Health and Quality Risk Assessment of Bottled Water

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Abstract. The risk and quality assessment paper is dedicated to estimation of impact (for human health) of bottled drinking-water package (especially PET one). The investigation is concentrated on using one integral method for different risk types (factors connected with potential carcinogenicity: concentrations of antimony, formaldehyde, diethylhexylphthalate; and organoleptic factors: turbidity, colour, and pH). We imply the nature of organoleptic (quality assessment) factors close to risk ones because their indirect influence on polluting power of chemicals can be amplifying. The acceptable risk levels for these types are fixed as 10-1 and 10-5 respectively. The research is based on Russian and International (principally, American) scientific researches and standards. The calculation of risk metric is proposed to be estimated in dimensionless number (hazard quotient – HQ). HQ can be transformed in probabilistic numbers in conversion to events per million (Risk Index – RI and risk of olfactory-reflectory impact factors, Integral Index of Water Risk). In the article we used the idea of "chronic daily intake" (CDI) as an acceptable risk-free measure of factors of potential carcinogenicity, which is an adequate evaluation of permissible concentration. 5 brands of Russian bottled water were analyzed, it turned out that one of them had an exceeded acceptable level of risk.

1. Introduction
Nowadays almost all residents of big cities of Russia face an actual problem of safe drinking water source selection. According to statistics [1], 38% of Russian respondents believe that poor quality of drinking water is an important factor for assessment of urban ecological situation as «unfavorable and disastrous». It is one of the reasons why bottled water has a firm position in the structure of water consumption (there are people’s justified and unjustified reasons to trust the quality of tap water). According to surveys periodically conducted by Russian sites [2], about 13% of Russians use tap water for consumption, 17% take water from a reliable water source or hydrant, 29% buy bottled water, and 41% use various household water filters. Bottled water production level is steadily growing every year in the world, in 2015 the market will reach 233 billion liters [3]. Nowadays more than 95% of Russian beverage package market (over 60% of alcoholic drinks) are presented by PET materials [4]. In 1989 polyethylene terephthalate came into wide use for plastic bottles production [5]. A large number of bottled water brands of different domestic and imported manufacturers are presented in Russian market network. When Russians choose a brand of bottled water, they usually rely on advice of their friends or colleagues, the mass-media reports or on the results of self-initiated independent
expertise at specialized chemical laboratories. However, they don’t consider two important nuances. Firstly, bottled water can’t be the fully functional equivalent of drinking tap water because the second one is more regular and more thoroughly monitored by the government. Secondly, bottled water production is concerned with using of different package materials which are more or less harmful for people. Chemical compounds of food and beverage containers are the potential danger source for human’s health because they can migrate with varying degrees of intensity from packing material in drinking water according to concentration gradient.

The consequences of such hazardous substances migration from bottle materials are hard-to-predict because of their impact on different age groups, synergetic, cumulative, differential effects, developmental toxicity and other factors that are not successfully studied. In our opinion, the above-described issues are quite unfairly overlooked by Russian hygienists. Specialists of the research institute of human ecology and environmental health of Russian Academy of Medical Sciences (RAMS) attempted to highlight this problem in the guideline 2.1.4.1184-03. However, the sixth appendix of this document titled «Assessment of chemical pollutants migration in bottled water from polymer package materials and glass containers» doesn’t contain a complete list of water contaminants. We notice that the guideline is not obligatory for implementation for bottled water manufacturers and is not used in control of finished water. That’s why we contribute the method of bottled water integral risk assessment. It considers evidently harmful factors (such as migration carcinogenic substances from package into water) and perception factors (turbidity, colour and pH) together. We have chosen antimony, formaldehyde and di-(2-ethylhexyl)-phthalate for carcinogenic substances migration analysis because they are rather common pollutants of bottled water according to some researches [6]. The problem of safety targets defining is rather controversial [7], for this reason we try to base assessment on dimensionless risk values.

2. Materials and methods
The authors took a poll of 191 respondents (students and teaching staff, 63% female and 37% male) in Far Eastern State Transport University (FESTU) that identified five the most popular bottled water brands. The selected water brands are produced in different regions of Russia and well distributed throughout its territory. Water samples for chemical analysis were taken from branded PET-bottles with a nominal capacity of 1.5 liters bought in supermarkets of Khabarovsk in April 2015 (5 samples of each brand). They were depersonalized in the laboratory of FESTU.

Turbidimeter 2100N HACH was used for water turbidity measurement with accuracy ±2%. It was standardized by stabilized formazin turbidity test gage. pH was measured with a portable analyzer «ANION-7000» (accuracy ±0.02 pH, ±2 mV) calibrated with standard buffer solutions. The colour of bottled waters was evaluated photometrically (the chrome-cobalt colour scale (CCU or Cr-Co units) stored in memory of spectrophotometer DR2800 HACH (according to the requirements of GOST R 52769-2007)).

Chemical pollutants’ (antimony, formaldehyde and di-(2-ethylhexyl)-phthalate) concentration was measured by the methods specified in table 1. Actual pollutant concentration of bottled water is an average estimation of results measured three times. Characteristics of pollutants were taken from substance specifications compiled in Chemical Abstracts Service (CAS). We showed the body systems that are intensively exposed to toxic substances migrating from package material into bottled water (according to CAS).

Toxic effects are described for oral way of delivery. Pollutant Maximum Contaminant Levels (MCLs) were taken from the current Sanitary Norms and Rules 2.1.4.1116-02 for the first category of bottled water (for Russian practice it means: water which is origin-independent and permanently safe for drinking, meets organoleptic, epidemiologic, chemical and radiological requirements). Statistical analyses was performed using the MS Excel software. A significance level matches p=0.05.
3. Description of main risk calculation methods

The system of Health Risk Assessment (HRA) involves indirect use of MCL measures. Adequate simulation of pollutant ingestion is important for determination of damaging effects. It should be done through the index of substance reference dose. The concept of reference doses (RfD) (equation 1) is based on the fact that it is calculated by multiplication of MCL by the margin of safety (Ks):

\[ \text{RfD} = \text{MCL} \times K_s \] (1)

The first, second, third, fourth hazard class are assigned the values of Ks, respectively equal to 7.5; 6; 4.5; 3. The values of RfD for each pollutant are calculated in table 1.

| Bottled water pollutant | Method of measurement | CAS Number | Toxic effects of oral water consumption by human | Hazard class | Factor Ks | MCL, (mg/l) | Reference dosage, RfD (mg/kg/day) |
|------------------------|-----------------------|------------|-----------------------------------------------|--------------|-----------|-------------|---------------------------------|
| Antimony               | ICP-AES (Federal Environmental Regulatory Documents 14.1:2.4.135-98; ed. 2008) | 7440-36-0 | endocrine and cardiovascular systems           | 2            | 6         | 0.005       | 3.00*10^{-2}                    |
| Formaldehyde           | Reaction gas chromatography (methodical instructions 4.1.653-96) | 50-00-0 | gastrointestinal tract, central nervous system, kidneys, growth and development of human | 2            | 6         | 0.005       | 3.00*10^{-2}                    |
| Di-(2-ethylhexyl)-phthalate (DEHP) | Gas chromatography (methodical recommendations № 01.025-07) | 117-81-7 | endocrine and cardiovascular systems           | 2            | 6         | 0.006       | 3.60*10^{-2}                    |

The next stage of the model’s practical improving needs evaluation of pollutants intake. Thereto other quantitative parameters of this process (in addition to the pollutant concentration) must be taken into account. The system of HRA introduces the CDI (chronic daily intake) index which is the comparison base of pollutants’ impact on the body [8]. The transformation of actual concentrations into CDI is shown in table 2.

Calculation of CDI, mg/kg (equation 2), is calculated according to the formula:

\[ \text{CDI} = C \times DI \times EF \times ET \times (BW \times AT)^{-1} \] (2)

where C – actual pollutant concentration in water, [mg/l]; DI – average daily intake rate (2 [l/day]); EF – exposure frequency (365 [days]); ET – exposure time (30 [years]); BW – body weight (70 [kg]); AT – average life span (30 [years]). The formula constants are taken from Russian procedures [9] that average out foreign counterparts.

Risk indicator calculation for chemical pollutants requires estimation of dimensionless measure – hazard quotient (HQ) (equation 3) presented in table 3 according to the formula:
CHQ = DI \times (\text{RfD})^{-1} \quad (3)

### Table 2. Results of pollutants concentrations measuring.

| Bottled pollutant | water | Actual pollutant concentration for bottled water brands, (mg/l) | 1 | 2 | 3 | 4 | 5 |
|-------------------|-------|---------------------------------------------------------------|---|---|---|---|---|
| Antimony          |       |                                                               | 0.0040 | 0.0040 | 0.0040 | 0.0040 | 0.0050 |
| Formaldehyde      |       |                                                               | 0.0100 | 0.0100 | 0.0400 | 0.0100 | 0.0100 |
| DEHP              |       |                                                               | 0.0009 | 0.0009 | 0.0009 | 0.0040 | 0.0040 |

\textit{Chronic daily intake (CDI) for bottled water brands, (mg/kg/day)}

| Bottled pollutant | water | CDI for bottled water brands |
|-------------------|-------|-----------------------------|
| Antimony          |       | 0.0417                      |
| Formaldehyde      |       | 0.1043                      |
| DEHP              |       | 0.0094                      |

Thus, according to the idea of HQ, there is the value that separates acceptable and dangerous levels of pollutant consumption – it is HQ=1. If HQ<1, pollutant intake is allowable. If the control parameter exceeds 1, it is harmful for human health. Di-(2-ethylhexyl)-phthalate has the lowest level of substance migration to water in three samples; the acceptable level is slightly exceeded in two other brands (№ 4 and 5). Antimony compounds show the average risk in the studied samples. The migration of formaldehyde from plastic material to water is definitely dangerous in absolute values. CDI multiple transcending of safe level is detected in bottled water brand №3 (according to the input data of the model).

According to the risk assessment theory, we can operate with not only dimensionless quantities, like HQ, but also with indicators of risk. Risk Index (RI) is introduced in HRA for solving of this problem. We suggest using the probability of hazardous phenomena occurrence equal to one in million events to happen for that purpose (we use international experience explaining that unacceptable event happening once in a million events can be considered satisfactory). RI calculation requires multiplication of HQ value by $10^{-6}$ (see table 3). This transformation is for further arithmetic actions.

Additionally we calculate the risk for olfactory-reflex impact factors (see table 4). Table 4 shows that the Russian hygienic standards of bottled water’s turbidity and colour are more stringent than the American ones. Organoleptic parameters of bottled waters (turbidity, colour, pH, odor, taste and other sensory characteristics) are often put together. We assessed the first three ones of these indicators in our work. Standardization of risks can be achieved by analyzing of the factor deviation from the optimal value. This operation means calculation of intermediate dimensionless characteristic PROB for all factors (equations 4-6) in this group according to the formulae [9]:

\[ 1. \text{PROB}_{Co} = -3.33 + 0.067 \times Co, \quad (4) \]
2. PROB_T = -3 + 0.25 * T ,
3. PROB_pH = \begin{cases} 
4 - \text{pH}, & \text{if pH} \leq 7 \\
-11 + \text{pH}, & \text{if pH} > 7 
\end{cases}

where Co – Colour of water in (chrome-cobalt units), T – water turbidity in (NTU), pH - measure of water acidity.

Then we define the risk value (equation 7) using PROB and the normal distribution law (see table 5). We make a transition to the risk indicators using Laplace’s function:

\[
\text{Risk} = (2\pi)^{0.5} \int_{-\infty}^{\text{PROB}} e^{t^2/2} dt
\]

Table 4. Hygienic characteristics of olfactory-reflex impact factors.

| Factors                        | US EPA Secondary Drinking Water Regulations | Russian Sanitary Norms and Rules 2.1.4.1116-02 | Adverse effect                                      |
|--------------------------------|--------------------------------------------|-----------------------------------------------|----------------------------------------------------|
| pH                            | 6.5-8.5                                    | 6.5-8.5                                       | impairs taste & odor, influences the rate of chemical reactions |
| Turbidity, [NTU]              | 5                                          | 1                                            | interferes with UV-treatment and disinfection during water preparation |
| Colour, [colour units]        | 15                                         | 5                                            | aesthetic, no direct health impact                  |

The total olfactory-reflex risk is calculated by summing up the individual risks for pH, turbidity and colour. The highest risk value was detected in water brand №1 (8.25*10^-3), it can be explained by the influence of sample acidity (close to allowable lower limit). The advantage of this approach is confirmed by making of risk sources more obvious.

Table 5. Risk calculation for olfactory-reflex impact factors.

| Factors                        | Number of water brand |
|--------------------------------|-----------------------|
|                                | 1        | 2        | 3        | 4        | 5        |
| pH                            | 6.500    | 8.000    | 7.000    | 7.300    | 6.700    |
| Turbidity [NTU]               | 0.120    | 0.080    | 0.040    | 0.050    | 0.040    |
| Colour [Cr-Co units]          | 1.000    | 0.000    | 0.000    | 0.000    | 1.000    |
| PROB                          | -2.500   | -3.000   | -3.000   | -3.700   | -2.700   |
| pH                            | -2.970   | -2.980   | -2.990   | -2.988   | -2.990   |
| Turbidity                     | -3.263   | -3.330   | -3.330   | -3.330   | -3.263   |
| Colour                        | -3.263   | -3.330   | -3.330   | -3.330   | -3.263   |

4. Integral Index of Water Risk (IIWR)

IIWR calculation allows to compare the total risk with acceptable level for both groups: potentially carcinogenic substances (table 3) and indicators with olfactory-reflex effects (table 5). According to the methodology [10], the risk of 10% (or 0.1) is permissible for the group of olfactory-reflex impact (theoretically it means that one occurrence has a chance of the order of one in ten to happen). This low
barrier is established by the reason that the indicators of this group are less dangerous in comparison to carcinogens. In this table we see that main adverse effects relate to aesthetic perception of water by consumers. In this article we suppose chemical substances migrating from the packing material into water are not evident carcinogens. Nevertheless, Chemical Abstracts Service, CAS [11], says that formaldehyde shows limited evidence of a carcinogenic effect; antimony is harmful by inhalation and if swallowed; DEHP may impair fertility and may cause harm to the unborn child.

We notice that formaldehyde and acetaldehyde form as the by-products during the PET blow molding (it happens if temperature and pressure equipment modes are not observable) [12]. This problem may cause aldehyde condensation on bottle inside surface [13,14]. Antimony (III) oxide is used as a fire retardant [15,16] and a catalyst of polymerization reaction between ethylene glycol and phthalic compounds [17,18,19,20] during PET plastics production. The most probable route of DEHP migration is through food and bottled water, with an average contribution of DEHP from food of 0.25 milligrams per day (mg/d) [21]. DEHP gets into food from plastics (the substance is used as popular plasticizer) during processing and storage.

International Agency for Research on Cancer (IARC) informs that formaldehyde [22] belongs to risk group 1 (carcinogenic to humans), DEHP [23] and antimony(III) oxide (CAS № 1309-64-4) [24] belong to risk group 2B (possibly carcinogenic to humans). At the same time toxic effects may depend on the characteristics of the water (minerals, CO₂ content, pH) [25-28]. In the paper we suppose the concentration of these 3 substances is the source of potentially carcinogenic risk.

Mostly, the risk level of 10⁻⁶ is considered to be acceptable for a wide range of cases, but this value is almost practically unattainable. So, we focus on risk not exceeding 10⁻⁵. The majority of standards recommended by international organizations hygienic set risk at this level (including cases of carcinogenic substances). We notice that the average risk degree, which lies in the range of 10⁻⁵ – 10⁻³, is the maximum allowable limit for occupational risks and unacceptable for civil cases. As a comparison, International Commission on Radiological Protection recommends that risk level of heavy metals shouldn’t exceed the value of 5*10⁻³ (in terms of one year). The risk level of 10⁻³ is unacceptable under any circumstances, and its reduction is required.

Calculation of bottled water optimal risk level takes multiplying of the final results from tables 3 and 5 by 10⁻⁴ and 10⁻⁵, respectively. The acceptable value should be set to 1. If the ratio in one of the groups exceeds 1, then it indicates danger source, and vice versa. For example, table 6 shows that the water brand №3 has danger source from the group of potentially carcinogenic substances (1.556>1).

| Group name                     | Acceptable level of risk | Number of water brand |
|-------------------------------|--------------------------|-----------------------|
|                               |                          | 1        | 2        | 3        | 4        | 5        |
| Indicators with olfactory-    | 1.00*10⁻¹               | 0.083    | 0.032    | 0.032    | 0.020    | 0.054    |
| reflex effects                |                          |          |          |          |          |          |
| Potentially carcinogenic      | 1.00*10⁻⁵               | 0.513    | 0.513    | 1.556    | 0.603    | 0.637    |
| substances                    |                          |          |          |          |          |          |
| IIVR                          | 1.000                    | 0.596    | 0.545    | 1.587    | 0.623    | 0.691    |

Calculation of IIVR takes summarizing of individual risks (olfactory-reflex and potentially carcinogenic). This procedure is possible due to bringing into compliance independent indicators and their acceptable risk levels. Obviously, in this case the target value will be a less or equal to 1. Our results prevent synergistic effect of risk factors for human health in bottled water consumption. Although olfactory-reflex factors have no direct relevance to human health we find it important that values (of turbidity, colour, pH) of above permitted meanings can seriously reduce the effectiveness of chemical and microbiological water purification. It can indirectly affect man health. It turned out that IIVR exceeded the allowable value only for water brand №3, mainly due to the presence of high risk of potential carcinogens.
5. Conclusion
It is evident that nowadays the demand for bottled water is increasing in Russia and in the world. The reasons of it can differ (the order of the day, distrust of tap water quality and others) but water safety is the main characteristic for consumers of this product. There is no the only one scheme of risk assessment. Our paper shows offered step-by-step calculation (see figure 1) procedure of IIWR using Russian bottled waters as an example. It enables to assess potential human health risks of bottled water consumption. Interim stages shows also HQ and olfactory-reflex risk calculation. More over IIWR allows to make a well-considered decision of drinking water source for daily consumption and to choose the best packing material for bottled waters. One of the effective ways of bottled water quality improving is to refuse buying brands with a high IIWR level because it signalizes about toxic substances and other negative effects for humans. In addition, IIWR allows to monitor water quality by multiparameter analysis (for example, concurrent influence of both carcinogenic and organoleptic factors).

![Figure 1. Calculation pattern “Integral Index of Water Risk” (IIWR).](image-url)
6. References

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