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Wokshop: Current trends regarding food safety and food security in Romania

BOTTLED WATER CONSUMER RISK EXPOSURE IN ROMANIA

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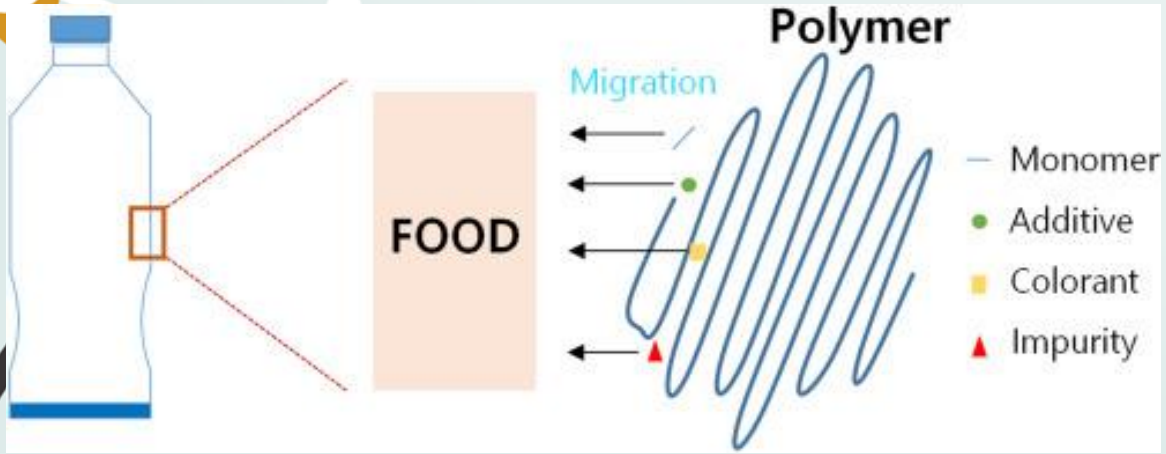
INTRODUCTION

Materials used in the food industry include glass, plastics, metals, paper and cardboard, multilayer materials, but the most used are **plastics packaging** obtained from polyolefins (PE, PP), polyesters (PET), polyvinyl chloride and polyvinylidene chloride, polystyrene, polyamide.

Beside the monomers, such as ethylene, propylene, esters, amides, plastic materials contain, also, various **chemical additives**, like plasticizers, antioxidants, flame retardants, dyes and pigments and many others.

These chemical additives, which are **metals-based**, can be released into the food products in certain conditions, process known as „**migration**".

Bisphenol A (BPA), phtalates, acetaldehyde and **potentially toxic elements** are the most studied chemical additives presents in food packaging and food products.



The **aim** of this study was evaluation of contamination degree of bottled water from Romanian market with BPA and pottentially toxic elements and assessment of carcinogenic and non-carcinogenic risk of target contaminants through ingestion pathway for 2 age categories.

ANALYSIS OF POTENTIALLY TOXIC ELEMENTS CONTENT IN BOTTLED WATER FROM ROMANIAN MARKET

Sample collection

69 **botted drinking water** samples collected between 2019-2021 were tested

50 samples of **regular bottled water** coded P1 – P50 → 36 brands were Romanian samples and 14 samples were imported

- 7 samples of sparkling water
- 43 samples of still water
  - 2 samples of table water
  - 1 sample of artesian water
  - 25 samples of mineral water
  - 15 samples of spring water

19 samples of **baby bottled water** coded P1' – P19' → 4 brands were Romanian samples and 15 samples were imported

- 19 samples of still water
  - 1 samples of table water
  - 10 samples of mineral water
  - 8 samples of spring water

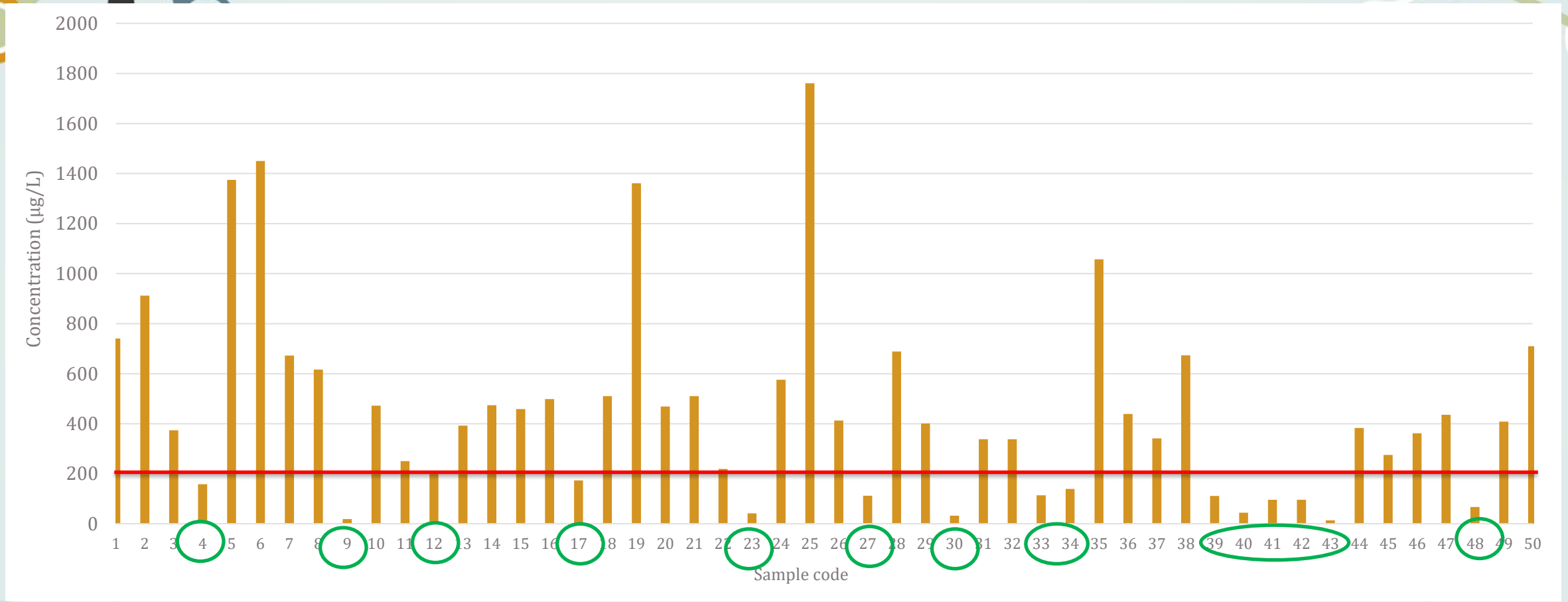
THE CONTENT OF POTENTIALLY TOXIC ELEMENTS IN REGULAR AND BABY BOTTLED WATER

Element	Concentration range ± SD (µg/L) in regular bottled water	Concentration range ± SD (µg/L) in baby bottled water	Directive (EU) 2020/2184 (µg/L)	Law no. 311/2004 (µg/L)	Directive 98/83/EC (µg/L)	WHO 2017 (µg/L)
Ba	< LOD – 10.47 ± 0.71	< LOD – 16.76 ± 0,32	-	-	-	1300
Co	< LOD – 0.89 ± 0.007	< LOD – 0.25 ± 0.05	-	-	-	-
Cu	0.38 ± 0.009 – 5.63 ± 0.540	0.38 ± 0.002 – 1.75 ± 0.03	2000	100	2000	200
Zn	0.67 ± 0.04 – 15.20 ± 0.80	0.96 ± 0.07 – 4.47 ± 0.22	-	5000	-	-
Mn	< LOD – 7.41 ± 0.12	< LOD – 4.17 ± 0.20	50	50	50	-
Ni	0.16 ± 0.002 – 3.77 ± 0.07	0.31 ± 0.006 – 2.25 ± 0.06	20	20	20	70
Li	< LOD – 12.30 ± 0.76	< LOD – 7.28 ± 0.36	-	-	-	-
Fe	**18.80 ± 1.37 – 1450.63 ± 35.64**	**62.38 ± 6.13 – 1688.58 ± 39.24**	200	200	200	-
Pb	**< LOD – 6.00 ± 0.02**	0.11 ± 0.006 – 1.79 ± 0.02	5	10	10	10
Cd	< LOD	< LOD	5	5	5	3
Cr	< LOD – 4.02 ± 0.09	< LOD – 0.16 ± 0.007	25	50	50	50
Sb	< LOD – 0.64 ± 0.04	< LOD – 0.13 ± 0.001	10	5	5	20

- acc. to **Directive (EU) 2020/2184** → **iron and lead** exceed the limits imposed
- acc. to **Law no. 311/2004** and **Directive 98/83** → **iron** exceed the limit imposed

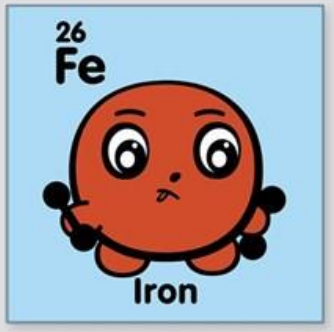
iron is most prevalent in surface waters, in groundwater and springs, due to their **high concentrations** in the lithosphere

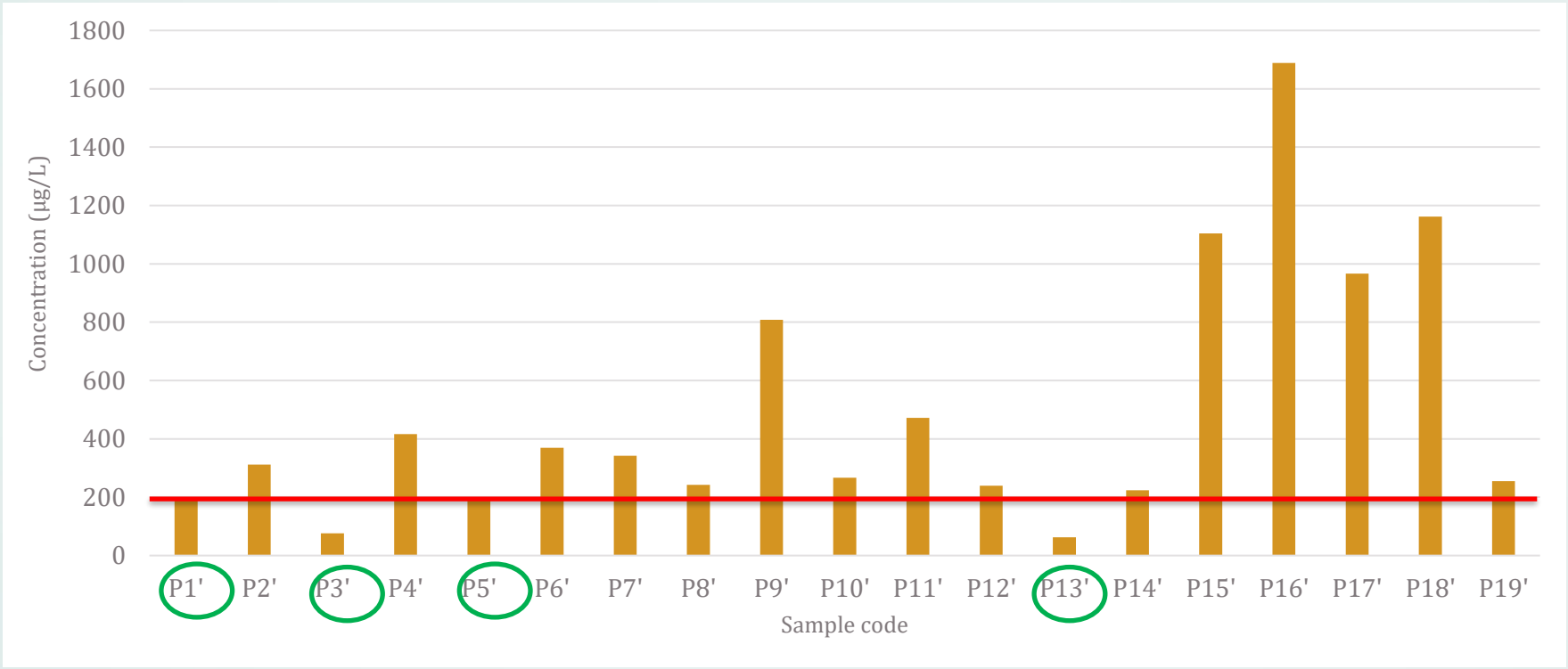
Fe EXCEEDINGS IN REGULAR BOTTLED WATER



30 % of tested samples were **below** the imposed limit of 200 µg/L

Fe EXCEEDINGS IN BABY BOTTLED WATER

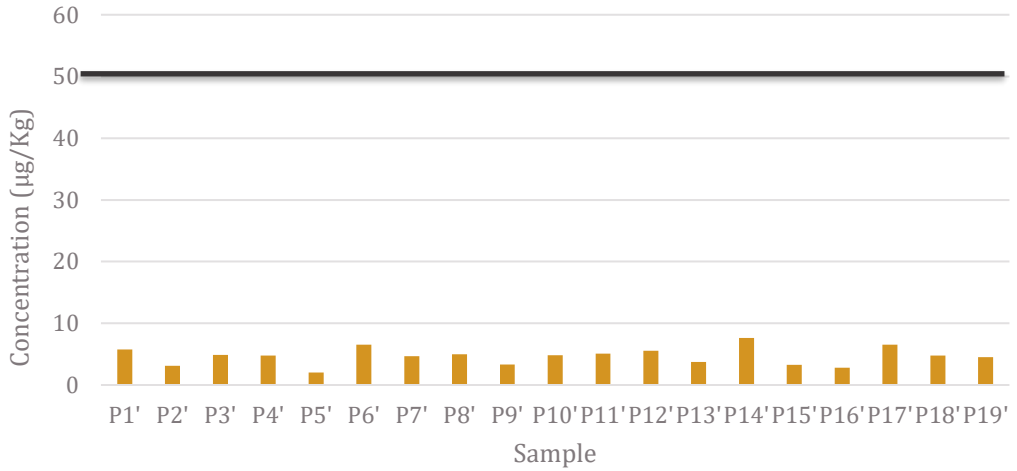




21% of tested samples were **below** the imposed limit of 200 µg/L

ANALYSIS OF BPA CONTENT IN BOTTLED WATER

BPA LEVELS IN REGULAR AND BABY BOTTLED WATER

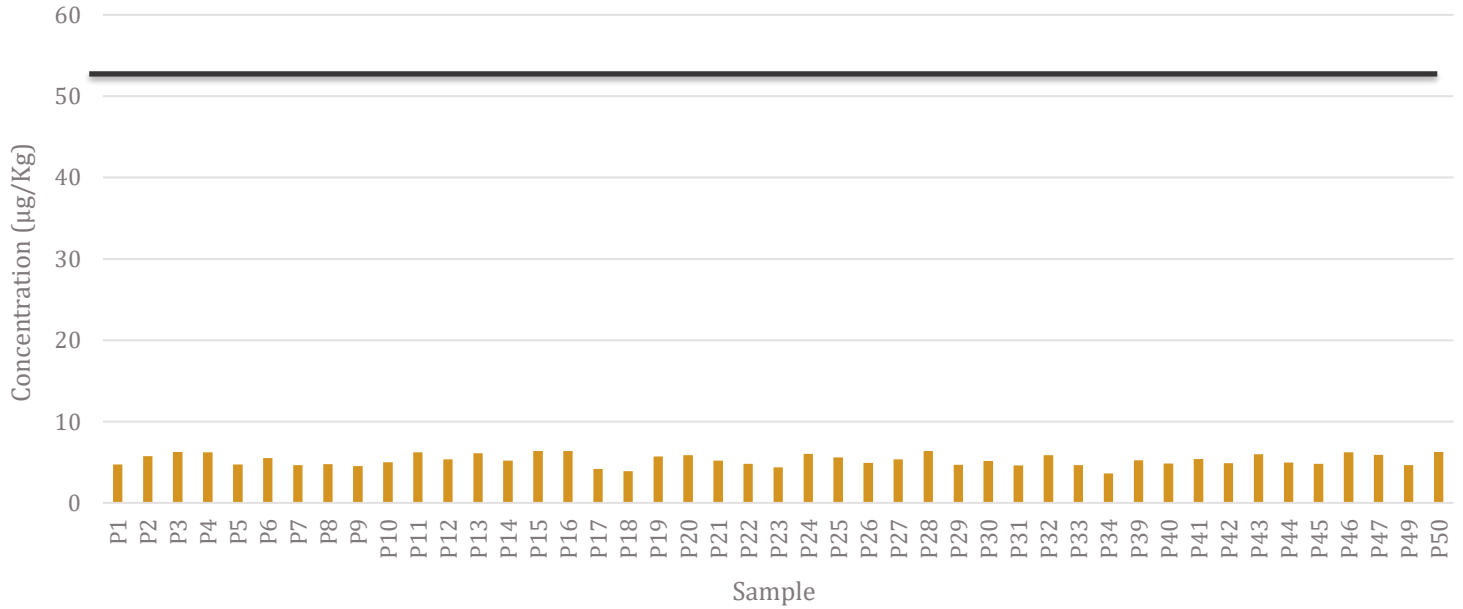


BPA levels in baby bottled water

- Person correlations **didn't show any correlation** between potentially toxic elements and BPA levels

all the concentrations obtained are **below the maximum imposed limit of 50 µg/Kg (Regulation EU 213/2018)**

BPA levels in regular bottled water



HEALTH RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS AND BPA, FOR ADULTS AND CHILDREN

NON - CARCINOGENIC ANALYSIS

- involves estimation of the **dose of exposure (D), the hazard quotient (HQ)** and the **hazard index (HI)**
- the estimation – acc. to the model presented in **PHA Guidance manual, 2005**
  - for **an adult** (70 years, 70 kg wight and a water intake rate of 2 L/day)
  - for a **child** (2 years, 10 kg weight and a water ingestion rate of 1 L/day)

Parameters equations

- **Exposure dose:** **D = (C X IR X EF) / BW**, where D is exposure dose (mg/kg/day), C is contaminant concentration (mg/L), IR is intake rate of water (L/day), EF is exposure factor (unitless), BW is body weight (kg).
- **Hazard Quotient (HQ):** **HQ = D / RfD**, where D is exposure dose (mg/kg/day), RfD is reference dose (mg/kg/day), which represents the tolerable daily intake of the metal via oral exposure.

- **Hazard Index (HI):**

$$HI = HQ_{Pb} + HQ_{Cd} + HQ_{Cr} + HQ_{Cu} + HQ_{Zn} + HQ_{Mn} + HQ_{Ni} + HQ_{Ba} + HQ_{Co} + HQ_{Li} + HQ_{Fe} + HQ_{Sb} + HQ_{BPA}$$

NON - CARCINOGENIC ANALYSIS OF REGULAR BOTTLED WATER FOR ADULTS

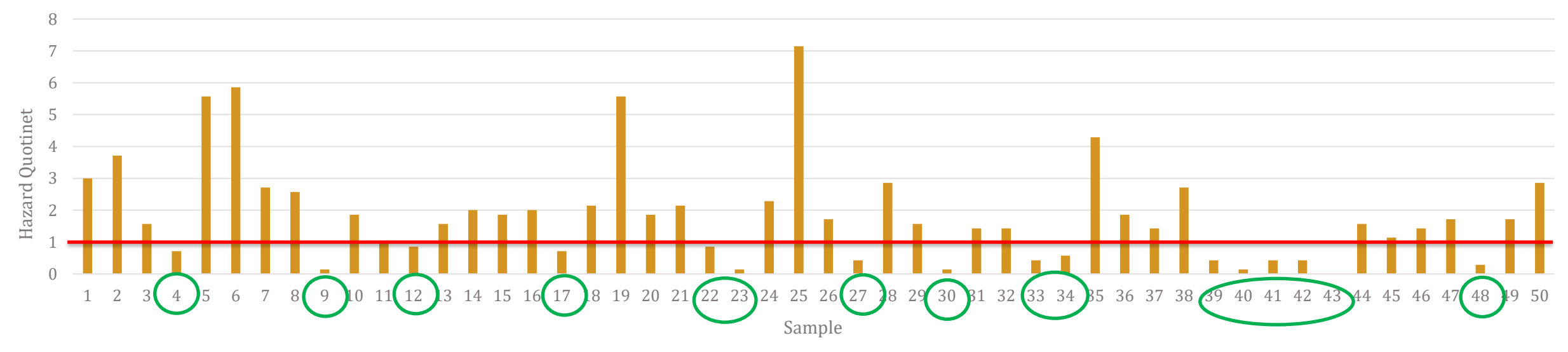
Element	D (µg/kg/day)			HQ		
	max	min	mean	max	min	mean
Ba	2.99E-04	0.00	5.45E-05	4,27E-03	0,00E+00	7,79E-04
Co	2.54E-05	0.00	3.19E-06	1,27E-03	0,00E+00	1,59E-04
Cu	5.54E-04	1.00E-05	4.13E-05	1,50E-01	2,70E-03	1,11E-02
Zn	4.34E-04	1.91E-05	9.04E-05	1.45E-03	6.38E-05	3.01E-04
Mn	2.12E-04	0.00	1.17E-05	4.60E-03	0.00	2.55E-04
Ni	1.08E-04	3.71E-06	3.46E-05	5.39E-03	1.86E-04	1.73E-03
Li	3.51E-04	0.00	4.77E-05	1.26E-02	0.00	1.70E-03
Fe	5.00E-02	0.00	1.30E-02	**7.17E+00**	**0.00**	**1.86E+00**
Pb	1.71E-04	0.00	1.85E-05	4.76E-02	0.00	5.13E-03
Cd	0.00	0.00	0.00	0.00	0.00	0.00
Cr	1.15E-04	0.00	8.01E-06	3.83E-02	0.00	2.67E-03
Sb	1.83E-05	0.00	2.34E-06	5.22E-02	0.00	6.68E-03
BPA	1.03E-04	1.95E-04	1.55E-04	2.07E-03	3.89E-03	3.10E-03
HI	7.18E+00	1.73E-02	1.89E+00			

except Fe, all elements tested had HQ values less than 1

- the ascendent trend of **Exposure Dose** is:
  Cd < Sb < Co < Cr < Mn < Pb < Ni < Cu < Li < Ba < Zn < BPA < Fe
- the ascendent trend of **Hazard Quotient** is:
  Cd < Co < Mn < Zn < Ba < Li < Ni < Cr < BPA < Pb < Sb < Cu < Fe
- ⬇ values of D and HQ - Cd
- ⬆ values of D and HQ - Fe

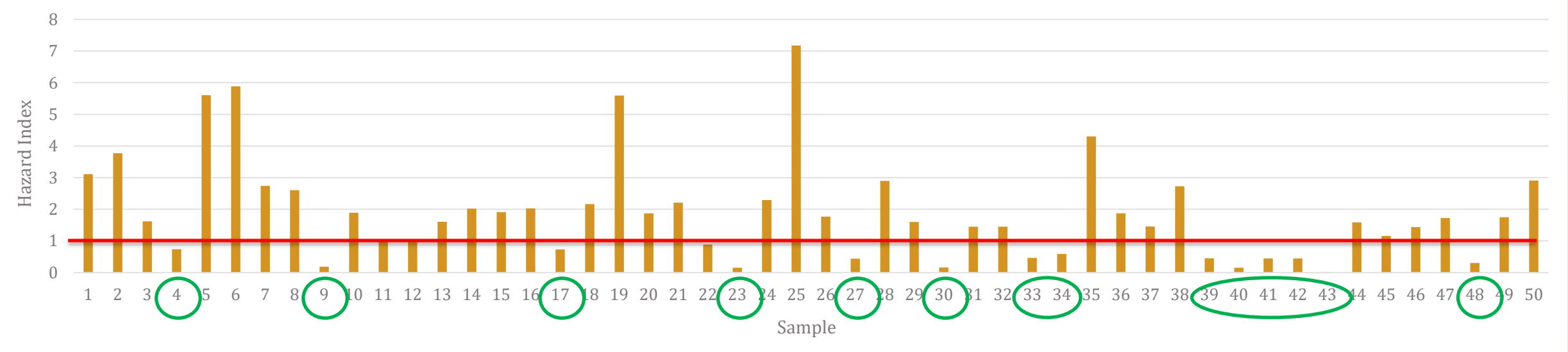
If the **HQ** value is **less or equal to coefficient 1**, repeated exposure **may not cause side** effects, but if the value is **greater than 1**, then consumers are exposed to a **non-carcinogenic risk**.

EXCEEDINGS OF THE HAZARD QUOTIENT OF FE IN REGULAR DRINKING WATER



32% of tested samples had HQ values **lower than 1** → repeated consumption doesn't cause adverse effects

HAZARD INDEX VALUES OF REGULAR BOTTLED WATER



32% of tested samples had HI values **lower than 1** ⟶ no side effects will occur

- if HI is higher than 1: some adverse effects, but non-carcinogenic, can appear
- if HI is less than or equal to 1: no side effects will occur after chronic exposure

NON - CARCINOGENIC ANALYSIS OF BABIES BOTTLED WATER

Element	D (µg/kg/day)			HQ		
	max	min	mean	max	min	mean
Ba	1.68E-03	0.00	3.87E-04	2.39E-02	0.00	5.52E-03
Co	2.50E-05	0.00	7.95E-06	1.25E-03	0.00	3.97E-04
Cu	1.75E-04	3.80E-05	9.60E-05	4.73E-02	4.25E-03	2.54E-02
Zn	4.47E-04	9.60E-05	2.04E-04	1.49E-03	3.20E-04	6.81E-04
Mn	4.17E-04	0.00	3.51E-05	9.07E-03	0.00	7.62E-04
Ni	2.25E-04	3.10E-05	1.06E-04	1.13E-02	1.55E-03	5.12E-03
Li	7.28E-04	0.00	1.72E-04	2.60E-02	0.00	6.13E-03
Fe	1.69E-01	6.20E-03	4.39E-02	**2.41E+01**	**8.86E-01**	**7.50E+00**
Pb	1.79E-04	1.10E-05	4.36E-05	4.97E-02	3.06E-03	1.19E-02
Cd	0.00	0.00	0.00	0.00	0.00	0.00
Cr	1.60E-05	0.00	1.32E-06	5.33E-03	0.00	4.39E-04
Sb	1.30E-05	0.00	1.60E-06	4.33E-03	0.00	5.44E-04
BPA	3.92E-04	6.38E-04	5.35E-04	7.83E-03	1.28E-02	1.07E-02
HI	3.50E+02	9.22E-01	2.53E+01			

- the ascendent trend of **Exposure Dose** is:

  Cd < Cr < Sb < Co < Mn < Pb < Cu < Ni < Li < Zn < Ba < BPA < Fe.

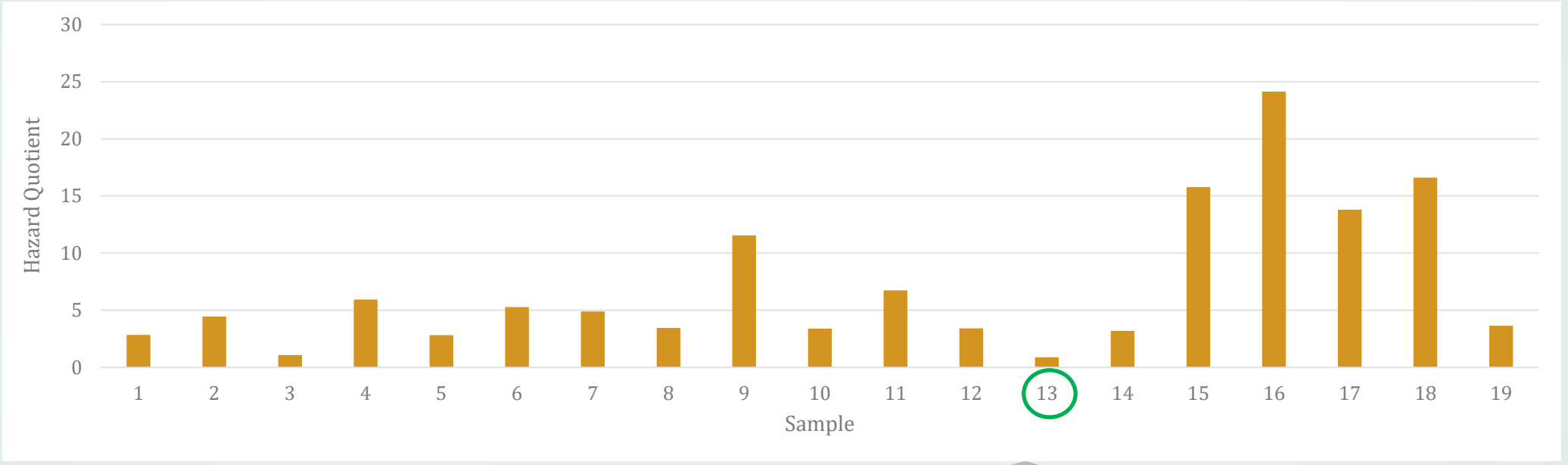
- the ascendent trend of **HQ** is:

  Cd < Co < Cr < Sb < Zn < Mn < Ni < Ba < Li < BPA < Pb < Cu < Fe.

- ↓ values of D and HQ - Cd
- ↑ values of D and HQ - Fe

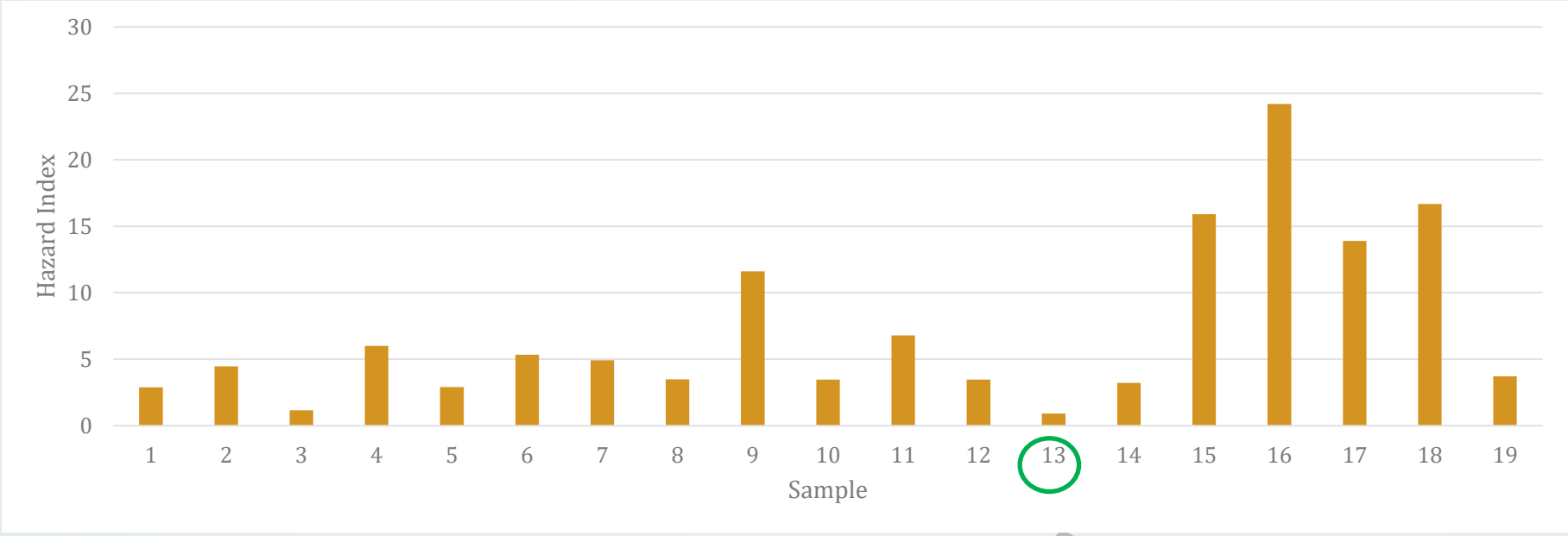
except Fe, all elements tested had HQ values less than 1

EXCEEDINGS OF THE HAZARD QUOTIENT VALUES OF FE IN BABY DRINKING WATER



only sample P13' had the **HQ value lower than 1**

HAZARD INDEX VALUES OF BABY BOTTLED WATER



only sample P13' had the **HI value lower than 1**

CARCINOGENIC ANALYSIS

- involves estimation of the **Cancer risk (CR) and Total Cancer Risk (TCR)**

Parameters equations

- **Cancer risk (CR):** **CR = D / CSF**, where D is exposure dose in mg/kg/day and CSF is Cancer Slope Factor, in mg/kg/day

- **Total Cancer Risk (TCR):** **$TCR = CR_{Pb} + CR_{Cd} + CR_{Cr} + CR_{Ni}$**, where Cr_{Pb}, Cr_{Cd}, Cr_{Cr} and Cr_{Ni} represent values of CR of the 4 metals.

Interpretation

- a value less than $1x10^{-6}$ is insignificant
- a value above $1x10^{-4}$ is harmful
- the acceptable level for TCR is $1x10^{-5}$

CARCINOGENIC ANALYSIS OF REGULAR AND BABY BOTTLED WATER

Regular bottled water

Metal	Cancer risk		
	max	min	mean
Pb	1.46E-03	0.00	1.57E-04
Cd	0.00	0.00	0.00
Cr	4.71E-03	0.00	3.28E-04
Ni	9.05E-05	3.21E-06	2.90E-05
$CR_{(Total)}$	4.86E-03	4.00E-05	5.14E-04

- the ascending trend of **CR** is: **Cd < Ni < Pb < Cr;**
- **TCR: 28%** of the samples are in the **acceptable level**, while **72%** of the samples are **harmful, which can lead to a type of cancer;**

Baby bottled water

Metal	Cancer risk		
	max	min	mean
Pb	1.53E-03	9.35E-05	3.63E-04
Cd	0.00	0.00	0.00
Cr	6.56E-04	0.00	5.39E-05
Ni	1.89E-04	2.60E-05	8.61E-05
$CR_{(Total)}$	**1.58E-03**	**1.69E-04**	**5.03E-04**

- the ascending trend of **CR** is: **Cd < Cr < Ni < Pb;**
- **TCR**: all 19 samples were in the **tolerable range;**

⬇ values of CR and TCR – for Cd, in both, regular and baby bottled water

WATER QUALITY DETERMINATION

- involves estimation of the **contamination factor (Cf) and contamination degree (Cd)**

Parameters equations

- **Contamination factor (Cf):** **$Cf = CA/CN$,** where CA is the measured concentration of the potentially toxic metal and CN is the maximum allowable concentrations (MAC) of the metals of interest.

- **Contamination degree (Cd):** **$Cd = Cf_1 + Cf_2 + \ldots + Cf_n$,** where Cd is degree of contamination, Cf_1, Cf_2, Cf_n are contamination factor of each contaminant.

Interpretation

Contamination factor classes	Description	Contamination degree classes	Description
CF <1	low contamination	Cd < 6	low degree of contamination
1 < CF < 3	moderate contamination	6 < Cd < 12	moderate degree of contamination
3 < CF < 6	considerable contamination	12 < Cd < 24	considerable degree of contamination
CF >6	very high contamination	Cd >24	high degree of contamination

REGULAR BOTTLED WATER QUALITY

Element	Contamination factor		
	max	min	mean
Ba	-0.97	-1.00	-0.99
Cu	-0.94	-1.00	-0.99
Zn	-0.99	-1.00	-1.00
Mn	-0.85	-1.00	-0.99
Ni	-0.81	-0.99	-0.94
Fe	**7.81**	-0.93	**1.25**
Pb	-0.40	-1.00	-0.94
Cd	**-1.00**	**-1.00**	**-1.00**
Cr	-0.92	-1.00	-0.99
Sb	-0.87	-1.00	-0.98
Cd	-1.06	-9.88	-7.58

- ⬇ values of Cf and Cd - cadmium
- ⬆ values Cf and Cd - iron
- except iron, all other metals ⟶ Cf < **1** ⟶ **low contamination;**
- the ascending trend of Cf is: **Cd < Zn < Cr < Ba < Mn < Cu < Sb < Pb < Ni < Fe;**
- Cd < **6** ⟶ **low degree of contamination;**
- the downward trend of Cd is: **Fe > Ni > Pb > Sb > Ba > Cu > Mn > Cr > Zn > Cd;**

BABY BOTTLED WATER QUALITY

Element	Contamination factor		
	max	min	mean
Ba	-0.94	-1.00	-0.99
Cu	-0.98	-1.00	-0.99
Zn	-1.00	-1.00	-1.00
Mn	-0.92	-1.00	-0.95
Ni	-0.89	-0.98	-0.95
Fe	7.44	-0.68	1.47
Pb	-0.82	-0.99	-0.96
Cd	-1.00	-1.00	-1.00
Cr	-1.00	-1.00	-1.00
Sb	-0.97	-1.00	-0.99
Cd	-1.38	-9.64	-7.40

- ⬇ values of Cf and Cd - Cd, Cr and Zn
- ⬆ values of Cf and Cd - Fe
- except iron, all other metals ⟶ Cf **< 1** ⟶ low **contamination;**
- the ascending trend of Cf, is: **Cd < Cr < Zn < Sb < Mn < Cu < Ni < Pb < Co < Fe;**
- Cd < **6** ⟶ **low degree of contamination;**
- the downward trend of Cd is: **Fe > Mn > Ni > Pb > Ba > Cu > Sb > Zn > Cr > Cd;**

GENERAL CONCLUSIONS

- Concentrations of potentially toxic elements in regular bottled water were **lower** than imposed limits, except for **Fe** and **Pb**;
- In baby drinking water, only **Fe** exceed the imposed limit;
- Concentrations of BPA in regular and baby bottled water were **lower** than imposed limit;
- In case of regular drinking water, only Fe had **HQ > 1** and 30% of samples has **HI value > 1**.
- For baby bottled water, except Fe, all other metals had **HQ values < 1** and only one sample has **HI < 1**.
- **30%** of the samples had values of HI for potentially toxic elements + BPA < 1 and 70% > 1;
- For baby water, all the HI values for potentially toxic elements + BPA were **> 1**;
- Except Fe, all the metals from regular and baby bottled water had a contamination factor **< 1**, which means **low** contamination;
- Contamination degree of regular and baby bottled water were **< 6**, which means a **lower** degree of contamination.

RECOMMENDATIONS

For consumers

- Maintain the bottled water in proper conditions protected from direct sunlight or high temperatures;
- Limits sparkling water consumption;
- Avoid using plastic bottles or containers from polycarbonate because many of them contain BPA;
- Use plastic bottle certified as BPA free, or bottles obtained from polyethylene or polypropylene.

For producers and retailers

- Keep bottled water in optimal light and temperature conditions;
- Improve the pre-bottled water treatments (especially for baby water);
- Use of less hazardous packaging materials.

RECOMMENDATIONS

For the authorities

1. The levels of potentially toxic elements, BPA, and other chemical contaminants, from food and water, must be assessed regularly;
2. Measures must be taken to minimize environmental contamination, the main factor for food contamination;
3. It must organize consumer education campaigns related to storing of food, but also about the effects of chemical contaminants on human health;
4. The allocation of funds and grants for this type of research study, but which should include a much larger number of contaminants, carried out on other food products.

Thank you for your attention!