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Analysis of the fluoride levels of well water and tea consumed by the Moroccan population in different rural areas

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ABSTRACT

Fluoride plays a fundamental part in human health. However, continued ingestion of excessive fluoride may cause significant negative health effects on people, ranging from mild dental fluorosis to crippling skeletal fluorosis, depending on the level and time of exposure to fluorides. In provincial areas, the presence of fluoride in well water may be due to natural factors or human activities. The reason for our work was to evaluate the level of tainting of groundwater by fluorides from various areas in Morocco situated in rural and agricultural areas, where the main wellspring of consumable water is well water, and the reasons for fluorosis in this area. The 44 samples were taken in seven Moroccan regions: Had Soualem-Berrechid, Kenitra, Fez, Tit Mellil, Sidi Slimane-Sidi Kacem-Zirara, Larache, and Brachoua, and 12 samples of tea were taken from different souks and commercials in Morocco. Fluoride dosing measurements in well water were performed using the potentiometric technique using the fluoride-specific ion electrode (HI-4110) at room temperature, while the determination of fluorine in tea is done by the spectrophotometric method. The results of fluoride levels revealed in different well waters from different regions range from 0.2 to 6.58 mg/l. For the green and black tea samples, the fluorine content varies between 0.48 and 1.60 mg/l for the 10 min infusion and between 0.93 and 2.7 mg/l for the 30 min infusion. These results make it possible to warn the population facing the risk of developing dental fluorosis by limiting the amount of fluoride ingested by the consumed foods.

1. Introduction

Fluoride is an essential element for the human body at a level of between 1.0 and 1.5 mg per day [1]. In low doses, fluoride is important for growth and the maintenance of bone tissue and teeth. It also poses a significant health risk if levels exceed health if levels exceed 1.5 mg/day [2]. Fluorides are found in the environment both naturally (through rock erosion and volcanic emissions) and as a result of certain human activities such as mining and rock phosphate processing, aluminum manufacturing, and water fluoridation [3–5]. Some foods naturally contain fluoride, such as table salt, tea, fish, spinach, and some mineral waters. Some foods, such as tea, are thought to be a significant source of fluoride exposure [6]. Several studies have highlighted different mechanisms by which fluoride disrupts the formation of enamel and leads to the formation of an unaesthetic porous enamel. Excessive fluoride consumption inhibits ameloblasts, changes absorption characteristics, and the surface properties of enamel crystals, resulting in unsightly porous enamel [7–9].

In Morocco, various studies have revealed the exposure of the population to groundwater in phosphate regions, which leads to the development of dental fluorosis. [10,11]. Few studies have been conducted at the level of food sources on fluoride toxicity in the Moroccan fluorides in the Moroccan population. In Morocco, the population is characterized by its very particular diet, marked by a high consumption of tea, in which fluoride is present with a remarkable content.

This study aims to highlight fluoride content in green and black teas and in well water consumed by the population located in

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seven rural Moroccan regions and to determine the risks of fluoride.

2. Materials and methods

2.1. Materials

Between September 2020 and February 2021, 44 samples were taken in 8 Moroccan regions (*P*1 to P44): Had Soualem-Berrechid, Kenitra, Fez, Tit Mellil, Sidi Slimane-Sidi Kacem-Zirara, Larache, and Brachoua (Table 1), and 12 samples of tea were taken from different souks and commercials in Morocco.(See Table 2.).

Table 1
Fluoride (mg/l) content of well water samples in the different regions.

Sample	Region	Location	Fluoride (mg/l)
P1	Had Soualem-Berrechid	Had Soualem	1.400
P2	Had Soualem-Berrechid	Had Soualem	6.580
P3	Had Soualem-Berrechid	Harcha	0.400
P4	Had Soualem-Berrechid	Ouled Bouziri	2.550
P5	Kenitra	Douar Bourhma	0.790
P6	Kenitra	Douar Bourhma	0.530
P7	Kenitra	Douar Bourhma	1.660
P8	Kenitra	Kenitra	0.530
P9	Kenitra	Kenitra	0.290
P10	Fez	Douar Bsais	0.730
P11	Fez	Douar Bsais	0.680
P12	Fez	Douar Chejeaa	0.450
P13	Fez	Douar Chejeaa	1.640
P14	Fez	Taaounyat Birda, Btamat Boujlafa	0.770
P15	Fez	Taaounyat Elfarah	0.970
P16	Fez	Taaounyat Ghalya	0.980
P17	Fez	Moulay Yacoub	0.850
P18	Fez	Moulay Yacoub	0.870
P19	Fez	Moulay Yacoub	0.090
P20	Fez	Moulay Yacoub	0.140
*P*21	Fez	Moulay Yacoub	0.180
P22	Tit Mellil	Tit Mellil	1.290
*P*23	Tit Mellil	Tit Mellil	1.470
P24	Tit Mellil	Tit Mellil	0.500
P25	Sidi Kacem-Sidi Slimane	Lkhawass	4.110
P26	Sidi Kacem-Sidi Slimane	Lkhawass	2.060
P27	Sidi Kacem-Sidi Slimane	Zirara	1.170
P28	Sidi Kacem-Sidi Slimane	Zirara	0.270
P29	Sidi Kacem-Sidi Slimane	Sidi Kacem	0.200
P30	Larache	Oulad Hamou Lghaba	0.750
*P*31	Larache	Oulad Hamou Lghaba	0.013
*P*32	Larache	Oulad Hamou Lghaba	0.004
P33	Larache	Oulad Hamou Lghaba	0.090
P34	Larache	Oulad Khssiss	0.200
P35	Brachoua	Enakhlat	0.650
P36	Brachoua	Enakhlat	0.790
P37	Brachoua	Enakhlat	0.330
P38	Brachoua	Enakhlat	0.460
P39	Brachoua	Brachoua	0.870
P40	Brachoua	Brachoua	0.270
P41	Temara	Jammat sbah, wladhbri	0.240
P42	Temara	Jammat sbah, wladhbri	0.250
P43	Temara	Jammat sbah, oulad mssoun rkhokha	0.220
P44	Temara	Jammat sbah, oulad mssoun rkhokha	0.040

Table 2
Fluoride level in green and black teas (10 and 30 mintes of infusion).

Sample	Nature	F^- mg/l (preparation 10 min)	F- mg/l (preparation 30 min)
1	Green tea	0.92	2.70
2	Green tea	1.17	2.20
3	Green tea	0.80	0.93
4	Green tea	1.40	1.93
5	Green tea	1.62	2.40
6	Green tea	0.50	1.94
7	Green tea	1.28	1.50
8	Green tea	0.69	2.55
9	Black tea	1.09	1.37
10	Black tea	1.26	1.75
11	Black tea	0.48	1.35
12	Black tea	1.26	1.36

2.2. Methods

Fluoride dosing has been made utilizing the potentiometric technique using the Fluoride specific ion electrode (HI-4110) at room temperature. HI-4110 is an ISE fluoride combination ideal for detecting free fluoride in drinking water, soft drinks, wine, plants, emulsion food products, and electrodeposition acids. The HI-4110 allows accurate measurement of the total concentration of fluoride.

The levels of fluoride in tea extracts (in duplicate tests) are determined by the Belcher-West colorimetric method with Alizarin complexone in polyethylene tubes [12]. In the presence of Alizarin complexone, lanthanum nitrate gives a red coloration in an aqueous medium. In the presence of F-anion, a blue-colored complex is formed. The new complex is soluble in acetone and was determined by spectrophotometry at 618 nm. The absorbance of the samples is subtracted from that of a control in which the tea extract is replaced by distilled water. The fluoride concentration of the samples is calculated by analysis against the calibration curve.

3. Results and discussion

Fluoride levels in well waters *P*2, *P*4 in Had Soualem-Berrechid, P7 in Kenitra, and P26 in Sidi Kacem exceed the WHO standard of less than 1.5 mg/day [1]. The *P*2 well water sampled from the rural region of Had Soualem had the highest fluoride value, with a fluoride content of 6.58 mg/l, making it the probable cause of dental fluorosis in this area. We suspected that the high fluoride level in this well water was due to pollution from an aluminum plant in the region, but an analysis of the discharged water from this plant revealed a fluoride value of 1.04 mg/l, proving that the plant is not responsible for the naturally high fluoride level in this well (Table 1). Barbier's research revealed that the naturally occurring presence of fluoride in the water table could be attributed to anthropogenic and industrial contaminations or geological inputs [13].

Well P13, which is located in the region of Fez, exceeds the standards set by the WHO, with a value of 1.64 mg/l. This region is known to be an agricultural area, and this well is located on agri-

cultural land where the use of pesticides is excessive (Table 1). According to the study by Naamane A., who conducted a survey on the use of pesticides in a Moroccan region, he found that all the farmers who participated in the survey used pesticides [14]. Perhaps it is the use of fluorinated pesticides that seep into the soil and contaminate it, increasing the level of fluoride in the water of these wells [15].

In the regions of Sidi Kacem and Sidi Slimane (khawass), it has been observed that a large number of the population suffer from dental fluorosis to different degrees; this is explained by the presence of a well in the region, in which fluorine reaches 4.11 mg/l (Table 1). This value, which exceeds the norms set by the WHO, confirms that water is the probable factor that causes dental fluorosis in this region.

There are many factors responsible for the high or low fluoride concentration in well water, such as rain precipitation. Fluoride concentrations for the two seasons were significantly different from each other [16]. A group of samples was taken during the winter season and on rainy days, so the fluoride value in these wells may be much higher if they were taken during non-rainy seasons. Another factor affecting fluoride concentration is the depth of the well. In a study by Y. E. Ibrahim, it was shown that the water in the deepest well (45 m) had a low and very stable fluoride concentration of 0.25 ppm, while the deepest well (93 m) had a tenfold higher and slightly variable fluoride concentration (2.56 ppm) [17].

The excess fluoride in these waters can be removed by using the waste mud. Indeed, the results of the study by Baris Kemer et al. demonstrated the effectiveness and feasibility of waste mud (original, acid-activated, and precipitated) for the removal of fluoride ions from an aqueous solution [18].

Another study conducted by Venkataraman Sivasankar et al. demonstrated the potential for defluoridation of water by disposed earthenware (DWE). The DWE with dispersed manganese dioxide showed an ability to lower the fluoride concentration to acceptable levels and improved the defluoridation efficiency of unmodified DEW [19].

Wells in rural areas of Tit Mellil, Larache, Brachoua, and Temara do not exceed the WHO standards, indicating that water is not the main source that causes dental fluorosis in these areas. We suspect that the dental fluorosis in these areas depends on the diet of the population and other factors (Table 1).

Fluoride levels revealed during 30-minute brewing times are higher than those of 10 min. After a 30-minute infusion, fluoride levels reach values of 2.7 mg/l (green teas) and 1.75 mg/l (black teas). These results are similar to previous studies citing values of 0.32 to 4.54 mg of fluoride per liter of brewed black tea [20], and 0.57 to 3.72 mg/l of black tea brewed for 5 min [21].

The fluoride content of tea and the consumption pattern of the population reveal risks of fluoride toxicity and dental fluorosis. This risk is even higher according to dietary habits and customs. The results observed in a family preparation are likely to increase in large tea consumers with variations in the quantity of tea granules used and the boiling time.

Fluorosis does not depend on a single factor but the bioaccumulation of several factors, such as the consumption of fluoridated water and other foods, mainly tea.

4. Conclusion

The use of groundwater for agricultural and human consumption may be restricted by the presence of fluorides in this water. They pose risks to human health at high concentrations, including dental and bone fluorosis. Fluoride pollution from natural or human sources, like industrial or agricultural by the use of fluorinated pesticides, may be the cause of the high concentrations seen in well water in several Moroccan regions. Aquifer mineralogy research is required to determine the depths of lithological facies with significant fluoride content. To encourage the growth of the localized population in rural areas, it is crucial to be aware of the significance of water supply, sanitation, and personal hygiene.

In the regions where the level of fluoride is below the recommendation of the WHO, we suspect that the prevalence of dental fluorosis in these regions is influenced by other factors as well as the local diets, mainly tea.

Fluoride levels vary according to the type of tea consumed by the population, the quantity, and the duration of consumption. The fluoride content of boiled teas is higher than that of teas brewed for 30 or 10 min. Three types of green tea and one black tea have fluoride levels above the recommended standards. Fluoride levels in tea preparation water taken from well water are higher than in urban sewage water. Dietary habits and living in rural areas could induce involuntary overconsumption of fluoride and, consequently, an increase in the prevalence of dental fluorosis.

Fluorinated food consumption should be monitored in children (before the age of six) in order to limit fluorinated food consumption.

CRediT authorship contribution statement

Issam Essebbahi: Methodology, Resources, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Chadia Ouazzani:** Methodology, Supervision, Resources, Validation, Writing – review & editing, Project administration. **Abdellah Moustaghfir:** Validation, Writing – review & editing. **Azzeddine Er-ramly:** Validation, Writing – review & editing. **Youssef El Baroudi:** Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Abdallah Dami:** Supervision, Validation, Writing – review & editing. **Lhoussine Balouch:** Supervision, Validation, Writing – review & editing.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] World Health Organization. Guidelines for drinking-water quality (Fourthedition), Fluroride. 2011; 12.1: 371-373

[2] World Health Organization. Exposure to inadequate or excess fluoride: A major public health concern, 2019;https://apps.who.int/iris/bitstream/handle/10665/329484/WHO-CED-PHE-EPE19.4.5-eng.pdf?ua=1.

[3] M.E. Kaseva, Contribution of trona (magadi) into excessive fluorosis a case study in Majiya Chai ward, northern Tanzania, Sci. Total. Environ. 366 (1) (2006) 92–100, https://doi.org/10.1016/j.scitotenv.2005.08.049.

[4] R.N. Janardhana, Prevalence of fluorosis in the fluoride enriched groundwater in semi-arid parts of eastern India: geochemistry and health implications, Quat. Int. 443 (B) (2017) 265–278, https://doi.org/10.1016/j.quaint.2016.05.028.

[5] C. Anirban, K.A. Mrinal, M. Arnab, D. Prasanta, D. Debasis, Critical review on geochemical and geological aspects of fluoride belts, fluorosis and natural materials and other sources for alternatives to fluoride exposure, J. Hydrol. 574 (2019) 333–359, https://doi.org/10.1016/j.jhydrol.2019.04.033.

[6] K. Alenka, T. Gašper, P.S. Maja, Fluoride in teas of different types and forms and the exposure of humans to fluoride with tea and diet, Food Chem. 130 (2) (2012) 286–290, https://doi.org/10.1016/j.foodchem.2011.07.037.
[7] K. Tanimoto, T. Le, L. Zhu, J. Chen, J.D.B. Featherstone, W. Li, P. DenBesten, Effects of fluoride on the interactions between amelogenin and apatite crystals, J. Dent. Res. 87 (1) (2008) 39–44, https://doi.org/10.1177/154405910808700106.
[8] A.L.J.J. Bronckers, D.M. Lyaruu, P.K. DenBesten, The impact of fluoride on ameloblasts and the mechanisms of enamel fluorosis, J. Dent. Res. 88 (10) (2009) 877–893, https://doi.org/10.1177/0022034509343280.
[9] P. Chandna, N. Srivastava, S. Ali, Remineralizing agents: the next frontier, Curr. Clin. Pharmacol. 11 (3) (2016) 211–220, https://doi.org/10.2174/1574884711666160607084813.
[10] M. Mountadar, H. Garmes, A. Bouraji, K. Yousrani, Contamination des eaux souterraines et des sols par tes fluorures et leur impact à proximité des mines et d'usines d'exploitation des phosphates (Maroc), J. Eur. Hydrol. 5 (1) (2010) 61–69, https://doi.org/10.1051/asees/20000501061.
[11] R. El Jaouadi, M. Ait El Cadi, Y. Bouslimane, M. Fekhaoui, A. Bouklouze, Y. Cherrah, Teneur en fluorures des eaux de puits des régions rurales au Maroc, Trop. Dent. J. 37 (146) (2014) 42–48.
[12] H. Tsunoda, M.H. Yu, Selected Papers from the 14th Conference of the International Society for Fluoride Research, Fluoride Research, Japan, 1985, pp. P3–P.
[13] Barbier J. L'origine du fluor dans l'eau des sources de France. European Journal of Water Quality - J. Eur. Hydrol., Cahiers de l'ASEES 2012 ;17:7–16. DOI: https://doi.org/10.1051/asees/2012003
[14] Naamane A., Enquête sur l'utilisation des engrais et pesticides chez les agriculteurs de la région de Casablanca-Settat | Revue Marocaine des Sciences Agronomiques et Vétérinaires (agrimaroc.org), 2020. 8 (3) : 279-85
[15] D.A.M. Alexandrino, C. Marisa, R. Almeida, A.P. Mucha, M.F. Carvalho, Revisiting pesticide pollution: the case of fluorinated pesticides, Environ. Pollut. 292 (1) (2022), https://doi.org/10.1016/j.envpol.2021.118315.
[16] M. Kwm, M. Wrl, E.A. Fabiano, study of fluoridegroundwater occurence in Nathenje, Lilongwe, Malawi, Phys. Chem. Earth 32 (2007) 1178–1184, https://doi.org/10.1016/j.pce.2007.07.050.
[17] Y.E. Ibrahim, A.H. Abuaffan, K. Bjorvatn, Prevalence of dental fluorosis in Sudanese children from two villages with 0.25 and 2.56-ppm fluoride in the drinking water, Int. J. Paediatr. Dent. 5 (4) (1995) 223–229, https://doi.org/10.1111/j.1365-263x.1995.tb00183.x.
[18] B. Kemer, D. Ozdes, A. Gundogdu, V.N. Bulut, C. Duran, M. Soylak, Removal of fluoride ions from aqueous solution by waste mud, J. Hazard. Mater. 168 (2–3) (2009) 888–894, https://doi.org/10.1016/j.jhazmat.2009.02.109.
[19] V. Sivasankar, T. Ramachandramoorthy, A. Darchen, Manganese dioxide improves the efficiency of earthenware in fluoride removal from drinking water, Desalination 272 (1–3) (2011) 179–186, https://doi.org/10.1016/j.desal.2011.01.021.
[20] E. Malinowska, I. Inkielewicz, W. Czarnowski, P. Szefer, Assessment of fluoride concentration and daily intake by human from tea and herbal infusions, Food Chem. Toxicol. 46 (3) (2008) 1055–1061, https://doi.org/10.1016/j.fct.2007.10.039.
[21] E. Emekli-Alturfan, A. Yarat, S. Akyuz, Fluoride levels in various black tea, herbal and fruit infusions consumed in Turkey, Food Chem. Toxicol. 47 (7) (2009) 1495–1498, https://doi.org/10.1016/j.fct.2009.03.036.