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Article

FOOD CHEMICAL CONTAMINANTS

Monitoring of Fluoride Content in Drinking Water by Ion Chromatography: A Case Study in the Suzhou Urban Area, China

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Abstract

Background: Both deficient and excessive intake of fluoride can lead to adverse health problems.
Objective: The aim of this study is to investigate the fluoride content in three types of drinking water in Suzhou urban area.
Method: Ion chromatography was employed to conduct the validation of analysis of fluoride ion in water and the method was applied to analyze the concentration of fluoride in 22 drinking water samples, including tap water, purified water, and commercially available bottled water, collected from five municipal districts of Suzhou urban area.
Results: The method was validated in the range of 0.05–2.00 mg/L with good repeatability and accuracy. Results of water analysis indicated that fluoride content in tap water ranged from 0.267 to 0.336 mg/L (average 0.304 mg/L), and the levels of fluoride in purified water and bottled water were 0.068–0.317 mg/L (average 0.134 mg/L) and 0–0.120 mg/L (average 0.080 mg/L), respectively.
Conclusions: The amount of fluoride in all samples analyzed were lower than the limit set for fluoride in drinking water according to the China standard (1.0 mg/L). Low fluoride exposure for the population in the studied area was observed, and the replacement of tap water with purified and bottled water could further aggravate the deficiency of fluoride intake for local residents.
Highlights: The present study is the first to characterize the fluoride content in these three types of drinking water in Suzhou urban area by ion chromatography.

Fluoride is an indispensable micronutrient for the human body, especially for the maintenance of teeth and bone health (1). Fluoride enters the body through drinking water, food uptake, and inhalation (2) and the most important route is drinking water, with a rate of 75% (3). Lower or higher than standard level of fluoride intake can lead to adverse health effects, including tooth decay when exposed to fluoride in drinking water with low concentrations of less than 0.5 mg/L (4, 5), fluorosis in long-term use of drinking water containing fluoride when concentration is higher than 1.5 mg/L, and other health problems such as digestive disorders, hypertension, infertility, Alzheimer's, thyroid disease, neurological problems, arthritis, which have been reported in related with chronically excessive fluoride intake (6–11). High levels of fluoride in drinking water exist in many parts of the world, especially in some regions of South Africa, America, India, Iran, and China (12–16). The monitoring of fluoride content in drinking water is a key factor in preventing negative health consequences. To protect human health, the maximum permissible limits of fluoride in drinking water established by the World Health Organization (WHO) and the Standardization Administration of China are 1.5 and 1.0 mg/L, respectively (17).

Suzhou is one of the developed areas in China with surface water as its main water source, which has significantly different hydrogeological conditions from other reported areas (18, 19). Moreover, one prevalent trend in recent years in various

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countries, including China, is the utilization of purifier devices to remove harmful chemicals in drinking water, such as lead ion, arsenic ion, and nitrate ion (20). Another trend among consumers is the replacement of their daily water with bottled water, possibly due to apprehension about contaminants in natural water supplies (21, 22). Therefore, this research determined to study the fluoride content in three types of drinking water, including terminal tap water samples collected from five municipal districts, purified tap water samples obtained from home water purification system in these areas, and four of the most popular domestically produced bottled waters of different brands collected from local stores. To the best of the researchers' knowledge, this present study was the first to characterize the fluoride content in these three types of drinking water in Suzhou urban area by ion chromatography (IC). The results of this study could provide scientific and useful information of fluoride content in drinking water for consumers in these areas.

Experimental

Area Studied

This study was carried out in Jiangsu province, Suzhou city, in 2020. Suzhou is located in the southeast of China. According to the latest census, the population in this city is 10 459 890 (city: 7 329 514, village: 3 130 376). The city has six municipal districts, which are Gusu district, Xiangcheng district, Suzhou new district (SND), Suzhou industrial park (SIP), Wuzhong district, and Wujiang district. The main water source of this city is surface water from Tai Lake and the drinking water for residents in these six districts is supplied from five main water sources, including Xujiang, Xiangcheng, Baiyangwan, Wuzhong, and SND water works. The water for both Gusu and Xiangcheng districts is supplied from Xiangcheng water works. Three different collection sites of terminal tap water provided from each water works were selected randomly, so that water samples collected from five municipal districts, not including Xiangcheng district, were analyzed. The studied area is shown in Figure 1.

Instruments and Chemicals

Stock fluoride standard 1000 mg F^-/L was obtained from National Nonferrous Metal and Electronic Materials Analysis and Testing Center (Beijing, China). Sodium hydroxide, sodium carbonate, and sodium bicarbonate with guaranteed reagent (GR) grade were all purchased from Aladdin (Shanghai, China) and used as supplied.

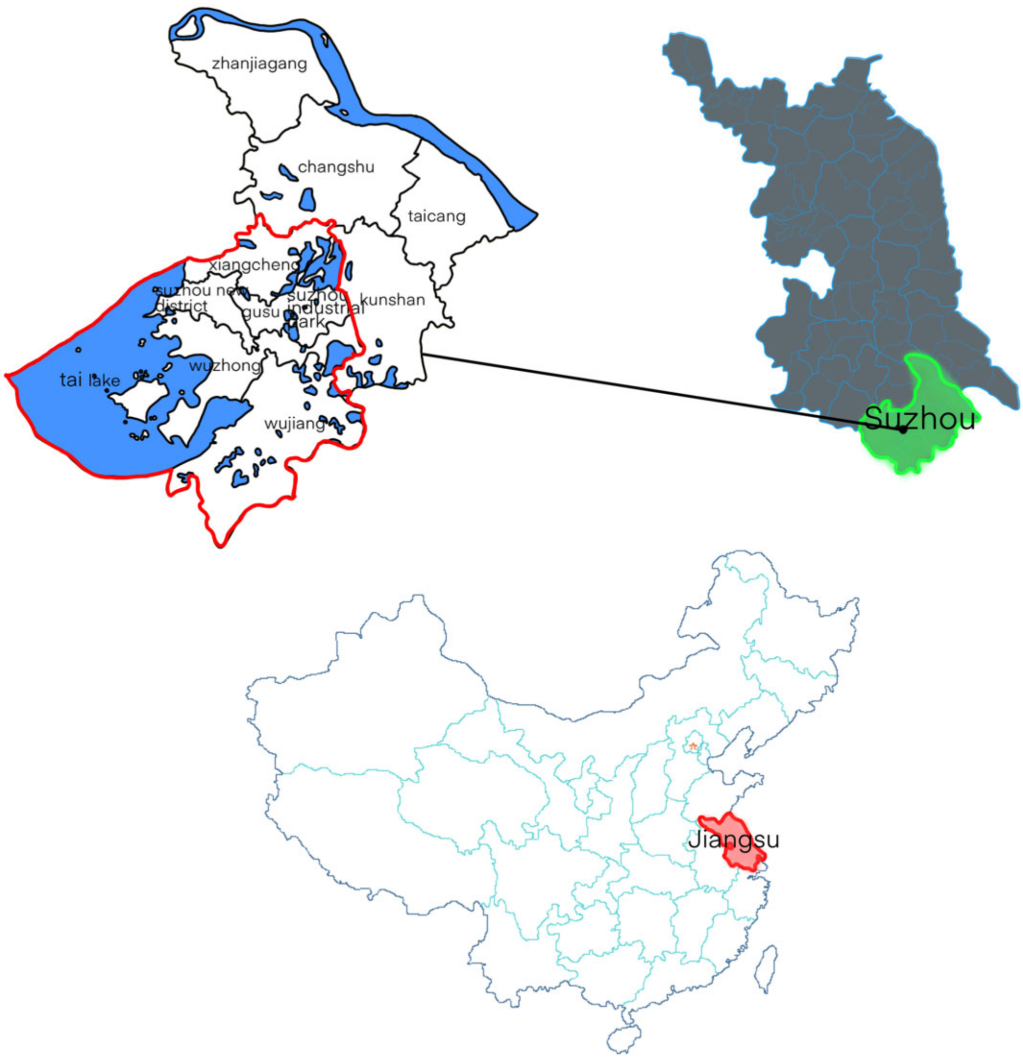

Figure 1. A view of the studied area.

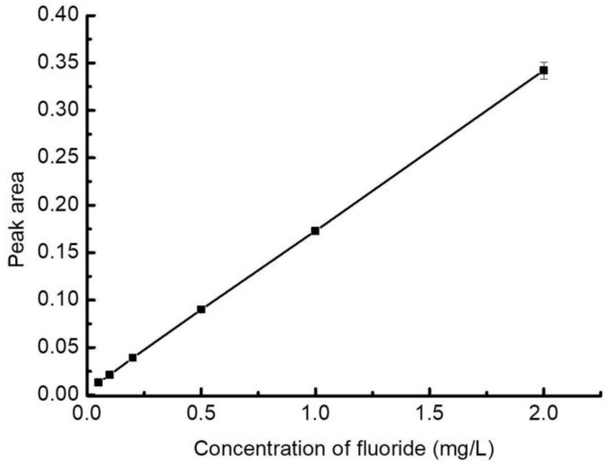

Figure 2. The calibration curve in the range of 0.05 to 2.00 mg/L fluorides in water (replicates: 3).

Table 1. The results of precision of fluoride analysis

Sample of 1.00 mg/L F⁻, No.	Determined value, mg/L	Mean, mg/L	SD, mg/L	RSD, %
1	0.941	0.945	0.019	1.96
2	0.968			
3	0.924			
4	0.966			
5	0.928			
6	0.944			

Sample Collection

Fifteen tap water and three purified tap water sites were selected randomly in thefive districts. All tap water and purified water samples were collected in sterile 50 mL polyethylene terephthalate (PET) tubes according to the standard method (23), and then transported to the laboratory. Based on a questionnaire survey, the four most popular domestically produced bottled waters under different brands were collected from local stores. Three of the waters are labeled "mineral water" and one is named "pure water". The bottled water samples were stored in their original closed containers with plastic screwcaps until the actual analysis. After sampling, they were preserved in standard conditions (24). All collected water samples were colorless, odorless, and no particulate presented. Prior to measurement, each water sample was shaken, and then 10 mL aliquots were filtered through a 0.45 μm filter membrane.

Preparation of Standard Solution

The stock fluoride standard solution of 1000 mg/L was firstly diluted with ultrapure water (the conductivity is 15.2 μs/cm) to give an intermediate solution (50 mg/L) in a 100 mL volumetric flask. Then, the intermediate solution was further diluted to give working standard solutions of 0.05, 0.1, 0.2, 0.5, 1.0, and 2.0 mg/L (25).

Fluoride Determination

The fluoride ion in water samples and standard solutions was determined by IC (ECO-IC, Vantone, Swiss), equipped with a suppressed conductivity detector (MSM-A Rotor A 6.2832.000). An anion analytical column (Metrosep A supp 5–150/4.0) was employed for analysis at 25°C. The mobile phase was 3.2 mmol/L of sodium carbonate with 1 mmol/L of sodium hydrogen carbonate. Run time was set as 7 min per injection. The sample volume injected was 25 μL, and the flow rate was 0.7 mL/min, with the column pressure 7.55 MPa (26). The quantification was measured through the peak height or area. All samples were measured in triplicate.

Results and Discussion

Reliability of the Method

Standard curve.—The method was calibrated by a series of standard fluoride solutions with different concentrations. The settings for the chromatograph are listed in *Fluoride Determination*. Six standard fluoride samples with concentrations between 0.05 and 2.00 mg/L were measured in triplicate and the mean values were used to construct the standard curve. The linear relationships of the obtained data are shown in Figure 2 and the linear regression was done from the peak area (μs/cm·min) and concentration (mg/L). The equation for linear regression is

$$y = 0.169x + 0.00474$$

and the linear correlation coefficient R^2 is 0.9999.

The LOD was expressed as the equation

$$LOD = 3.3\sigma/S$$

where σ = residual SD of the intercept and S = slope of the calibration curve. The LOD for determining fluorides in this method was 0.013 mg/L.

The LOQ was calculated as:

$$QL = 10 \cdot \sigma/S$$

where σ = residual SD of the intercept and S = slope of the calibration curve. The LOQ for determining fluorides in this method was 0.039 mg/L.

Repeatability.—To evaluate the precision of fluoride determination, the repeatability of this method was investigated by measuring six standard solutions with a concentration 1.00 mg/L (the permission level in drinking water of the Bureau of China standards) under the selected experimental conditions, as exhibited in Table 1. The analyses of these six solutions were executed by the same analyst using the same apparatus in the same laboratory within 1 day. The RSD was calculated as 1.93%.

Recovery.—The recovery was investigated to evaluate the accuracy of fluoride determination. Three randomly selected water samples were spiked at one concentration level of fluoride (1.00 mg/L, the permission level of fluoride in drinking water of the Standardization Administration of China) before treatment by filtration membrane. The samples were measured in triplicate and the average values of fluoride ion determined in the three original water samples were used as the initial concentration of fluoride. The percentage recovery values were calculated by comparing fluoride concentration obtained from the spiked samples with the actual added fluoride concentrations. As presented in Table 2, the percentage recovery values were in the range of 95.3–97.2%, indicating the reliability of our method.

Table 2. The results of measured spiked samples

Sample of tap water, No.	Initial F⁻ concm, mg/L	Added F⁻ concn, mg/L	Total F⁻ concn determined, mg/L	Recovery, %
8	0.316 ± 0.010	1.00	1.270	96.5
10	0.307 ± 0.013	1.00	1.246	95.3
12	0.292 ± 0.011	1.00	1.257	97.2

Table 3. Fluoride content in tap waters

Sample No.	Sample source	Content of fluoride, mean ± SD, mg/L	RSD, %
1	Tap water (SIP)	0.314 ± 0.013	4.14
2	Tap water (SIP)	0.317 ± 0.012	3.79
3	Tap water (SIP)	0.329 ± 0.007	2.13
4	Tap water (SND)	0.302 ± 0.015	4.97
5	Tap water (SND)	0.305 ± 0.008	2.62
6	Tap water (SND)	0.336 ± 0.011	3.27
7	Tap water (Wuzhong District)	0.311 ± 0.010	3.22
8	Tap water (Wuzhong District)	0.316 ± 0.010	3.16
9	Tap water (Wuzhong District)	0.267 ± 0.005	1.87
10	Tap water (Wujiang District)	0.307 ± 0.013	4.23
11	Tap water (Wujiang District)	0.312 ± 0.008	2.56
12	Tap water (Wujiang District)	0.292 ± 0.011	3.77
13	Tap water (Gusu District)	0.284 ± 0.009	3.17
14	Tap water (Gusu District)	0.287 ± 0.013	4.53
15	Tap water (Gusu District)	0.284 ± 0.005	1.76

Water sample analysis.—Fluoride contents in all collected water samples were investigated by this validated IC method. Each sample was measured in triplicate. The determined values are presented as the mean ± SD (mg/L) as exhibited in Tables 3 and 4.

The fluoride content in tap water samples (No. 1–15) ranged from 0.267 to 0.336 mg/L. The average of samples was calculated as 0.304 mg/L, and the SD was 0.019 mg/L. Among them, water sample No. 9 containing the lowest concentration of fluoride was collected from Wuzhong district, and No. 6 with the highest value was collected from SND. According to the values determined, the concentration levels of fluoride in tap water of these five districts from high to low are: SIP 0.320 (± 0.008); SND 0.314 (± 0.019); Wujiang district 0.304 (± 0.010); Wuzhong district 0.298 (± 0.027); and Gusu district 0.285 (± 0.017) mg/L. In conclusion, all tap water samples from the studied area are lower than the permission level of fluoride in drinking water of the Standardization Administration of China (1.0 mg/L). The results of this study were compared with studies conducted in other parts of the world. According to the study of Zhang et al. (27 fluoride content in tap drinking water of 29 provinces of China was determined as 0.10–2.14 mg/L, in which the level of fluoride in Jiangsu province was measured as 0.19–3.04 mg/L. The tap water fluoride in the present study (0.267 to 0.336 mg/L) was in this reported range, which shows consistency in results. In another study, the level of fluoride in deep and shallow well water of Chiang Mai city, Thailand, was measured as 2.21 (±3.17) and 0.65 (±0.76) mg/L, respectively, which was higher than the obtained result in this study (28). Similarly, the pooled level of fluoride in Iranian drinking water was reported as 0.51 mg/L, higher than Suzhou urban area (12). Biglari et al. (29) investigated the groundwater fluoride in Sistan and Baluchistan

Table 4. Fluoride content in purified waters and bottled waters

Sample No.	Sample source	Content of fluoride, mean±SD, mg/L	RSD, %
16	Purified water (purifier 1)	0.068 ± 0.003	4.41
17	Purified water (purifier 2)	0.017 ± 0.002	11.76
18	Purified water (purifier 3)	0.317 ± 0.013	4.10
19	Bottled mineral water (Brand: Dongting mountain)	0.120 ± 0.005	4.17
20	Bottled mineral water (Brand: Nongfu spring)	0.041 ± 0.0015	3.66
21	Bottled pure water (Brand: C'estbon)	ND[a]	
22	Bottled mineral water (Brand: Master Kong)	ND	

[a]ND = Not detected.

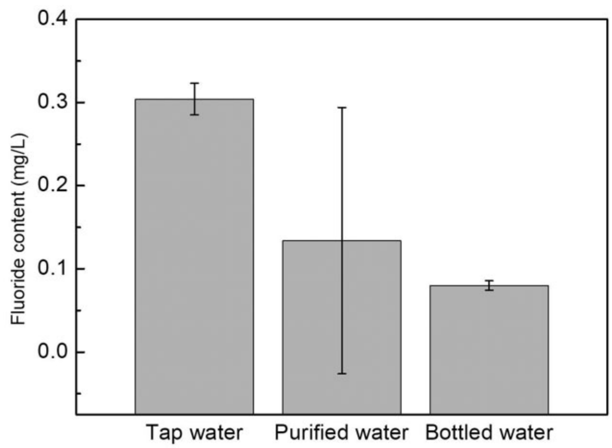

Figure 3. The distribution of the sample population related to their fluoride level.

provinces, Iran. The obtained results showed many changes of fluoride concentration in groundwater, from 0.125 to 1.71 mg/L, which exhibited a relatively larger difference of fluoride amount in groundwater due to hydrological conditions, compared with samples taken from the drinking water distribution network in this study.

Samples 16–18 were purified water collected from home water purification systems of different brand names, which are denoted as purifier 1, 2, 3, as shown in Table 4. The determined concentration levels of fluoride was 0.068–0.317 mg/L, and the average was 0.134 (± 0.160) mg/L. As compared to tap water, the fluoride content decreased significantly in purified water samples 16 and 17, whereas no obvious change was observed in 18. A large difference in fluoride concentration among purified water samples was observed, which indicates that some purifier devices removed most fluoride ions, whereas others tended to retain the original fluoride ion in water as a result of the utilization of different purification principles by home purifiers (30). The obtained results were consistent with the study of Eftekhar et al. (20) in 2015. They evaluated the effectiveness of six domestic brands of home water purification systems in Iran on the amount of fluoride in drinking water and the fluoride concentration was significantly decreased after using purifier devices (20).

Since bottled water is frequently used as an alternative source of drinking water, it has gradually become another important source of fluoride (21, 22). The concentrations of fluoride in the four most popular domestically produced bottled waters in the local area were analyzed. Among them, the fluoride levels in samples 21 and 22 were too low to be determined, and the fluoride contents in samples 19 and 20 were 0.120 and 0.041 mg/L, respectively. The levels of fluoride in bottled water in this study were 0–0.120 mg/L, and the mean value of fluoride content in the other two bottled water samples was 0.080 (± 0.056) mg/L. Similarly, Ghaderpoori et al. studied fluoride levels in 10 brands of bottled water sold in Sanandaj city, Iran by IC. The results showed that the amount of fluoride ranged from 0.04 to 0.32 mg/L (31). In a study by Amanlou et al. (32), 18 commercial brands of bottled water in Iran were investigated and fluoride concentration was in the range of 0.039–0.628 mg/L. According to another study reported by Ahmad et al. (33) they evaluated the bottled water and tap water in Yanbu city, Saudi Arabia. The determined fluoride content in 14 brands of bottled water was in range of 0.06–1.2 mg/L, with no significant difference between bottled water and tap water. As compared with studies in other countries, it is noted that the measured amount of fluoride in bottled water in the present study was lower than those studies conducted in parts of Iran and Saudi Arabia. Furthermore, the loss of fluoride in domestic bottled water was significant compared with local tap water.

Despite the fact that purified water and bottled water are usually considered as safer and healthier drink than tap water, the levels of fluoride in all three types of drinking water were carefully monitored. The distribution of the sample population related to their fluoride level is exhibited in Figure 3. According to the obtained results, all measured values are lower than both the WHO and China standard, which indicates that drinking water in the studied area is of good quality and poses no threat of fluorosis. Nevertheless, the World Health Organization recommends the concentration of 0.5–1.0 mg/L to prevent tooth decay (17). Hence, adding fluoride to public drinking water is suggested to prevent the risk of dental cavity increases in people (34). Furthermore, local residents should elevate fluoride intake by using fluoride supplements, such as toothpaste and tea drinks containing fluoride (35).

Conclusions

In this study, the results of validation exhibited high sensitivity, good precision, and accuracy of the implemented IC method, which indicates the reliability of determined fluoride concentrations. The fluoride levels measured in these three types of drinking water in Suzhou urban area were in the order of tap water > purified water > bottled water. All water samples were lower than the China standard (1.0 mg/L), but no sample analyzed exceeded the recommended lower limiting set by the WHO (0.5 mg/L). Based on these results, a low fluoride exposure for the population in the studied area can be observed, and the replacement of tap water with purified and bottled water could further aggravate the deficiency of fluoride intake for local residents. Therefore, continuous monitoring is necessary to guarantee safe drinking water and further investigations on water samples from more collection points and other sources of drinking water are highly recommended.

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Conflict of Interest

The authors declare that there is no conflict of interest.

References

1. Azami-Aghdash, S., Ghojazadeh, M., Pournaghi Azar, F., Naghavi-Behzad, M., Mahmoudi, M., & Jamali, Z. (2013) *J. Dent. Res. Dent. Clin. Dent. Prospects* **7**, 1–7
2. Dobaradaran, S., Fazelinia, F., Mahvi, A.H., & Hosseini, S.S. (2009) *Fluoride* **42**, 228–232
3. Battaleb-Looie, S., Moore, F., Malde, M.K., & Jacks, G. (2013) *J. Food Compos. Anal.* **29**, 94–99
4. Rahmani, A., Rahmani, K., Dobaradaran, S., Mahvi, A.H., Mohamadjani, R., & Rahmani, H. (2010) *Fluoride* **43**, 179–186
5. Yousefi, M., Ghoochani, M., & Mahvi, A.H. (2018) *Ecotoxicol. Environ. Saf.* **148**, 426–430
6. Kheradpisheh, Z., Mirzaei, M., Mahvi, A.H., Mokhtari, M., Azizi, R., Fallahzadeh, H., & Ehrampoush, M.H. (2018) *Sci. Rep.* **8**, 2674–2680
7. Dobaradaran, S., Mahvi, A.H., Dehdashti, S., Dobaradaran, S., & Shoara, R. (2009) *Fluoride* **42**, 50–53
8. Mohammadi, A.A., Yousefi, M., Yaseri, M., Jalilzadeh, M., & Mahvi, A.H. (2017) *Sci. Rep.* **7**, 17300
9. Yousefi, M., Mohammadi, A.A., Yaseri, M., & Mahvi, A.H. (2017) *Fluoride* **50**, 343–353
10. Yousefi, Z., Mohammadpour Tahmtan, R.A., & Kazemi, F. (2016) *J. Mazandaran Univ. Med. Sci.* **26**, 69–80
11. Karami, M.A., Fakhri, Y., Rezania, S., Alinejad, A.A., Mohammadi, A.A., Yousefi, M., Ghaderpoori, M., Saghi, M.H., & Ahmadpour, M. (2019) *Int. J. Environ. Res. Public Health* **16**, 4261–4270
12. Keramati, H., Miri, A., Baghaei, M., Rahimizadeh, A., Ghorbani, R., Fakhri, Y., Bay, A., Moradi, M., Bahmani, Z., Ghaderpoori, M., & Mousavi Khaneghah, A. (2019) *Biol. Trace Elem. Res.* **188**, 261–273
13. Ghaderpoori, M., Najafpoor, A.A., Ghaderpoury, A., & Shams, M. (2018) *Data Brief.* **18**, 1596–1601
14. Adimalla, N. (2019) *Expo. Health* **11**, 109–123
15. Wang, B., Zheng, B., Zhai, C., Yu, G., & Liu, X. (2004) *Environ. Int.* **30**, 1067–1073
16. Singh, G., Kumari, B., Sinam, G., Kumar, N., & Mallick, S. (2018) *Environ. Pollut.* **239**, 95–108
17. WHO (2008) Guideline for drinking-water quality, 3rd edition: Volume1 - Recommendations, https://www.who.int/water_sanitation_health/publications/gdwq3rev/en/
18. Wang, F.Q., Li, Y.J., Tang, D.X., Zhao, J.N., Yang, X., Liu, Y.Q., Peng, F.T., Shu, L.P., Wang, J.S., He, Z.X., & Liu, Y. (2021) *Environ. Pollut.* **270**, 116227
19. Li, M., Qu, X., Miao, H., Wen, S., Hua, Z., Ma, Z., & He, Z. (2020) *Environ. Sci. Pollut. Res. Int.* **27**, 20281–20291
20. Eftekhar, B., Skini, M., Shamohammadi, M., Ghaffaripour, J., & Nilchian, F. (2015) J Dent (Shiraz) **16**, 278–281
21. Aldrees, A.M., & Al-Manea, S.M. (2010) *Saudi Dent. J.* **22**, 189–193
22. Semerjian, L.A. (2011) *Environ. Monit. Assess.* **172**, 275–285
23. Standardization Administration of China (2006) Standard examination methods for drinking water - General principles. (SAC GB/T 5750.1-2006), http://down.foodmate.net/standard/sort/3/11165.html

24. Rice, E.W., Baird, R.B., & Eaton, A.D. (2017) *Standard Methods for the Examination of Water and Wastewater*, 23rd Ed., American Water Works Association, Washington DC, USA
25. Szmagara, A., & Krzyszczak, A. (2019) *J. Geochem. Explor.* **202**, 27–34
26. Bondu, J.D., Selvakumar, R., & Fleming, J.J. (2018) *Indian J. Clin. Biochem.* **33**, 86–90
27. Zhang, L., Huang, D., Yang, J., Wei, X., Qin, J., Ou, S., Zhang, Z., & Zou, Y. (2017) *Environ. Pollut.* **222**, 118–125
28. Chuah, C.J., Lye, H.R., Ziegler, A.D., Wood, S.H., Kongpun, C., & Rajchagool, S. (2016) *Sci. Total Environ.* **545-546**, 266–279
29. Biglari, H., Chavoshani, A., Javan, N., & Mahvi, A.H. (2016) *Desalin. Water Treat.* **57**, 22392–22399
30. Clasen, T., & Menon, S. (2007) *Int. J. Environ. Health Res.* **17**, 83–93
31. Ghaderpoori, M., Mirzaei, N., Sharafi, K., Rezaei, S., Adabi, S., Ahmadpour, M., Fouladi-Fard, R., & Farhang, M. (2018) *Int. J. Pharm. Res.* **10**, 328–333
32. Amanlou, M., Hosseinpour, M., Azizian, H., Khoshayand, M.R., Navabpoor, M., & Souri, E. (2010) *Int. J. Pharm. Res.* **9**, 37–42
33. Ahmad, M., & Bajahlan, A.S. (2009) *Environ. Monit. Assess.* **159**, 1–14
34. Guissouma, W., Hakami, O., Al-Rajab, A.J., & Tarhouni, J. (2017) *Chemosphere* **177**, 102–108
35. Wong, M.H., Fung, K.F., & Carr, H.P. (2003) *Toxicol. Lett.* **137**, 111–120