

Article

Human Health Risk Assessment of Trace Elements in Tap Water and the Factors Influencing Its Value

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Abstract: (1) Background: The influence of tap water fittings construction and internal pipe-work on the release of heavy metals was investigated. (2) Methods: A statistical approach was applied for the examination of the chemistry of tap water in five different cities in southern Poland. In total, 500 samples were collected (from 100 to 101 samples in each city). The sampling protocol included information on the construction of the water supply network and the physicochemical parameters of measured tap water. (3) Results: The statistical analysis allowed to extract the crucial factors that affect the concentrations of trace elements in tap water. Age of connection, age of tap, age of pipe-work as well as material of connection, material of pipe-work and material of appliance reveal the most significant variability of concentrations observed for As, Al, Cd, Cu, Fe, Mn, Pb, and Zn. Calculated cancer risks (CRs) decrease with the following order of analysed elements Ni > Cd > Cr > As = Pb and can be associated with the factors that affect the appearance of such elements in tap water. The hazard index (HI) was evaluated as negligible in 59.1% of the sampling points and low in 40.1% for adults. For children, a high risk was observed in 0.2%, medium in 9.0%, negligible in 0.4%, and low for the rest of the analysed samples.

Keywords: trace elements; aquatic environment; tap water; risk assessment; hazard Index; multivariate statistics



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1. Introduction

In recent years, great importance has been placed on the protection of human health. Increased attention is paid to toxic components of the environment, which occur naturally (e.g., metals, metalloids) or are introduced artificially by humans (e.g., pesticides), and which harm human health. Risk analysis deals with the issues of the harmful effects of various substances on human health. It is an issue more commonly discussed in scientific articles that present risk associated with, e.g., acceptable daily intake (ADI), lowest no observed adverse effect level (NOAEL), drinking water equivalent level (DWEL), cancerogenic risk (CR), non-cancerogenic risk (NCR), and related to the introduction of harmful substances by different routes into the human body, e.g., ingestion, dermal contact, inhalation [1–13]. The total risk related to the substances considered is therefore expressed in the form of the hazard quotient (HQ) or hazard index (HI), which, depending on their value, indicate low or high risk.

In every chemical research on natural water (ground-, surface, geothermal) including water intended for human consumption, it must be ensured that the obtained results are reliable. This requirement cannot be fulfilled without properly conducting quality control of the research and collecting representative samples in accordance with international standards and norm series.

Water quality tests are carried out routinely, but there is a lack of a harmonized water samples collection protocol from the water supply network despite the clear requirements of the directive of the European Council 98/83/EC of 3 November 1998, the Regulation of the Minister of Health of 7 December 2017 [14–18] and the revised Directive of the European Parliament and of the Council [19], all on the scope of water intended for human consumption. Therefore, the results obtained from research conducted at the same place but with the application of different protocols during sampling collection can differ significantly [20,21].

One of the main problems is to accept only one, universal method of water samples collection which ensures obtaining reliable results from the research conducted in points of drawing, treating, distribution and tap of the end-user. It also implies a difficulty in the application of an integrated quality assurance/quality control programme (QA/QC) and estimation of results uncertainty related to all stages of the research. The recommendations considering sampling of water intended for drinking purposes were described in a standard ISO 5667-5 [22] Water quality—Sampling—Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems, but no harmonized methodology or volume of tap water that should be collected is pointed out [23]. In some worldwide research, samples of volumes 50, 100 or 250 mL were collected [24,25]. In compliance with the guidelines there, samples for assessment of the quality of drinking water should be collected from different points in the water supply network [10]. Special attention should be paid to the elements placed directly before the next stage of the water treatment process. The International Water Association [26–28] recommends conducting water quality research on the whole way of water flow—from the source to the end-user's tap. Regardless of the sampling methodology used, the most important is to ensure the good quality of water for the end-user. Therefore, it is necessary to identify the factors that can affect the results of drinking water analyses. This information is necessary to develop one universal sampling protocol which will consider all important variables and sources of variation in the water composition.

The quality of tap water can change over a time since the processes of secondary pollution in water network installation systems (WNISs) take place constantly. The WNISs kind and intensity are conditioned by the type of material used for its construction, network project, implementations and usage conditions. The deterioration of water quality can be due to changes in physical parameters (colour, turbidity), chemical parameters (undesirable increase in heavy metals concentrations), and bacteriological parameters. The effect of these changes may be the dissatisfaction of end-users with the quality of tap water or the incapacity of water for human consumption [29].

One of the most important issues related to water quality research is the influence of water stagnation time in the water network and therefore the time of its contact with internal elements of installation, and appliance on a water chemical composition. Errors arising from the determination of the concentration levels of heavy metals in water intended for human consumption are related to the insufficient flush of installation before collection of water samples [20,21,30–32].

All the above-mentioned factors can influence the quality of water mainly by changes in concentrations of some metals and metalloids and, therefore, pose a risk to human health. The non-carcinogenic and carcinogenic effect of drinking water on human health is usually calculated for raw water or based on samples collected directly from the waterworks [3,5,7,12,13,33–41]. Only a few studies consider tap water samples [42,43].

Chemometric methods are successfully implemented for the assessment of groundwater [44,45] and surface water quality [46–49], analysis of pollutants in wastewater [50] and groundwater [51], characterisation of groundwater chemistry [52,53], contamination of aquifers [54], assessment of spatial variability of curative water [55], or identification of the correlations between different components of water intended for human consumption and tap water [21,32,56–63].

The aim of the presented research is to indicate the human health risk arising from the consumption of water containing elevated concentrations of selected harmful elements originated from installation. The main factors that can affect the final results of drinking water analyses and should therefore be included in the drinking water sampling protocol were also indicated. Water chemical composition and selected physical parameters as well as house characteristics (kind of household) and water connection system features (material and age of the connections, pipes and tap) were taken into consideration. This is one of the first such complex research that includes the wide scale of different factors associated with tap water chemical composition. Multivariate analysis of variance (MANOVA) was implemented to find out if the chemical composition differs within the categories of the analysed parameters. If so, the parameters were deemed relevant for the sampling protocol. Otherwise, the influence of the parameters on the elemental content is insignificant.

2. Study Area

Research was conducted in the five cities located in southern Poland (Figure 1).



Figure 1. Location of the study area.

Poland has a warm temperate transitional climate. The climate zone is crossed by air masses from the Atlantic Ocean and Eurasian landmass [64]. The average annual precipitation is approximately 700 mm in central Poland, and toward the south, it increases to 780 mm in the uplands belt and 1100 mm in the mountains [64]. In case of evapotranspiration, this parameter can affect the chemical composition of drinking water, the main source of which is surface water such as in Krakow. The annual average value of evapotranspiration in Krakow based on the observation made by the meteorological station is 657.9 mm (<http://meteo.kdwd.webd.pl/wxetseason.php?r=wxetseason.php>, accessed date: 8 November 2021).

The examined area lies within the mountain–upland hydrogeological province where fresh groundwater is formed in the Sudetic Massif (MS), Carpathian Massif (MC), Świętokrzyski Massif (MSt) and Kujawski Massif (MKu). Within described massifs, the dominant bedrock is the fissured crystalline rocks (MS), Neogene–Paleogenic and cretaceous flysch rocks of fissure-pore nature (MK), fissure–karst Devonian carbonate rocks and Jurassic–Cretaceous carbonate rocks, as well as fissure–pore Jurassic–Cretaceous sandstone formations (MSt). The Kujawski massif is built mainly from Jurassic rocks of karst–fissure nature [65,66]. Detailed information on the geological setting within each city is presented in Table 1.

Table 1. Geological setting of groundwater used as a source of drinking water.

City	Geological Setting
Myszkow	Carbonate series of Middle Triassic (Muschelkalk), formed as cracked karstic fissured dolomites and limestones
Jaworzno	Formations of carbonate series of Lower and Middle Triassic and sandstone series of Upper Carboniferous
Raciborz	Pleistocene groundwater reservoir with sandy and gravelly formations
Kamienna Gora	Pleistocene groundwater reservoir with gravelly formations, covered with loams, silts, and contemporary river alluvia

3. Materials and Methods

Samples were taken from households in five Polish cities, Krakow, Raciborz, Jaworzno, Myszkow, and Kamienna Gora in accordance with the ISO 5667-3 [67]. The samples were collected at a random time of the working day directly from the tap without previous flushing (random daytime (RDT) samples) [23]. The collected information included 10 metals and metalloids: Al, As, Cd, Cr, Cu, Fe, Mn, Zn, Ni, and Pb and auxiliary chemical indices such as major ions to control the correctness of the chemical analyses made. In total, 500 samples were collected (from 99 to 101 samples in each city). Blank samples (deionized water treated in the same way as normal samples) were also taken at 10 randomly selected locations in each city. In the field, pH and electrical conductivity (EC) (using automatic compensation to 25 °C) were measured using a Multi 350i meter, WTW, Weilheim, Germany, according to ISO 10523 [68] and EN 27888 [69] standards. Basic information about the water source, mean values of TDS (calculated as a sum of all analysed cations and anions), pH, EC, concentration of Ca, Mg, SO₄, HCO₃ ions and water treatment process in each city are summarised in Table 2. The dominating major ions in water analysed are HCO₃ and Ca. The hydrochemical type of water from Jaworzno, Kamienna Gora and Myszkow is HCO₃–SO₄–Ca–Mg, in Krakow it is HCO₃–SO₄–Ca water and in Raciborz HCO₃–Ca–Mg.

The water samples were analysed in the laboratory of the Department of Hydrogeology and Engineering Geology, AGH University of Science and Technology, Krakow, Poland. The analyses of Al, As, Cd, Cr, Cu, Fe, Mn, Zn, Ni, Pb were performed using inductively coupled plasma mass spectrometry (ICP-MS) with an ELAN 6100 spectrometer (Perkin Elmer, Waltham, MA, USA) in compliance with ISO 17294-2 [70]. Ca, Mg and S (recalculated on SO₄) were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) with an Optima 7300 DV spectrometer (Perkin Elmer, Waltham, MA, USA) according to ISO 11885 [71]. Titration methods were implemented for alkalinity (HCO₃[−]) determination. The laboratory has implemented an internal QA/QC programme. As a part of quality control, it participates in proficiency tests and interlaboratory comparisons (PT/ILC), including in the field of heavy metal analysis in water intended for human consumption, achieving satisfactory results. Moreover, the duplicate samples and certified reference materials (TMDA 63.4) with a known matrix underwent the analysis during routine laboratory work. Basic method parameters were evaluated based on the results of multiple analyses of the certified reference material. The precision obtained

during the chemical analyses was lower than 10%, and the accuracy was in the range of 80% to 120%. The relative pair difference calculated for duplicate samples did not exceed 13%. The relative expanded uncertainty calculated for the analysed elements varied from 10% to 18%.

Table 2. Basic water parameters.

City	Water Source	Number of Samples	TDS [mg/L]	pH	EC [μS/cm]	Ca ²⁺ [mg/L]	Mg ²⁺ [mg/L]	SO ₄ ^{2−} [mg/L]	HCO ₃ [−] [mg/L]	Water Treatment Process
			Mean ± SD							
Krakow	Surface water	101	178 ± 19	7.1 ± 0.4	294 ± 24	41.7 ± 5.0	5.8 ± 0.7	45.8 ± 7.7	111 ± 12	ozonation coagulation sedimentation filtration disinfection
Jaworzno	groundwater	100	450 ± 37	7.5 ± 0.1	760 ± 17	74.9 ± 8.0	40.4 ± 3.8	123 ± 16	266 ± 18	disinfection
Kamienna Gora		100	175 ± 7	6.8 ± 0.1	270 ± 6	32.6 ± 2.1	9.1 ± 0.9	62.2 ± 7.2	81.7 ± 6.5	untreated
Raciborz		100	315 ± 46	7.4 ± 0.2	560 ± 64	82.6 ± 13.2	16.1 ± 3.1	47.8 ± 8.0	274 ± 43	aeration filtration disinfection
Myszkow		100	346 ± 21	7.3 ± 0.1	568 ± 26	71.0 ± 9.0	35.5 ± 4.3	58.1 ± 14.4	322 ± 15	aeration disinfection (if necessary)

SD: standard deviation.

In addition, anonymous voluntary survey data was collected for the research. The information was gathered from the adult household residents during a short-field voluntarily given interview in accordance with the current Polish law on data protection (The Personal Data Protection Act, no. 1000 of 2018). The experimental protocol, which included sampling procedures and the gathering of additional information from householders, was approved by the Polish National Committee of COST Action 637 “MetEAU” (Metals and Related Substances in Drinking Water). All respondents were of legal age (over 18 years) and gave their informed consent to participate in the study. Among others, the questionnaire contained inquiries about the kind of household, water rating by end-user, age and material of pipe-work, connections and appliance and water stagnation time. These factors that could affect the results of the drinking water analysis were categorised according to the information collected during the field interview. The list of categories for each factor is available in Table 3.

Table 3. Categories established for survey descriptive variables collected during the field interview.

Factor	Categories
City	Krakow Jaworzno Kamienna Gora Raciborz Myszkow
Kind of household	public building block of flats house
Age of connection	10 years 10–30 years 30 years
Age of pipe-work	10 years 10–30 years 30 years

Table 3. Cont.

Factor	Categories
Age of tap	10 years 10–30 years 30 years
Stagnation time	1 h 1 h
Material of connection	stainless steel iron plastic galvanised steel other
Material of pipe-work	stainless steel copper iron plastic galvanised steel other
Material of appliance	stainless steel other
Water rating by end-user	good unacceptable

3.1. Data Analysis

Data were interpreted using different statistical methods. Box-and-whiskers plots were used to show the variation in selected elements concentrations depending on the factor selected. Pearson correlation was applied to indicate dependencies between the analysed elements.

As a final part of the statistical analysis, multivariate analysis of variance (MANOVA) was applied [72]. The R package [73] was used to perform the MANOVA analysis. It was implemented to verify our hypothesis that the studied water sampling factors affect the concentrations of metals in water. The test was performed for each dependent variable (factor). To meet the assumptions of MANOVA, the univariate and multivariate outliers were identified and removed from each category. Only independent variables (metals and metalloids concentrations) characterised by the normal distribution for each category underwent MANOVA. The number of samples in each category range from 10 to 296, and the lowest was achieved for the different types of connection, pipe-works, and taps materials. Since the assumption of the covariance equality between categories was violated and the data were unbalanced (sizes of categories were not equal), the MANOVA test may have lost some sensitivity and thus Pillai's statistic was applied. The null hypothesis stated that there is no statistically significant difference in the metals content between the categories and the alternative hypothesis stated otherwise. The null hypothesis failed to be rejected with *p*-values above the established threshold equal to 0.05. All values below 0.05 indicated that there is enough evidence to reject the null hypothesis and conclude that the metals content differs significantly between the categories. This further leads to regard these factors as potentially influencing the metals content during the water sampling and indicates that the variability related to this factor is remarkable and therefore this factor should be controlled during sampling.

3.2. Risk Assessment

Trace elements that occur in drinking water can pose a health risk to consumers primarily by ingestion [5,7,11–13,33,34,42,74]. For this reason, the human health risk (carcinogenic and non-carcinogenic) was assessed in relation to Al, As, Cd, Cr, Cu, Fe, Mn, Zn, Ni and Pb. Chronic daily intake (CDI), hazard quotient (HQ), hazard index (HI) as a

sum of the HQ arising from each element in the analysed samples, and cancer risk (CR) were calculated using the following formulae (Equations (1)–(4)) [11,42,67,68]:

$$CDI = \frac{CW \cdot IRW \cdot EF \cdot ED}{BW \cdot AT} \quad (1)$$

$$HQ = \frac{CDI}{RfD} \quad (2)$$

$$HI = \sum HQ \quad (3)$$

$$CR = CDI \cdot SF \quad (4)$$

where CDI is chronic daily intake (mg/kg/day), CW is concentration of selected elements in water (mg/L), IRW is water ingestion rate (L), EF is exposure frequency (day/year), ED is exposure duration (years), BW is body weight (kg), AT is average exposure duration time (days), RfD is reference dose of a specific element (mg/kg/day), HQ is hazard quotient (-), HI is hazard index (-), CR is cancer risk (mg/kg/day), and SF is slope factor (-). Risk was assessed in the division to two groups of people, children and adults. The values of the parameters used to estimate the exposure assessment of the analysed elements in the water samples are summarized in Table 4.

Table 4. Parameters used to estimate exposure assessment of analysed elements in water samples [11,34,42,74–78].

Parameters	Unit	Value	
		Children	Adult
IRW	L	1	2
EF	day/year	365	365
ED	Year	6	30
BW	Kg	15	70
AT (non-carcinogenic)	Days	2190	25,550
AT (carcinogenic)	Days	25,550	
RfD (As)	mg/kg/day	0.0003	
RfD (Al)		1	
RfD (Cd)		0.001	
RfD (Cr)		0.003	
RfD (Cu)		0.04	
provisional RfD (Fe)		0.7	
RfD (Mn)		0.14	
RfD (Ni)		0.02	
RfD (Pb)		0.014	
RfD (Zn)		0.3	
SF (As)	µg/g/day	1.5	
SF (Al)		not assessed	
SF (Cd)		6.3	
SF (Cr)		0.5	
SF (Cu)		not assessed	
SF (Fe)		not assessed	
SF (Mn)		not assessed	

Table 4. Cont.

Parameters	Unit	Value	
		Children	Adult
SF (Ni)	µg/g/day	1.7	
SF (Pb)		0.0085	
SF (Zn)		not assessed	

Non-carcinogenic risk expressed as HI (as a sum of HQ for each element) was classified as negligible ($HI < 0.1$), low risk ($0.1 \leq HI < 1$), medium ($1 \leq HI < 4$) and high ($HI \geq 4$) [76,79]. An acceptable value of the carcinogenic risk calculated as CR was adopted at the level of 1×10^{-4} [80].

4. Results

The concentrations of the major ions differ significantly between cities and are mainly associated with the natural composition of the water distributed in the analysed regions. The differences between cities mostly come from the type of distributed water (i.e., surface or groundwater) and their chemical composition before any treatment (the so-called raw water), and the type of treatment processes applied in water treatment plants. Therefore, only total concentrations of selected heavy metals and metalloids which present in drinking water is related to the water distribution system properties rather than to natural factors, were analysed [23,81].

The results obtained for the blank samples were below the method detection limits. Basic statistics for the concentrations of elements analysed in the collected water samples, together with the maximum permissible concentrations in drinking water set in European (EU 2020 [19]) and worldwide (WHO 2017 [82]) standards are presented in Table 5.

Table 5. Statistics for trace elements concentrations in the collected water samples.

Variable	Parametric Value [7] [µg/L]	Guideline Value [47] [µg/L]	Mean [µg/L]	5% Trimmed Mean [µg/L]	Median [µg/L]	Standard Deviation [µg/L]	Minimum [µg/L]	Maximum [µg/L]
As	10	10	0.72	0.70	0.65	0.38	0.18	3.39
Cr	50	50	4.85	4.64	4.45	2.97	0.03	44.26
Zn	— ¹	—	650	525	365	930	5	11,377
Al	200	—	11.64	10.52	3.19	17.42	0.15	149.4
Cd	5	3	0.53	0.42	0.18	0.74	0.002	4.73
Mn	50	—	16.26	12.00	6.08	28.34	0.04	336.9
Cu	2000	2000	38.21	18.92	11.01	118.1	0.09	1610.0
Ni	20	70	3.73	2.28	1.93	19.91	0.02	433.8
Pb	10	10	5.43	4.21	1.77	8.68	0.10	75.69
Fe	200	—	202	159	104	282	13	2331

¹ Parametric or guideline value is not established.

The variability of the concentration of trace elements between the categories of the descriptive variables is shown in the form of box plots (Supplementary Materials Figure S1). In Figure 2, selected results for Fe and Mn are presented for which the differences were most pronounced. The results were also compared with the requirements of European [19] and international [82] regulations.

Human health risk was calculated for both children and adults, taking into account oral exposure. CDI, HQ, HI and CR were computed individually for each sampling point. Table 6 presents the range and mean values of the calculated parameters.

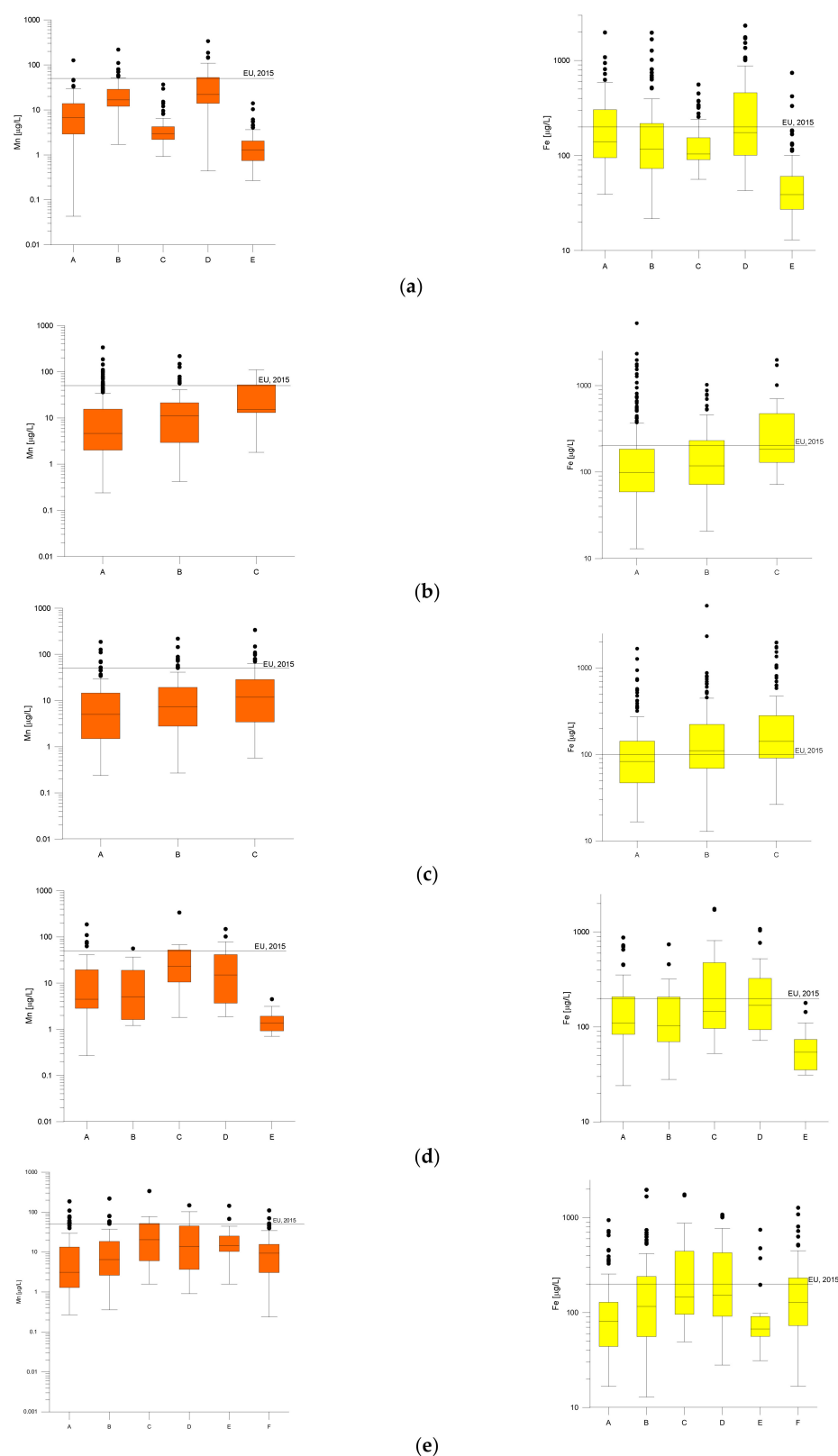


Figure 2. Fe and Mn concentrations in the water analysed by selected categories of factors. (a) City: A, Krakow; B, Jaworzno; C, Kamienna Gora; D, Raciborz; E, Myszkow. (b) Age of tap: A, <10 years; B, 10–30 years; C, >30 years. (c) Age of pipe-work: A, <10 years; B, 10–30 years; C, >30 years. (d) Material of connection: A, PCV; B, steel; C, galvanised steel; D, stainless steel; E, other. (e) Material of pipe-work: A, PCV; B, steel; C, galvanised steel; D, stainless steel; E, copper; F, other.

Table 6. Basic statistics for calculated risk.

Element	Statistic	CDI (Non-CarcinoGenic)		HQ		HI		CR	
		Children	Adults	Children	Adults	Children	Adults	Children	Adults
As	range	1.2×10^{-5} – 2.3×10^{-4}	2.2×10^{-6} – 4.2×10^{-5}	4.0×10^{-2} – 7.5×10^{-1}	7.3×10^{-3} – 1.4×10^{-1}	range: 9.3×10^{-2} – 4.4 mean: 5.8×10^{-1}	range: 1.7×10^{-2} – 8.1×10^{-1} mean: 1.1×10^{-1}	1.5×10^{-6} – 2.9×10^{-5}	3.3×10^{-6} – 6.2×10^{-5}
	mean	4.8×10^{-5}	8.8×10^{-6}	1.6×10^{-1}	2.9×10^{-2}			6.2×10^{-6}	1.3×10^{-5}
Cr	range	n.c. -3×10^{-3}	n.c. -5.4×10^{-4}	n.c. -9.8×10^{-1}	n.c. -1.8×10^{-1}			n.c. -1.3×10^{-4}	n.c. -2.7×10^{-4}
	mean	3.2×10^{-4}	5.9×10^{-5}	1.1×10^{-1}	2.0×10^{-2}			1.4×10^{-5}	3.0×10^{-5}
Zn	range	3.1×10^{-4} – 7.6×10^{-1}	5.7×10^{-5} – 1.4×10^{-1}	1.0×10^{-3} – 2.53	1.9×10^{-4} – 4.6×10^{-1}			not assessed	
	mean	4.3×10^{-2}	8.0×10^{-3}	1.4×10^{-1}	2.7×10^{-2}			not assessed	
Al	range	1.0×10^{-5} – 1.0×10^{-2}	1.9×10^{-6} – 1.8×10^{-3}	1.0×10^{-5} – 1.0×10^{-2}	1.9×10^{-6} – 1.8×10^{-3}			not assessed	
	mean	8.4×10^{-4}	1.5×10^{-4}	8.4×10^{-4}	1.5×10^{-4}			not assessed	
Cd	range	1.3×10^{-7} – 3.2×10^{-4}	2.4×10^{-8} – 5.8×10^{-5}	1.3×10^{-4} – 3.2×10^{-1}	2.4×10^{-5} – 6.02×10^{-2}			7.2×10^{-8} – 1.7×10^{-4}	1.5×10^{-7} – 3.7×10^{-4}
	mean	3.5×10^{-5}	6.5×10^{-6}	3.5×10^{-2}	6.5×10^{-3}			1.9×10^{-5}	4.1×10^{-5}
Mn	range	2.9×10^{-6} – 2.3×10^{-2}	5.3×10^{-7} – 4.1×10^{-3}	2.0×10^{-5} – 1.6×10^{-1}	3.8×10^{-6} – 3.0×10^{-2}			not assessed	
	mean	1.1×10^{-3}	2.0×10^{-4}	7.7×10^{-3}	1.4×10^{-3}			not assessed	
Cu	range	5.9×10^{-6} – 1.1×10^{-1}	1.1×10^{-6} – 2.0×10^{-2}	1.5×10^{-4} – 2.7	2.7×10^{-5} – 4.9×10^{-1}			not assessed	
	mean	2.6×10^{-3}	4.7×10^{-4}	6.4×10^{-2}	1.2×10^{-2}			not assessed	
Ni	range	n.c. -2.9×10^{-2}	n.c. -5.3×10^{-3}	n.c. -1.5	n.c. -2.7×10^{-1}			n.c. -4.2×10^{-3}	n.c. -9.0×10^{-3}
	mean	2.5×10^{-4}	4.6×10^{-5}	1.2×10^{-2}	2.3×10^{-3}			4.0×10^{-5}	8.0×10^{-5}
Pb	range	n.c. -5.1×10^{-3}	n.c. -9.3×10^{-5}	n.c. -3.6×10^{-1}	n.c. -6.6×10^{-2}			n.c. -3.7×10^{-6}	n.c. -7.9×10^{-6}
	mean	3.6×10^{-4}	6.6×10^{-5}	2.6×10^{-2}	4.7×10^{-3}			2.6×10^{-7}	5.6×10^{-7}
Fe	range	n.c. -1.6×10^{-1}	n.c. -2.9×10^{-2}	n.c. -2.2×10^{-1}	n.c. -4.0×10^{-2}			not assessed	
	mean	1.3×10^{-2}	2.5×10^{-3}	1.9×10^{-2}	3.5×10^{-3}			not assessed	

n.c., not calculated due to the concentration below the detection limit.

5. Discussion

The parametric values (PVs) were exceeded for cadmium, manganese, nickel, lead and iron. PVs for lead must be decreased to 5 µg/L by 12 January 2036 and for chromium to 25 µg/L [19]. Taking into account these PVs, some exceedances occur also in terms of the observed Cr concentrations. Selected results close to PVs were detected for copper, chromium and aluminium. When related expanded uncertainty is also included in the decision process, more results should be classified as above PVs. However, for the purpose of the presented evaluation, the simple deterministic method was used. It can be observed that the oldest connections during the long-time of work have been undergoing material corrosion; therefore, a significant amount of lead, zinc and iron can be released into the tap water. The new ones which are produced of copper can enrich tap water in Cu ions during the first years of work. While the copper material ages, it is covered with a patina that prevents further releasing Cu ions into water. From the collected data, heavy metals and metalloids such as As, Cd, Cr, Cu, Fe, Mn, Ni and Pb showed the relationship between their concentrations in tap water and facilities used to provide water to households (Figures 2 and S1). As many authors suggest (e.g., [83–85]) the usage of Al-based coagulants may result in an increase of Al concentration in tap water. Some studies proved that up to 11% of the aluminium input could remain in the treated water [83]. This phenomenon is typical in situations where surface water is used as a source of raw water. As the results indicated, the age of connection, pipe-work and tap mostly influence As, Cr, Cd, Cu, Ni and Pb concentrations regardless of the city. The material of installation affects the final amount of Al, As, Cd and Cr. Figure 3 graphically presents the correlations for trace elements that are preferentially released to tap water. It can be seen that Fe occurs more often with Mn (natural co-existence) and Cd, Pb and Zn usually appear together. It is well understood since galvanised steel is produced from Zn-Pb ores containing Cd as an accessory metal. The corrosion of Zn alloys leads to the release of those metals in various proportions. It is typical for pipes older than 25–30 years.

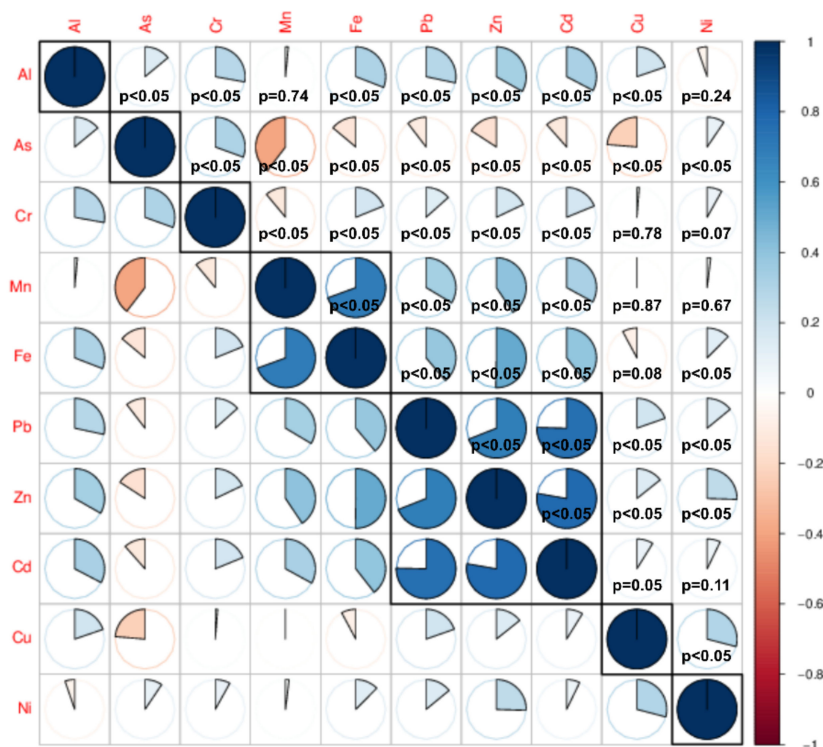


Figure 3. Correlations between heavy metals in tap water. Correlation is statistically significant when the *p*-value is equal to or lower than 0.05.

However, the concentrations of Fe, Mn and Zn, Pb, Cd can have a major source in the material and the length of the distribution pipes [86]. The results of the presented research show that the concentrations of Fe and Mn increase with the growth of the age of the tap and pipe-works (Figure 2). The differences also occur depending on the material of connection and pipe-work and are particularly visible in terms of As, Al, Cd, Cr, Fe, Mn, Pb and Zn concentrations (Figures 2 and S1, Table 7) and are statistically significant (Figure 3). Gao et al. [87] reported that among the inorganic compounds found in the pipe scales and loose deposits, Fe had the highest concentration which was followed by Al, Mn, Zn, Cu, Ni, Cr, Pb, As and Cd. Iron can also be released in the ferrous form from corroded, old galvanised pipes [88].

Table 7. Results of MANOVA for selected trace elements concentrations in tap water.

Factor	Variables	MANOVA <i>p</i> -Value
City	Zn, Mn	<i>p</i> 0.05
Age of connection	As, Cr, Cu, Ni	<i>p</i> 0.05
Age of pipe-work	Cr, Cu, Ni	<i>p</i> 0.05
Age of tap	Cr, Zn, Fe	<i>p</i> 0.05
Material of connection	As, Zn, Cu, Ni, Pb, Fe	<i>p</i> 0.05
Material of pipe-work	Zn, Ni, Fe	<i>p</i> 0.05
Material of appliance	Zn, Cu, Ni, Fe	<i>p</i> 0.05
Water rating by end-user	Cr, Zn, Ni, Fe	<i>p</i> 0.05

The lowest concentrations of Zn, Pb and Cd were found in the case of taps, pipe-works and connections in the age below 10 years, whereas the Cu concentration in this group reached the highest values. Both Zn and Pb can be affected by brass corrosion, although Zn can be preferentially released (Figure 3). This is reflected in the correlation found during the investigation carried out (Figure 3). This type of corrosion, called “dezincification” [14,89,90] is generally less desirable than uniform corrosion because it persists over time which can lead to device failure [90]. Dezincification is also considered a major promoter of lead release [90,91]. Replacing or connecting of aged lead pipes with stainless steel ones can affect the Pb release to drinking water due to galvanic corrosion. The concentration of Pb decreases with pH and the higher chloride to sulphate mass ratio [92–94]. The network water supply system made of brass devices or lead solders may constitute a major source of Pb in tap water, not only in old but also in new buildings [24,25,89,95].

The source of increased concentrations of zinc and copper can be correlated, among others, with a time of water stagnation in pipes [96,97]; however, in the presented research, this correlation was not indicated (Figure 3). Besides the pipe material and water stagnation time, the flow rate established before sampling affects the concentration of heavy metals in tap water [94]. The highest concentration of Cu in the new installation may result from the material of pipe-work and connection. Popular copper pipes in the first years of use can cause the entrance of Cu to the water (Figure 2). Furthermore, in Poland, the pipes used for the construction of the connection and internal pipe-work were covered with zinc from the Olkusz Pb-Zn ores in which accompanying metals such as cadmium occur. The zinc refining process in the past did not allow for full separation; therefore, all these metals are present in the galvanised cladding. With the progress of zinc corrosion and increasing porosity of the Zn covering, some amounts of Pb and Cd may be released to the water.

The most significant differences in trace elements concentrations were observed between the five cities as shown in Figure 2 and Supplementary Materials Figure S1. Water rating by end-user is the most difficult factor to assess. It can be considered as Supplementary information. The results are difficult to interpret because of the subjective nature of this information.

The grouping seems much less pronounced for the age of tap, connection or pipe-work, Material of connection or pipe-work factors. Material of appliance and water rating by the end-user factors demonstrate the remarkable overlap between categories.

Table 7 briefly summarises the variables considered for running the MANOVA test for each factor. Note that MANOVA was not performed for kind of household and stagnation time dependent variables due to the lack of normally distributed independent variables. The *p*-values pointed out if the differences of the trace elements concentrations between factor categories were statistically significant at the assumed level ($\alpha = 0.05$). Assuming $\alpha = 0.05$ is associated with a 5% risk of concluding that a difference exists when there is actually no difference. Thus, the test is statistically significant if $p < 0.05$. This result was obtained for all factors and the conclusions are that the differences of metals and metalloids concentrations differ statistically significantly between the studied factors categories. In other words, there is enough evidence to reject the null hypothesis and conclude that the metals content differs significantly between the categories. Thus, all factors should be controlled during water sampling since they all introduce significant variability in the metals content.

The most probable source of Cr and Ni are the alloys of taps, while Cu and Zn could be released from pipes and taps' corpuses made of bronze or brass [98]. High concentrations of Ni in tap water were also determined, i.e., by Andersen et al. [99], especially in samples collected directly from the taps without prior installation flush. They connected the occurrence of Ni in tap water with the materials of valves and chromium–nickel plated taps. The highest concentrations of Fe were found in installations made of stainless-steel and in samples collected after more than 1 h of water stagnation, which is most likely related to the progressive process of corrosion [100,101]. Meanwhile, Cu contents were higher in water samples collected from new installations. The release of Cu from the material of connection is controlled by many factors, such as the water temperature or pH [100,102]. Zn can release from the galvanised pipes and other brass parts of water installation systems [103]. Clark et al. [104] found a strong correlation between Pb and Zn in samples collected from water systems containing galvanised steel pipes. Differences in Zn concentration in the City category can also be influenced by the groundwater intake located in the city of Jaworzno, which lies within the mining area of Zn–Pb ores. The zinc concentration in raw groundwater in Jaworzno was the highest compared to four other cities, and is on average 0.3 mg/L, while in other cities, it is absent (not measured/below the limit of detection of the analytical method) or it was quantified at the level of a dozen $\mu\text{g/L}$ [65].

Results of hazard analysis are presented in Figure 4.

For adults, HI was assessed as negligible in 59.1% of the sampling points and low in 40.9%. Medium and high risk was not observed in the area analysed. Taking into consideration the non-carcinogenic risk for children, high risk was observed in one sample (0.2%), medium in 45 samples (9.0%), negligible in two samples (0.4%) and low for the rest of the analysed samples (Figure 4). The high and medium risk (HI above 4 and between 1 and 4, respectively) evaluated for children arose mostly from medium HQ values for copper, zinc, lead and nickel. Elevated concentrations of these elements in water can be related to the age and material of the internal water installation (Table 7). The order of non-carcinogenic risk caused by the elements considered was $\text{As} \cong \text{Zn} > \text{Cr} \cong \text{Pb} > \text{Cu} > \text{Cd} > \text{Fe} > \text{Ni} > \text{Mn} > \text{Al}$. In addition, Tian et al. [43] indicated the impact of water stagnation time in galvanised steel pipes on human health risk. Cancer risk (R) was evaluated only for As, Cd, Cr, Ni and Pb because of the lack of carcinogenic character and, therefore, slope factor value for the rest of the elements considered. An unacceptable cancer risk for children was observed in one sample (0.2%) for chromium, 18 samples (3.6%) for nickel and 11 samples (2.2%) for cadmium. Meanwhile, in the case of calculations made for adults, the exceedance of the acceptable limit of $1\text{E-}04$ was indicated in two samples (0.4%) for chromium, 64 samples (12.3%) for nickel and 57 samples (11.4%) for cadmium (Figure 4). As MANOVA results indicated, both Cr and Ni concentrations depend on

the age of pipe-work and age of connection. Additionally, the material of connection, pipe-work and appliance influence nickel concentration in tap water. The values of HQ, HI and CR determined individually for each city using mean concentrations of each element indicated that the carcinogenic risk for adults arises from nickel in the water of Kamienna Gora (Table 8). Low non-carcinogenic risk expressed as HI occurs in each city in a case of children oral exposure and in Jaworzno, Kamienna Gora and Raciborz in a case for adults.

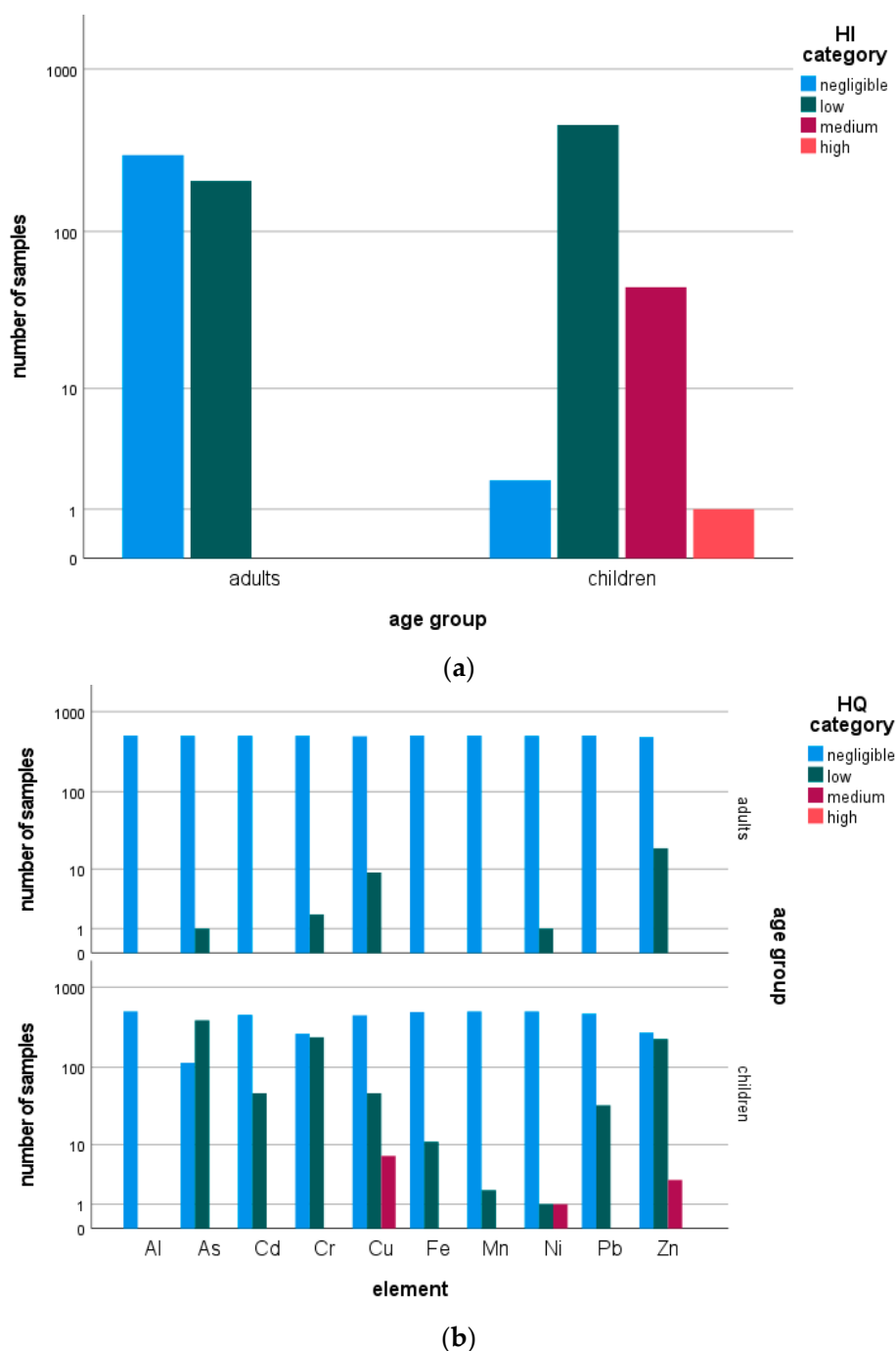


Figure 4. Cont.

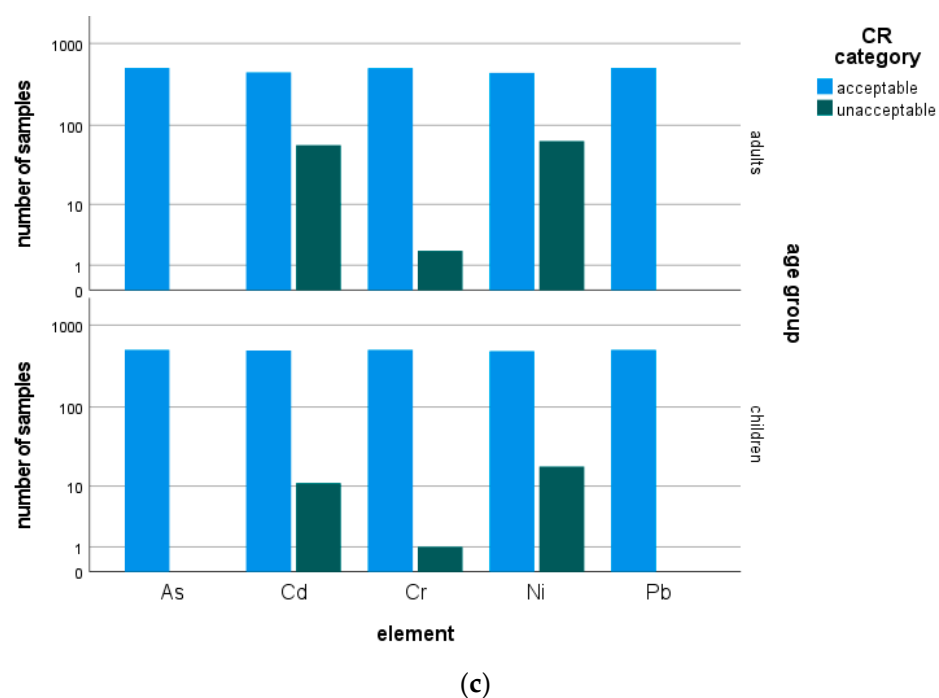


Figure 4. Summarised results for (a) HQ, (b) HI, and (c) CR.

Table 8. HQ, HI and CR values in each city.

City	Element	HQ		HI		CR	
		Children	Adults	Children	Adults	Children	Adults
Jaworzno	As	1.6×10^{-1}	3.0×10^{-2}	7.8×10^{-1}	1.4×10^{-1}	6.2×10^{-6}	1.3×10^{-5}
	Cr	1.6×10^{-1}	2.9×10^{-2}			2.0×10^{-5}	4.3×10^{-5}
	Zn	2.4×10	4.4×10^{-2}			n.a.	n.a.
	Al	1.7×10^{-3}	3.2×10^{-4}			n.a.	n.a.
	Cd	8.2×10^{-2}	1.5×10^{-2}			4.4×10^{-5}	9.4×10^{-5}
	Mn	5.0×10^{-3}	9.2×10^{-4}			n.a.	n.a.
	Cu	3.7×10^{-2}	6.8×10^{-3}			n.a.	n.a.
	Ni	9.1×10^{-2}	1.7×10^{-3}			2.6×10^{-5}	5.7×10^{-5}
	Pb	6.9×10^{-2}	1.3×10^{-2}			7.0×10^{-7}	1.5×10^{-6}
	Fe	2.2×10^{-2}	4.1×10^{-3}			n.a.	n.a.
Kamienna Gora	As	6.2×10^{-2}	1.1×10^{-2}	6.2×10^{-1}	1.1×10^{-1}	2.4×10^{-6}	5.2×10^{-6}
	Cr	9.4×10^{-2}	1.7×10^{-2}			1.2×10^{-5}	2.6×10^{-5}
	Zn	1.8×10^{-1}	3.4×10^{-2}			n.a.	n.a.
	Al	2.0×10^{-4}	3.6×10^{-5}			n.a.	n.a.
	Cd	2.5×10^{-2}	4.5×10^{-3}			1.3×10^{-5}	2.9×10^{-5}
	Mn	1.2×10^{-2}	2.2×10^{-3}			n.a.	n.a.
	Cu	1.8×10^{-1}	3.2×10^{-2}			n.a.	n.a.
	Ni	2.3×10^{-2}	4.2×10^{-3}			6.6×10^{-5}	1.4×10^{-4}
	Pb	2.7×10^{-2}	4.9×10^{-3}			2.7×10^{-7}	5.8×10^{-7}
	Fe	2.2×10^{-2}	4.0×10^{-3}			n.a.	n.a.

Table 8. Cont.

City	Element	HQ		HI		CR	
		Children	Adults	Children	Adults	Children	Adults
Krakow	As	1.7×10^{-1}	3.1×10^{-2}	5.1×10^{-1}	9.4×10^{-2}	6.6×10^{-6}	1.4×10^{-5}
	Cr	1.1×10^{-1}	2.0×10^{-2}			1.4×10^{-5}	3.0×10^{-5}
	Zn	1.1×10^{-1}	2.1×10^{-2}			n.a.	n.a.
	Al	2.0×10^{-3}	3.6×10^{-4}			n.a.	n.a.
	Cd	1.9×10^{-2}	3.6×10^{-3}			1.1×10^{-5}	2.3×10^{-5}
	Mn	2.0×10^{-3}	3.6×10^{-4}			n.a.	n.a.
	Cu	6.7×10^{-2}	1.2×10^{-2}			n.a.	n.a.
	Ni	7.5×10^{-3}	1.4×10^{-3}			2.2×10^{-5}	1.4×10^{-3}
	Pb	8.8×10^{-3}	1.6×10^{-3}			9.0×10^{-8}	1.9×10^{-7}
	Fe	1.3×10^{-2}	2.5×10^{-3}			n.a.	n.a.
Myszkow	As	1.7×10^{-1}	3.2×10^{-2}	5.5×10^{-1}	1.0×10^{-1}	6.7×10^{-6}	1.4×10^{-5}
	Cr	9.6×10^{-2}	1.8×10^{-2}			1.2×10^{-5}	2.7×10^{-5}
	Zn	1.4×10^{-1}	2.6×10^{-2}			n.a.	n.a.
	Al	2.4×10^{-4}	4.4×10^{-5}			n.a.	n.a.
	Cd	4.1×10^{-2}	7.6×10^{-3}			2.2×10^{-5}	4.8×10^{-5}
	Mn	1.9×10^{-2}	3.4×10^{-3}			n.a.	n.a.
	Cu	1.2×10^{-2}	2.2×10^{-3}			n.a.	n.a.
	Ni	7.4×10^{-3}	1.4×10^{-3}			2.2×10^{-5}	4.6×10^{-5}
	Pb	2.1×10^{-2}	3.8×10^{-3}			2.1×10^{-7}	4.5×10^{-7}
	Fe	3.3×10^{-2}	6.0×10^{-3}			n.a.	n.a.
Raciborz	As	2.3×10^{-1}	4.3×10^{-2}	4.3×10^{-1}	7.9×10^{-2}	9.0×10^{-6}	1.9×10^{-5}
	Cr	8.9×10^{-2}	1.6×10^{-2}			1.1×10^{-5}	2.5×10^{-5}
	Zn	4.6×10^{-2}	8.4×10^{-3}			n.a.	n.a.
	Al	8.0×10^{-5}	1.5×10^{-5}			n.a.	n.a.
	Cd	9.3×10^{-3}	1.7×10^{-3}			5.0×10^{-6}	1.1×10^{-5}
	Mn	8.7×10^{-4}	1.6×10^{-4}			n.a.	n.a.
	Cu	2.7×10^{-2}	4.9×10^{-3}			n.a.	n.a.
	Ni	1.6×10^{-2}	2.9×10^{-3}			4.6×10^{-5}	9.8×10^{-5}
	Pb	5.4×10^{-3}	1.0×10^{-3}			5.5×10^{-8}	1.2×10^{-7}
	Fe	5.9×10^{-3}	1.1×10^{-3}			n.a.	n.a.

n.a., not assessed.

6. Conclusions

The statistical approach applied in this study can be used for the investigation of the tap water chemical composition, especially in relation to the release of heavy metals. The MANOVA test clearly pointed out that the concentration levels of some heavy metals present in tap water are affected by a series of factors, which therefore must be considered in the water sampling protocol. Disregarding them may lead to erroneous and unreliable water quality analyses and may hinder drawing valid conclusions, at least for the metals considered for MANOVA. In future research, information on the composition of water and the factors that may influence it should be collected with greater care, especially to maintain balanced data for each category (equally sized categories) and thus receive more reliable MANOVA results. The information gathered during the field interview was collected in the extensive database that was used for further statistical calculations on the extraction of factors that can affect favourable enrichment of tap water with significant amounts of trace elements. The results showed a positive correlation between concentrations of heavy

metals such as Fe, Mn, Zn, Pb, Cd and the material of fittings/appliance used as well as with the material of pipe-work. Observed dependencies between the age of connection, age of pipe-work and installation material and concentrations of trace elements found in tap water suggest that additional information about construction properties of the distribution system should be gathered. The knowledge about the discussed parameters can help in the interpretation of results, and as a consequence, it enables the development of optimal methods for decreasing higher concentrations of trace elements in tap water. Although these concentrations are over the maximum permissible levels regarding EU and WHO standards, health-related problems can occur. It is visible in the high value of HI and CR. The CR decreases with the following order of the analysed elements $Ni > Cd > Cr > As = Pb$. If during sampling the information about necessary factors are collected, the source of higher concentrations of metals and related substances can be more easily found.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11111291/s1>, Figure S1: Trace elements concentrations in the analysed water by different categories of factors. (a) City: A—Krakow, B—Jaworzno, C—Kamienna Gora, D—Raciborz, E—Myszkow. (b) Type of building: A—public building, B—house, C—flat. (c) Age of connection: A—<10 years, B—10–30 years, C—>30 years. (d) Age of tap: A—<10 years, B—10–30 years, C—>30 years. (e) Age of pipe-work: A—<10 years, B—10–30 years, C—>30 years. (f) Stagnation time: A—<1 h, B—>1 h. (g) Material of connection: A—PCV, B—steel, C—galvanised steel, D—stainless steel, E—other. (h) Material of pipe-work: A—PCV, B—steel, C—galvanised steel, D—stainless steel, E—copper, F—other. (i) Material of appliance: A—steel, B—other. (j) Water rating by end-user: A—good, B—unacceptable.

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