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Determination of Fluoride in Tap Water in Morocco using a Direct Electrochemical Method

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Abstract This study aimed to analyze the fluoride concentration in tap drinking water in different cities of Morocco using an electrochemical ion-selective method. Three samples were collected from each thirteen selected cities in the period between March and May 2011. The median value of fluoride was 0.94 mg/L (0.21–2.97). High fluoride concentrations (>0.8 mg/L) were found in sixteen cities. Very high values were found in phosphate regions such as Khouribga which is known to be an endemic dental fluorosis area. This study has shown that the concentration of fluoride in drinking water exceeds the limit especially in phosphate regions.

Keywords Tap water · Fluoride · Electrode · Morocco

Fluoride is an essential trace microelement for human health at low levels and is a potentially toxic element at higher levels. The adequate intake for fluoride from all sources is set at 0.05 mg/day/kg body weight; this intake is recommended for all ages greater than 6 months and in general, drinking water, beverages, dentifrices and other dental agents are regarded as the main dietary contributors to human fluoride intake (DRI 1997). Drinking water is typically the largest single contributor to daily fluoride intake (Murray et al. 1993). Smaller quantities in the order of 1.0 mg/L in ingested water are usually considered good to have a beneficial effect on the rate of occurrence dental carries, particularly among children (WHO 1997). Chronic exposure to high levels of fluoride has been associated to multiple health problems. Some are characterized by mineralization changes in skeletal deformities (Sarala Kumari et al. 1993; Krishnamachari et al. 1986). Along with it metabolic changes have been reported on soft tissues such as thyroid, reproductive organs, brain, liver and kidney (Raja-Reddy et al. 1979).

According to WHO (DRI 1997) permissible limit for fluoride in drinking water is 1.0 mg/L, whereas, USPHS (United States Public Health Service) has set a range of allowable concentrations for fluoride in drinking water for region depending on its climatic conditions because the amount of water consumed and consequently the amount of fluoride ingested being influenced by the air temperature (USPHS 1962). In Morocco, the climate is Mediterranean in the North and in some mountains (West of Atlas), which becomes more extreme towards the interior regions. In the south of Morocco, the climate is desert. With this climate, the Moroccan population tends to consume a large amount of water especially during the hot period. In Morocco, the concentration of fluoride in groundwater varies by region. In the plateau of Benguerir (center of Morocco), the fluoride concentration exceeds acceptable standards. Fluoride contamination in this region is attributed to the phosphate deposits that cause endemic fluorosis, which is widespread among the population supplied directly from wells (Haikel et al. 1989; Abdennebi et al. 1995). Concerning the fluoride content in drinking water, no large study has been conducted in Morocco. The majority of Moroccans consume tap water as a drinking water source.

Various methods, like direct potentiometry (Pavić et al. 1999; Van Staden et al. 1999; Conceição et al. 2008; Santos et al. 2007), gas chromatography (Pham et al. 1991), ion liquide chromatography (Lefler et al. 2011),

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atomic absorption spectrometry (Morés et al. 2011), titrimetry (Borissova et al. 1993) and UV/V is absorption spectrometry (Zolgharnein et al. 2009), were applied for the determination of fluoride in different matrix. The aim of this work was to determine the fluoride level in drinking water supplies of different cities in Morocco using a fluoride selective electrode.

Materials and Methods

All reagents were of analytical grade and all solutions were prepared using MilliQ water (Millipore, France). Commercial fluoride standard was purchased from Merck. A fluoride ion-selective electrode (Consort, Belgium) combined with Ag/AgCl reference electrode was used for all measurements. The potentials were recorded at room temperature with a microprocessor ionalyser (Istek, Korea).

Samples of drinking water were collected from thirteen cities of Morocco (Fig. 1) in the month of March, April and May, 2011. Three drinking water samples were collected from different localities of each city. Tap water samples of 500 ml each were collected (in triplicate) in clean fluoride polyethylene plastic bottles after water was allowed to run for at least 15 min. In order to determine if there were variations in fluoride concentrations during the day, water samples were obtained three times a day (8 h a.m, 12 and 6 h p.m). All samples were stored at 4 °C until they were analyzed.

Fluoride content in the samples of drinking water was determined directly after dilution with equal volumes of TISAB (Total Ionic Strength Adjustment Buffer). The composition of TISAB was as follows: 58 g of NaCl, 4 g of CDTA (Cyclohexylene diamine tetraacetic acid) and 57 ml of glacial acetic acid per liter and NaOH 5 M was added to obtain a pH of 5.2–5.4 (Singh et al. 2007). Calibration curve was frequently carried out with fresh fluoride standards of 0.2 up to 10 mg/L. A linear regression between pF^- concentration in standards and potential (mV) was constructed using the Microsoft Excel software and used to calculate the F^- concentration in each water sample. In our study, we have taken into account only calibration curves which had a slope more than 55 mV/decade and r^2 0.99. Repeatability was confirmed by corresponding coefficient of variation of 3.01 %. Recovery values of 97 % indicated adequate accuracy of the method. During

Fig. 1 Cities of sampling in Morocco

measurements, freshly prepared quality controls were used. High values of F^- were verified by ion chromatography.

All data were classified according to the fluoride concentration in mg/L in four groups: (1): from 0.01 to 0.30 mg/L (very low F^- concentration); (2): from 0.31 to 0.59 mg/L (low F^- concentration); (3): from 0.60 to 0.80 mg/L (optimum F^- concentration) and (4): above 0.81 mg/L (high F^- concentration).

Data are expressed as mean ± SD, median and interquartile range (25–75) or as a percentage. After testing for data normality (Kolmogorov–Smirnov test), the Student's *t* test was used for Gaussian data; however, the Mann-Witney and the Wilcoxon rank-sum test for non-Gaussian data. One-way analysis of variance, ANOVA and repeated measures ANOVA followed by Bonferroni's post hoc comparisons tests were used to obtain statistical analysis regarding the fluoride level in drinking water in differences groups. Differences were considered to be statistically significant if the p values were <0.05. All analyses were performed using the SPSS software version 13 for windows (SPSS, Inc., Chicago, IL, USA).

Results and Discussion

The study has concerned thirteen cities of Morocco. The population of all these cities corresponds to more than 70 % from the total population in the country. It can be estimated that this work covers drinking water of almost all inhabitants of the country. The median value of fluoride in drinking water was 0.94 mg/L (0.48–1.51) with 0.21 mg/L as a minimum and 2.97 mg/L as a maximum value which was found in Khouribga. Fluoride concentrations of each city were presented in Table 1. Four cities presented very low natural F^- concentration, whereas six showed low natural F^- concentration. Optimum F^- concentration was found in three cities and high F^- concentration in sixteen cities. These frequencies were given in Fig. 2. No variation in fluoride concentrations during the day was found ($p = 0.85$).

According to the Moroccan standard of drinking water quality, the upper limit of fluoride concentration is 0.7 mg/L (SNIMA 1991). Based on this reference, 60 % of analyzed samples were not compliant. However, this is not a fixed value but it tends to vary depending on local climate conditions and fluoride content in water and soil (USPHS 1962). The recommended level to help reduce tooth decay is 1 mg/L, while the minimum recommended value is 0.5 mg/L (DRI 1997). The WHO maximum guideline value of fluoride in drinking water is 1.5 mg/L; 23.3 % of analyzed samples had values above this limit.

The highest values of fluoride were found in phosphate regions, these values were significantly higher than those found in other regions ($p < 0.001$). Regions of Khouribga, Youssoufia, Bengrir, Safi and Eljadida are known to be rich in phosphates and the water in these regions usually exceeds the fluoride standards. This fluoride contamination is

Table 1 Fluoride concentration in drinking water

City	C (mg F/L)
Agadir	2.16 ± 0.05
Benguerir	2.91 ± 0.04
Beni mellal	0.84 ± 0.08
Casablanca	0.28 ± 0.07
El Jadida	1.19 ± 0.11
Errachidia	1.47 ± 0.14
Essaouira	2.43 ± 0.04
Fes	0.29 ± 0.09
Guelmim	1.08 ± 0.11
Kalaa seraghena	0.76 ± 0.12
Kenitra	0.57 ± 0.09
Khouribga	2.97 ± 0.05
Larach	0.43 ± 0.11
Marrakech	1.01 ± 0.14
Meknes	0.36 ± 0.05
Mohammedia	1.35 ± 0.09
Ouad zem	0.54 ± 0.06
Ouarzazate	0.98 ± 0.14
Rabat	0.27 ± 0.06
Safi	1.48 ± 0.15
Sale	0.27 ± 0.06
Settate	1.86 ± 0.06
Taddaret	0.93 ± 0.08
Tanger	0.68 ± 0.09
Tantan	2.15 ± 0.05
Taza	0.68 ± 0.14
Témara	0.38 ± 0.05
Tinjdad	1.01 ± 0.14
Tetouan	0.45 ± 0.07
Youssoufia	2.10 ± 0.03

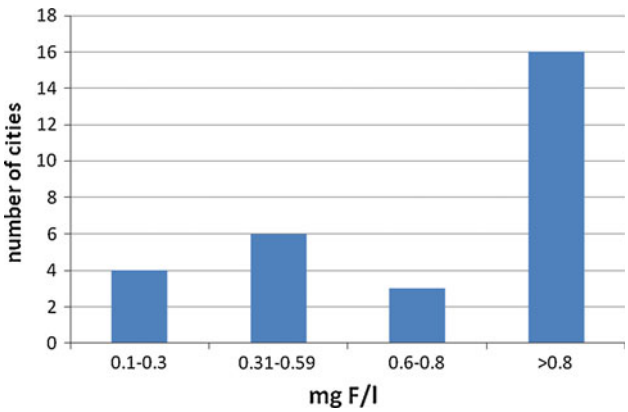

Fig. 2 Frequencies of fluoride concentration in tap water

attributed to the phosphate deposit (Tahaikt et al. 2007). Khouribga, where we found the highest value of fluoride (2.97 mg/L), is an endemic dental fluorosis area; this pathology is known as "Darmous" in Morocco (Benoit et al. 1973). Due to excessive fluoride intake, dental fluorosis is manifested as colored spot or horizontal streaks on dental enamel. The degree of dental fluorosis depends on the amount of fluoride exposure up to the age of 10 years (Denbesten et al. 2011). Skeletal fluorosis can also be observed after chronic exposition to high amounts of fluoride which can cause pain and damage to bones and joints.

If we consider that the adult daily water consumption is 2 L; the intake of fluoride, for a person weighing 70 kg, is 0.06 mg/kg/day in Youssofia, Tantan and Agadir; 0.07 mg/kg/day in Essaouira and 0.08 mg/kg/day in Khouribga and Bengrir; these values are superior to the safe threshold: 0.05 mg/kg/day (WHO 2011). In Tantan, which is an arid region, water consumption becomes more important, this leads to high ingestion of fluoride. In addition, tea and dates are widely consumed in this region and are considerable source of fluoride. Their fluoride content is about 2.9 mg/kg (Messaitfa et al. 2007), accordingly, they can contribute significantly to increase the amount of fluoride intake.

There are few publications about fluoride content in the drinking water in Morocco; but the National office for drinking water (ONEP Co) has made great efforts to remove fluoride from water (Tahaikt et al. 2007). High values of fluoride were found in water in the region Khouribga (Haikel et al. 1989) but no study covering the whole country regarding tap water has been yet published.

This study has shown that, if the concentration of fluoride in drinking water is optimal in several Moroccan cities, it exceeds the limit of fluoride concentration in phosphate regions exposing the inhabitants of these regions at high risk of fluorosis. More controls are needed in these areas to normalize the content of fluoride in drinking water and prevent fluorosis whose prevalence is estimated at 12.2 % among adults aged 35–44 in Morocco (Ministry of health Morocco 1999).

Potentiometric method using selective electrode seems to be very suitable to determine the concentration of F^- in water because it is simple, rapid end economical. It can be concluded that the fluoride content in drinking water in some region in Morocco is very high. The risk for a high prevalence of dental fluorosis is very likely in these areas due to the high fluoride content in the drinking water. This risk is increased in areas where water consumption is important.

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