Region are given in Table 2. In general, the temperature of the groundwater studied varies between 6.2 and 15.3 °C, which allows it to be classified as cold water according to the water classification. It should be noted that lower temperatures are determined for wells with a depth of more than 100 m. The pH was found to be between 6.93 and 8.55. Only slightly elevated values were noted for facies II. The pH in the present study aligns with the levels of WHO guidelines for drinking water (WHO, 2017). A comparable range of pH (6.5-8.5) is observed for groundwater in the Chelyabinsk Region (Nokhrin & Davydova, 2020). pH for groundwater of the Leningrad Region of Russia varies between 5.0-8.7 (Vinograd et al., 2019). Groundwater samples from the Varaha River basin in India have pH ranging from 7.1 to 8.2 (Rao, 2012). Groundwater in Busan City, South Korea, displays a pH range from 6.2 to 7.9 (Venkatramanan et al., 2014).

The redox potential of the groundwater under investigation ranged between 95-389 mV, thus indicating the prevalence of weak to moderately oxidizing conditions and. the presence of dissolved elements such as oxygen, Fe^{3+}, Cu^{2+}, and Pb^{2+} in the water. A study by Ayejoto et al. (2021) revealed an oxidizing and reducing environment with Eh values ranging from -280 to 303 mV in the Bazman basin groundwater system, Iran.

The mineralization of the groundwater examined revealed a broad variation ranging from 208 to 3088 mg/l. It should be highlighted that facies I and II exhibited higher mineralization

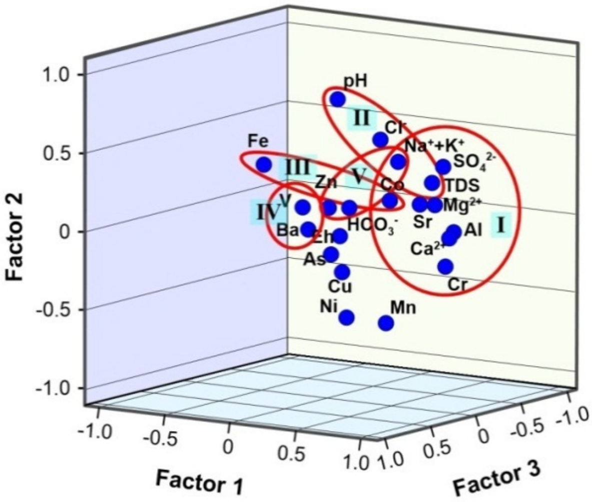

Fig. 3. Diagram of factor loadings for the groundwater in the Pre-Volga Region.

values. It has been observed that 67% of samples from facies I and 73% of samples from facies II exceed the recommended WHO limits for salinity and therefore are deemed unsuitable for human consumption (salinity above 1000 mg/l) (WHO, 2017). It has been previously reported that the calcium sulphate waters in the Pre-Volga Region, near facies I and II, with a relatively high degree of mineralization are a result of natural processes of gypsum dissolution in water-bearing rocks (Nuriev, 2002). It should be noted that hydrocarbonate magnesium-calcium groundwater in the Pre-Volga Region typically exhibits a mineralization range of 200 - 400 mg/l in waters from the active water exchange zone, beyond the areas where evaporite distribution occurs (Nuriev, 2002). The Permian formations of the Kazan sulphate-carbonate formation (P_2kz) and the Urzhum terrigenous-carbonate formation (P_2ur) are water-uppers. The Upper Permian sediments are overlain by the mentioned layers, leading to the division of the section into active and slow water exchange zones. Consequently, at depths between 60-180 m, there are bodies of water with mineralization exceeding 1 g/l and up to 6 g/l (Nuriev, 2010). By contrast, the mineralization levels of calcium groundwater in the Chelyabinsk Region are comparatively lower, ranging from 25-1050 mg/l (Nokhrin & Davydova, 2020). Groundwater in St. Petersburg and the Leningrad Region of Russia has levels of minerals ranging from 67 to 8368 mg/l (Vinograd et al., 2019). The Varaha river basin in India has groundwater mineral levels that range from 850 to 3380 mg/l (Rao, 2012).

Metal content in groundwater

Trace metals in the groundwaters were tested (Table 3). It can be seen that gypsum waters (facies I) were relatively enriched in Sr (up to 9409 μg/l), Mn (up to 987 μg/l), Fe (up to 614 μg/l), Al (up to 77.5 μg/l), Co (up to 5.5 μg/l) and Cr (up to 0.8 μg/l), while deep-seated mirabilite waters (facies II) show slightly elevated levels of Ni (up to 11.0 μg/l), As (up to 8.1 μg/l) and Pb (up to 2.7 μg/l). The sodic groundwater in facies III displays elevated Fe levels (up to 1640 μg/l) and Cu levels (up to 4.8 μg/l), while the shallow hydrocarbonate freshwater in facies IV features marginally higher amounts of Ba (up to 262 μg/l), Zn (up to 24.1 μg/l) and V (up to 6.7 μg/l). Previous research demonstrated that the concentration of trace metals in groundwater located in the Pre-Volga Region in the Republic of Tatarstan was as follows: Cu 0.1-10 μg/l, Pb 2-34 μg/l, Zn 4-89 μg/l, and Cd 0.1-0.9 μg/l (Nuriev, 2002). These values were marginally higher than those found in present study. When comparing the groundwater between the Chelyabinsk Region in Russia and the Pre-Volga Region, it was determined that the latter

Table 3. Metals content in the groundwater of the Pre-Volga Region.

Hydrochemical facies		Metal content in water, μg/l													
		Al	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb	As	Fe	Ba	Sr	V
I	min	0.0	0.20	1.50	2.00	0.0	0.20	0.50	0.10	0.50	0.50	0.50	1.80	990	0.50
	max	77.5	0.80	987	5.50	4.60	1.70	13.8	0.10	0.50	0.50	614	44.1	9409	0.90
	mean	31.3	0.51	133	3.72	0.87	0.31	2.14	0.10	0.50	0.50	178	14.0	4998	0.53
II	min	1.40	0.00	3.30	0.30	0.00	0.20	0.50	0.10	0.50	0.50	3.40	1.20	236	0.50
	max	4.90	0.60	58.3	4.00	11.0	0.60	17.7	0.10	2.70	8.10	169	19.7	3789	4.20
	mean	2.70	0.26	18.1	2.11	1.78	0.27	2.44	0.10	1.09	1.78	35.8	6.71	1492	0.84
III	min	2.10	0.20	18.0	1.90	0.30	0.20	0.50	0.10	0.50	0.50	3.30	11.6	1479	0.50
	max	2.40	0.30	60.9	4.20	0.60	4.80	5.30	0.10	0.50	0.50	1640	18.2	1639	0.50
	mean	2.25	0.25	39.5	3.05	0.45	2.50	2.90	0.10	0.50	0.50	822	14.9	1559	0.50
IV	min	0.0	0.0	0.0	0.40	0.0	0.20	0.50	0.10	0.50	0.50	0.00	1.20	348	0.50
	max	25.9	0.70	367	3.00	5.10	1.80	24.1	0.10	0.50	6.30	40.3	262	1699	6.70
	mean	4.53	0.33	59.5	1.34	1.64	0.76	4.40	0.10	0.50	1.11	8.24	52.1	699	1.60
MPC*		200	50	500	100	20	2000	3000	3	10	10	300	700	-	-

* The maximum permitted concentration

Table 4. Groundwater quality indices of the Pre-Volga Region.

Facies		PIG	TMEI	CI	TMPI	TMTI	HI	CR
I	min	0.78	0.28	0.00	3.53	17.0	0.40	0.65
	max	4.18	3.25	1.05	6.49	867	3.60	2.86
	mean	2.26	1.26	0.24	4.34	146	1.63	1.10
II	min	0.73	0.26	0.00	3.84	12.8	0.17	0.86
	max	3.42	1.71	0.00	22.9	71.4	1.24	8.89
	mean	2.04	0.61	0.00	7.21	30.7	0.53	2.02
III	min	0.91	0.25	0.00	3.56	39.1	0.36	0.79
	max	1.12	5.83	4.45	6.66	65.2	0.75	0.94
	mean	1.01	3.04	2.23	5.11	52.1	0.56	0.87
IV	min	0.35	0.20	0.00	3.53	6.35	0.16	0.62
	max	1.02	1.44	0.00	13.6	408	1.70	4.14
	mean	0.54	0.54	0.00	5.13	95.2	0.54	1.68

contains significantly higher amounts of Sr while other metals were found to be present in lower concentrations (Nokhrin & Davydova, 2020). Groundwater in Busan City, South Korea, contains Fe concentrations between 1-140 μg/l and Mn concentrations between 1-500 μg/l, which are similar to the waters of facies II and IV of the Pre-Volga Region, and Zn contents between 40-260 μg/l, Cu 1-240 μg/l and Cd 1-3 μg/l, which are higher than the values obtained in the present study (Venkatramanan et al., 2014).

Recently, agricultural activities have been causing an increase in the pollution of groundwater with trace metals (Li et al., 2013; Nuriev, 2002). This process involves the use of significant amounts of organic and mineral fertilizers and pesticides, as well as the storage of animal waste (Santos et al., 2002). Trace metals can leach into underlying groundwater when there is sufficient surface water infiltration (Nouri et al., 2008). Developed farming is widespread in the Pre-Volga Region, which is likely the primary cause of anthropogenic impact on groundwater.

Assessment of groundwater quality

Trace metal contamination assessment of groundwater in the Pre-Volga Region was conducted by computing water quality indices and indices for evaluating public health risks (Table 4). Effect of metal and ion content on water quality indices and public health risks shown in the figure 4. The PIG is a significant tool for evaluating the quality of drinking groundwater (Rao, 2012; Egbueri et al., 2020). Calculation of the PIG showed that the index ranging from 0.35 to 4.18 (Table 4). Revealed that 34.1% of the sampled wells had insignificant pollution levels, while 6% and 6% of the wells had low and moderate pollution levels, respectively. Additionally, 4% and 26.8% of the wells were classified as having high and very high pollution levels, respectively. On average, facies I and II have a high level of contamination. Groundwater

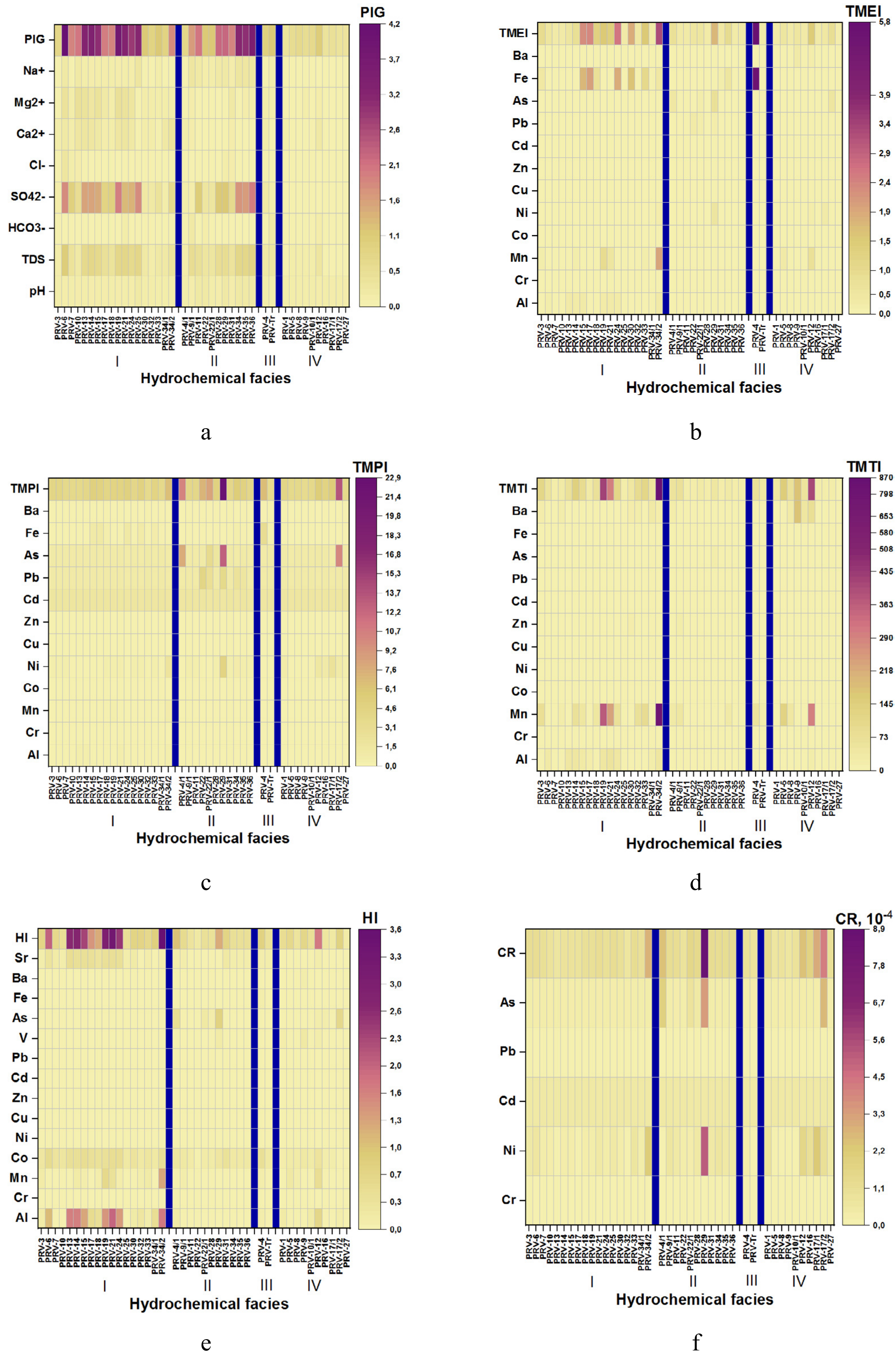

Fig. 4. Effect of metal and ion content on water quality indices and public health risks: a. PIG; b. TMEI; c. TMPI; d. TMTL; e. HI; f. CR

with a high pollution classification was identified for boreholes situated on different livestock farms, the wells that supplies water to the kindergarten and water village. Groundwater with low pollution levels is available for facies III and IV. According to figure 4a, high mineralization and SO_4^{2-} concentrations have the most impact on the PIG. This is also the case for the Mg^{2+} content of facies I. For instance, it was discovered that 20% of groundwater samples taken from southeast Nigeria were severely contaminated and unsuitable for human consumption (Egbueri, 2020). The PIG for groundwater in Varaha river basin, India, ranges from 0.83 to 2.55, with a zone of very high contamination is observed where waters are associated with Cl^- (Rao, 2012). The PIG computed for the Tebessa basin in north-east Algeria range from 0.46 to 8.19 (Djebassi et al., 2021). Both the present study and Djebassi et al. (2021) found that the PIG is affected by high salinity and concentrations of SO_4^{2}.

The range of TMEI for the studied waters was between 0.29 and 5.83. Based on the index, most of the groundwaters are suitable for domestic use. Specifically, 29.3% are classified as very pure and 41.5% as pure. However, there are also slightly affected waters (17.1%), moderately affected waters (9.8%), and strongly affected waters (2.4%). The TMEI showed that some groundwater boreholes in facies I were "moderately affected" (a spring in the church font, boreholes on farms) and for facies III groundwater, a "strongly affected" borehole was identified on a farm in the village of the Chuvashskie Kishchaki village. Water in facies II and IV is graded from "very pure" to "slightly affected". High Fe content has the most impact on the TMEI, with Mn less significant (figure 4b). The TMEI (HEI) varies widely in groundwater from other districts. For instance, groundwater from Arang in Chhattisgarh State, India has a notably higher TMEI measure, ranged from 2 to 42 (Singha, 2020). For Semi-arid Coastal Aquifers on the Maputaland coastal plain in South Africa, the HEI ranged from 0.08 to 10.25 (Mthembu et al., 2022).

In the study area, the CI ranges from 0.00 to 4.45. The investigation revealed that 95.2% of wells in the Pre-Volga Region have low levels of water pollution. Moderate pollution was found in 2.4% of the wells, while high pollution was found in 2.4% of them. Facies I, II, and IV exhibit low pollution classes on average. The water of facies I in the borehole of the farm has a moderate pollution class. Water of facies III is on average moderately polluted, but the water in the borehole for the water supply of the Ishmurzino-Surinsk village is highly polluted. The CI in polluted waters of the Pre-Volga Region is affected by the amount of Fe and Mn present. When compared, the CI of groundwater from Arang in Chhattisgarh State, India ranged from 0 to 37 (Singha, 2020). For the ground water found in Busan City, South Korea, the CI categorizes 85% of the samples in the medium contamination zone, with only 5% in the high contamination (Venkatramanan et al., 2014).

The study of groundwater in the Pre-Volga Region revealed that the TMPI ranges from 3.53 to 22.9. Of the wells studied, 97.5% had water with low pollution levels. One of the boreholes for water supply in the Ishmurzino-Surinsk village, where the water belongs to the facies II, shows a moderate level of contamination. Overall, all groundwater investigated presents a TMPI below the critical level. The TMPI shows a sensitivity to As content while Pb and Ni are less influenced (figure 4c). TMPI (HMPI) has been employed internationally for water quality assessment in numerous research studies. Thus, the groundwater HPI in Arang, Chhattisgarh State, India, has a range of 5 to 396 (Singha, 2020). For the groundwater in the Maputaland coastal plain located in Africa, the HPI exhibited a range from 0.28 to 128 (Mthembu et al., 2022). The groundwater in Busan City, South Korea, had HPI ranging from 3 to 135 (Venkatramanan et al., 2014).

The TMTI ranged from 6.4 to 867 in the present study. In the Pre-Volga Region, the majority of groundwater (75.6%) has a low toxicity level, 17.1% of the waters have moderate toxicity, while 4.8% and 2.4% have high and very high toxicity levels, respectively. According to TMTI calculations, the collected samples of groundwater mirabilite (facies II) and sodic water (facies III) are classified as having a low toxicity level. Hydrocarbonate waters of facies IV generally exhibit low toxicity, however, moderate toxicity levels were observed in two boreholes located in farms, and high levels were detected in a borehole situated in a farm in the Yembulatovo village. Gypsum groundwater (facies I) generally exhibits moderate toxicity, however, the

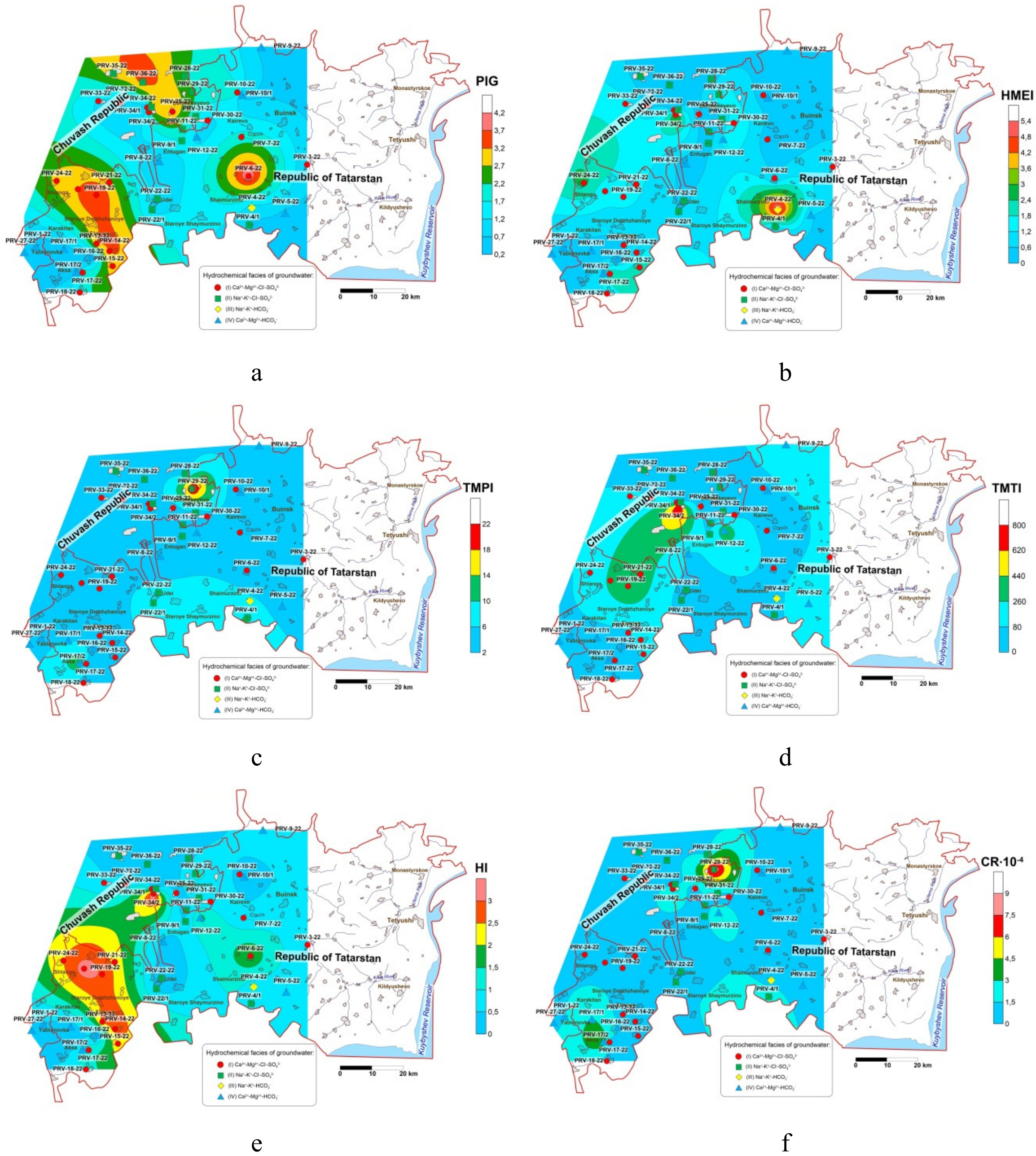

Fig. 5. Maps of water quality indices and health risks of the population in the Pre-Volga Region: a. PIG; b. TMEI; c. TMPI; d. TMTI; e. HI; f. CR

water at two specific sites, namely a borehole at the farm and a spring in the church, displays very high and extremely high toxicity, respectively. In this study, Mn and Ba were found to influence the toxicity index (figure 4d). Higher TMTI (HMTL) were discovered in the Lower Cretaceous Abakaliki aquifer in Ameka area, Nigeria, with a range from 3599 to 16796 mg/l (Ayejoto et al., 2021).

Overall, HI index for the study area range from 0.16 to 3.60. Out of the sampled wells, 31.7% have HI above the threshold of 1. The HI indicates that all facies III waters have low non-carcinogenic risks. On average, the waters in facies II and IV are non-carcinogenic. However, there are observed boreholes where the non-carcinogenic risk exceeds the threshold value (village's water supply borehole, the boreholes at the village and the village's farm). On average, gypsum waters (facies I) have the highest non-carcinogenic risk (e.g. a spring in the church well and several boreholes on farms). The study found that the HI of groundwater in the Pre-Volga Region is primarily affected by Al concentrations, with Mn, Co, and As concentrations having a lesser impact (figure 4e). For comparison in Semi-arid Coastal Aquifers in South Africa, the hazard index values of groundwater samples ranged from 0.02 to 2.14, with Co showing the highest non-carcinogenic health risk (Mthembu et al., 2022).

The CR range from $0.62\cdot10^{-4}$ to $8.89\cdot10^{-4}$. It is worth noting that 61.0% of wells have CR values above the threshold, which indicates potential carcinogenic effects on the local population of the Pre-Volga Region. The CR indicates that consumption of the examined sodic waters (facies III) poses a low probability for cancer formation. Average CR for the waters of other facies surpass the threshold values, while the highest values were observed for the mirabilite waters of facies II. High CR values were discovered in boreholes intended for supplying water to the villages. The CR value is most significantly affected by the concentrations of As and Ni (figure 4f).

The Pre-Volga region's groundwater generally exhibits lower values of TMEI, CI, TMPI and TMTI. This is because the concentration of metals in the groundwater of the study region is lower. The PIG has values comparable to those obtained in other regions, which is likely due to the similarity in the distribution of soluble salt concentrations and major ion concentrations. Overall, the groundwater pollution level in the Pre-Volga Region can be considered satisfactory based on the analysis of various indices. This conclusion has been reached because there is a significant amount of uncontaminated water available. However, it has also been identified that some wells have high levels of contamination.

The data obtained from the indices shows that the gypsum waters in facies I have greater pollution as measured by the PIG, TMTI, and HI. High contents of SO_4^{2-}, mineralization, Mn, Al, Co and Fe are responsible for polluting of this facies. Mirabilite groundwater in facies II displays higher values of PIG, TMPI and CR, which are correlated with increased levels of SO_4^{2-}, mineralization, As, Pb and Ni. Based on the TMEI and CR, sodic groundwater in facies III is highly susceptible to contamination as a result of elevated levels of Fe. Hydrocarbonate waters in the facies IV experience less pollution, but the indices show significant influence from As, Ba, Mn, Al, and Ni. Overall, it can be deduced that the water quality indices and health hazards for the population in the Pre-Volga Region are impacted considerably by the presence of SO_4^{2-}, mineralization, and the concentrations of Fe, Mn, Al, Ni, and As, while the concentrations of Ba, Pb, and Co have a lesser impact. Sources of these metals can originate from either natural or anthropogenic activities. There is evidence to suggest that agricultural activities may be related to the presence of Pb, Ni, As, and Co in groundwater. This is due to elevated levels of these metals being found in agricultural soils and wastewater (Ullah et al., 2022).

Spatial visualization maps indicating the levels of groundwater pollution in the Pre-Volga Region have been produced through index calculations (figure 5). The maps identify the following areas: phase I waters in the wells at the farms in the Novye Ishli village (PRV-19) and the Starye Tinchali village (PRV-6); phase I waters in the church font spring in the Almancikovo village (PRV-34/2); and phase II waters in the water supply well in the Ishmurzino-Surinsk village (PRV-29) and in the pig farm well in the Toisi village (PRV-36). Significant differences exist between the maps, which are related to the methods used to calculate the indices. The various methods for calculating indexes incorporate different characteristics, such as the relative importance weights of the metal, maximum allowable concentrations, toxicity values, and risk factors based on metal properties, among others. Consequently, each index has its own list of metals with the highest priority. The TMPI and CR index maps are exceptions in this paper. These indices are mainly influenced by the As and Ni concentrations in the present study, which explains their similar spatial distributions. The complexity of territorial pollution assessment is emphasized by differences in index calculation methodologies. However, this allows for a more accurate assessment and a complete list of priority pollutants.

High levels of metals when consumed can have severe toxic effects on human biochemistry. There is evidence to suggest that an excessive amount of Fe in the human body can lead to an increased risk of liver disease, kidney disease, heart failure, diabetes mellitus, osteoarthritis, and osteoporosis (Berg et al., 2001; Jamshaid et al., 2018). Acute exposure of Mn has potential neurological and muscle dysfunction effects, while long-term consumption of large quantities can cause neurological effects, giving rise to Parkinson's and Alzheimer's diseases (Avila et al., 2013; Mitra et al., 2022). High levels of Al in the body have effects on the nervous system, leading to memory loss and loss of coordination (Flaten, 2001). Some additional health complications that can arise due to Al toxicity are dermatitis, respiratory issues, anemia, hindered iron absorption, nervous system disorders, damage to the brain and bones (Becaria et al., 2002; Dahiya, 2022). Nickel has been found to chronic bronchitis, decreased lung function, asthma, lung cancer, sinus cancer, and laryngeal cancer (Genchi et al., 2020; Sonone et al., 2021). Arsenic consumption by humans results in neurodegenerative and circulatory diseases, endometrial cancer, hypertension, liver damage, diabetes mellitus, lung, kidney (Garza-Lombo et al., 2019; Mitra et al., 2022). Exposure to barium compounds in humans has been found to gastroenteritis, hypokalemia, acute hypertension, cardiac arrhythmias, renal failure, skeletal muscle paralysis, pulmonary edema, gastric and intestinal bleeding (CDC, 2003; Kravchenko et al., 2014). Chronic exposure to Pb may result in intellectual disability, hyperplasia, renal failure, chronic cirrhosis, atherosclerosis, hypertension, thrombosis, bowel cancer, lung cancer (Mitra et al., 2022; Singh et al., 2023). Cobalt toxicity has been found to induce systolic cardiac depression, impaired coordination, visual impairment, and several hematological, neurological, cardiovascular, and endocrine disorders (Packer, 2016; Leyssens et al., 2017).

The studies conducted have led to the conclusion that groundwater in the Pre-Volga Region should be purified before consumption to protect and maintain public health. The study has identified a range of groundwater parameters in the Pre-Volga Region that pose a significant threat to the health of the local population. There are significant variations in the concentrations of trace metals in groundwater, pollution indices, and potential health risks across various parts of the Pre-Volga Region. Therefore, it is recommended that specific policies be developed to reduce anthropogenic impacts on groundwater and that strict adherence to environmental regulations be enforced for certain sites in the Pre-Volga Region.

CONCLUSION

Groundwater research conducted in the Pre-Volga Region has determined that the majority of groundwater is a blend of calcium and sodic waters in terms of cation composition, with an insignificant contribution from the magnesium component. Based on the anionic composition analysis, the investigated groundwater primarily falls into the hydrocarbonate and sulphate categories. The analysis shows that the concentrations of Al, Mn, Sr, Co, Cr, and Fe are relatively high in gypsum groundwaters, Ni, Pb, and As are enriched in mirabilite waters, Cu and Fe are more abundant in sodic waters, and Zn, Ba and V are enriched in hydrogen carbonate waters. High mineralization is detected in facies I and II, rendering majority of these samples unsuitable for drinking.

An evaluation of the groundwater quality in the Pre-Volga Region is presented through the use of different indices and a corresponding assessment of public health risks. Gypsum waters demonstrate greater contamination as indicated by the PIG, TMTI and HI indices, due to their elevated levels of SO_4^{2-}, TDS, Mn, Al, Co and Fe content. Mirabilite waters exhibit elevated levels of PIG, TMPI, and CR indices as a result of increased amounts of SO_4^{2-}, TDS, As, Pb, and Ni. According to TMEI and CR, sodic groundwater is the most prone to contamination due to its elevated Fe content. Hydrocarbonate waters are less polluted, but the indices are influenced by As, Ba, Mn, Al and Ni. Groundwater pollution indices in the Pre-Volga Region generally show more significant influence from SO_4^{2-}, TDS, Fe, Mn, Al, Ni, and As, and comparatively less influence from Ba, Pb, and Co concentrations. On average, bodies of water have levels ranging from "pure" to "moderately polluted", moderate toxicity, carcinogenic and non-carcinogenic potential risks close to the thresholds. However, some boreholes have water that is very polluted, extremely toxic, and can cause carcinogenic and non-carcinogenic risks. The factor analysis conducted has revealed that groundwater pollution in the Pre-Volga Region is likely caused by both natural geological factors, such as the presence of interlayers of easily soluble minerals in water-bearing rocks, and anthropogenic influences. Anthropogenic sources that have the potential to affect groundwater in the Pre-Volga Region include agriculture, food processing, and municipal discharges.

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STATEMENTS AND DECLARATIONS

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The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

No life science threat was practiced in this research.

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