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## Koncentracija fluorida u vodovodnoj vodi i komercijalnim napitcima

### *The Concentration of Fluorides in tap Water and Commercial Bottled Beverages*

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#### Sažetak

**Svrha:** Zadatak istraživanja bio je izmjeriti koncentraciju fluorida u vodovodnoj vodi u sjevernom hrvatskom gradu Čazmi i u komercijalno dostupnim napitcima. **Materijali i metode:** Koncentracija fluorida određena je fluorid-selektivnom elektrodom u uzorcima vode iz vodovoda i komercijalno dostupnih napitaka. Pritom je pH određen ion-selektivnom elektrodom za vodik. **Rezultati:** Sadržaj fluorida u vodovodnoj vodi iznosio je 0,313 mg F/L. Od komercijalno dostupnih napitaka najveća koncentracija izmjerena je u gaziranoj mineralnoj vodi (0,34 – 1,5 mg F/L) te u ledenim čajevima (0,06 – 0,74 mg F/L). Negazirane vode i sokovi te gazirani sokovi imali su vrlo nizak sadržaj fluorida i iznosili su redom <0,01 mg F/L, 0,06 – 0,15 mg F/L i 0,02 mg F/L. U gaziranim napitcima pH je iznosio od 2,36 do 2,68, a u sokovima od 3,08 do 3,64. **Zaključak:** Niska koncentracija fluorida u napitcima te kombinacija niskog pH i dodanih šećera mogla bi imati visoki kariogeni potencijal. Rezultati ovog istraživanja mogli bi se iskoristiti za planiranje preventivnih mjera.

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#### Ključne riječi

gazirana pića; mineralna voda; čaj; fluoridi, ion-selektivna elektroda, vodikovi ioni, koncentracija; kariogene tvari

#### Uvod

Prema stajalištu Svjetske zdravstvene organizacije (SZO) karijes je još uvijek velik javnozdravstveni problem u većini industrijaliziranih zemalja gdje pogađa od 60 do 90 posto djece školske dobi i većinu odrasle populacije (1). U državama sa sve većom incidencijom zubnog karijesa, SZO preporučuje niz metoda dodatnog unosa fluorida, uključujući i fluoridirane zubne paste te protokole za fluoridaciju vode, soli ili mlijeka (1,2).

U mnogim zajednicama, uključujući i grad obuhvaćen ovim istraživanjem, dokazana je povećana konzumacija komercijalnih voda i napitaka te je zato potrebno odrediti razinu fluorida u tim napitcima kako bi se što točnije procijenio unos tih spojeva.

Sadržaj fluorida u prirodnim vodama ovisi o koncentraciji u tlu, geološkim svojstvima područja kroz koje vode protječu, topljivosti minerala koji sadržavaju fluoride te prisutnosti drugih elemenata, npr. kalcija, aluminijska i željeza koji

#### Introduction

According to the World Health Organization (WHO), caries still represents an important public health issue in the majority of industrialized countries where it affects 60 – 90% of schoolchildren and the vast majority of adult population (1). In countries with growing incidence of dental caries, WHO recommends various methods of fluoride delivery, including the use of fluoridated toothpastes and water, salt or milk fluoridation schemes (1, 2).

In many communities, including the town assessed in this study, there is evidence of increasing consumption of bottled water and manufactured beverages. There is therefore a need to determine the fluoride level of these beverages to assess fluoride intake.

The content of fluorides in ground waters depends on their concentration in soil, geologic formation of the area through which water passes, solubility of the fluoride containing minerals and the presence of other elements, e.g. cal-

mogu stvarati komplekse s tim spojem. Koncentracija fluorida u onečišćenim slatkim površinskim vodama iznosi do 0,2 mg/L (7), a u morskoj vodi je od 1,2 do 1,5 mg F/L (8). Ljudska djelatnost može utjecati na razinu fluorida u okolišu, premda je u današnjem razvijenom svijetu taj utjecaj obično malen. Skjelkvåle (9) je ustanovio da izvori vode u Norveškoj u blizini pogona za preradu aluminija sadržavaju i do 10 puta veću koncentraciju fluorida u usporedbi s izvorima koji nisu u blizini takve industrije. No, s tehnološkim napretkom mogu se očekivati i niže emisije fluorida iz takvih pogona.

Drugi znatni izvori fluorida su industrija fosfatnih gnojiva koja može povisiti prirodnu koncentraciju fluorida i za više od 100 puta, zatim proizvodnja kemikalija kao što su fluorovodična kiselina, kalcijev i natrijev fluorid te sumporni heksafluorid, proizvodnja opeke i crijepova, keramike i stakla te korištenje pesticida s fluoridima (8,10,11).

U posljednjih nekoliko desetljeća tiskano je mnogo studija o sadržaju fluorida u velikom broju namirnica, jela i napitaka u različitim zajednicama i različitim zemljama (3–6, 12).

U Hrvatskoj je prevalencija karijesa vrlo visoka, oralna higijena loša je čak i među visokoobrazovanim pojedincima te je karijes glavni uzrok ekstrakcije zuba (13–15).

Svrha ovog istraživanja je odrediti sadržaj fluorida u vodovodnoj vodi i komercijalno dostupnim napitcima u gradu Čazmi u sjevernoj Hrvatskoj.

## Materijal i metode

Uzorak vode uzet je iz vodovodne mreže u plastični spremnik. Komercijalne negazirane vode (čiste i aromatizirane), gazirane mineralne vode, gazirani i negazirani sokovi i čajevi nabavljeni su u mjesnom trgovačkom centru. Sadržaj fluorida u vodovodnoj vodi i u komercijalno dostupnim napitcima u boci određen je ion-selektivnom elektrodom za fluor. Ta elektroda pretvara aktivnost određenog iona u otopini u električni potencijal koji se mjeri voltmetrom. Mjerna elektroda (ionski specifična membrana) uparena je s referentnom elektrodom i zajedno s otopinom elektrolita (uzorak) čini elektrokemijski članak. Napon izmjeren voltmetrom predstavlja funkciju logaritma ionske aktivnosti, odnosno koncentraciju promatranog iona, što je izraženo Nernstovom jednačinom:  $E = E^{\circ} + S \log A$ , ( $E$  – potencijal na mjernoj elektrodi;  $E^{\circ}$  – referentni potencijal (konstanta);  $A$  – aktivnost fluoridnih iona u otopini;  $S$  – nagib elektrode) (16). Za mjerenje koncentracije fluoridnih iona uporabljen je ionski analizator ORION EA 940 (Orion Res Inc, SAD) kalibriran prema fluoridnim standardima od 0,19 do 1,9  $\mu\text{g/mL}$  i opremljen ion-specifičnom elektrodom (Orion 96-09, Boston, Mass., SAD).

Prije analize gazirani su napitci 12 sati držani na sobnoj temperaturi radi uklanjanja ugljičnog dioksida (17).

Svaki uzorak ili standard pomiješan je u količini od 4,5 ml s 0,5 ml pufera TISAB III (Total Ionic Strength Buffer). TISAB sadržava reagense koji oslobađaju fluoridne ione iz kompleksa s metalnim ionima (Fe, Al, Mg) i održava pH iz-

cium, aluminum and iron, which may bond with fluoride. The average fluoride value in unpolluted surface waters is usually up to 0.2 mg/L (7). The fluoride concentration in sea water ranges from 1.2 to 1.5 mg F/L (8).

Human activities can also have influence on fluoride levels in the environment, although these usually play a small role in the developed world. Skjelkvåle (9) found that some Norwegian water sources in the vicinity of an aluminum industry may contain more than 10 times the concentration of fluorides compared to those outside the aluminum industry vicinity. However, with the advances in technology, lower F emissions are expected. Other major sources of fluorides are in the phosphate fertilizers industry, which increases the natural concentration of fluorides more than 100 times, followed by the industry producing chemicals such as hydrogen fluoride, calcium fluoride, sodium fluoride and sulfur hexafluoride as well as brick, ceramics and glass industry, the usage of pesticides containing fluorides (8, 10, 11).

In the last few decades, a number of studies have reported on the fluoride content in a large number of food and beverages in different communities and in different countries (3 – 6, 12).

In Croatia, the prevalence of caries is very high, oral hygiene is poor, even among highly educated people, and the main reason for teeth extraction is caries (13 – 15). The objective of this study was to determine the fluoride content of tap water and commercially available beverages in the town of Čazma in northern Croatia.

## Materials and Methods

The sample of potable tap water was collected from the water supply system into a plastic container. Commercial bottled non carbonized water (plain and aromatized), carbonated and natural fruit juices, teas were obtained from local groceries. The fluoride content in tap water and commercial bottled drinks was determined using an ion selective electrode. The electrode records the activity of a specific ion dissolved in a solution into an electrical potential, measured by a voltmeter. The indicating electrode is an ion-specific membrane, which together with the reference electrode, and electrolyte solution (sample solution) makes up an electrochemical cell. The voltage measured by the voltmeter is dependent on the logarithm of the ionic activity i.e. concentration, as stated in the Nernst equation:  $E = E^{\circ} + S \log A$ , ( $E$  – measured electrode potential;  $E^{\circ}$  – referential potential (constant);  $A$  – activity of fluoride ions in the solution;  $S$  – electrode incline) (16).

The fluoride was determined with the use of an ORION EA 940 ion analyzer (Orion Res Inc, USA) calibrated with the fluoride standards from 0.19 – 1.9  $\mu\text{g/mL}$ , equipped with an ion-specific electrode (Orion 96-09, Boston, Mass., USA). Before the analyses, carbonated beverages were maintained at room temperature for 12 h for de-carbonation (17). 4.5 mL of each sample or standard were mixed with 0.5 mL of Total Ionic Strength Buffer (TISAB III). TISAB contains reagents that release fluorides from the complexes with metal ions (Fe, Al, Mg) and maintains pH around 5-6, which is

**Tablica 1.** Koncentracija fluorida u komercijalnim napitcima  
**Table 1** The concentration of Fluorides in Commercial Bottled Beverages

Proizvod • Product	Proizvođač • Manufacturer	pH napitka • pH of the beverage	pH nakon što je dodan TISAB II • pH after adding TISAB	Koncentracija F <sup>-</sup> • Conc. of F <sup>-</sup> (mg/L)
<b>Negazirane vode • Non-carbonated waters</b>				
JANA	Jamnica d.d, Getaldićeva 3, Zagreb, Hrvatska • Croatia	7.65	4.86	0.080
BISTRA	Coca-Cola, Beverages, M. Sachsa 1 Zagreb, Hrvatska • Croatia	6.96	5.09	0.092
JANA JAGODA	Jamnica d.d, Getaldićeva 3; Zagreb, Hrvatska • Croatia	3.21	5.02	0.050
JANA LIMUN	Jamnica d.d, Getaldićeva 3, Zagreb, Hrvatska • Croatia	3.29	4.96	0.052
<b>Gazirane mineralne vode • Carbonated waters</b>				
JAMNICA	Jamnica d.d, Getaldićeva 3; Zagreb, Hrvatska • Croatia	8.35	4.93	0.632
MIVELA	Nova sloga Kneginje Milice 81/1 Trstenik, Srbija • Serbia	7.34	4.96	0.378
STUDENAC	Podravka d.d. A. Starčevića 32 Koprivnica, Hrvatska • Croatia	7.00	5.15	1.500
DONAT MG	Droga Kolinska Kolinska cesta 1 Ljubljana, Slovenija • Slovenia	7.89	5.65	0.015
<b>Gazirani sokovi • Carbonated soft drinks</b>				
SPRITE	Coca-Cola, Beverages, M. Sachsa 1 Zagreb, Hrvatska • Croatia	2.68	4.91	0.020
FANTA	Coca-Cola, Beverages, M. Sachsa 1 Zagreb, Hrvatska • Croatia	2.86	4.93	0.020
COCA COLA Plastična boca • Plastic bottle	Coca-Cola, Beverages, M. Sachsa 1 Zagreb, Hrvatska • Croatia	2.36	4.99	0.018
COCA COLA Limenka • Can	Coca-Cola NBC, Trestev Strasse 91, Beč • Vienna, Austrija • Austria	2.43	4.99	0.018
<b>Čajevi • Teas</b>				
ICE TEA STUDENA	Podravka d.d. A. Starčevića 32 Koprivnica, Hrvatska • Croatia	3.33	4.95	0.180
ETERNA	Eurobev d.o.o. Borongajska cesta 104, Zagreb, Hrvatska • Croatia	2.84	4.89	0.062
GREEN TEA	Podravka d.d. LERO d.o.o. Tome Stržižića 8, Rijeka, Hrvatska • Croatia	3.34	4.88	0.375
VITAO	Coca-Cola, Beverages, M. Sachsa 1 Zagreb, Hrvatska • Croatia	3.07	4.93	0.738
<b>Voćni sokovi • Fruit soft drinks</b>				
VINDIJA JABUKA	Vindija d.o.o. Međimurska 6 Varaždin, Hrvatska • Croatia	3.26	5.00	0.146
VINDIJA BRESKVA	Vindija d.o.o. Međimurska 6 Varaždin, Hrvatska • Croatia	3.47	5.01	0.099
VINDIJA BOROVNICA	Vindija d.o.o. Međimurska 6 Varaždin, Hrvatska • Croatia	3.08	4.69	0.116
MARASKA NARANČA	Maraska d.d. Biogradska c. 64A Zadar, Hrvatska • Croatia	3.64	4.88	0.064
MARASKA MULTIVITAMIN	Maraska d.d. Biogradska c. 64A Zadar, Hrvatska • Croatia	3.27	4.92	0.080

među 5 i 6, što je iznimno važno jer ion-selektivna fluoridna elektroda reagira na promjene koncentracija  $\text{OH}^-$  iona (16). Fluoridni standardi pripremljeni su serijskim razrjeđivanjem komercijalnog standarda (0,1 M otopina fluorida, Orion 940906). Tijekom mjerenja su se standardi i uzorci miješali konstantnom brzinom magnetskim štapićem u magnetskom mikseru. Uzorci su od podloge miksera bili izolirani komadom polistirena kako bi tijekom mjerenja temperatura ostala nepromijenjena. Fluoridi su u svakom uzorku određeni tri puta izravnim mjerenjem (18). Rezultati su izraženi u mg/L fluorida. pH uzorak izravno je izmjeren kombiniranim pH staklenom elektrodom (Model 91 02 BN, Orion) kalibriranim korištenjem pufera pH 4,01 (Orion 910104) i pH 7,00 (Orion 910107, Orion Research, Inc., SAD). pH svakog uzorka određen je prije i dodavanja otopine TISAB-a te nakon toga.

## Rezultati

Izmjerena koncentracija fluorida u vodovodnoj vodi iznosila je 0,3137 mg/L.

Rezultati analize s pomoću ion-selektivne elektrode za fluor i pH u uzorcima komercijalno dostupnih napitaka prikazani su u tablici 1. Koncentracija fluorida u gaziranim mineralnim vodama iznosila je 0,34 do 1,5 mg F/L, a u ledenim čajevima 0,06 do 0,74 mg F/L. Komercijalno dostupne negazirane vode sadržavale su koncentraciju fluorida manju od 0,01 mg F/L, gazirani sokovi 0,02 mg F/L, a voćni sokovi od 0,06 do 0,15 mg F/L.

## Rasprava

Noviji epidemiološki podaci pokazuju da je karijes još uvijek javnozdravstveni problem u mnogim zemljama u razvoju u kojima je zabilježen porast incidencije kod školske djece i odraslih (2,19, 20).

Hrvatska se ubraja u zemlje s lošim oralnim zdravljem, uključujući i visoku prevalenciju karijesa (12,14,15,21). Premda je u 1970-ma i 1980-ma postojao trend smanjenja prevalencije karijesa, istraživanja provedena u posljednjih nekoliko desetljeća pokazuju negativni smjer u oralnom zdravlju (12,14). Čimbenici koji tome pridonose uključuju ratna zbivanja u ranim devedesetima, što je rezultiralo znatnim pogoršanjem stanja. Neprovođenje preventivnih mjera nakon privatizacije ordinacija dentalne medicine pridonijelo je lošem oralnom zdravlju. Na globalnoj razini, pak, porastu prevalencije karijesa pridonosi povećana konzumacija šećera i nedostatna izloženost fluoridima (2).

Iz navedenih razloga preporučuje se kontrola karijesa dobro poznatim i iskušanim metodama korištenja fluorida, s posebnim naglaskom na javnozdravstveni pristup koji uključuje fluoridaciju vode, mlijeka i soli, razvoj cjenovno prihvatljivih fluoridiranih zubnih pasti, topikalnu primjenu fluorida te ponovne edukacijske programe u školama (četkanje zuba, korištenje zubne svile, prehrabene navike, redovite kontrole) (2).

Sve češća konzumacija komercijalnih negaziranih mineralnih voda i voćnih napitaka još je jedan čimbenik koji mo-

very important since the fluoride ion selective electrode reacts to the changes in the concentration of  $\text{OH}^-$  ion (16). Fluoride standards were prepared by serial dilution of a stock-standard containing 0.1 M of fluoride (Orion 940906).

During the measurements, standards and samples were mixed at a constant rate using a magnetic mixer and a magnetic stick. Between the mixer and the vessel a piece of polystyrene was placed in order to keep the temperature constant during measurement. The concentrations of the samples were determined by comparison to the standards. Fluoride was directly analyzed in all samples in triplicate (18). The results were reported in mg/L fluoride. The pH of the samples was measured directly with a combined pH glass electrode (Model 91 02 BN, Orion) calibrated using buffers of pH 4.01 (Orion 910104, Orion Research, Inc., USA) and pH 7.00 (Orion 910107, Orion Research, Inc., USA). The pH of each sample was measured before and after TISAB adding.

## Results

The recorded concentration of fluorides in tap water equaled 0.3137 mg F/L.

The results of the analysis of fluorides concentration by fluoride selective electrode and pH in different samples of commercially available beverages are shown in Table 1. The fluoride concentration in carbonated mineral waters ranged from 0.34 to 1.5 mg F/L; in ice teas it ranged from 0.06 – 0.74 mg F/L. Commercial bottled non-carbonated waters contained a fluoride concentration below 0.01 mg F/L. Commercial bottled carbonated soft drinks contained fluoride at 0.02 mg F/L and fruit juices contained 0.06 – 0.15 mg F/L.

## Discussion

Recent epidemiologic data show that dental caries remains a public health problem in many developing countries, where significant increase in dental caries prevalence has been recorded in schoolchildren and adults (2, 19, 20).

Croatia is among the countries with poor oral health, including high caries prevalence (12, 14, 15, 21). Although in the 1970's and 1980's there was a decreasing trend in caries prevalence, the research in the last few decades has shown negative oral health trends (12, 14).

The factors contributing to the negative trends in oral health in Croatia include the war in the early nineties which caused significant problems. Reduced access to preventive dentistry procedures following the privatization of dental profession also contributed to a deterioration of oral health. On the global level, such a trend in caries prevalence is attributed to the increasing consumption of sugar and inadequate exposure to fluorides (2).

For this reason, it is recommended that caries should be controlled by applying well known and established fluoride implementation methods, with the emphasis on public health approaches including: water, salt and milk fluoridation, the development of affordable fluoride toothpastes, topical application of fluorides, (re)introduction of educational programs in schools (tooth brushing, dental floss usage, nutrition, paying regular visits to dental office) (2).

že utjecati na pojavu karijesa. Glavni razlozi za odabir vode u boci umjesto vode iz slavine jest u brizi o mikrobiološkoj sigurnosti vodovodne vode te strah od moguće prisutnosti kemikalija za dezinfekciju (klor). Drugi razlog je okus vode iz vodovoda (22). U ovom istraživanju koncentracija fluorida u negaziranim vodama (0,050 – 0,080 mg F/L) bila je niža nego u vodovodnoj vodi (0,313 mg F/L), a koncentracija u komercijalnim gaziranim mineralnim vodama (0,378 – 1,5 mg F/L) bila je viša nego u vodovodnoj vodi. Rezultati dobiveni analizom negaziranih voda slažu se s rezultatima australске studije (22), no ako se u obzir uzmu rezultati gaziranih mineralnih voda, koncentracije fluorida i razlike među njima nisu zanemarive.

Razina fluorida u vodovodnoj vodi daleko je od optimalne razine od 1 mg F/L i uz niske zabilježene koncentracije u negaziranim komercijalnim vodama ne smanjuje pojavu karijesa kod osoba koje ih piju. Sadržaj fluorida bio je naznačen samo na nekoliko proizvoda, a izmjerene vrijednosti odgovarale su navedenima. Studije u SAD-u pokazale su da tek pet posto proizvoda ima naznačenu koncentraciju fluorida, dok u Kanadi svi proizvodi prema zakonu moraju imati deklariranu količinu toga spoja (23,24). Wienberger (23) je ustanovio da deklaracije u nekim slučajevima nisu bile točne.

Čimbenik koji, uz nisku koncentraciju fluorida u vodovodnoj vodi i komercijalnim napitcima, pridonosi većem indeksu KEP-a jest konzumacija niskomolekularnih ugljikohidrata, posebice među djecom (25). U pojedinim dijelovima Hrvatske, KEP 12-godišnjaka doseže 9,5 i u korelaciji je s niskom koncentracijom fluorida u vodi za piće (26). Prema izvještaju Svjetske zdravstvene organizacije iz 2003. indeks KEP-a među 12-godišnjacima bio je od 2,7 do 4,4 (20). Smanjivanje incidencije karijesa kod predškolske djece nižeg socijalno-ekonomskog statusa u Brazilu dogodilo se nakon fluoridacije vode (27). Većina populacije u našoj studiji pila je vodu iz vodovoda koja u Hrvatskoj nikada nije bila fluoridirana, a razina fluorida daleko je ispod preporučene u preventivnim mjerama. Detaljna analiza populacije s odgovarajućim podacima o indeksu KEP-a mogla bi predstavljati razumnu osnovu za provedbu fluoridacije vode, posebice u područjima koja su jako ugrožena karijesom. Prema nekim izvještajima ukupna dnevna količina konzumiranog šećera ostala je ista, no promijenio se način na koji ga se uzima – danas se uglavnom unosi slatkim sokovima (28). pH tih napitaka vrlo je nizak (pH=3,08 – 3,64), mnogo niži od 5,5, vrijednosti koja se smatra kritičnom u procesu demineralizacije hidroksilapatita, premda gubitak minerala može nastati i u manje kiselim uvjetima (29). Sadržaj fluorida u komercijalnim sokovima također je bio iznimno nizak (0,06 – 0,14 ppm F<sup>-</sup>), što im dodatno povećava kariogeni potencijal. Ako se pH poveća iznad 4,5, a fluoridni ioni dostupni su u niskoj koncentraciji, fluor-hidroksilapatit se precipitira na površini, dok se hidroksilapatit u dubljim slojevima i dalje otapa. Povećanjem pH iznad 5,5 i dostupnošću fluoridnih iona nastaje remineralizacija cakline i dentina. Hidroksilapatitni kristali s uklopljenim fluoridima tijekom remineralizacije manje su topljivi od kalcijeva hidroksilapatita (30). Koncentracija fluorida u napitcima pojedinih multinacionalnih tvrtki različita je u različitim zemljama i ovisi o koncentraciji u lokalnoj

The increasing consumption of commercial noncarbonated mineral waters and soft drinks is another factor potentially impacting upon dental caries experience. The main reasons why people choose bottled waters over tap water relate to concerns about the microbiologic safety of tap water and possible chemicals in it, including chlorine added for disinfection. Other concerns with tap water include taste issues (22). The concentration of fluorides in non carbonated waters (0.050 – 0.080 mg F/L) was lower than in tap water (0.313 mg F/L), while the concentration of fluorides was higher in bottled carbonated waters (0.378 – 1.5 mg F/L) than in tap water. The results considering non carbonated water are in concordance with Australian survey (22), however when taking bottled carbonated water results into account, the fluoride concentrations are not negligible. The level of fluorides in tap water was significantly below the optimal level of 1 mg F/L, and the recorded low value of fluorides in majority of commercial waters does not contribute in any way to caries incidence decrease in individuals consuming them. The fluoride concentration was declared in only a few products and the values recorded in our study corresponded to the declared values. It was reported that in the USA less than 5% of the products had the concentration of fluoride declared, while in Canada, where the declaring of fluoride content is obligatory, all products had the fluoride concentration stated in the declaration (23, 24). Wienberger (23) investigated the accuracy of the declared values and reported that they are not correct in all cases.

Besides low fluoride concentration value in tap water and commercial drinks, the factor contributing to increasing DMFT index is the increasing consumption of low molecular carbohydrates, especially among children (25). In some parts of Croatia DMFT among 12 year olds reaches 9.5 and is in correlation with the low concentration of fluorides in tap water (26). According to the WHO report from 2003, DMFT index among 12-year olds was 2.7 – 4.4 (20). The decrease in caries incidence in pre-school children of lower economic status in Brazil occurred following the commencement of water fluoridation (27). The majority of the population in our study consumed tap water. The tap water in Croatia has never been fluoridated, and is much below the level recommended in preventive measures. Careful screening of the population with adequate DMFT data could be a basis for implementation of water fluoridation, especially in areas with high caries prevalence.

According to some reports, net daily consumed quantity of sugars remained the same over the years, but the form in which they are consumed has changed – today they are mostly consumed via soft drinks (28). The pH of soft drinks in this study was very low (pH=3.08 – 3.64), much lower than pH 5.5, which is considered the critical acidity value for hydroxyapatite demineralization, although the loss of tooth mineral content can occur in a less acidic environment (29). The fluoride content of soft drinks was also very low (0.06 – 0.14 ppm F<sup>-</sup>) which makes them even more cariogenic. If the pH was higher than 4.5 and the fluoride ions available in low concentration, fluor hydroxyapatite would precipitate within the surface layer, while the hydroxyapatite in deeper enamel

vodi kojom se proizvođač koristi u proizvodnji. Na primjer, u Meksiku je koncentracija fluorida u pojedinim napitcima 0,49 ppm (u rasponu od 0,10 do 1,62 ppm) (31), što je znatno više nego u našoj studiji. S obzirom na to da fluoridi imaju visok afinitet prema staklu i metalu, može se očekivati da će njihova koncentracija biti nešto manja u napitcima pakiranim u metalnoj ili staklenoj ambalaži (32). Razlog zašto nismo pronašli znatnu razliku vjerojatno je u činjenici da su razlike u koncentracijama bile jako niske te je i mjerenje bilo otežano. Visoka koncentracija fluorida pronađena je u gaziranim mineralnim vodama – jedna od njih sadržavala je 1,5 ppm fluorida, što je vrijednost veća od preporučene u preventivnim mjerama protiv karijesa. Taj bi se rezultat morao uzeti u obzir i pri predlaganju preventivnih mjera za odrasle pacijente s visokim rizikom od karijesa. Isto tako treba imati na umu da pretjerana konzumacija mineralnih voda bogatih fluoridima, uz unos fluorida iz drugih izvora, može rezultirati dentalnom fluorozom.

Nešto veća koncentracija fluorida pronađena je u ledenim čajevima. Jedan od proizvoda sadržavao je 0,7 ppm toga spoja i te su vrijednosti blizu preporučenih u preventivnim mjerama (1 ppm). Slični rezultati dobiveni su analizom pojedinih gaziranih sokova i mineralnih voda (0,7 – 0,9 ppm) (33). Svježi i ledeni čajevi mogu imati koncentracije fluorida u rasponu od 0,5 do 4 mg/l, ovisno o mjestu rasta biljke i koliko su dugo listići čaja bili namočeni (34, 35).

Broj studija o koncentraciji fluorida u hrani i piću jako se povećao u posljednjih nekoliko desetljeća, a mnogobrojne su i studije o prevalenciji dentalne fluoroze zajedno sa smanjenjem prevalencije karijesa povezane s javnozdravstvenom fluoridacijom vodovodne vode i korištenjem fluorida u terapijske svrhe (3,36). Istaknuto je da kod 1 ppm fluorida u pitkoj vodi 50 posto ljudi razvije blagu dentalnu fluorozu. Također je dokazano da stupanj fluoroze izravno ovisi o uporabi fluorida i zato je potrebno optimalno fluoridirati vodu, ovisno o higijenskim navikama populacije, posebice djece (30). Stoga, kako bi se teoretski organizirale i provele učinkovite preventivne mjere u borbi protiv karijesa, potrebne su detaljne informacije o načinima i količini unosa fluorida u populaciji kako bi se izbjegli nepoželjni učinci fluorida, a postigli optimalni zaštitni učinci od karijesa (2,36). Detaljne spoznaje o indeksu KEP-a u populaciji i oralnohigijenskim mjerama također su potrebne kako bi se mogli planirati dodatni izvori fluorida u sklopu javnozdravstvenih mjera (ev. fluoridacija vode) i edukacija o oralnoj higijeni.

Rezultati ove studije pokazuju sadržaj fluorida u različitim napitcima. Zajedno s dodatnim studijama o unosu fluorida iz drugih izvora mogu biti upotrijebljeni u planiranju i provedbi preventivnih mjera protiv karijesa, uključujući i fluoridaciju, u ovom hrvatskom gradu.

layers would dissolve. With pH growing above 5.5 and available fluoride ions, remineralization of enamel and dentine would take place. Hydroxyapatite crystals with incorporated fluoride in remineralization process are less soluble than calcium hydroxyapatite (30).

The fluoride content in commercial beverages of some multinational companies differs among countries and depends on the fluorides concentration in the local water from which the drinks are made. For instance, the fluoride concentration in some beverages in Mexico is 0.49 ppm (in the range from 0.10 to 1.62 ppm) (31), which is significantly higher than in our study. Furthermore, we did not find any significant difference in fluoride concentration of carbonated soft drinks beverage in plastic bottle and tin, which is not in concordance with the results of the study in Mexico (31). Since the fluorides have high affinity towards glass and metals, it could be expected that their concentration would be lower in tin or glass bottle (32). The reason why we did not record any difference between carbonated soft drinks in plastic or tin lies probably in the fact that the differences in concentrations were very low and difficult to detect.

Higher fluoride concentration was found in carbonated mineral waters. One of them contained 1.5 ppm of fluorides which is a higher value than the one recommended in caries prevention. This fact can be taken into consideration when suggesting preventive measures in adult, high caries risk patients, but it should also be noted that excessive consumption of high fluoride content mineral water combined with increased input of fluorides from other sources may lead to dental fluorosis.

Somewhat higher fluoride concentration was found in ice teas. One product showed the value of 0.7 ppm. This concentration is close to the value recommended in caries prevention (1 ppm or 1 mg/L). Similar concentrations were found in some carbonated soft drinks of fruit flavor and some mineral waters and (0.7 – 0.9 ppm) (33). Fresh made tea or ice tea can have the concentration of fluorides from 0.5 – 4 mg/l, and the concentration is dependent on the place of growth of tea plants and the dipping time of tea leaves (34, 35).

The number of reports on fluoride content in foods and beverages has increased in the last few decades, as the reported increase in the prevalence of dental fluorosis together with the reduction in caries prevalence had been related to the community water fluoridation and fluoridated therapeutic products usage (3, 36). It has been reported that with 1 ppm fluoride in drinking water, 50% of subjects exhibit mild fluorosis. It has also been reported that the degree of fluorosis is directly dependent on the fluoride usage. Therefore, care should be taken to optimally fluoridate water, depending on oral hygiene habits of the population, especially children (30).

For that reason, in order to theoretically organize and implement effective caries preventive measures in a certain community, it is important to have a thorough knowledge about the ways of fluoride intake and its quantity, in order to get the optimal caries preventive effect of fluoride and avoid undesired consequences such as dental fluorosis (2, 36). A detailed study on population DMFT burden and oral hy-

giene habits is necessary to properly plan and implement additional fluoride sources as a part of public health measures, including water fluoridation and increased efforts in oral hygiene education.

The results of this study will provide information about the fluoride sources in different beverages. Together with the additional studies on fluoride intake by other sources, they can be used in planning and implementing caries preventive measures including fluoride supplements in this northern Croatian town.

## Zaključci

Koncentracija fluorida u vodovodnoj vodi bila je 0,3137 mg/L, a od komercijalno dostupnih napitaka su gazirane mineralne vode i ledeni čajevi imali najveće koncentracije fluorida (0,34 – 1,5 mg F/L i 0,06 – 0,74 mg F/L). U negaziranim vodama te u gaziranim i negaziranim sokovima koncentracije fluorida bile su jako niske (<0,01 mg F/L, 0,02 mg F/L i 0,06 – 0,15 mg F/L). Nizak pH sokova može zajedno s niskom koncentracijom fluorida djelovati vrlo kariogeno.

## Conclusion

Concentration of fluorides in tap water was 0.3137 mg/L; Of commercially available beverages, carbonated mineral waters and ice teas contained the highest level of fluorides: 0.34 – 1.5 mg F/L and 0.06 – 0.74 mg F/L respectively. In bottled noncarbonated waters, carbonated and non-carbonated juices, fluoride concentration was very low: below 0.01 mg F/L, 0.02 mg F/L and 0.06 – 0.15 mg F/L respectively. Soft drinks of low pH can, together with the low fluoride concentration, be very cariogenic.

### Abstract

**The aim** of this study was to measure the concentration of fluorides in tap water in northern Croatian town Čazma and commercially available bottled drinks. **Materials and Methods:** Fluoride content was assessed by fluoride-selective electrode in tap water and commercial drinks from public supply. The pH was assessed by hydrogen ion-selective electrode. **Results:** Fluoride content in tap water was 0.313 mg F/L. In commercially available bottled drinks fluoride concentration was the highest in carbonated mineral water (0.34 – 1.5 mg F/L), followed by some ice tea drinks (0.06 – 0.74 mg F/L). Non-carbonated waters, carbonated soft drinks and noncarbonated soft drinks had very low fluoride concentration and it amounted to <0.01 mg F/L, 0.02 mg F/L and 0.06 – 0.15 mg F/L, respectively. The pH in carbonated drinks was 2.36 – 2.68 and 3.08 – 3.64 in juices. **Conclusion:** Low concentration of fluorides in soft drinks and low pH in combination with added sugars could be cariogenic. The results obtained in this investigation could be used in planning preventive measures.

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### Key words

Carbonated Beverages; Mineral Waters;  
Tea; Fluorides; Water; Ion-Selective  
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