Croatian Journal of Food Science and Technology
journal homepage: www.ptfos.unios.hr/cjfst/

Original scientific paper

DOI: 10.17508/CJFST.2018.10.2.14

Population exposure of Zagreb city area to contaminants from drinking water

DANIJELA STRAŽANAC[1], LEONARD MATIJEVIĆ[1], JASENKA PETRIĆ[1], DARIO ČAGALJ[1], JASENKA BABIĆ[2], BRIGITA HENGL[1*]

[1]*Croatian Food Agency, I. Gundulića 36b, 31000 Osijek, Croatia*
[2]*City of Zagreb, City Office for Health, Department of Health Ecology, Draškovićeva 15/III, 10000 Zagreb, Croatia*

ARTICLE INFO

Article history:
Received: April 20, 2018
Accepted: June 26, 2018

Keywords:
drinking water,
contaminants,
HBGVs,
exposure assessment

ABSTRACT

Availability of drinking water is considered to be the essential prerequisite for health, and the presence of contaminants under the maximum levels guarantees that it will not cause adverse effect to consumer's health during their lifetime. The presence of contaminants in drinking water is the result of pollution from agriculture, industry, but also of human activity. Increased exposure to certain water contaminants can contribute to develop health disorders usually connected with particular contaminants, such as methaemoglobinemia, various neurological disorders, cardiovascular and kidney diseases and osteoporosis, and, in exceptional cases, death. Health-based guidance values (HBGVs) were established on the basis of chemical exposure assessment for certain contaminants, obtained from experimental studies on animals and corrected by a safety factor (10x10). In this way, it is possible to determine contaminant concentration to be entered into body during whole lifetime without any adverse health effects. This paper presents population exposure assessment of Zagreb city area to contaminants from drinking water.

Introduction

Water is a substance, a beverage, a nutrient, a potential source of other nutrients, and as such is essential for life and health. However, water can also contain contaminants from different sources. Increased presence of certain contaminants in water contributes to their increased intake into human body and thus possible emergence of various health disorders. The most of the contaminants in drinking water are regulated by guidelines issued by the World Health Organization (WHO) and the EU legislation. Contaminants in drinking waters have a variety of different sources.

Cyanide concentrations in natural waters are generally low, and the occurrence of increased concentrations is a consequence of industrial contamination, or discharge of wastewater with high cyanide content. It has also been found out that chlorine cyanide can appear during processing of drinking water, and its disintegration lead to cyanides. Cyanides can reduce vitamin B_{12} in the body (WHO, 2003).

In natural waters, cadmium is found mainly in sediment layers and suspended particles (Friberg et al., 1986). Contamination of drinking water may occur as a result of the presence of cadmium as an impurity in the zinc galvanized pipes, pipe joints containing cadmium, water heaters and coolers. Cadmium can accumulate in kidneys and lead to increased blood pressure (Rosborg, 2015).

Mercury occurs in nature as a result of a series of natural processes, such as volcanic activity. Lower exposure levels are associated with non-specific neurological and physiological symptoms, and acute effect can cause disorders in the functioning of the nervous system and kidneys (WHO, 2005a).

Aluminium is naturally found in drinking water as a result of the passage of water through the ground, whereby parts of mineral rocks dissolve in water. At neutral pH, dissolved aluminium concentration is lower than 0.1 mg/L. However, in acidic soil,

[*]Corresponding author E-mail: bhengl@hah.hr

concentration is higher. Another way of contamination is use of aluminium salts as a coagulation agent for purification of drinking water. Increased concentrations of aluminium in drinking water may be related with dementia and Alzheimer's disease (WHO, 2010).
Nitrates are easily soluble in water, and in groundwater most often come from agricultural fields where fertilizers and inorganic fertilizers were used (WHO, 2011a). Natural concentration of nitrates in groundwater is less than 10 mg/L. There are two main sources of nitrates entering surface waters: from underground resources associated with agricultural activities and urban waste water, which also contain ammonia (HAH, 2014).
Nitrification in combination with anaerobic conditions (which is a consequence of microbial activity in water supply systems) may increase nitrite levels, as well as the chloramination of drinking water (WHO, 2011a). Even a lower dose of nitrate and nitrite can cause methaemoglobinemia, especially in children (Vasić-Rački et al., 2010).
Chlorites and chlorates are by-products of disinfection where chlorine dioxide is used as a disinfectant and odour and taste control for drinking water. In addition, it may come into water supply system from industrial waste water. The most significant health adverse effect of exposure to chlorite and chlorate is related to oxidative stress resulting in changes in red blood cells (WHO, 2005b). Arsenic is present in natural waters mainly in inorganic form (about 90%). The toxicity of arsenic depends on the form in which it is found. Extremely toxic is water-soluble arsenic (V) and arsenic (III) which is difficult to isolate (Habuda-Stanić and Kuleš, 2002). In general, it can be said that the population is the most exposed to arsenic from drinking water and food, while exposure from air is insignificant (according to WHO exposure, arsenic exposure from air is less than 1 μg/day).
This paper presents an exposure assessment of the Zagreb city population to contaminants (cyanide, cadmium, mercury, aluminium, nitrite, nitrate, chlorates, chlorites, arsenic) from drinking water and risk assessment using HBGVs.

Materials and methods

Materials

Contaminants data in drinking water were collected by the City Office for Health, City of Zagreb in 2016, as part of the water quality monitoring for the Zagreb city area.

Methods

Following ISO methods were used for determination of certain contaminants: total cyanide HRN ISO 6703-1:1998; aluminium and cadmium HRN EN ISO 17294-2:2016; mercury HRN EN ISO 12846:2012 mod; nitrate and nitrite HRN EN ISO 10304-1:2009/Corr.1:2012; chlorate and chlorite HRN EN ISO 10304-4:2001; arsenic ISO 17378-2:2014.
Exposure assessment was made by computer model "Improrisk 1.3.1., which is built in "MS Excel" and used to calculate the exposure of the population to certain contaminants through water intake (Improvast, 2016). This model combines food consumption dataset with data of particular contaminant occurrence in food (in this case in water) and calculates exposure rates for the population. Food consumption data came from the National Nutrition Research Program of the Adult Population in the Republic of Croatia, HAH 2011-2012 (consumer data were used only). The model shows exposure in three scenarios: in the "LB" (lower bound) scenario it is assumed that the values of results that were lower than the LOQ (limit of quantification) are equal to zero, in the "MB" (middle bound) scenario it is assumed that the values lower than the LOQ have values of the half LOQ value, while in the "UB" (upper bound) scenario exactly LOQ value was used.

Results

Table 1 shows the average concentrations of certain contaminants with respect to the MB scenario. All monitored contaminants have average values lower than the prescribed (<MPC, maximum permitted concentration) and lower than the established average concentrations in the world, as well as the values recommended by the WHO.
Fig. 1 shows the exposure to HBGV of certain contaminants for Zagreb city population for all three scenarios. It can be seen that the values for cyanide, cadmium, mercury, aluminium, nitrite and chlorite are below 1.5% HBGV, while nitrate and chlorate exposure values are higher, 6.16-6.75%. Nitrates and aluminium were quantified in all samples and therefore there is no difference in exposure in different scenarios, while the other contaminants have not been quantified in concentration higher that LOQ what led to differences in exposure depending on different scenarios.
Exposure for arsenic has been evaluated with a different approach because it is a genotoxic carcinogen with no single value at which an adverse response occurs but the range of values. The EFSA Panel of contaminants in the food chain concluded that $BMDL_{01}$ between 0.3 and 8 μg/kg b.w. per day

presents an increased risk for lung, skin and bladder cancer, as well as skin lesions (EFSA, 2009). Regarding to the established presence of arsenic in water from this monitoring, it was estimated that its daily intake would be 0.007 µg/kg b.w.

Discussion

The contribution of cyanide from drinking water to total cyanide intake in humans is significantly dependent on the occurrence and concentrations of cyanogen chloride in drinking water after water treatment, but average daily cyanide intake is estimated to be less than 1.0 µg (HAH, 2014). However, studies indicate that water is the dominant route of cyanide intake to a general population if we exclude exposition to cyanogen glycoside from food and cigarettes smoke. Increased exposure from drinking water is mainly a consequence of an unexpected incident (ATSDR, 1997).

Table 1. Average concentrations of drinking water contaminants, MPC values, values from guidelines and standards for drinking water contaminants

Contaminant	Average conc. in water (Zagreb)	MPC	Average conc. in water	Guidelines and standards for conc. in water
Cyanide (total)	5.37 µg/L	50 µg/L	-	70 µg/L (WHO) 50 µg/L (EU)
Cadmium	0.11 µg/L	5 µg/L	0.21 µg/L (EU)	3 µg/L (WHO) 5 µg/L (EU)
Mercury	0.05 µg/L	1 µg/L	0.1 µg/L (EU)	6 µg/L (WHO) 1 µg/L (EU)
Aluminium	11.74 µg/L	200 µg/L	10 µg/L (Germany) 101 µg/L (Canada) 30 – 100 µg/L (USA)	900 µg/L (WHO) 200 µg/L (EU)
Nitrite	0.0264 mg/L	0.5 mg/L	< 0.1 mg/L (WHO – world)	3 mg/L (WHO) 0.5 mg/L (EU)
Nitrate	13.6 mg/L	50 mg/L	< 10 mg/L (WHO – world)	50 mg/L (WHO) 50 mg/L (EU)
Chlorate	7.57 µg/L	400 µg/L	33.5 µg/L (EU)	700 µg/L (WHO)
Chlorite	5.18 µg/L	400 µg/L	-	700 µg/L (WHO)
Arsenic	0.42 µg/L	10 µg/L	2.61 µg/L (EU)	10 µg/L (WHO) 10 µg/L (EU)

MPC –maximum permitted concentration according to the Regulation on parameters compliance and water analysis methods for human consumption (OG 125/2013); WHO – World Health Organization; EU – European Union

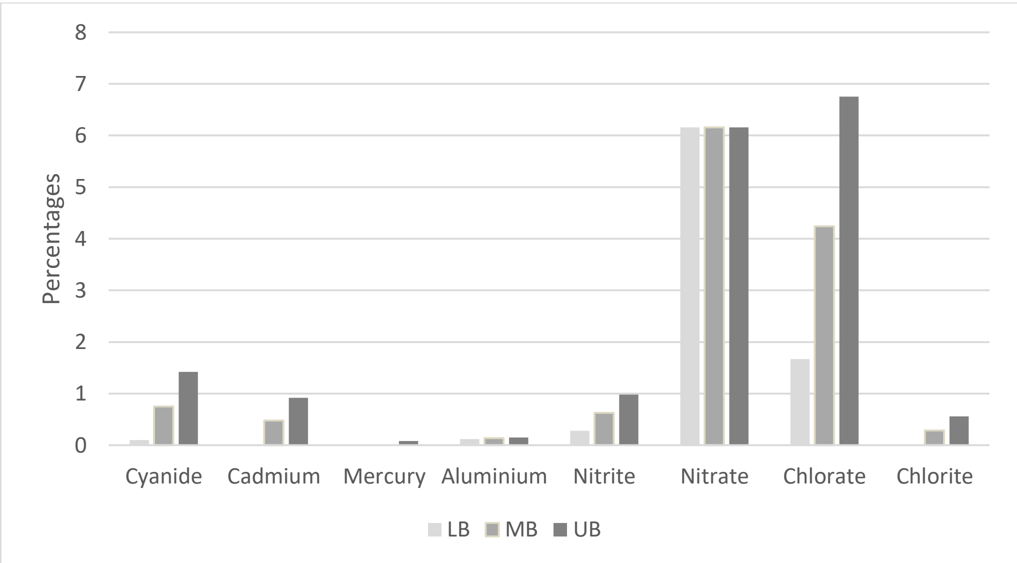

Fig. 1. Exposure to HBGV values (%) of certain contaminants for Zagreb city population due to different scenarios. (LB - lower bound, using 0 for all results <LOQ; MB - middle bound, using 1/2 LOQ or all results <LOQ; UB - upper bound, using exactly LOQ for all results < LOQ

Average cyanide concentration in this study was 5.37 µg/L, much lower than MPC. Therefore, an estimated exposure is about 1.5% HBGV, which presents a very small contribution to daily intake.

Food is the main exposure route for cadmium with a daily intake 10 to 35 µg. The intake from drinking water is usually less than 2 µg/day (JECFA, 1989). Smoking will increase daily intake of cadmium. In Western Europe, Australia and the USA, average daily intake of cadmium by non-smokers living in unpolluted areas is 10–25 µg (HAH, 2014). Estimated lethal oral dose for humans is 350–3500 mg of cadmium; a dose of 3 mg of cadmium has no acute effects on adults (Krajnc et al., 1987). Drinking water from shallow wells of areas in Sweden where soil had been acidified contained concentrations of cadmium approaching 5 µg/L (Friberg et al., 1986). The levels of cadmium could be higher in areas supplied with low pH soft water, as this would tend to be more corrosive in plumbing systems containing cadmium (WHO 2011b). In the Netherlands, in a survey of 256 drinking water plants from 1982, cadmium (0.1–0.2 µg/L) was detected in only 1% of the drinking water samples (Ros and Slooff, 1987). The average concentration in drinking water in Zagreb city area was 0.11 µg/L and exposure assessment for the Zagreb city population in the UB scenario ranged below 1% HBGV cadmium intake.

Naturally occurring levels of mercury in groundwater and surface water are less than 0.5 µg/L, although local mineral deposits may produce higher levels in groundwater. The concentration range for mercury in drinking water is the same as in rainwater, with an average of about 25 ng/L (WHO, 2005a), which is lower than the average values found in the Zagreb city area (0.05 µg/L). Mercury intake from the drinking water is below 0.5% HBGV, which makes it almost negligible.

In Germany, levels of aluminium in public water supplies averaged 0.01 mg/L in the western region, whereas levels in 2.7% of public supplies in the eastern region exceeded 0.2 mg/L. In Canada, the average total concentration of aluminium in water was 0.1 mg/L and in the USA 0.03 to 0.1 mg/L (WHO, 2010). The average aluminium concentrations of 11.74 µg/L in Zagreb are lower than the concentrations found in Canada and the USA and are in line with the lower values established in Germany, and aluminium intake from the water is almost negligible.

The nitrate concentration in surface water according to WHO (2011) ranges from 0 to 18 mg/L but can reach high levels as the result of application from agricultural surfaces. Their concentration fluctuates significantly due to the seasons and wastewater, rich in nitrates, swirling into river. Nitrate concentrations have gradually increased in many European countries in the last few decades and sometimes have doubled over the past 20 years. In most states, nitrate levels in drinking water do not exceed 10 mg/L. According to WHO data (2011a), about 10 million people use drinking water with a nitrate concentration greater than 50 mg/L. With an average value of 13.6 mg/L, the concentration of nitrate in drinking water in Zagreb is lower than MPC. The presence of nitrates in surface waters from 1 to 30 mg/L is considered to be low (Denžić Lugomer et al., 2016), which corresponds with our average nitrates concentration of 13.6 mg/L. The contribution to nitrate intakes from water for the population in the Zagreb city area is slightly more than 6% and is among the largest inputs for the contaminants covered in this study.

Nitrite levels in drinking water are usually below 0.1 mg/L, which corresponds to the results obtained for water from Zagreb city area. These values in the UB scenario were less than 1% of the total HBGV value.

Chlorites appear in drinking water when chlorine dioxide is used for purification purposes. According to the WHO data (2005b), chlorine levels in water ranged from 3.2 to 7.0 mg/L, which is significantly higher than amount in water that was tested in Zagreb city area. Given that water is considered to be the major route of exposure for chlorine dioxide, chlorites and chlorates (WHO, 2005b), exposure in this study using UB scenario was slightly less than 7%. This result indicates a relatively low exposure, although this exposure is the highest in comparison to other contaminants.

Except for individuals who are occupationally exposed to arsenic, the most important route of exposure is through the intake of food and drinking water, including beverages made from drinking water. The average arsenic daily intake from drinking water is generally less than 10 µg; however, in those areas where drinking water contains elevated concentrations of arsenic, this source will make a significant contribution to the total intake of inorganic arsenic. Regarding to diet studies in North America, estimated daily intake of arsenic from food is 12–14 µg of inorganic arsenic (Yost et al., 1998), and according to WHO (2011 c) in areas where rice, soups or similar dishes are usual part of the diet, the drinking water contribution through preparation of food will be even larger. At the beginning of year 2000 the determination of arsenic concentration in water of twelve cities in eastern Croatia was carried on. It was found out that arsenic appeared in elevated concentrations in well water in the areas of Donji Miholjac, Valpovo, Čepin, Vinkovci and

Andrijaševci, sometimes at concentrations above 500 µg/L (Habuda-Stanić and Kuleš, 2002). However, studies conducted on water from the Zagreb city area showed an average concentration of 0.42 µg/L, which complies with the maximum permitted concentration and exposure assessment of 0.007 µg/kg b.w. is far below the dose values causing harmful responses.

Conclusion

Based on the estimates, drinking water is not a significant source of human exposure to contaminants, which is consistent with the fact that all average values are lower than the MPC values. This is especially important to emphasize for arsenic whose water concentrations in some parts of Croatia represent a significant public health problem. The values from this study are lower than the values from the WHO and EC guidelines, and from average concentrations established on the global and European scale, except in the case of nitrates which were slightly higher than the world average.

References

ATSDR (1991): Case studies in environmental medicine. Atlanta, GA, United States Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

ATSDR (1997): Toxicological profile for cyanide. Atlanta, GA, United States Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

Denžić Lugomer, M., Jaki Tkalec, V., Pavliček, D., Kiš, M., Sokolović, J., Majnarić, D. (2016): Analiza pitke vode na sabiralištima mlijeka Bjelovarsko-bilogorke županije. Croatian Journal of Food Technology, Biotechnology and Nutrition 11 (3-4), 176-181.

EFSA (2009): Scientific opinion on Arsenic in Food, EFSA Journal, 7(10):1351

Friberg L., Nordberg G. F., Vouk V. B. (1986): Handbook of the toxicology of metals. Vol. II. Amsterdam, Elsevier, pp. 130–184.

Habuda-Stanić M., Kuleš M. (2002): Arsen u vodi za piće, Prehrambeno-tehnološki fakultet, Osijek.

HAH (2014): Znanstveno mišljenje o označavanju prirodne mineralne vode navodom „pogodna za pripremu hrane za dojenčad“, Hrvatska agencija za hranu, Osijek. https://www.hah.hr/pregled-upisnika/?preuzmi_misljenje=20. Accessed April 20, 2017

Improvast (2016): http://www.improvast.com/. Accessed April 17, 2017

IPCS (1990): Methylmercury. Geneva, World Health Organization, International Programme on Chemical Safety (Environmental Health Criteria 101).

JECFA (1989): Toxicological evaluation of certain food additives and contaminants. Geneva, World Health Organization, Joint FAO/WHO Expert CommiTMee on Food Additives; Cambridge, Cambridge University Press, pp. 163–219 (WHO Food Additives Series No. 24).

Krajnc, E. I. et al. (1987): Integrated criteria document. Cadmium — Effects. Appendix. Bilthoven, National Institute of Public Health and Environmental Protection (Report No. 758476004).

Regulation on parameters compliance and water analysis methods for human consumption (OG 125/2013).

Ros, J. P. M., Slooff, W. (1987): Integrated criteria document. Cadmium. Bilthoven. National Institute of Public Health and Environmental Protection (Report No. 758476004).

Rosborg I. (2015): Drinking Water Minerals and Mineral Balance, Springer, 2015.

Vasić – Rački, Đ., Galić, K., Delaš, F., Klapec, T., Kipčić, D., Katalenić, M., Dimitrov, N., Šarkanj B. (2010): Kemijske i fizikalne opasnosti u hrani, Hrvatska agencija za hranu (HAH), Osijek.

Way J. L. (1984): Cyanide intoxication and its mechanism of antagonism. Annual Review of Pharmacology and Toxicology, 24:451–481.

WHO (2003): Cyanide in Drinking water http://www.who.int/water_sanitation_health/dwq/cyanide.pdf. Accessed April 20, 2017

WHO (2005a): Mercury in Drinking water http://www.who.int/water_sanitation_health/dwq/chemicals/mercuryfinal.pdf . Accessed April 20, 2017

WHO (2005b): Chlorite and Chlorate in Drinking water http://www.who.int/water_sanitation_health/dwq/chemicals/chlorateandchlorite0505.pdf. Accessed April 20, 2017

WHO (2010): Aluminium in Drinking water http://www.who.int/water_sanitation_health/water-quality/guidelines/chemicals/aluminium.pdf?ua=1. Accessed April 19, 2017

WHO (2011a): Nitrate and nitrite in Drinking water http://www.who.int/water_sanitation_health/dwq/chemicals/nitratenitrite2ndadd.pdf. Accessed April 20, 2017

WHO (2011b): Cadmium in Drinking water http://www.who.int/water_sanitation_health/dwq/chemicals/cadmium.pdf. Accessed April 19, 2017

WHO (2011c): Arsenic in Drinking water http://www.who.int/water_sanitation_health/dwq/chemicals/arsenic.pdf. Accessed April 19, 2017

Wilhelm, M., Idel, H. (1995): Aluminium in drinking water: a risk factor for Alzheimer’s disease? Forum, Städte, Hygiene, 46:255–258 (in German).

Yost, L. J., Schoof, R.A., Aucoin, R. (1998): Intake of inorganic arsenic in the North American diet. Human and Ecological Risk Assessment, 4:137–152