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Sodium Levels in the Spring Water, Surface and Groundwater in Dalmatia (Southern Croatia)

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1. Introduction

A great number of water resources used for water supply occasionally have sodium concentrations exceeding 20 mgL-1 (Tuthill & Calabrese, 1975; EPA, 1996). Thus, in Massachusetts more than 50% of water from community collectors has more than 20 mgL-1 Na. In some areas the sodium concentration exceeds 100 mgL-1. In order to obtain data used for bringing national decisions on monitoring sodium in drinking water Tuthill & Calabrese (1975), from the University of Massachusetts in Amherst, analyzed blood pressure in students from two adjacent water intake areas where all environmental conditions, except the sodium concentration in drinking water, were similar. The students in the water intake area with 105 mgL-1 Na had significantly higher blood pressure than students in the area with a 5 mgL-1 Na concentration. This study points to the necessity of carrying out longitudinal investigations on sodium concentration together with an increased number of data on health.

In view of the influence sodium in blood has upon the increase in blood pressure, the author decided to classify water as hypotensive (< 10 mgL^{-1} Na), normotensive (from 11 to 20 mgL^{-1} Na) and hypertensive (>20 mgL^{-1} Na) according to the same principle of sodium levels in drinking water.

However, there are significant variations in sodium intake among different individuals as well as from one day to another for each individual (Bauber, 1967). In Western Europe and North America the present consumption of sodium chlorides is estimated to be 5-20 gday-1, with an average of approximately 10 gday-1 (i.e. 4g of sodium per day) (WHO, 1979). The minimum daily sodium demand is ca 50 mg in average adults (WHO, 1984). The average daily sodium demand for adults varies from 2-5 g (WHO, 1979). The allowed sodium levels from food and water have been estimated for various groups of adults and children (WHO, 1984).

Excessive sodium concentration can be easily detected through taste. In solutions at room temperature the taste threshold for sodium present in salts as sodium chloride and sodium sulfate is ca 130 to 140 mgL^{-1}. Generally, the taste is bad at a concentration of <200 mgL^{-1} (regardless whether it is a chloride or sulfate). However, sensitive individuals can detect a bad taste at concentrations varying from 175 to 185 mgL^{-1} (WHO, 1979). Therefore, there are built-in restrictions for allowed sodium levels in drinking water. The threshold for sodium taste in water can be changed and it depends on bonded anions, the solution temperature and personal habits for salt intake.

Sodium plays an important role in nutrition (Weast, 1983), contributes to electrolytes regulated by kidneys (Howard & Schrier, 1990), maintains water balance in the body, and affects muscle contraction and the production of adrenaline and amino acids. However, high concentrations of sodium can disrupt cell or blood chemistry. The excessive consummation of sodium may significantly contribute to many diseases, especially hypertension (Dahl & Love, 1957; Hoffman, 1988; Rutan et al., 1988). Sodium is also toxic to plants in high concentrations (Driscoll, 1986). Sodium concentrations above 70 mgL^{-1} are problematic for irrigation if water is absorbed by leaves (Bouwer, 1978). High concentrations of sodium applied to soils can reduce permeability and produce alkali conditions in which vegetation cannot grow. Elevated sodium levels can also cause problems for industrial uses - for example, foaming in steam boilers.

There is no maximum contamination level (MCL) for sodium, but its guidance level is 20 mg L^{-1} (EPA, 1996). Sodium-restricted diets can often limit one's total intake to less than 1000 mg day^{-1}. Assuming a water intake of 2 L mg day^{-1}, drinking water can contribute substantially to one's total sodium intake at concentrations above 100 mg L^{-1}. For patients on low sodium diets, drinking water may account for more that 60% of total sodium intake.

Considering the importance of sodium for human health the objectives of the investigations were 1) the systematic monitoring of the sodium levels in the spring water, surface and groundwater in Dalmatia and 2) identification of potential causes of the wide variability in this parameter.

2. Study area

Dalmatia belongs to karst regions with abundant rainfall. However, it is characterized by insufficient quantities of water since water sinks underground through fissures (Štambuk-Giljanović, 1999).

The groundwater in Dalmatia can be classified as fissure water which, according to hydrochemical and hygienic characteristics, resembles surface water. Groundwater becomes turbid and has to be treated before entering the water supply system. It is moderately hard with a fairly quick flow. Karst waters can be generally classified as calcium-hydrocarbonate water and differ according to the content of sulfates, chlorides, magnesium, sodium and dissolved CO_2 (Štambuk-Giljanović, 2006).

The majority of karst water resources have high quantities of chlorides resulting from the seawater intrusion, i.e. due to the direct mixing of seawater with fresh water or with groundwater flows. These water resources, in addition to increased chlorides content, have increased sulfates, sodium and magnesium contents.

3. Methods

Individual water samples in Dalmatia (29 taken from spring waters, 25 from surface water and six samples from groundwater) were taken monthly at 60 measurement stations (Figure 1) from January 1, 2010, to January 1, 2011.

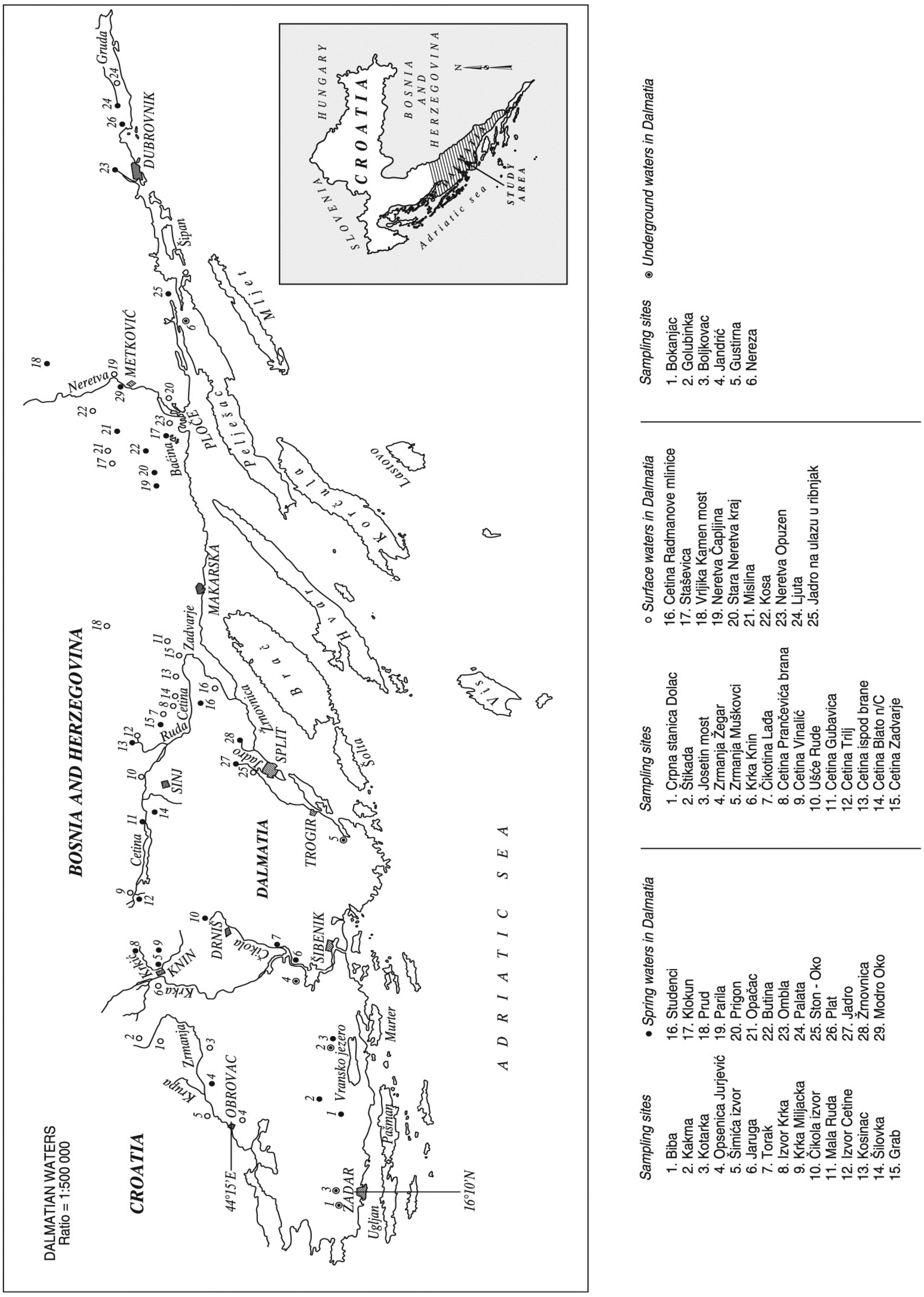

Fig. 1. Sampling sites of waters in Dalmatia

The sulfates concentrations were measured by employing the turbidimetric method, chlorides by the argentometric method and hardness by the complexometric method according to American standard methods (1995).

According to the concentrations of the mentioned quality parameters the following coefficients were computed: K_1 (Larson & Scold, 1958) (the ratio between the chlorides and sulfates sum and the carbonate hardness) and K_2 (the ratio between noncarbonate and carbonate hardness). Sodium was computed from the difference between K_1-K_2 and carbonate hardness according to the author's formula (Štambuk-Giljanović, 2003, 2004, & 2005).

$$Na\ (mgL^{-1}) = (K_1\text{-}K_2) \cdot 2\ HCO^-_3 \cdot M\ (Na) \qquad (1)$$

Wherein M (Na) = 23 $gmol^{-1}$.

According to coefficient K_1 values, the water types were classified into three groups (Štambuk-Giljanović, 2006):

a. non-corrosive water with K_1 lower than 0.2;
b. water with low corrosiveness, K_1 from 0.2 to 0.65;
c. very corrosive water with K_1 higher than 0.65.

The annual results of investigations of waters in Dalmatia were statistically analyzed. They were presented as arithmetic means and medians, since the average concentration values expressed by a median are better than those expressed by an arithmetic mean since the distribution of sodium concentrations is asymmetric. Standard deviations and variability coefficients were computed and the maximum and minimum sodium concentrations in the measurement stations were presented. Statistically analyzed data are presented in Tables 1-3. The tables also present the corrosiveness coefficient K_1 for all the measurement stations.

4. Results

Sodium concentrations in spring water, surface and groundwater in Dalmatia are presented in Tables 1-3 for 2010 at 60 measurement stations. Sodium concentrations expressed by a median are presented in Figures 2, 4 and 6 while the corrosiveness coefficient K_1 is presented in Figures 3, 5 and 7.

In the spring waters in Dalmatia (Table 1) the sodium concentrations expressed by a median (Figure 2) ranged from 1.8 (Ombla and Biba) to 17.6 mgL^{-1} (Klokun). The highest variations were noted at the Kotarka station (217%), and the lowest at Opsenica Jurjevići (32%). At the Šilovka station the sodium concentration was 21 mgL^{-1} with a significant variation (152%). That type of water is classified as hypertensive. According to corrosiveness coefficient K_1 (Figure 3) it is very corrosive water.

Maximum sodium concentrations in spring water varied from 4.6 (Opsenica Jurjevići) to 617 mgL^{-1} (Kotarka) while the minimum concentrations ranged from less than 0.1 (Biba, Kakma, Torak, Kosinac and Studenac) to 2.9 mgL^{-1} (Ston-Oko). The corrosiveness coefficient K_1 was from 0.1 in Parila water (Vrgorac area) to 0.88 in Kotarka (Zadar region). Out of 29 spring water resources analyzed, 83% can be classified as noncorrosive and 17% as water with a low degree of corrosiveness; 75.8% are classified as hypotensive, 20.7% as normotensive and 3.5% as hypertensive.

Sampling sites	Sampling sites number	Aritmetic mean concentration	Standard deviation	Median	Variability coefficient, %	Maximum concentration	Minimum concentration	Corrosion coefficient K_1
1. Biba	12	4.9	6.8	1.8	138.7	21.9	<0.1	0.18
2. Kakma	12	14.6	27.2	9.1	186	99	<0.1	0.20
3. Kotarka	12	80.9	176.1	11.9	217	617	0.5	0.88
4. Opsenica Jurjevići	12	2.5	0.8	2.2	32	4.6	1.5	0.19
5. Šimića izvor	12	8.1	7.2	7.3	88.8	21.8	0.1	0.17
6. Jaruga	12	13.5	12.2	9.6	90.3	36.4	2.0	0.16
7. Torak	12	8.6	8.6	6.3	100	27.7	<0.1	0.20
8. Izvor Krka	12	5	4.5	3.7	90	14.2	0.1	0.18
9. Krka Miljacka	12	13.8	10.3	13.2	74.6	32.7	0.9	0.17
10. Čikola izvor	12	2.9	3.3	1.9	113	11.7	0.4	0.16
11. Mala Ruda	12	3.2	2.7	2.9	84.3	9.8	0.3	0.20
12. Izvor Cetine	12	9.9	11.7	4.8	118	34.7	0.2	0.18
13. Kosinac	12	5.0	5.1	3.6	102	17.4	<0.1	0.19
14. Šilovka	12	35.7	54.6	21	152	199	0.2	0.66
15. Grab	12	3.2	2.4	2.6	75	9.5	0.2	0.11
16. Studenci	12	4.7	3.4	5.1	72.3	10	<0.1	0.10
17. Klokun	12	16.6	9.2	17.6	55.4	32.9	0.5	0.35
18. Prud	12	14.5	17.8	9.8	122	59.9	1.1	0.7
19. Parila	12	7.2	6.2	4.8	86	19.3	1.1	0.1
20. Prigon	12	13.5	18.3	7.1	135	55.8	0.5	0.5
21. Opačac	12	5.3	3.2	5.8	60.3	10.2	0.2	0.19
22. Butina	12	17.8	11.8	16.1	66.2	41.3	4.0	0.18
23. Ombla	12	2.4	1.5	1.8	86.2	6.1	0.9	0.20
24. Palata	12	5.5	3.7	5.1	67.2	14.3	0.0	0.19
25. Ston-Oko	12	10.8	4.7	12	43.5	19.9	2.9	0.25
26. Plat	12	3.3	2.4	1.8	72.7	8.4	0.8	0.21
27. Jadro	12	5.5	4.4	3.3	80	13.7	0.9	0.18
28. Žrnovnica	12	4.2	2.0	3.7	47.6	8.7	1.5	0.18
29. Modro Oko	12	13.1	14.3	9.4	109	52.1	0.5	0.68

Table 1. Sodium concentrations (mgL^{-1}) in Dalmatian spring waters (2010)

Sampling sites	Sampling sites number	Aritmetic mean concentration	Standard deviation	Median	Variability coefficient, %	Maximum concentration	Minimum concentration	Corrosion coefficient K_1
1. Crpna stanica Dolac	12	3.3	2.2	3.0	66.6	7.8	0.8	0.18
2. Štikada	12	2	1.3	1.6	65	4	0.2	0.16
3. Josetin Most	12	1.4	1.4	1.0	100	3.4	<0.1	0.17
4. Zrmanja Žegar	12	2.5	2.4	1.7	96	8.2	0.4	0.16
5. Zrmanja Muškovci	12	2.6	1.8	2.5	69.2	5.7	<0.1	0.19
6. Krka Knin	12	10.1	4.5	10.6	44.5	19.9	0.1	0.19
7. Čikotina Lađa	12	14.7	12.5	12.2	85	38.5	0.4	0.17
8. Cetina Prančevića brana	12	8.7	11.3	4.3	129	39.7	<0.1	0.16
9. Cetina Vinalić	12	17.2	18.1	9.6	105	63.9	1.1	0.10
10. Ušće Rude	12	4.5	3.4	3.5	75.5	9	0.3	0.10
11. Cetina Gubavica	12	9.3	8.3	7.5	89.2	24.8	0.4	0.12
12. Cetina Trilj	12	4.5	2.5	4.6	55.5	96	<0.1	0.17
13. Cetina ispod brane	12	17.2	21.9	6.3	127	74	2.0	0.19
14. Cetina Blato n/C	12	11.2	9.6	8.8	85.7	33.5	0.0	0.18
15. Cetina Zadvarje	12	13.7	6.8	14.4	49.6	23	1.6	0.19
16. Cetina Radmanove mlinice	12	22	15.3	22	69.5	46.9	0.9	0.17
17. Staševica	12	16.1	6.6	17.6	40	28	6.3	0.18
18. Vrljika Kamen most	12	2.6	2.1	2.6	80.7	6.4	<0.1	0.17
19. Neretva Čapljina	12	22.8	14.8	17.1	64.9	53.9	10.6	0.20
20. Stara Neretva kraj	12	177.9	217.2	95.3	122	733	4	2.1
21. Mislina	12	329.2	423.7	42.5	128	1144	1.9	3.2
22. Kosa	12	368	587	43.2	159	1793	3.0	2.6
23. Neretva Opuzen	12	642.6	722.7	502	112	2153	4.3	0.17
24. Ljuta	12	3.4	4.3	2.4	126	15.3	<0.1	0.19
25. Jadro na ulazu u ribnjak	12	4.1	3.9	3.1	95	12.3	<0.1	0.2

Table 2. Sodium concentrations (mgL^{-1}) in Dalmatian surface waters (2010)

In surface waters in Dalmatia (Table 2), sodium concentrations expressed by a median (Figure 4) varied from 1.0 (Josetin Most) to 502 mgL-1 (Neretva Opuzen). The sodium concentrations were highest at the Kosa station (159%) and lowest at Staševica (40%). The water at the Neretva Opuzen station is hypertensive and very corrosive (Table 2, Figure 5). Increased sodium concentration at that station results from the infiltration of seawater into the Neretva River due to level oscillations. The seawater influence is greatest from the Neretva estuary to Opuzen while it decreases towards Metković. After the Metković Bridge the seawater action is no longer felt. In other words, after the Metković Bridge the riverbed rises by 2-2.5 m which decreases the infiltration of seawater into the riverbed after the bridge. Maximum sodium concentrations in surface water were from 3.4 (Josetin Most) to 2153 mgL^{-1} at the Neretva-Opuzen station, while the minimum concentrations varied from less than 0.1 (Josetin Most, Cetina-Prančević Dam, Cetina-Trilj, Cetina-Blato on/C, Ljuta, Jadro at the fishpond entrance) to 10.6 mgL^{-1} (Neretva-Čapljina). The corrosiveness coefficient K_1 varied from 0.1 (Cetina-Vinalić and Ruda estuary) to 3.2 at Mislina so that this water can be classified as very corrosive water.

Sampling sites	Sampling sites number	Aritmetic mean concentration	Standard deviation	Median	Variability coefficient,%	Maximum concentration	Minimum concentration	Corrosion coefficient K_1
1. Bokanjac	12	19.5	16.1	14.1	82.5	53.2	3.1	0.84
2. Golubinka	12	14.1	10.9	11.1	77.3	34.7	3	1.8
3. Boljkovac	12	173	161	124.3	93	578	<0.1	1.6
4. Jandrić	12	23	28.4	15.3	123	111	5.6	0.8
5. Gustirna	12	25	23.1	14.4	92.4	71.2	5	0.6
6. Nereza	12	276	497.4	72.7	180	1610	2.5	0.7

Table 3. Sodium concentrations (mgL^{-1}) in Dalmatian underground waters (2010)

Among all analyzed 25 surface water resources according to K_1, 84% of them can be classified as noncorrosive water and 165% as very corrosive water; 64% of surface water can be classified as hypotensive, 20% as normotensive and 16% as hypertensive.

In the Dalmatian groundwater (Table 3) the sodium concentrations expressed by a median (Figure 6) varied from 11.1 mgL^{-1} at Golubinka to 124.3 mgL^{-1} at Boljkovac. The greatest variations were recorded at the Nereza station (Dubrovnik area), i.e. 180% while the lowest variations were observed at Golubinka (Zadar area), i.e. 77.3%. At the gauging station Boljkovac the sodium concentration expressed by a median was 124.3 mgL^{-1} while at Nereza it was 72.7 mgL^{-1} so that it can be classified as hypertensive water.

According to corrosiveness coefficient K_1 all analyzed groundwater resources are very corrosive (Figure 7). The maximum sodium concentrations in the groundwater ranged from 34.7 (Golubinka) to 1610 mgL^{-1} (Nereza) while the minimum concentrations varied from less than 0.1 (Boljkovac) to 5.6 mgL^{-1} (Jandrići). The analyzed groundwater can be classified as normotensive (67%) and hypertensive (33%).

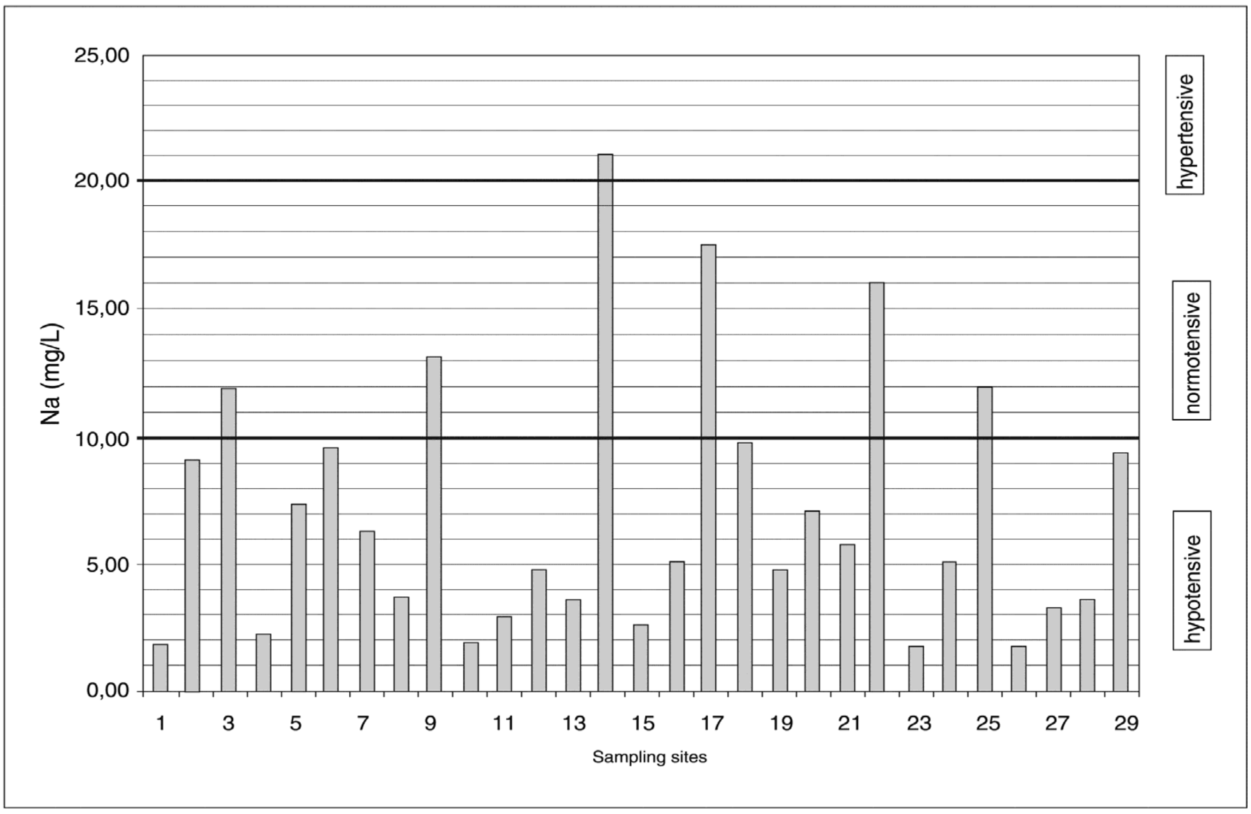

Fig. 2. Sodium concentrations (mgL^{-1}) expressed by the median in Dalmatian spring waters (2010)

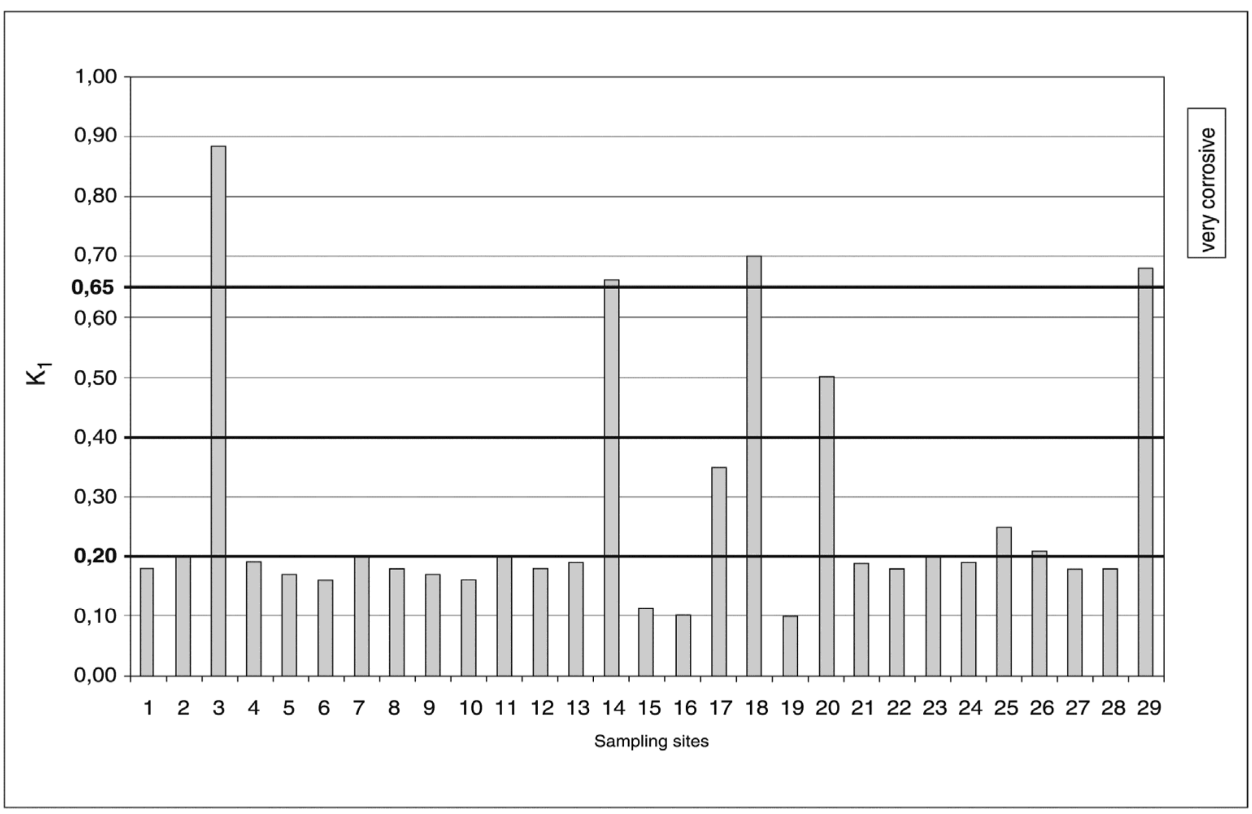

Fig. 3. Corrosion coefficient K_1 in Dalmatian spring waters (2010)

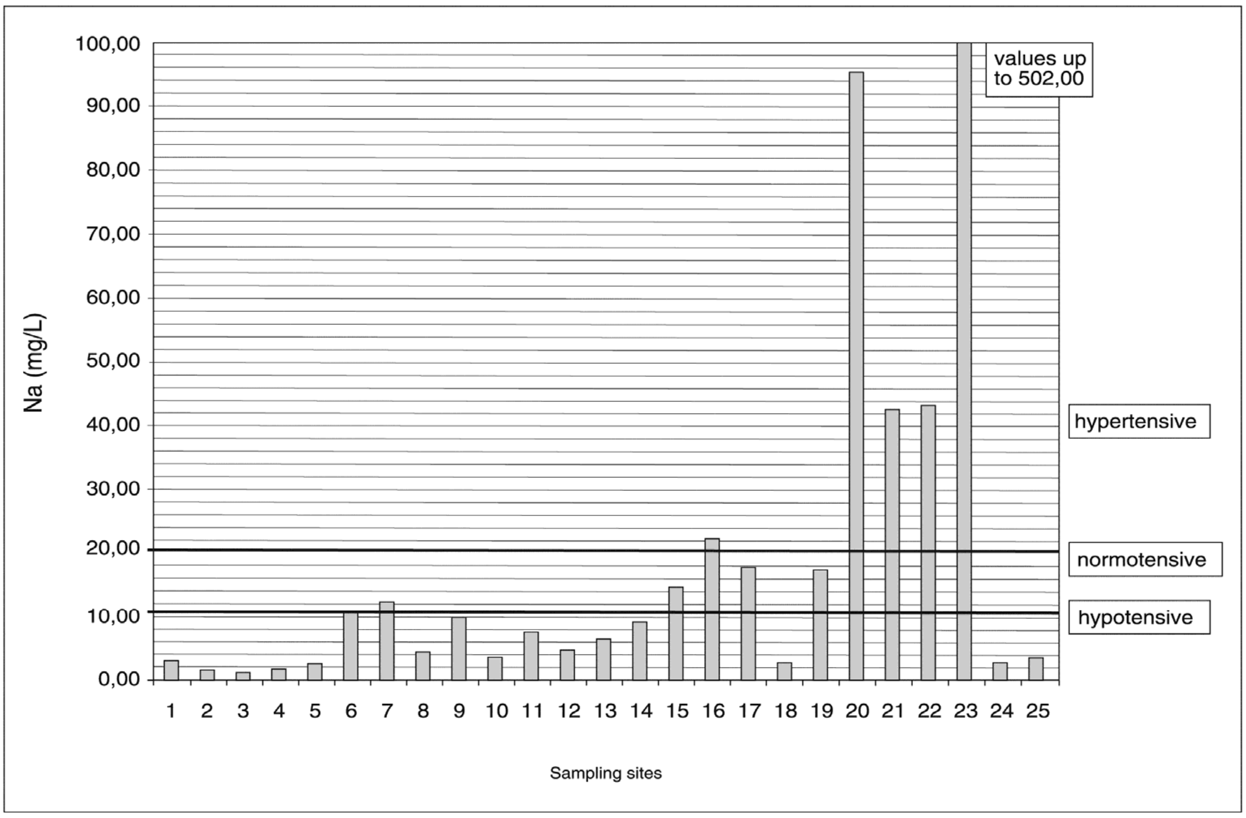

Fig. 4. Sodium concentrations (mgL-1) expressed by the median in Dalmatian surface waters (2010)

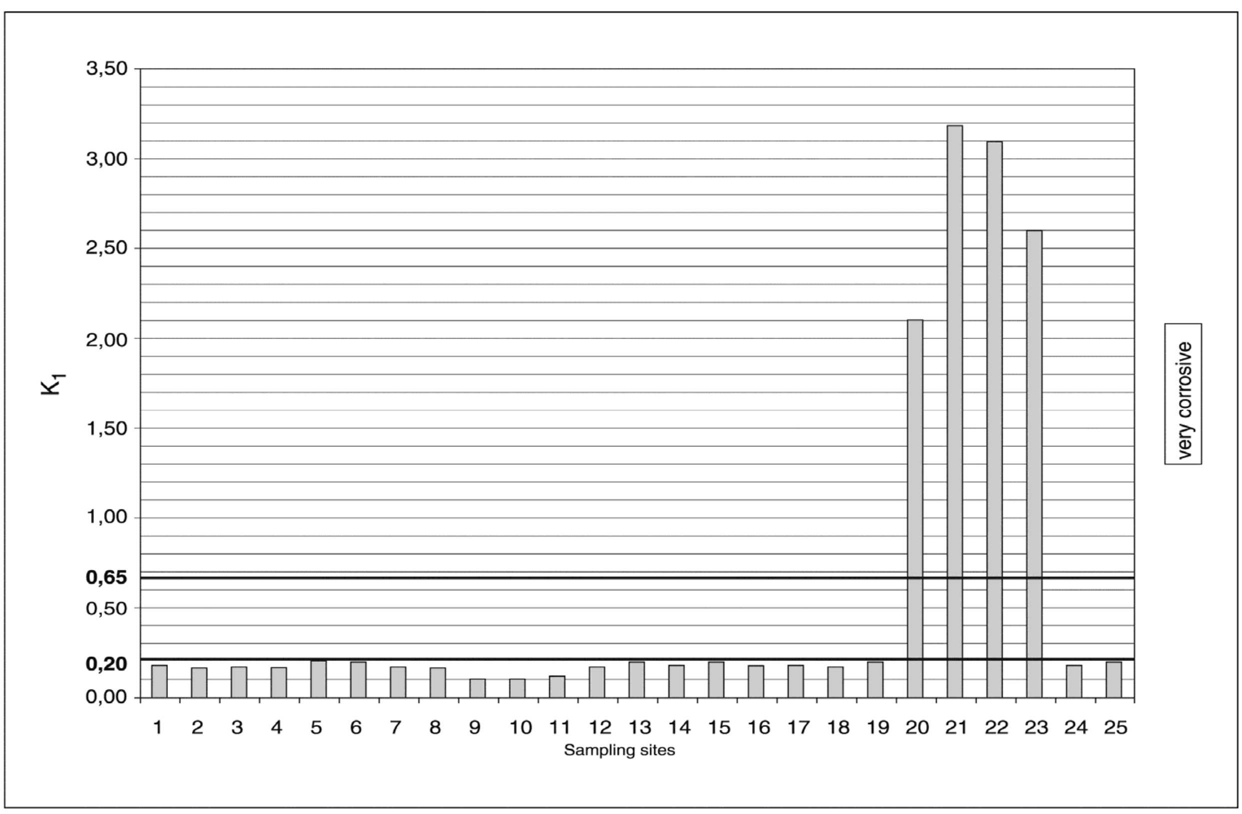

Fig. 5. Corrosion coefficient K_1 in the surface Dalmatian water (2010)

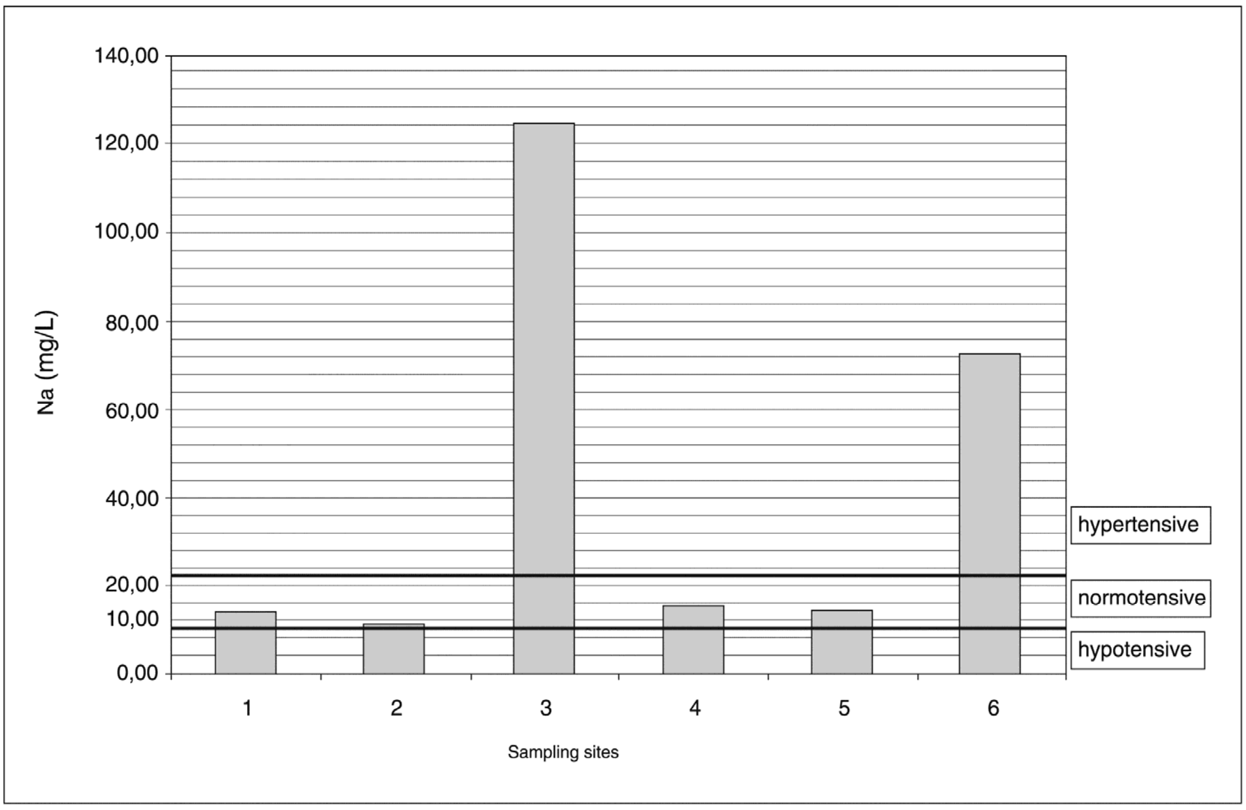

Fig. 6. Sodium concentrations (mgL[-1]) expressed by the median in Dalmatian underground waters (2010)

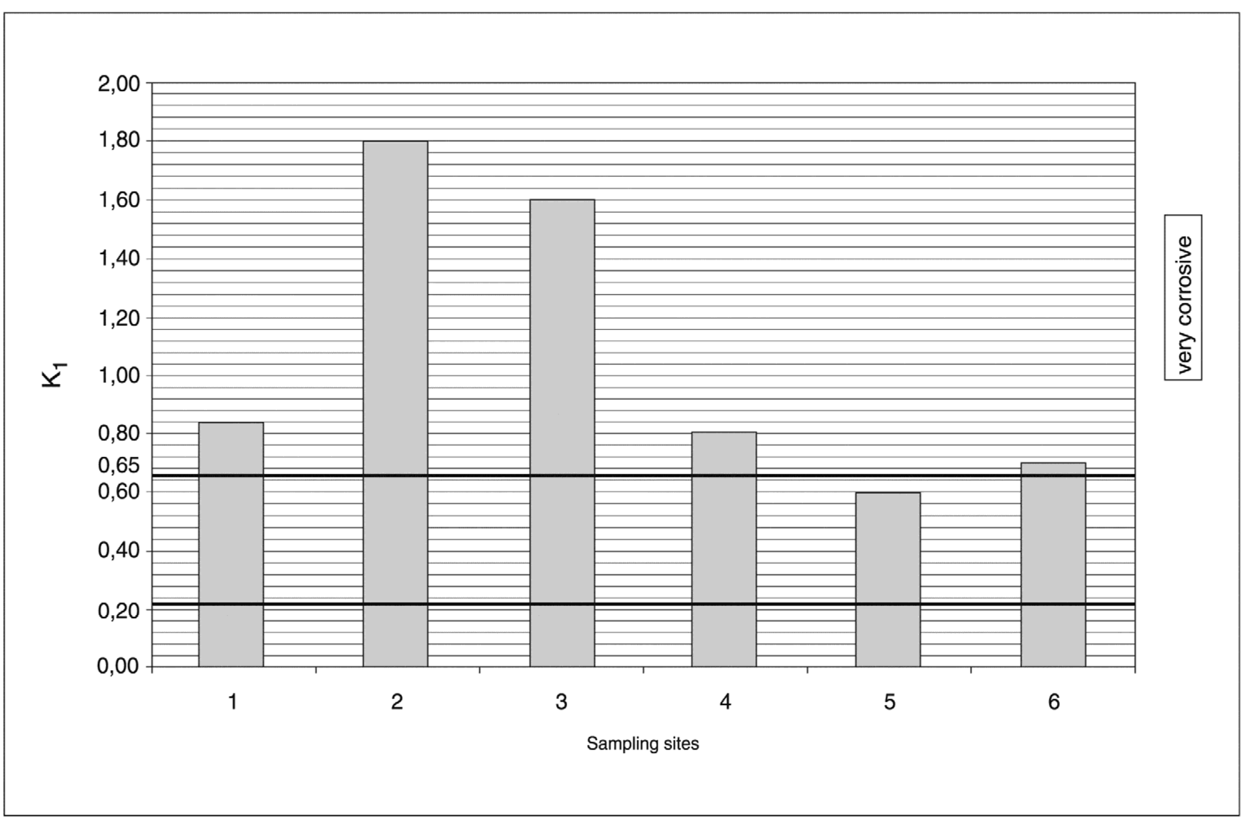

Fig. 7. Corrosion coefficient K_1 in the Dalmatian underground waters (2010)

5. Discussion

Dalmatia belongs to the karst region with surface and groundwater karst phenomena; the latter are more complex and result from the geological composition of karst. Thus, karst regions are characterized by permeable limestone with fissures caused by faults and folding. Rainfall water is lost from the surface by sinking underground through limestone fissures which expand due to water outflows and thus create a large storage of groundwater. The groundwater, stored in limestone, flows down to sea level; however, its flow is prevented by impermeable layers or rock layers of low permeability from different lithological formations. Dolomites and dolomite limestone are most important in stopping the groundwater outflow. Those rocks act as insulators preventing groundwater circulation. As barriers, they stop the groundwater flow and force it to appear on the surface in the form of concentrated springs; sometimes groundwater flows can act as siphons and appear in the sea as submarine springs. This barrier is often formed by the sea itself which slows down groundwater flows so that water appears as coastal springs. In the most abundant Dalmatian coastal springs groundwater comes to the surface, flowing from distant karst regions and flooded poljes (fields). It then sinks underground along faults in impermeable rocks or through ponors (swallow holes) along the mountains boundaries.

Closed karst poljes in Dalmatia are catchment areas in which the water is collected and then sinks underground, however, in some places it comes to the surface. (Štambuk-Giljanović, 2006). The majority of springs were used as bases for water intakes for city water supplies in Dalmatian coastal areas. Thus, the Bokanjac groundwater is used for the Zadar area water supply, the Kakma and Biba Springs supply Biograd and Benkovac, the Čikola Spring is used for the Drniš water supply, the Jaruga and Jandrić Springs for Šibenik, the Jadro Spring for Split and Trogir, the Klokun Spring for Ploče, the Ombla Spring for Dubrovnik and the Duboka Ljuta Spring for the water supply of Cavtat and Ćilipe. The Mala Ruda Spring is used for the new Sinj water collector while the Prud Spring supplies Pelješac and Korčula. The above mentioned large springs represent the only sources of water supply from by springs. The intakes for Dalmatian rivers are on the Cetina River near Gata and Zadvarje and on the Zrmanja River; soon there will be a new intake on the Krka River.

The water resources in Dalmatian karst have more bicarbonates than chlorides and sulfates since water frequently comes into contact with limestone and dolomites while layers of sulfate minerals are rare and less soluble and there are no chloride minerals. In many karst water resources there are significant chlorides concentrations which result from seawater either by direct mixing with freshwater or infiltrating into the groundwater flows. In these flows, apart from increased chlorides concentrations, the sodium and magnesium concentrations are also increased. Sulfates and chlorides in some karst water resources, unlike bicarbonates, vary significantly and depend upon groundwater levels, i.e. rainfall quantities.

Sodium concentrations in Dalmatian water resources expressed by a median during 2010, varied from 1.8 mgL^{-1} in spring water to 502 mgL^{-1} in surface water. According to a study carried out in Canada (Subramanian & Méranger, 1984) sodium concentrations expressed by a median ranged only from 0.3 to 242 mgL^{-1}.

According to the author's classification of drinking water as hypotensive (<10 mgL^{-1} Na), normotensive (from 11 to 20 mgL^{-1} Na) and hypertensive (>20 mgL^{-1} Na) by relating sodium concentration projectively with the arterial pressure and knowing that an increased concentration of sodium in blood increases blood pressure, the following can be concluded: among all analyzed 60 water resources in Dalmatia, 64% can be classified as hypotensive, 20% as normotensive and 16% as hypertensive which means that they exceed the recommended concentration of 20 mgL^{-1} which is characteristic both for hypotensive and normotensive drinking water.

According to the corrosiveness coefficient K_1 out of all analyzed 60 water samples in Dalmatia, 70% can be classified as noncorrosive water (K_1 lower than 0.2), 6.7% as water with low corrosiveness (K_1 from 0.2 to 0.65) and 23.3% can be classified as very corrosive water (K_1 higher than 0.65).

According to Freis (1973) the primary factor connecting sodium and hypertension is the out-cell volume which includes the plasma volume. Sodium is important for hypertension since it is the main factor in the formation of out-cell liquid. Excessive salt in food can be processed by a normal kidney without increasing the volume of out-cell liquid. However, if the kidney does not function properly this volume is increased and hypertension intensified even after a moderate sodium intake. Conversely, at that time sodium quantity should be limited in the diet until the out-cell liquid is reduced which will then significantly decrease blood pressure.

People suffering from hypertension should drink normotensive or even hypotensive water. Sodium concentration in drinking water should be longitudinally analyzed together with an increased number of health data. It is of special importance that data gathered in this way will facilitate the systematic monitoring of sodium in drinking water and ensure quick preventive actions for decreasing sodium concentrations, either by reverse osmosis or by substitution of drinking water sources. Sodium should be included in water quality monitoring since its concentrations can be important to doctors prescribing diets for their patients.

6. Conclusion

During the year 2010, sodium concentrations were monitored in spring water, surface and groundwater in Dalmatia, in order to study their influence upon human health, i.e. arterial hypertension and cardiovascular diseases.

Sodium concentrations expressed by a median in the spring water varied from 1.8 to 17.6 mgL^{-1} with variations from 32% to 217%. According to the corrosiveness coefficient K_1, 83% of the spring water can be classified as non-corrosive (K_1 lower than 0.2), 17% are waters with low corrosiveness (K_1 from 0.2 to 0.65). Out of 29 samples of analyzed spring water, 75.8% were classified as hypotensive (<10 mgL^{-1} Na), 20% as normotensive (from 11-20 mgL^{-1} Na) and 3.5% as hypertensive (>20 mgL^{-1} Na).

Sodium concentrations expressed by a median in surface water ranged from 1-502 mgL^{-1} with variations from 40% to 159%. According to corrosiveness coefficient K_1, 84% of surface water can be classified as non-corrosive and 16% as corrosive. Out of 25 samples of analyzed surface water 64% is classified as hypotensive, 20% as normotensive and 16% as hypertensive.

Sodium concentrations expressed by a median in groundwater ranged from 11.1-124.3 mgL^{-1} with a variation from 77.3% to 180%. According to corrosiveness coefficient K_1 all groundwater can be classified as very corrosive water. The analyzed groundwater was normotensive (67%) and hypertensive (33%). Of all the analyzed 60 samples in Dalmatia, during the year 2010, 70% of the water resources can be classified as non-corrosive, 6.7% as water with a low degree of corrosiveness and 23.3% as very corrosive water.

According to the research results obtained on 60 water samples, 64% can be classified as hypotensive, 20% as normotensive and 16% as hypertensive.

Sodium concentrations and/or water corrosiveness determined by chloride should be used to study the health of each group's drinking water with different sodium (and/or chlorides) concentrations. It can also be used to epidemiologically correlate the pathological states such as arterial hypotension or hypertension with sodium intake from water; it should be also relevant to correlate other pathological states, such as stomach erosion due to water corrosiveness caused by chlorides.

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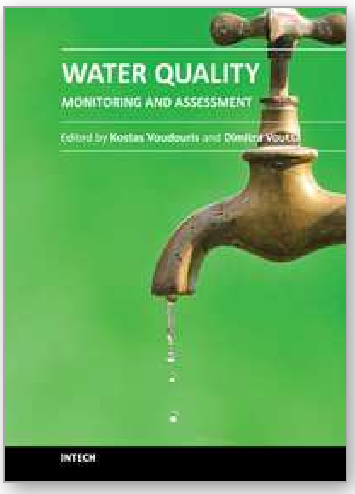

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