Distribution of Aluminium in the Water Supply System of Sofia City, Bulgaria

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Abstract: *Elevated concentrations of aluminium have been found at the outlets of the Drinking Water Treatment Plants (DWTPs) of Sofia city, Bulgaria and in separate sampling points in the water supply network. Cluster analysis is performed for multivariate data interpretation of the distribution of aluminium (Al) concentrations during 2019 at 19 water sampling points (2 DWTPs outlets and 17 points within the city water supply system). Although the concentration of aluminium in the outlet of the treatment plants differ significantly, both of them fall into the same cluster, as the concentrations during the year change in the same manner. The formed cluster of both the treatment plants and most of the studied sampling points indicate the mixed origin of the purified water and proves that the concentration of Al in tap water is dominated by the qualities and quantities from the different sources of the supplied water, rather than by the secondary processes in the network for areas with predominant steel and polyethylene pipes. A distinct exception are the areas with old asbestos cement pipelines where potential release of the metal from the cement affects the Al distribution in the water supply system.*

Keywords: *Aluminium, Drinking water, Distribution, Drinking Water Treatment Plants (DWTPs), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Cluster analysis.*

Introduction

Human exposure to aluminium (Al) through drinking water may be a contributing factor to Alzheimer's disease onset and related disease progression [11, 14, 18, 19, 21, 35]. Therefore, Al drinking water quality standards were devised worldwide with different permissible concentrations. African National Drinking Water Standard indicates an operational guideline limit for aluminium of 0.3 mg/L [29]. The Environmental Protection Agency (EPA) in the USA has recommended a Secondary Maximum Contaminant Level (SMCL) of 0.05-0.2 mg/L for aluminium in drinking water [16]. World Health Organization (WHO) demands residual Al concentration lower than 0.2 mg/L [36], as is the regulation in Bulgaria [27], while in some countries, the limits are even lower: ≤ 0.1 mg/L for France, Canada, Japan and Sweden [8] and ≤ 0.05 mg/L in the United States [28].

Generally, the aluminium concentration in the tap water of the urban water supply system depends on: i) raw water total Al content; ii) drinking water treatment methods and reagents used; iii) the composition of pipe deposits and; iv) the hydraulic conditions change. In natural surface waters, aluminium is present in the form of free ions, bound into insoluble inorganic compounds, or as organic complexes; in dissolved and undissolved form with typical concentrations ranging between 60 to 300 μg/L [9]. Irreversibly increased in the last decades, the poor surface water quality intended for human consumption necessitates the extensive use of Al-based coagulants for the reduction of heavy metals, organic matter, colour, turbidity, suspended particles and pathogens. Unfortunately, it inevitably causes residual Al contamination of the drinking water [19, 28, 30]. A high concentration of dissolved aluminium in the treated water may result from unsuitable coagulant dosage or coagulation operation, while the high concentration of particulate aluminium indicates a poor efficiency of the solid-liquid separation process [17, 22]. It has been reported that aluminium ubiquitously existed in corrosion scales and loose deposits within cast iron pipes, lead pipes, plastic pipes and cement-mortar lined pipes [37]. In the deposits of distribution systems, Al can exist in various forms such as amorphous $Al(OH)_3$, aluminosilicates and aluminium phosphates [32]. Li and co-workers [20] suggest that Al is mainly accumulated on the solid-water interface as it is not evenly incorporated into the main body of the iron corrosion products in metallic pipes. Deposition of aluminium might weaken disinfection efficiency, increase turbidity and interfere with water transport capacity. [37]. The aluminium in pipe scale and sediments may be released back into bulk water once the water chemistry (e.g., pH, electrical conductivity, dissolved oxygen content and presence of iron and manganese oxides and hydroxides) or hydraulic conditions (e.g., hydraulic shock) change [15, 20, 37]. Relatively high concentrations due to leaching from metal pipes of some metals (including Al) had been detected in samples from the ends of the distribution webs in Mount Amiata (Tuscany, Italy) when compared to values at sources [34]. Such a finding was also observed for Sofia, showing that the quality of drinking water in few city sampling points is somewhat worse than that at the drinking water treatment plants (DWTP) outlet [2].

The results from the mandatory monitoring of Al concentrations are usually assessed through multivariate statistical methods, used in water quality assessment at all stages – from the natural reservoir to the tap of the consumer [6, 7, 24, 26, 33]. Such approaches complement hydraulic modelling of the network, thus aiding the management of the whole water supply system. Tools, such as cluster analysis, could serve as a supplementary means of network description, resulting in increased safety [31]. Cluster analysis is a widely used multivariate statistical approach for the classification and interpretation of large data sets [23]. Clustering aims to reveal and visualize any structure of the studied data, mainly similarity between the objects or the variables that describe them.

In the last few years, increased concentrations of Al were found in the raw surface water coming from the Iskar Reservoir and entering the DWTP of Bistritsa and Pancharevo – the main plants in the drinking water supply system of Sofia, Bulgaria. Average Al concentration in the raw water influent to DWTP-Bistrica raised from 0.095 mg/L in 2016 and 0.087 mg/L in 2017 to 0.148 mg/L in 2018. Average Al concentration in the raw water influent to DWTP-Pancharevo decreased from 0.291 mg/L in 2016 and 0.297 mg/L in 2017 to 0.199 mg/L in 2018 [4]. The high and often excessive concentrations of Al at the inlet of DWTP-Bistritsa and DWTP-Pancharevo are a challenge for the treatment technology applied and the first prerequisite for the presence of the element in the urban water supply network [3]. Besides, the two DWTPs use the same Al-based coagulant, which has a positive effect on the concentration of Al in the treated water. Elevated levels of Al have been found at the outlets of drinking water treatment plants and in separate sampling points in the water supply network of the city of Sofia [2]. For the period 2016-2018 concentration of Al in the water treated in DWTP-Bistrica and DWTP-Pancharevo, is mainly in the range between 60 μg/L and 100 μg/L. In 2018, the percentage of samples with Al content in the range 110-150 μg/L rises rapidly in comparison to 2016 and 2017 and together with the samples having Al in the range 160-190 μg/L represents almost half (47.2%) of all test results [4]. Similar outcomes for elevated concentrations of Al in tap water were reported for European countries, such as Italy [12, 13] and Spain [5], Nigeria in Africa [1] and the USA [25].

The present work aims to study the Al distribution in the drinking water supply system of Sofia city by assessing the contribution of all three major factors – raw water Al content; Al-based coagulant use; possible accumulation and additional release of Al in the water supply network. Cluster analysis is performed to assess the distributions of Al concentrations during 2019 and also for multivariate data interpretation of the 17 water supply system locations and 2 outlets of DWTPs. The treated water origin and the distribution patterns for the different water supply system locations are presented.

Materials and methods

Sofia city water supply system

A relatively small amount of water in the drinking water supply system of Sofia city comes from Beli Iskar Reservoir and is treated in DWTP-Mala Tsarkva. These water quantities feed mainly separate neighbourhoods of the capital, located at the foot of Vitosha Mountain. The main drinking water source is the Iskar Reservoir. The raw water enters DWTP-Bistritsa and DWTP-Pancharevo and after treatment is distributed to the consumers (Fig. 1).

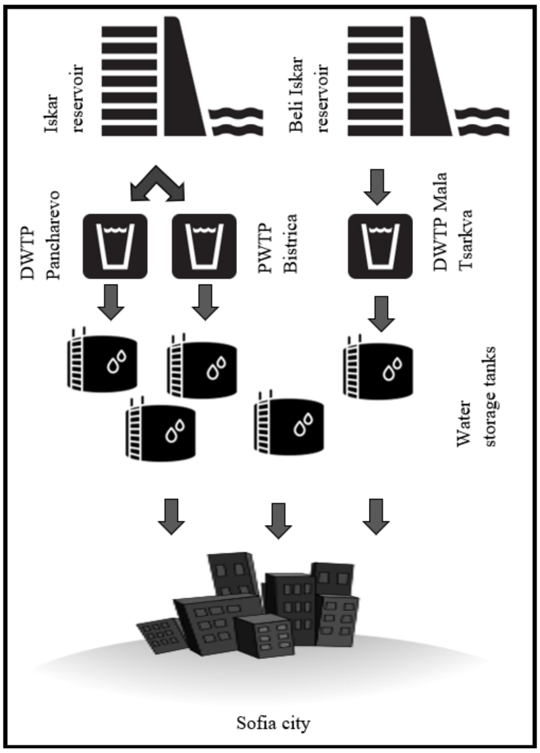

Fig. 1 Scheme of Sofia city water supply system

Sampling

Water samples were collected at the outlets of the two DWTPs (DWTP-Bistrica and DWTP-Pancharevo). Seventeen sampling points are located in the city water distribution network, including the neighbourhoods with the highest population density, as well as end quarters (Fig. 2). These sampling points are part of the Sofiiska Voda AD monitoring program, which is in line with Directive 98/83/EO [10]. The database includes only the sampling points with full data for the average monthly concentrations for the entire 2019. Sampling points with proven supply from DWTP-Mala Tsarkva, where increased concentrations of Al are never found, were excluded.

Fig. 2 Locations of the DWTPs and the sampling points

The water samples were filtered through a 45 μm membrane filter immediately after sampling. The filters were preliminarily soaked in diluted HNO_3 (Fisher Chemicals, Trace Metal Grade, CAS: 7697-37-2) and washed with deionized water. All containers, filters and syringes were preliminary washed with a mixture of HNO_3 (Fisher Chemicals, Trace Metal Grade, CAS: 7697-37-2) and deionized water (1:1) and soaked for 24 h in the same mixture. Before sampling, the containers were washed with water from the source.

Samples of 50 mL were acidified with the addition of 0.5 mL HNO_3 (Fisher Chemicals, Trace Metal Grade, CAS: 7697-37-2) with a concentration of 1 mol/L to obtain pH = 2 to prevent bacteriological activity and losses from the Al deposition on the walls of the vessel.

ICP-MS determination

The determination of Al was performed by inductively coupled plasma mass spectrometry ICP-MS (Perkin-Elmer SCIEX Elan DRC-e) with a cross-flow nebulizer in standard conditions (Table 1). The spectrometer was optimized (RF, gas flow, lens voltage) to provide minimal values of the ratios of oxides and double-charged ions and maximum intensity of the analytes.

Table 1. ICP-MS instrumental conditions

Instrument operating conditions	Value
Argon plasma gas flow	15 L/min
Auxiliary gas flow	1.20 L/min
Nebulizer gas flow	0.85 L/min
Lens voltage	6.00 V
ICP-RF power	1100 W
Dwell time	50 ms
Acquisition mode	Peak hop
Peak pattern	One point per mass at maximum peak
Number of runs	4
Sample flow	2 mL/min
Rinse time	180 s
Rinse solution	3% HNO_3

External calibration was performed using a single element Al standard (Fluka, CAS: 13473-90-0) with an initial concentration of 1000 mg/L. The calibration standard solutions were prepared in the concentration range 0.01 to 100 μg/L after appropriate dilution.

Trueness check

The trueness of the determination procedure was checked by analysis of certified reference materials (CRMs). The results for SPS-SW2 (Reference Material for Measurement of Elements in Surface Waters, Spectrapure Standards, Norway) and TM-23.5 (Environmental matrix reference material, Canada) are presented in Table 2. The recoveries are 99.6% and 97.0%, respectively. Normally, when recoveries are in the range of 85-110%, the method is considered to be fit-for-purpose.

Table 2. Comparison of the measured and certified values for the Al determination in CRMs

Analyte	SPS-SW2		TM-23.5	
	Measured value ± expanded uncertainty	Certified value ± expanded uncertainty	Measured value ± expanded uncertainty	Certified value ± expanded uncertainty
Al, ng/mL	251 ± 5	250 ± 1	98.6 ± 5.7	95.7 ± 10.1

Cluster analysis

As a preliminary step, a normalization of the raw input data (e.g., auto-scaling or *z*-transformation) is applied. The next step is to determine the similarity between the objects, which can be measured by calculating a correlation coefficient or Euclidean distance between them. The final step of the cluster analysis is the selection of an algorithm for linkage the objects in groups of similarity (clusters) and their graphical presentation, usually as a treelike scheme with a hierarchical structure (dendrogram). In this study, the hierarchical cluster analysis is performed using squared Euclidean distance as a similarity measure and Ward's method as a linkage algorithm. The statistical significance of the clusters formed is checked by the Sneath's criterion with ⅓D_{max} value, where D_{max} is the maximal linkage distance in the dendrogram.

Results and discussion

Distribution of aluminium concentrations at the DWTPs

The mean monthly Al concentrations for 2019 at the inlet and the outlet of DWTP-Bistritsa and DWPT-Pancharevo are presented in Fig. 3.

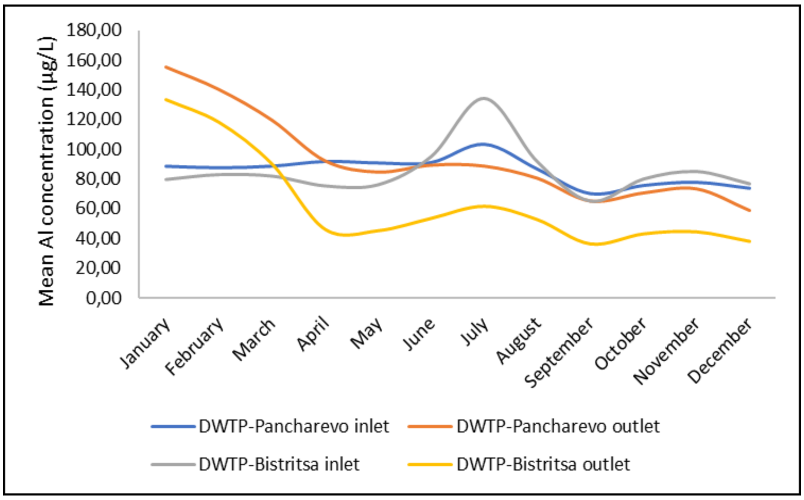

Fig. 3 Mean monthly concentrations of Al at the DWTPs, January-December 2019

Al concentrations at the inlet of both treatment plants are in the range of 75-130 µg/L. Similar results are reported for the DWTPs of Athens [31]. Mean monthly outlet concentrations are lower than the inlet concentrations, except for the first three months of 2019. A probable reason for the elevated Al concentrations in the treated water compared to the raw water are the deteriorating conditions for coagulation and flocculation due to the low temperature (ambient and of the raw water) during this period, which leads to the elevation of the Al concentrations in the water. This is the reason why the first cluster differs significantly from the others (see next section). The reported peak in the inlet concentrations of Al for the period June-August is associated with significant amounts of precipitation in the Sofia region from late June, early July and early August 2019 [3], but has hardly affected the treatment plants efficiency.

Outlet concentration trends follow the inlet concentration change for both plants. The concentrations of Al at the inlet and outlet of DWTP-Bistritsa show significantly lower values compared to the DWTP-Pancharevo, illustrating the direct relationship between these values. Still, the observed reduction of Al at the outlet proves the efficiency of the coagulation and filtration process applied in Sofia's drinking water treatment plants.

DWTP-Pancharevo's outlet Al concentrations are nearly 50% higher than the Al concentration in the treated water from DWTP-Bistrica, mainly due to the difference in the technological schemes of the two plants and the construction of the fast sand filters.

Cluster analysis

The data set consists of 12 variables – mean monthly Al concentrations for 2019 at 19 objects (17 sampling points in the water supply network and 2 at the outlets of DWTP-Bistritsa and DWTP-Pancharevo). Cluster analysis by variables is performed to study the seasonal distribution of Al concentrations in the network and identify possible significant differences in it during the 12 months of 2019. The hierarchical dendrogram (Fig. 4) shows the formation of four clusters.

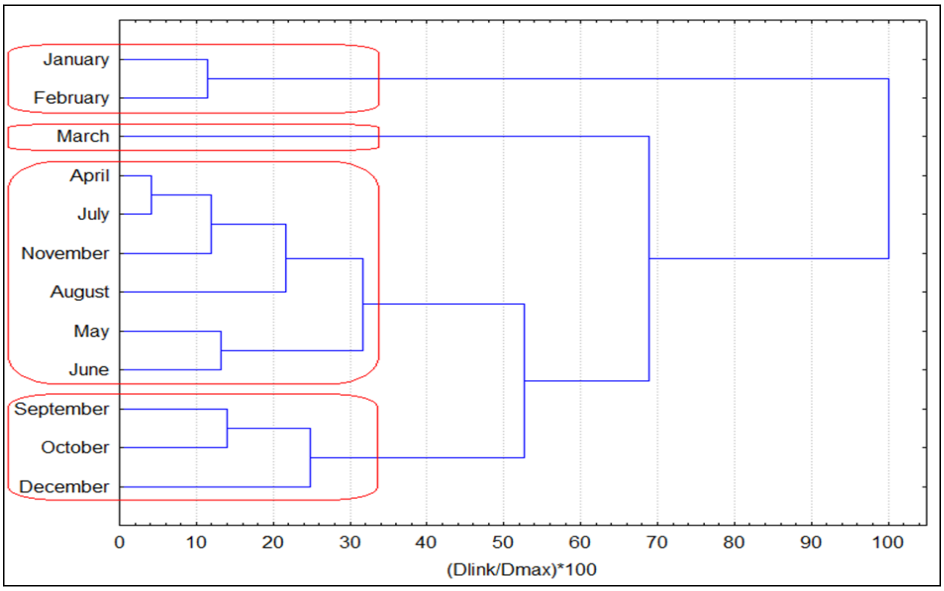

Fig. 4 Hierarchical dendrogram for clustering of the months in 2019

The first cluster (January and February) differs the most from the others, due to the higher concentrations of Al, probably caused by the use of a higher dose of Al-based coagulant in the cold winter months and unsatisfactory performance of the treatment processes. The most fluctuations in the Al concentrations within the 19 objects are found in March which separates it into a self-contained cluster. It presents the smooth transition between high winter metal content and the noticeably lower spring and summer concentrations that form the third cluster. The autumn months, except November, form the last cluster. During the autumn months in 2019, the lowest Al content is measured in all sampling points, but still, the average concentration differs from that of the third cluster with less than 20 µg/L.

Secondly, a cluster analysis by objects was performed for multivariate data interpretation. The resulting dendrogram for hierarchical clustering of the 17 water supply network sampling points and 2 outlets of DWTPs is presented in Fig. 5.

Three major clusters are formed – Cluster 1 consists of most of the sampling points and the outlets of both the DWTPs, Busmantsi separates into a self-contained cluster (Cluster 2), while Vrazhdebna, Mladost, Nadezhda and Republika form Cluster 3. Although the concentration of Al at the outlet of DWTP-Pancharevo is higher than in the outlet of DWTP-Bistritsa, both DWTPs fall into the same cluster, as the concentrations during the year change in the same manner. Moreover, the formation of one cluster consisting of 12 sampling points together with the DWTPs is a confirmation of the mixed origin of the treated water in the water supply network of Sofia city. The concentration of Al depends more on the qualities and quantities of the supplied water than on the secondary processes in the pipes in the first cluster. The results of the cluster analysis prove that Al distribution is not affected by the distance between the treatment plants and the sampling points, having the closest (Mladost) and the farthest (Republika) paired in the same cluster.

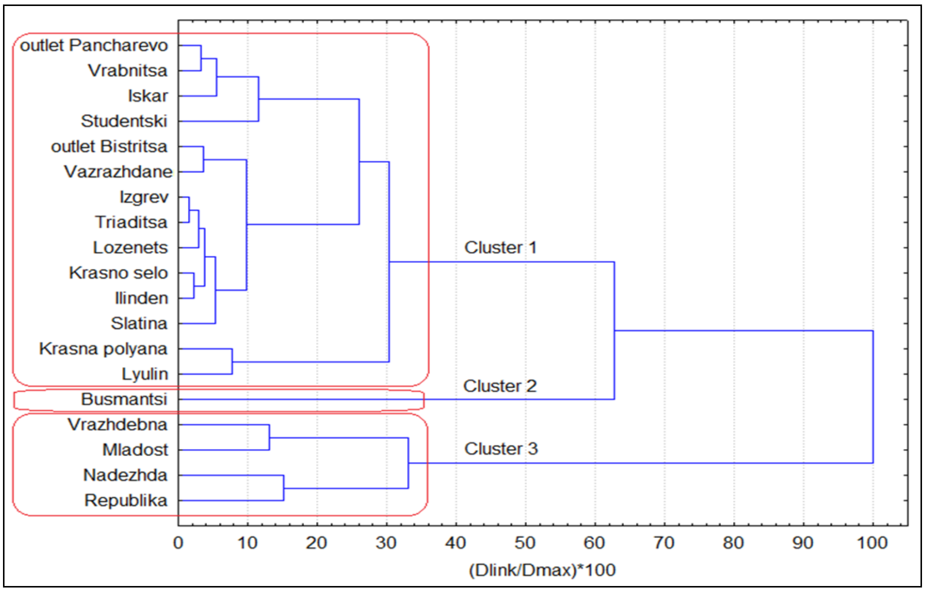

Fig. 5 Hierarchical dendrogram for clustering of the 17 sampling locations of the water supply system and 2 outlets of DWTPs

To find out the reasons for the presented grouping, the mean Al concentration in the formed three clusters was calculated (Fig. 6).

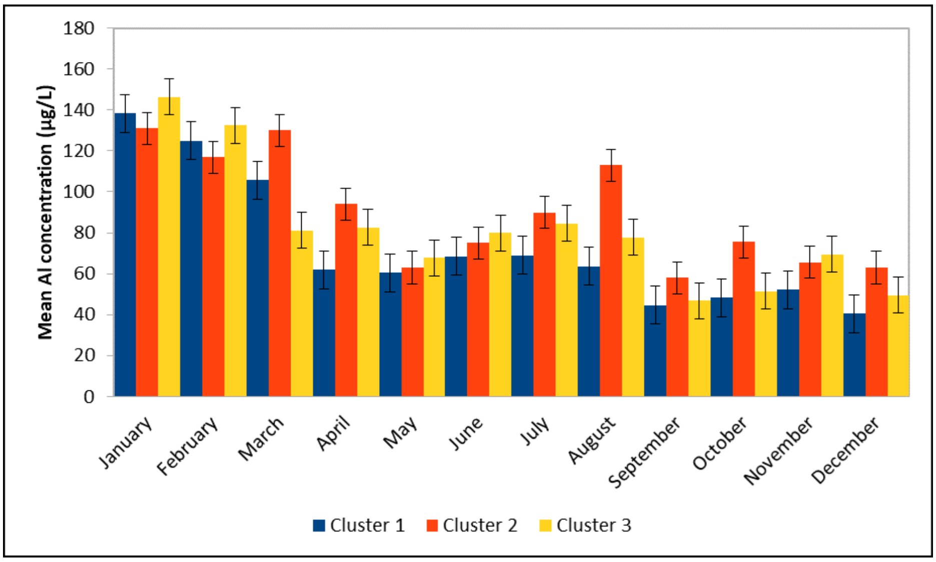

Fig. 6 Mean concentrations of Al in the formed clusters

The graph shows an obvious similarity in Al concentration distribution trends during the year in almost all sampling points, having the highest concentration in January and February (120-145 µg/L) and lowest in December (40-65 µg/L). The Al concentrations in the sampling points forming Cluster 3 are higher than those from Cluster 1, mainly during the spring and summer months of 2019. The similarities of Al concentrations at the outlet of the DWTPs and the different sampling points of Cluster 1 indicate the high degree of similarity and confirms that the Al distribution is dependent on the quality of the supplied water. An increase in the concentration of Al may be associated with some rapid (momentary) change in hydraulic conditions, for example a hydraulic shock, in which the Al, accumulated in the deposits on the pipes' walls (mainly co-precipitated with Fe and Mn-containing oxides and hydroxides), is liberated and released back into the water. In cases of such events, this increase in the Al concentration is short-lived to influence the monthly and annual average data.

Analysis of the network pipe material (Table 3) highlights an additional factor influencing Al distribution in urban water supply networks. Busmantsi water supply network was built more than 50 years ago, where the pipe material is 100% asbestos cement, thus relating the Al distribution to the known release of the metal from the cement and the pipe corrosion deposits. The formation of the third cluster is due to the synergic effect of manly asbestos cement and cast-iron pipes with cement mortar and the higher portion of water coming from DWTP-Pancharevo in Mladost.

Table 3. Pipe materials in Sofia water surly network

Sampling points locations	**Pipe material, (%)**				
	Asbestos cement pipes	**Steel pipes**	**Cast-iron pipes**	**PE pipes**	**other**
Vrabnitsa	29	16	27	23	5
Iskar	30	30	14.5	25	0.5
Studentski	5	20	41	33	1
Vazrazhdane	1	36	47	15.7	0,3
Izgrev	3	18.2	48	30	0,8
Triaditsa	12	15	39	30	4
Lozenets	3	12.5	47.5	35	2
Krasno selo	12,3	20.6	51.5	14.6	1
Ilinden	3	19.2	55.2	20	2.6
Slatina	16	12.3	42.2	28,5	1
Krasna polyana	8	18	42	20	12
Lyulin	14	18	41	24	3
Busmantsi	100	0	0	0	0
Vrazhdebna	67	14.7	5.3	9	4
Mladost	12.3	16	31	40	0.7
Nadezhda	27.5	10	35.5	26	1
Republika	70	25	0	5	0

Conclusion

In the last few years, increased concentrations of Al were found in the raw surface water coming from the Iskar Reservoir and entering the DWTP of Bistritsa and Pancharevo – the main plants in the drinking water supply system of Sofia, Bulgaria. Occasionally the quality of drinking water in few city sampling points was found to be somewhat worse than that at the DWTP outlet. Al concentrations at the outlets of the two drinking water treatment plants of Sofia city, Bulgaria follow the trend of the inlet Al concentrations, indicating the direct relationship between the raw water and the treated water quality. Multivariate statistical analysis (cluster analysis) of Al concentrations, grouping both the treatment plants and the most of the studies sampling points, indicates the mixed origin of the treated water in the water supply network. Al distribution is not affected by the distance between the treatment plants and the sampling points.

The largest quarters with the highest population density and the end quarters form 3 clusters based on the Al concentration variation in the pipe system, proving that Al distribution in tap water depends on the quality of the DWTP outflow, the ratio between the flows from the different plants and on the potential release of the metal from the cement or cement mortar of the asbestos and cast-iron pipes. Future research of the pipe scale composition will give insight into the potential quantity of the Al released back in the drinking water for consumers. Nevertheless, pipes should gradually be replaced to avoid such contamination risks.

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