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The Pilot Study of Water Chemistry in Municipal Fountains in Olsztyn (NE Poland)

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Abstract. The aim of the study was preliminary identification of water chemistry in selected fountains located in municipal parks in Olsztyn (NE Poland). These studies will be the basis for further analyzes, including microbiological and mycological ones - the authors assume that specific chemical composition of water is the environment of existence and growing of microorganisms and at the same time it can be modified by them. For the pilot studies 5 objects were selected and conventionally divided them into artificial, semi-natural and natural fountains. Artificial fountains are supplied with tap water. The water is disinfected with chlorine and replaced if necessary. The semi-natural fountains are partly supplied with tap water and partly with surface runoff. Natural ones are supplied only by surface drainage and collectors draining the area of the adjacent park. Water for testing was collected throughout the operating season, every 2 weeks, from 22.05 to 3.10.2017. Physicochemical analyzes were performed in accordance with the methodology adopted in hydrochemical research. There were no significant differences in the water temperature between the different types of fountains, while the relationship between water temperature and air temperature was shown by the following equations: $y = 0.9275x + 2.034$, $R^2 = 0.6611$ (for artificial) and $y = 0.4538 x + 8.6301$, $R^2 = 0.6642$ (for others) where x = water temperature in the fountain. It has been shown that chemical composition of water in artificial objects is definitely different from that which fills natural and semi-natural fountains. Water in artificial objects, compared to the other ones, was characterized by low concentration of iron (0-0.14 mg dm^{-3}) and manganese (0.02-0.07 mg dm^{-3}), constant, slight hyperoxia (maximum 116.7% O_2). The content of organic matter determined as COD-Mn was lower than in other objects, and we have improved that changes in the lifetime were insignificant. A highly significant relationship was found between the electrolytic conductivity and the concentration of NO_3^- and Cl^- (Spearman: 0.92 and 0.82 respectively) and between the concentration of free chlorine (Cl_2) and chlorides (Cl^-). The maximum concentration found during the studies was 21 mg Cl_2 dm^{-3}, and the smell was organoleptically felt as intensive even within about of five meters, generally throughout the whole research period. In all objects, the concentration of chlorides increased systematically during the lifetime of fountains. Constant increase in conductivity was observed, which indicates increased pollution. In addition, natural and semi-natural objects are exposed to increased pollution not only from people. Animal faeces and remains of feed scattered by people feeding birds, leaves and pollen are a big problem.

1. Introduction

There are 8 municipal fountains in Olsztyn. As an interesting architectural element, they diversify the city landscape, positively influencing the climate and favoring the rest and relaxation. The oldest, pre-war or some of the 70's of the last century, historical objects do not function as fountains anymore, but they are commemorative sculptural groups situated in parks. Some of the old objects are renovated and equipped with modern technical systems, and new fountains are being built, too

From the engineering point of view, the most important is the way of supplying them in the water and the construction of the basin. Therefore there are objects conventionally called artificial (with artificially created, concrete basin, supplied with tap water) and as their opposite in the city there are also fountains conventionally called natural or ponds. Their basins are a depression of the area filled with rainwater, supplied by drainage collectors from neighbouring park. There are also "semi-natural" objects with artificially created and concrete bowl, partially supplied with tap water, during the summer season also with surface runoff and drainage collectors of the adjacent terrain. All of them work in a closed system.

Fountains are often located in parks and play the role of recreation places for people and they are also living and watering places for animals [1]. Municipal fountains have filtering devices, artificial fountains and disinfecting devices, but biological tests, including microbiological and mycological ones, show significant water pollution [2, 3, 4]. Natural and semi-natural objects create specific ecosystems in which deterioration of physicochemical parameters resulting from progressive degradation is observed. It is largely associated with the growing anthropopressure [5, 6]. For this reason the research was undertaken. We want to show differences in water chemistry in various types of city fountains. These are preliminary studies that will be used as a background for biological research in the next stage.

2. Material and methods

The research was carried out on 5 objects: 3 artificial fountains, one natural and one semi-natural. Their basic features are listed in table 1. Research was carried out throughout the operating season, from May 22 to October 3, 2017. Water samples were collected every 2 weeks in the morning. Each time the air temperature was measured and photographic documentation was made. It was taken into account of the current situation - pollution of waterfowl with bread, spreading food for pigeons on the bank of reservoir, anglers fishing (in the case of natural and semi-natural objects) and the presence of birds using these objects as a living environment. In the vicinity of artificial objects, the intensity of chlorine odour in the air was determined organoleptically using a 5-degree scale. The temperature and oxygen content dissolved in water (mg dm^{-3}, % O_2) were measured using a ProOdo optical probe from YSI in the field. Water samples for laboratory analyzes were collected in PET containers. Additionally, from artificial objects, water was taken for glass, oxygen-type bottles, to determine the total chlorine (Cl_2) in the water samples the reaction (pH) and electrolytic conductivity were measured using of the WTWMultiLine F / SET-3 probe. The content of ammonium nitrogen ($N\text{-}NH_4$) and total chlorine (Cl_2), colour (HZ) and turbidity (NTU) was determined on a MERCK SQ118 spectrophotometer. The chloride concentration was made by the argentometric titration method, the alkalinity and hardness of water as well as the concentration of calcium and magnesium was determined by titration method. The tests were carried out in accordance with the methodology adopted in surface water studies [7].

The surface of basins (fountains) were measured using the tools available at geoportal.pl

The results were statistically analyzed in the Statistica 12. It was shown that the data distribution was different from normal, therefore the T test, Spearman's rank correlation, R2 and median were used. Significance was assumed with a probability of <0.05.

Artificial objects (A) are equipped with modern sand filters and automated dispensing disinfectant (sodium hypochlorite). The characteristics of the fountains are shown in table 1.

Table 1. Characteristics of research stations

Station	A kind of reservoir	Water surface [m^2]	Additional comments
A1/Central Park	artificial	635	The newest object in the town, built in 2014. 30 nozzles foaming water. Concrete bottom, recreation of people, watering animals, sometimes used for hygienic purposes
A2/ The Old Town	artificial	6	Renovation of the fountain in 2013 10 nozzles foaming water. A lot of pigeons
A3/ The Fish with a Child	artificial	430	After renovation in 2015, there was modern system of filters and water disinfection installed. Concrete bottom, 10 nozzles foaming water.
B/Kusociński Park	Semi-natural pond	1660	Concrete bottom, habitat elements - footbridges for birds (pigeons, ducks), a lot of fallen leaves. No water disinfection
C/Jakubowo Park	Natural pond with a fountain	9150	Fascines bottom, ducks, swans. Used by anglers. No water disinfection

3. Results

All objects were characterized by a similar course of temperature changes during the research period. The highest temperatures were noticed on 19.06 and 7.08, in September a diminish in the water temperature was noted. There were no statistically significant differences in the temperature of water between the different types of fountains. However, it was noted that the highest temperature was usually noted in the object B, the lowest - in A3.

The relationship between water temperature and air temperature described by the equations was shown:

$y = 0.9275x + 2.034$, $R^2=0.6611$ (for artificial) and

$y = 0.4538 x + 8.6301$, $R^2=0.6642$ (for the rest), x = temperature of water in the fountain.

The reaction of the water in all objects was within the limits of 7.9-8.5 pH. It oscillated to a small extent and there were no statistically significant differences between the different types of objects. Other hydrochemical parameters in individual stations are varied (Table 2).

Table 2. The range of changes in selected chemical parameters

Station	MC	Ca	Mn	Fe	TOC	DOC
	mval dm^{-3}	mg dm^{-3}	mg dm^{-3}	mg dm^{-3}	mg dm^{-3}	mg dm^{-3}
A1	2.4-5.3	23.6-75.7	0.01-0.05	0.00-0.03	1.82-10.01	1.82-8.41
A2	5.7-5.8	46.4-98.5	0.06-0.17	0.02-0.17	7.52-12.59	6.15-10.83
A3	2.1-5.8	21.1-83.2	0.01-0.06	0.00-0.03	4.73-6.30	3.82-6.17
B	1.4-3.3	16.7-43.0	0.16-0.47	0.25-0.67	8.53-13.97	5.94-11.24
C	2.1-3.9	23.7-56.4	0.03-0.24	0.01-0.18	9.99-17.77	9.43-13.11

Artificial fountains A: The colour of water in artificial tanks was low (1 - 17 HZ, median = 3), the turbidity was from 1 to 10 NTU. These values increased very strongly after rainfall, reaching 65 Hz

and 31 NTU. Spearman's rank correlation showed a relationship between the colour of water and the concentration of chlorine.
In the other reservoirs: the colour and turbidity were higher in the semi-natural B: 26 - 53 HZ (median = 28.6) and 9-29 NTU (median = 20.5), in reservoir C: 23-38 HZ (median = 26.8) and 3-30 NTU (median = 22). Similarly, after rainfall, these values increased to 217 (B) and 153 (C) HZ and 60 (B) and 48 (C) NTU, respectively.

In the whole research period, water in artificial facilities was generally characterized by low oxygenation reaching 116.7% O_2 (A1). Fluctuations in water oxygenation in other objects were significant, in natural C: 52.5-137% O2, in semi-natural B: 29.9-124.0% O2. In regard to oxygen content, objects B and C behaved like natural, heavily eutrophied artificially aerated reservoir.
The main difference between artificial and other objects originated from the disinfection of water using chlorine in artificial fountains A. Free chlorine concentrations in individual objects were different (figure1), the highest recorded in the smallest A2 fountain. In the air, organoleptically, the smell was specific, distinct or strong, even at a distance of about 5 m from the fountain. In other artificial objects (A1 and A3), even if chlorine was detected in water, the smell in the air was very weak or weak.

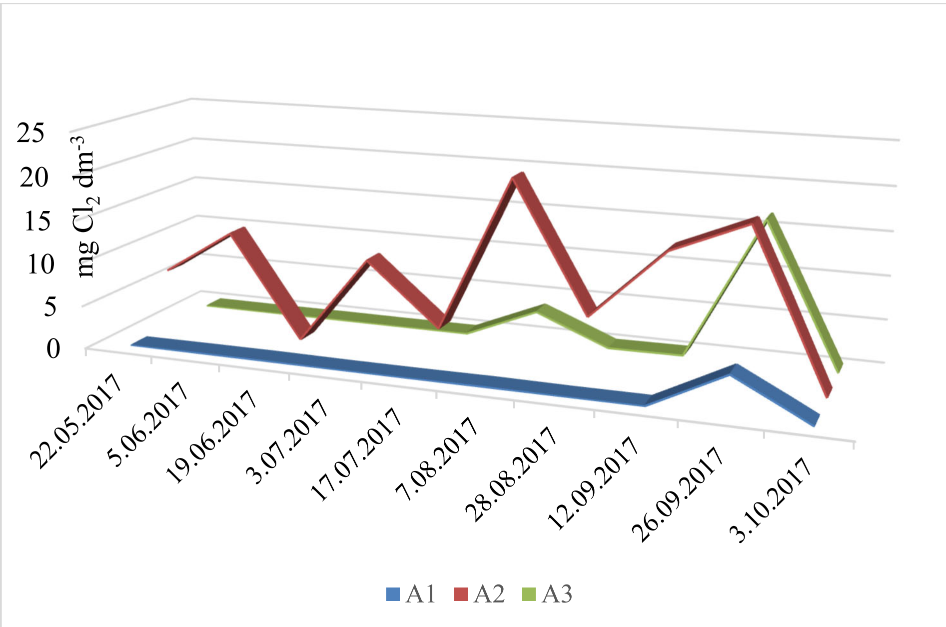

Figure 1. Concentrations of free chlorine in artificial fountains

The T test showed a significant relationship between chloride and total chlorine concentrations (T = -10.2998, $p < 0.05$, n = 27) in fountains A. $R^2 = 0.289$. The linear dependence is shown in figure 2.

During the operational season, from June to the end of August, a gradual increase in chloride concentrations in artificial objects (reaching up to 800 mg dm^{-3}) was observed, followed by a reduction or persistence of these higher values. In other objects (B and C) chloride concentrations were always significantly lower and no change trend was observed (figure 3).

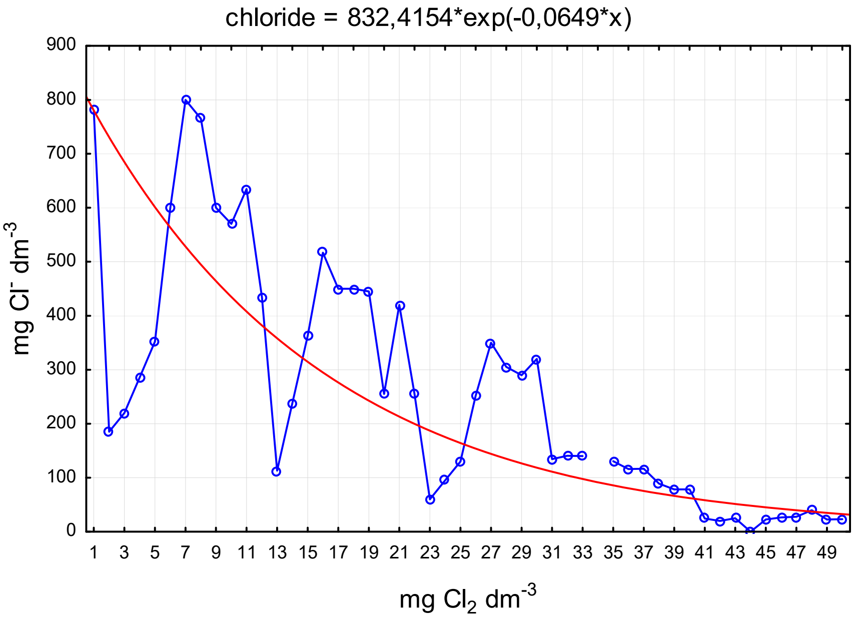

Figure 2. A linear relationship between the concentration of free chlorine and chloride in the water of artificial fountains.

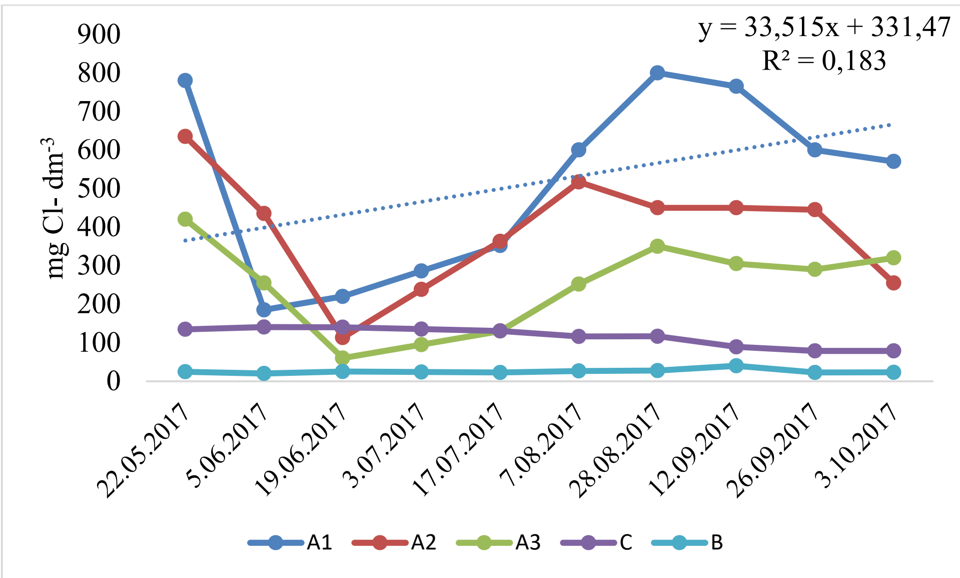

Figure 3. Concentration of chloride in the water of all fountains.

The individual types of objects differed among themselves with the values of electrolytic conductivity (figure 4). The highest values were found in artificial fountains A (figure 4), especially in A1 (median):1366µS cm^{-1}, while in natural reservoir B: 530µS cm^{-1}, and in natural C: 327µS cm^{-1}.

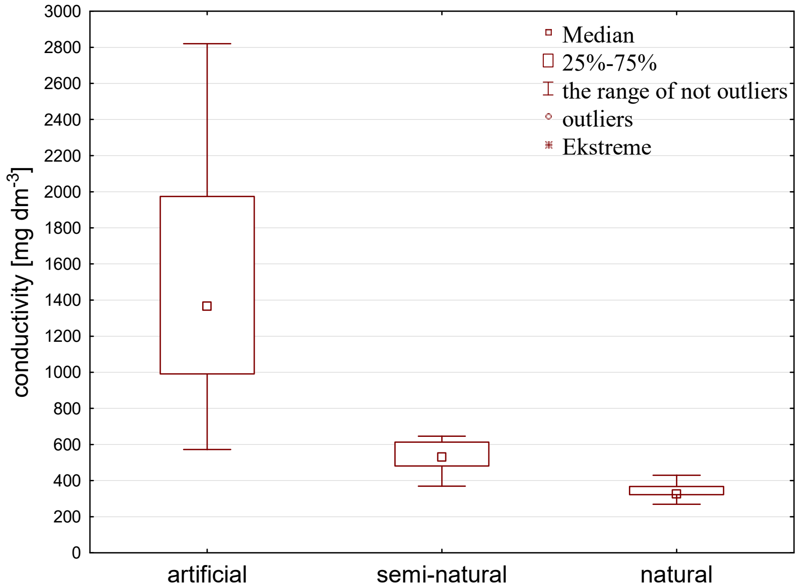

Figure 4. Median of conductivity values ($\mu S\ cm^{-1}$) for different types of fountains

The Spearman's rank correlation ($p < 0.05$, $n = 27$) for artificial object data showed a highly significant relationship between conductivity and chloride concentration (0.9221) and NO^{3-} (0.8196) and between nitrates and chlorides (0.7162). The dependence of conductivity on chlorides (0.9523), iron (0.8414) and manganese (0.6775) for other objects was significant, but in this case the correlation between conductivity and nitrates was not confirmed.

Individual types of objects were characterized by a varied content of organic matter, defined as COD-Mn. This component contained in the water of artificial A fountains was in the concentration of 9.6 ± 2.39 mg O_2 dm^{-3}, in the other stations concentration of organic matter was higher. The ranges of COD-Mn changes in objects B and C were similar (figure 5). Alike, the concentration of organic matter determined as TOC (median A: 6.77 mg C dm^{-3}, B: 10.91 mg C dm^{-3}, C: 10.91 mg C dm^{-3}, respectively). Analysis of the components of this parameter showed that this matter was mainly DOC, which in artificial objects generally exceeded 90% TOC and in 80% semi-natural.

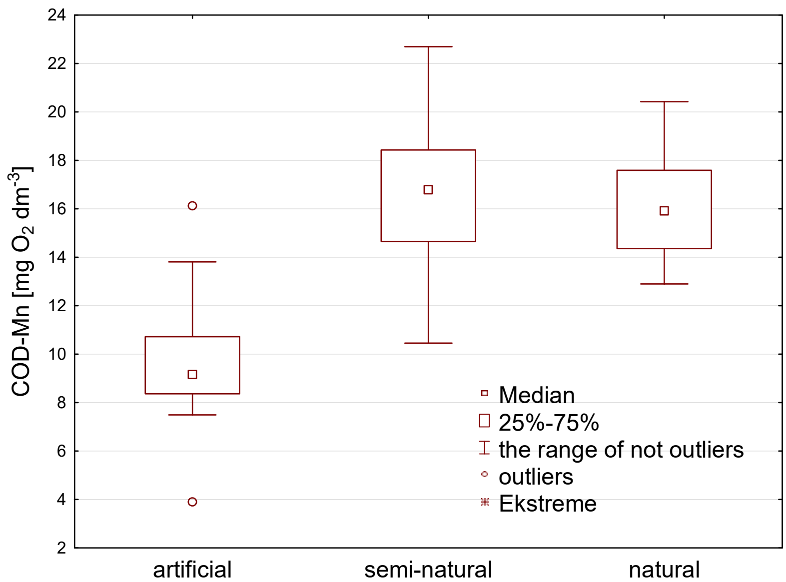

Figure 5. Median of COD-Mn for different types of fountains

The different types of objects differed in terms of biogenic elements content. Artificial ones were characterized by a low concentration of ammonium nitrogen (median = 0.026) and about 10-fold higher concentration of nitrate nitrogen (V). In the semi-natural object B and the natural C, the concentration of ammonia was higher than in natural A, the median value was 0.18 and 0.36 mg dm^{-3}, respectively. The concentration of nitrates was lower (figure 6), comparing to the ammonia and to stations A.

The highest concentrations of phosphorus were found in the natural fountain C in Jakubowo Park. Since mid-August, the concentrations of this ingredient have increased many times and remained at this level until the end of the research period, exceeding 0.49 mg P dm^{-3}. Significant among of the artificial objects were found in the A2 fountain in the Old Town. The concentrations of this component during the research period decreased from values approaching 0.3 mg P dm^{-3} to very low, below 0.1 mg P dm^{-3}. In other objects, the concentration of this component was even and low (figure 7).

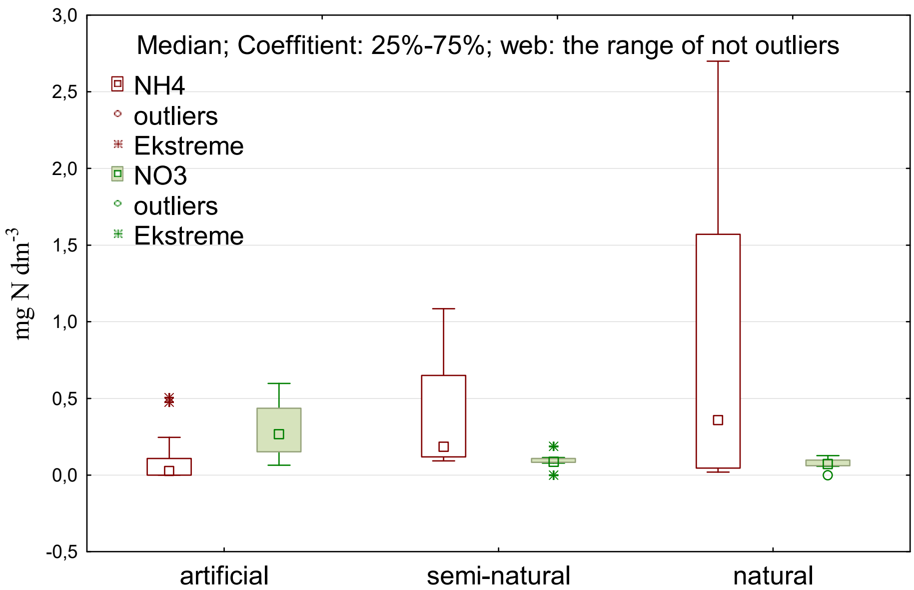

Figure 6. Median of NH_4^+ and NO_3^- for different types of fountains

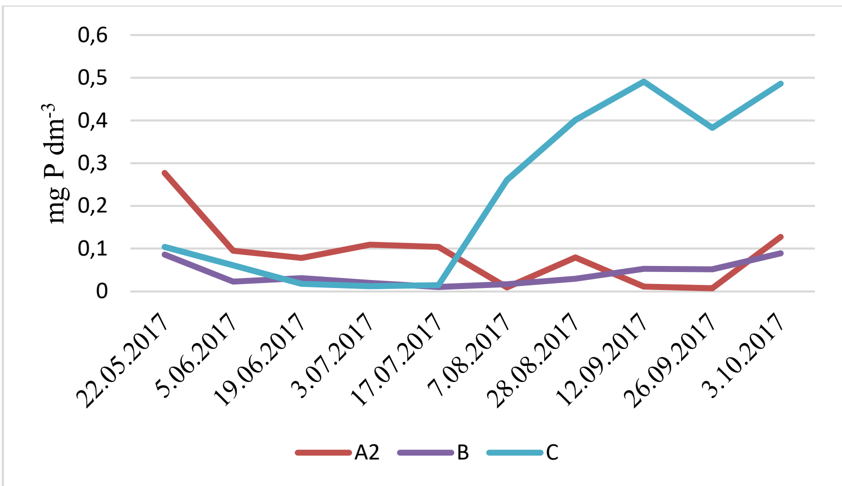

Figure 7. Median of PO_4^{3+} for different types of fountains

4. Discussion

This work contains the pilot results of water chemistry in urban fountains. Scientific literature on the quality of water in fountains theme focuses on presenting the results of biological research [1,2,3,4,5], omitting hydrochemical research. Meanwhile, hydrochemical parameters are the basis for the functioning of microorganisms using components contained in water for life and modifying the chemistry of water. Usually, natural and semi-natural fountains are also omitted in such research because contact with their water is smaller. However, the risk, although smaller, remains. Our preliminary research on all types of fountains fills this gap.

The main difference between artificial and other fountains is due to the construction of their basin and the method of water supplying. This entails differences in the perception of their recreational function in urban space. Artificial fountains are an element of urban architecture, it performs decorative functions and therefore, in accordance with the law, their water is not under control [8]. Water in artificial fountains is usually characterized by low colour (table 2) and therefore it is mistakenly considered clean. As evidenced by microbiological tests [5], fountains may pose a threat to the health of people who use them as a place for bathing, wading in water, or other direct contact. Considering the fact that they are located in open area, in water in fountains there may be various types of microbiological contamination from animals (birds, dogs) or humans. People can also contact with chemical impurities of unknown origination, dangerous to our health, especially for young children. Natural and semi-natural fountains similar strongly eutrophicated ponds, which is why (as confirmed by our research) in the urban space they constitute a place of living of birds, especially ducks and pigeons, they are also used for fishing.

Artificial fountains are equipped with modern sand filter systems and dosage of disinfectants, in this case - sodium hypochlorite. It is one of the most popular disinfectants used also for disinfection of water in swimming pools [9, 10]. The solution is dosed with a chlorinator, in the case of fountains located in special manholes under the pavement near the object. During the disinfection of water with chlorine, a number of chemical processes and reactions take place, as a result of which the chlorine oxidizes and chlorinates organic and inorganic compounds [11,12]. In water, a strongly oxidizing environment is formed and, as a consequence, the concentration of organic matter is low. It was confirmed by the results of COD-Mn and TOC.

The course and effectiveness of disinfection is determined not only by the number and type of microorganisms, but also by the physico-chemical composition of disinfected water. The main components of water affecting the course of disinfection include: pH, temperature, amount and type of reduced organic and inorganic substances as well as the number of suspensions. The pH value influences the type of active using disinfectant, and thus its bactericidal properties. The temperature of the water affects its penetration through the cell wall of the microorganism and then on the reaction rate, eg. with enzymes [12, 13]. Chlorine introduced into water reacts quickly with inorganic reductive compounds (in this case they may be Fe^{2+}, Mn^{2+}, which occurs in water despite the use of iron and manganese removal processes). In water containing nitrogen, ammonium chlorine, chlorine(I), and mainly chlorine (I) react with NH^{4+} ions to form chloramines, which are characterized by a lower bactericidal strength than the chlorine substrates of this reaction [7, 9, 11]. This explains why the artificial objects were characterized by clearly lower NH^{4+} concentrations compared to natural and semi-natural fountains.

Reactions which occur during chlorination of water [7, 13] in the subsequent stages resulted in the formation of very high concentrations of chlorides in the water of artificial objects (A) and, therefore, high values of electrolytic conductivity. In our research, it was shown that during the exploitation period, these parameters increased and exceeded the limit values for drinking water [14]. In the fountain A1, it correlated with a greater number of fungi and bacteria [3]. In the case of microbiological and mycological studies, there is evidence that consumption of such water or other direct contact may be dangerous to health [1, 4, 5]. Also, higher concentrations of NO_3^- were noted as a result of oxygenation of water in A-reservoirs, indicating the possibility of contamination. In objects B and C, the presence of these ions is the result of good oxygenation of water and nitrification [7].

Fountains are also a source of water aerosol, which may contain chlorine (its smell was palpable organoleptically in the air around the fountain) and bacteria of the genus *Legionellasp.* [15]. Mycological studies of the A1 fountain did not show the presence of microorganisms in atmospheric air [3].

Our research has shown large difference in water chemistry between natural and artificial fountains. This results from the construction of their bowl and filling water. The chemistry of water in natural fountains indicates high trophy [16, 17]. In the C fountain, there is noticeable impact of bottom sediments on the increase in phosphorus concentration in the water. The bottom of object B is cleaned before the summer season, the sediments do not build up, and hence the concentrations of this element are low as in artificial objects.

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