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Priority chemical pollutants of drinking water in the city of Kazan: approach based on risk assessment

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Abstract. Assessment of non-carcinogenic risks from chemical substances ingested with drinking water included peroral, skin and inhalation routes of contact with water. The study was carried out for children aged 3-6 years living in 4 districts (zones) of the city of Kazan. Regional exposure factors (REF) at the median (Me) and the 95-th Percentile (95P) levels were identified according to the results of the questionnaire survey. The value of total hazard indices (THI) calculated with application of REF at the median (Me) and the 95-th Percentile (95P) levels made $THI_{Me} = 14.2$ and 17.1, and THI $_{95perc} = 13.03$ and 16.3 in zones with a combined type of water supply. The ingestion of chemical substances with drinking water in different zones of the city of Kazan implies, alert and high levels of non-carcinogenic health risk for the child population.

1. Introduction

The quality of drinking water exercises significant influence over the public health. According to the data of the State Report of Rospotrebnadzor (The Russian Federal Service for Surveillance on Consumer Rights Protection and Human Wellbeing) "On the Status of Sanitary and Epidemiological Wellbeing of the Population in Russian Federation" last year, the number of deaths associated with consumption of polluted drinking water increased by a factor of three and reached almost 18.9 thousand in comparison with 5.9 thousand in the year of 2015 [1]. Morbidity associated with a water factor increased as well: last year 1.486 million cases of genito-urinary diseases, digestive diseases, skin and subcutaneous tissue disorders, musculoskeletal disorders, endocrine diseases, circulatory diseases and others (1.455 million according to the results of the year of 2015) were registered. The major negative effect on the human health is exerted by chemical impurities contained in the tap water, both of natural origin, for example nitrates, and industrial origin - metal compounds (iron, manganese, strontium, aluminium) and other substances [2-4]. The presence of chlorine compounds in drinking water remains an urgent problem [5-7]. Analysis of the present stage of the drinking water quality indicates that, uniform requirements for composition and properties of the drinking water are not unified on a world-wide scale and should take into account and reflect the national peculiarities of public water supply domestically [8]. The World Health Organization (WHO) underlines in the 4th Guidelines on the Control of the Drinking Water Quality that, the approaches based on the health risk assessment should be used for justification of managerial decisions on provision of the drinking water safety [9]. The dose-effect and dose-response relationships in children under 6 years old due to differences from the older children and the adults in structural and functional characteristics are responsible for their high vulnerability on exposure to chemical substances [10-13].

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2. Materials and methods

The study was carried out for children aged between 3-6 years living in 4 districts (zones) of the city of Kazan. The water supply source of selected zones (Kirovsky (the 1st zone) and Vakhitovsky districts (the 3rd zone)) is the "Volzhsky" water intake. The population of Sovetsky (the 2nd zone) and Privolzhsky districts of the city (the 4th zone) use drinking water of combined nature (the "Volzhsky" water intake and underground water sources). The assessment of non-carcinogenic risk was carried out according to the values of the upper limit of the 95% CI of the results of studies carried out on the basis of an accredited laboratory of the Federal State-Funded Healthcare Institution "The Center of Hygiene and Epidemiology in the Republic of Tatarstan" in keeping with Guidelines on the population health risk assessment (Guidelines P 2.1.10.1920-04) and the Environmental Protection Agency (US, EPA) [14 - 16]. The assessment of exposure to chemical substances via the ingestion, inhalation and dermal routes was carried out with application of the assessment of chronic daily intake (CDI) with application of standard formulas [14]. Information on maximum concentrations of pollutants corresponding to the upper limit of statistical confidence interval of the 95% probability was used in calculation due to the fact that, risk potentials, reference doses and concentrations used for assessing the "dose-effect" relationship are oriented on this particular criterion. The value of the absorbed dose calculated on the basis of a reference dose (RfDo) on peroral route of ingestion and absorption ratio in gastro-intestinal tract (GIABS) are used as an approximate measure of permissible skin effect (RfDd) of chemical substances [14]. The value of the absorbed dose on ingestion of chemical substances, when washing and taking a bath (a shower), is assessed in our study for children $3\geq 6$ years old on skin exposure. EPA applies various approaches to assessment of DAevent (absorbed dose per event $(mg \cdot cm^{-2}$ -event)) concerning non-organic and organic chemical substances [16] in current policy.

3. Results and discussion

In total, the risk assessment process consists of four steps: hazard identification, exposure assessment, dose-response assessment, and risk assessment. Regional exposure factors (REF) at the median (Me) and the 95-th Percentile (95P) levels were identified according to the results of the questionnaire survey [17]. Reference values for calculating the impact and risk assessments are given in table1.

Analysis of the total hazard indices (HI) calculated from the values of REF (Me and the 95th Perc) for the child population of the city of Kazan showed (apart from the 1st zone) the excess of the upper limit of the reference level (3.0) for three systems: the blood, the kidneys and the cardiovascular system. The major contribution to development of general toxic effects for the critical organs and systems on peroral ingestion is made by, oil products (from 29 to 54.7%) in the 2nd and the 4th zones; by chloroform (from 10 to 30.6%) and nitrates (from 12.8 to 35.9%) in all zones; by magnesium (up to 11.2%) in the 3rd zone; and by fluorides (from 13.7 to 14.3%) in the 1st and the 3rd zones. The peroral route of ingestion (65.4% - 83.3%) is the main route in all zones. Inhalation route makes from 16.01% to 33.2 % and is caused by chloroform (65.4%) in all zones, the proportion of the skin route being from 0.5% to 1.1% (table 2).

Ingestion of chemical substances with drinking water in different zones of the city of Kazan is indicative of alert and high levels of non-carcinogenic risk for the health of the child population living in the 2nd and the 4th zones. Quantitative assessment identified differences in regional exposure factors (Me and the 95th Perc) by a factor of 1.25, which are revealed on characterization of the exposure doses and hazard quotients of the chemical substances ingested in an integrated manner (simultaneously via several routes) with drinking water. The value of total hazard indices (THI) calculated with application of REF at the median (Me) and the 95th Perc levels made THI_{ME} = 14.2 and 17.8 and THI _{95perc} = 13.03 and 16.03 in the zones with combined type of water supply. The levels of non-carcinogenic risk in the 1st and the 3rd zones exceeded the upper limit of the reference level as well: at the Me level (6.1 and 9.1) and at the 95th Perc level (7.63 and 11.45).

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Input parameters	Unit	Values (for children), Me	Values (for children), 95 Perc	Reference
Concentration in water (CW)	$\mu g \cdot L^{\text{-1}}$	$\mu g \cdot L^{\text{-1}}$	$\mu g \cdot L^{-1}$	This study
Ingestion rate (IR)	L·day ⁻¹	1.0	2.0	[17]
Concentration in air (Cair)	$mg \cdot L^{-1}$	Calculation method	Calculation method	[14]
Ventilation rate (VR) Absorption efficiency in alveoli (AE)	$m^3 \cdot hour^{-1}$	0.5 (children)	0.5 (children)	[14] [14]
Water flow rate (QL) Dimensionless Henry's law constants (H)	L·hour ⁻¹	30	30	[14] IRIS
Water temperature (T)	44			This study
Air-water mass transfer efficiency (Theta)		Theta= $3000000/(2.5/Dw^{0.67})$ +[(R*T/(H*Da^{0.33})]		[14]
Universal gas constant (R)		8.31		[14]
Skin surface area (SA)	cm ⁻²	5400	7050	[18]
Fraction of skin in contact with water (F)	Percent	100	100	[18]
Water diffusion coefficient (Dw)	$\mathrm{cm}^2 \cdot \mathrm{c}^{-1}$	For organic substances, Dw=22*0.00001/MV ^{0.67} . For majority of non-organic substances, Dw is close to zero		[14]
Air diffusion coefficient (Da)	$\mathrm{cm}^2 \cdot \mathrm{c}^{-1}$	For organic substances, Da $=1.9/MV^{0.67}$. For majority of non- organic substances, Da is close to		[14]
	minute		Zero	
Exposure time (ET)	·dav ⁻¹	30	90	[17, 18]
Conversion factor (CF)	L·cm ⁻³	0,001	0,001	[14]
Exposure duration (ED)	year	3	3	[15]
Exposure frequency (EF)	day year ⁻¹	296	364	[17, 18]
Mean exposure time (AT)	day	ED-365	ED-365	[14, 15]
Body weight (BW)	kg	10.3	16.4	[17, 18]

Table 1. Input Parameters for Calculating Exposure and Intake.

 Table 2. Total hazard indices of chemical substances ingested with drinking water via different routes, REF (Me).

Research zones	Peroral route	Skin route	Inhalation route	Total risk (THI)
Zone 1	4.018 (65.8%)	0.059 (0.96%)	2.027 (33.2 %)	6.104
Zone 2	11.838 (83.3%)	0.098 (0.69%)	2.275 (16.01 %)	14.211
Zone 3	6.256 (68.3%)	0.100 (1.1%)	2.811 (30.7 %)	9.166
Zone 4	10.768 (82,6%)	0.069 (0.53%)	2.199 (16.9 %)	13.036

Forming a list of priority monitored indices constituting a real danger for the population health, and its sensitive groups in particular, it is an integral part of elaborating effective measures on prevention or minimization of possible negative effect on the health. The important task in this context is scientific justification not only of the sufficiency of the list of controlled chemicals with the account of nature and peculiarities of their impact on the body, but their priority as far as the probability of health damage is concerned. The concept of the drinking water safety based on the requirements of the sanitary rules and regulations, as well as the results of the population health risk assessment, is the basis for selection of priority monitored indices characterizing chemical pollution of drinking water and subject to constant monitoring [19]. The safety of drinking water in chemical composition is determined by its conformity with standards in composite indices, the content of harmful chemical substances due to anthropogenic origin and global widespread, as well as the presence of harmful chemical substances, which enter and are formed in water in the process of its treatment in the water-supply system, and the substances in the territory of a certain region or city. The priority pollutants of drinking water in the city of Kazan, which determine from 62.6 % to 99.0 % of the level of the total non-carcinogenic risk in all zones of Kazan, are oil products (in total), chloroform, nitrates (in NO3), magnesium and fluorides. Oil products are a complex mixture of certain hydrocarbons, and this fact complicates the identification of their toxicity in case of water pollution and implies that, traditional approaches to risk assessment for them (on inhalation and dermal routes) are considerably inappropriate. Currently, the content of oil products in drinking water (as well as the value of per oral reference level) is standardized only in RF, compared to the drinking water standards of EC, WHO and other countries [20]. There are data in the literature that, pre-chlorination results in a multiple increase in concentrations of chlorine-containing compounds when passing through the water purification stations, moreover, their content increases further on transportation in the water-supply system reaching the highest values in the outermost points of the system [21, 22].

The value of total hazard indices (THI) calculated with application of REF at the median and the 95-th Perc levels is indicative of alert and high risks on complex ingestion of chemical substances with drinking water. The obtained results imply the justification of managerial decisions on the health risk minimization for the child population of the Sovetsky (2nd zone) and Privolzhsky districts of the city (4th zone).

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