Optimal Fluoride Concentration in Drinking Water as a Function of Calcium Content

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Abstract. Fluoride (F-) is known to have both beneficial and adverse effects on humans, depending on the total intake. Drinking water, usually obtained from groundwater, is the primary source of fluoride intake. Estonian aquifer systems differ from each other in bedding conditions, hydraulic parameters and chemical composition and fluorides are released into the groundwater mostly through water-rock interaction. The present study bases on long term groundwater monitoring data and was undertaken to assess the occurrence of fluoride values in abstracted drinking water over the whole of Estonia and their relation to groundwater’s calcium content. Fluoride concentration in 4404 water samples ranges from 0 to 6.71 mg/l. Values higher than 1.5 mg/l were detected in 8 % of samples, mostly in Silurian-Ordovician aquifer system, composed of limestones and dolomites. Low fluoride area in southern Estonia coincides with the outcrop of Devonian sedimentary rocks, where the major source of drinking water is terrigenous Middle-Devonian aquifer system. The occurrence of fluorides is correlated to variations in groundwater chemical type, which is the function of the proportional content of main cations and anions. The highest F- values prevail in wells, which produce the water with low Ca2+ content and vice versa. Thus, the content of calcium ions in groundwater has an important effect on fluoride concentration, insofar as Ca is an element that removes F from water through CaF2 formation and precipitation. Generally, in terrigenous aquifer systems consisting of sand- and siltstones the optimal fluoride content (0.7-1.2 mg/l) is achieved at the calcium concentration within 30-120 mg/l, in carbonaceous Silurian-Ordovician aquifer calcium content which provides the optimal fluoride amount in carbonaceous aquifer system is 150-340 mg/l.

1. Introduction

Fluoride (F-) in drinking water is an important bioelement for the development of teeth and the bones. Fluoride deficiency (lower than 0.5 mg/l) promotes susceptibility to dental caries, but excessive content (higher than 1.5 mg/l) leads to toxic effect as dental fluorosis. Optimal intake of fluoride (0.7-1.2 mg/l) replaces hydroxyapatite with fluorapatite in enamel structure, which reduces enamel’s solubility in the acids. Values higher than 4 mg/l cause skeletal fluorosis known as an osteoporosis [1]. Fluoride concentration in Estonian groundwaters ranges within extensive limits. Consequently, there are different water types concerning the health effects - from cariogenic or optimal to causing fluorosis.

Drinking water, usually obtained from groundwater, is the primary source of fluoride intake. Thus, the occurrence of fluorides in groundwater has drawn worldwide attention, especially in granitic areas, where high F- concentrations are prevalent [2], [3], [4]. Fluorine is a ubiquitous element being the most electronegative and reactive of all elements and reacts with most of the elements. In natural waters,
fluoride exists as a free ion (F-) or forms several complexes. Fluorides are released into the groundwater mostly through water-rock interaction, anthropogenic origin is less frequent. The most common fluorine-bearing mineral in the geological environment is fluorite (CaF$_2$). Fluorine is also abundant in other rock forming minerals like apatite, micas, amphiboles, and clay minerals [5], [6], [7], [3].

Water-rock interactions, such as dissolution and leaching of the clay-rich sedimentary rocks and K-bentonites providing ion-exchange and adsorption sites for F-, are the main geological sources of F in Estonian groundwater [8], [9]. The chemical type of groundwater is the key factor controlling the dissolution of F in water. The content of calcium ions in groundwater has an important effect on fluoride concentration, insofar as Ca is an element that removes F from water through CaF$_2$ formation and precipitation. Thus, the purpose of this study is to examine the relationship between the occurrence of fluoride and calcium concentrations in all Estonian aquifer systems in order to estimate its effect to drinking water quality.

2. Geology and hydrogeology of study area

Estonia is situated in the north-western part of the East-European Platform, where crystalline Paleoproterozoic basement is overlain by Neoproterozoic (Vendian) and Palaeozoic (Cambrian, Ordovician, Silurian and Devonian) sedimentary rocks (Figure 1) covered by Quaternary deposits [10].

![Figure 1. Location of the study area, geological map with the position of the line of the cross section and north-south geological cross-section of Estonia.](image)

Hydrogeologically Estonian sedimentary rocks form a typical artesian basin, where five economically important aquifer systems (Middle-Devonian, Middle-Lower-Devonian, Silurian-Ordovician, Ordovician-Cambrian and Cambrian-Vendian) are isolated from each other by impervious beds (Table 1). The Upper-Devonian aquifer system, which has a very limited extent in south-eastern part of the country, and the uppermost Quaternary aquifer system are used as a drinking water sources mostly in private households.
Table 1. A Stratigraphy and hydrostratigraphy of Estonia [11].

| System            | Aquifer system | Aquitard           | Lithology                    |
|-------------------|----------------|--------------------|------------------------------|
| Quaternary        | Quaternary     | Sand, gravel, glacial till |
|                   | Upper-Devonian | Dolomite, limestone |
| Devonian          |                |                    | Snetaja Gora-Amata           | Clayey sandstone |
|                   | Middle-Devonian|                    | Narva                        | Sandstone, siltstone |
|                   | Middle-Lower-Devonian |      | Narva                        | Siltstone, marl, clay |
| Silurian-Ordovician| Silurian-Ordovician | Limestone, dolomite |
| Ordovician        | Ordovician-Cambrian | Sandstone, siltstone |
| Cambrian          | Cambrian-Vendian | Lükati-Lontova     | Clay, clayey siltstone       |
| Ediacaran         |                |                    | Sandstone, siltstone         |

The Middle-Devonian aquifer system (D2) is the main source of public water supply in southern Estonia. It consists of terrigenous material: sand- and siltstones with interlayers of clayey and dolomitized sandstone. Groundwater in aquifer system is mainly fresh, HCO3-Ca-Mg chemical type with total dissolved solids (TDS) of 0.2-0.6 g/l [11], [12].

Middle-Lower-Devonian (D2-1) aquifer system is isolated from overlying D2 aquifer system by Narva aquitard, but the water-bearing rocks consist also of fine-grained weakly cemented sand- and siltstones. Groundwater abstracted for drinking purposes is HCO3-Ca-Mg and HCO3-Mg-Ca chemical type [12]. The aquifer system is hydraulically connected with underlying Silurian strata, thus the association of water bearing rocks is named Devonian-Silurian (D2-1-S) aquifer system and used for public water supply in southern and southwestern Estonia [11].

Silurian-Ordovician aquifer system (S-O) is an important and often the only source of drinking water in central and western Estonia and on islands of the West-Estonian Archipelago. It consists of diverse limestone and dolomite with clayey interlayers. The upper portion of the water bearing rocks with the thickness of 30 m is intensively fractured and cavernous [11]. The aquifer system has a characteristic HCO3-Ca-Mg water type with TDS mainly below 0.6 g/l in its upper 30-50 m thick portion. In coastal areas and greater depths, the content of Cl and Na in groundwater increases and HCO3-Cl-Na-Mg-Ca type water with TDS between 0.3-1.5 g/l is widespread [12].

Ordovician-Cambrian aquifer system (O-Ca) is present in most of Estonia and consists of fine-grained sandstones and siltstones. Chemical type of water and the amount of TDS vary considerably in the aquifer system. The HCO3-Mg-Ca type water with the TDS content of 0.2–0.5 g/l occurs in northern Estonia. In southern Estonia and on the coastal area of western Estonia the Cl-HCO3-Na-Ca and Cl-Na water type is common [12]. The aquifer system is exploited in northern and central part of the country.

3. Data
Estonian groundwater monitoring database stored in Estonian Environment Agency (EEA) was used in this study. The data management department of EEA collects, processes, analyses water data, publishes domestic and international reports on groundwater, surface water and water use, and administers water related databases. For this study, the results of 4404 groundwater chemistry analyses from the monitoring period of 1960-2016 were used and the data was selected on the principle that both fluorine and calcium contents in all analyses were determined. The exact distribution of analytical results between discussed aquifer systems could be seen in Table 2. The number of F and Ca determinations is largest from Silurian-Ordovician aquifer system (n = 2791), which is the most problematic because of the high F values and extensive use as drinking water source in Estonia.
4. Results and discussions

Fluoride concentration in Estonian aquifer systems ranges within extensive limits. According to Estonian groundwater monitoring database used in this study fluoride concentration in 4404 water samples ranges from 0 to 6.71 mg/l. Values higher than 1.5 mg/l were detected in 8 % of samples, mostly in Silurian-Ordovician aquifer system. However, permissible fluoride concentration set by the Estonian as well as EU and WHO requirements (1.5 mg/l) are exceeded in all aquifer systems (Table 2). On the other hand, 37 % of the water samples contained fluoride less than 0.5 mg/l. Consumption of drinking water with such low fluoride content is insufficient to prevent dental caries.

Table 2. Statistical summary (range, mean and median values, mg/l) of the F- concentrations determined in groundwater. n – number of analyses; nF>1.5mg/l - number of analyses where F- content is above 1.5 mg/l

| Aquifer System                      | n   | Range       | Mean | Median | nF>1.5mg/l |
|-------------------------------------|-----|-------------|------|--------|------------|
| Middle-Devonian                     | 162 | 0.00-2.90   | 0.45 | 0.30   | 3          |
| Middle-Lower-Devonian               | 46  | 0.57-2.10   | 1.07 | 1.04   | 4          |
| Middle-Lower-Devonian-Silurian      | 12  | 0.71-2.50   | 1.43 | 1.30   | 4          |
| Silurian-Ordovician                 | 2791| 0.00-6.71   | 0.80 | 0.62   | 315        |
| Ordovician-Cambrian                 | 378 | 0.00-2.15   | 0.69 | 0.66   | 8          |
| Cambrian-Vendian                    | 1015| 0.04-3.00   | 0.62 | 0.61   | 6          |

Low fluoride area in southern Estonia coincides with the outcrop of Devonian sedimentary rocks, where the major source of drinking water is terrigenous Middle-Devonian aquifer system (Figure 1). Water supply in northern Estonia is based on Cambrian-Vendian and Ordovician-Cambrian terrigenous aquifer systems, which are exploited by wells penetrating through the complex of Ordovician carbonate rocks. The highest fluoride concentrations are detected in areas, where Silurian and Ordovician limestones and dolomites occur and the only drinking water source is Silurian-Ordovician aquifer system (Table 2). Elevated fluoride concentrations can also determined along the northern outcrop line of Devonian rocks (Figure 1). This is the area, where hydraulically connected Devonian and Silurian strata form the Middle-Lower-Devonian-Silurian aquifer system.

Permissible fluoride concentration set by the Estonian and international drinking water standards has been exceeded in all aquifer systems (Table 2). Generally, the groundwater has a good quality in terrigenous Cambrian-Vendian, Ordovician-Cambrian and Middle-Devonian aquifer systems. The fluoride contents in those aquifer systems vary from 0 to 3 mg/l, but the number of wells where its concentration does not meet the drinking water requirement is not high. However, in case of Middle-Devonian aquifer system, the mean and median fluoride values are the lowest (0.45 and 0.3 mg/l, respectively). This aquifer system is used in southern parts of the country where a strong correlation between natural fluoride levels and the prevalence of dental fluorosis has been reported [13].

The most serious problems are associated with Silurian-Ordovician carbonaceous aquifers, where fluoride contents reach up to 6.71 mg/l and approximately 11 % of the analyzed F- contents are above 1.5 mg/l (Table 2). The largest variations of F- concentrations in production wells are visible in this aquifer system (Table 2). However, in most of the northern and eastern Estonian wells F- concentrations are below the limit value, occasionally high concentrations are common in western Estonia [8].

Table 2 also shows that the highest mean and median fluoride values are found in Middle-Lower-Devonian and Middle-Lower-Devonian-Silurian aquifer systems, compared to the other Estonian aquifer systems. These aquifer systems are hydraulically connected with underlying Silurian strata,
which makes the water exchange between F-rich Silurian-Ordovician and forenamed aquifer systems in places possible.

The previous study on the hydrochemistry of Silurian-Ordovician aquifer system [8] has shown that the remarkable differences in relations between main cations and anions within this aquifer system can be followed and that the concentrations of fluorides are closely correlated to variations in groundwater chemical type (Figure 2).

![Piper diagram reflecting the chemical type of groundwater and proportional contents of F⁻ in Silurian-Ordovician aquifer system [8].](image)

Groundwaters with high F⁻ contents are generally HCO₃-Na-type waters, particularly poor in Ca²⁺ [14]. Same trend can be observed in Estonian Silurian-Ordovician aquifer system (Figures 2 and 3) – high F⁻ contents prevail in wells, which produce the water with low Ca²⁺ content. And the opposite, groundwater in Estonian aquifer systems is mainly HCO₃-Ca-Mg-type and owing to the high Ca²⁺ contents, quite low amounts of F⁻ in most of the aquifers may be mobilized (Figure 3).

Generally, the Na and Cl contents increase with depth and the groundwater changes towards Na-Cl-HCO₃ chemical type. Accordingly, geochemically favourable conditions for high dissolved F in groundwater dominate in deeper portions of aquifer systems. Thus, the content of calcium ions in groundwater has an important effect on fluoride concentration, insofar as Ca is an element that removes F from water through CaF₂ formation and precipitation. Generally, in terrigenous aquifer systems consisting of sand- and siltstones the optimal fluoride content (0.7-1.2 mg/l) is achieved at the calcium concentration within 30-120 mg/l (Figure 3A, B and D). Silurian-Ordovician aquifer system composed of limestones and dolomites exhibits high bicarbonate and calcium values. Calcium content which provides the optimal fluoride amount in carbonaceous aquifer system is higher – 150-340 mg/l (Figure 3C). Consequently, the excessive fluoride contents could be found in Estonian terrigenous and carbonaceous aquifers with Ca²⁺ content below 30 and 150 mg/l, respectively.
Figure 3. Bivariate plots of F and Ca contents in Estonian aquifer systems. A-Cambrian-Vendian, B-Ordovician-Cambrian, C-Silurian-Ordovician, D-Middle-Devonian (D2), Middle-Lower-Devonian (D2-1) and Middle-Lower-Devonian-Silurian (D2-1-S) aquifer systems.

Bivariate plots (Figure 3) show also, that in the terrigenous aquifer systems, especially in Ordovician-Cambrian and Middle-Devonian, large number of F concentrations are below 0.5 mg/l. Drinking water abstracted from those aquifer systems thus exhibits fluoride deficiency and promotes susceptibility to dental caries [13].

In conclusion, the Ca\(^{2+}\) content determined within routine water quality analyses is a simple indicator to assess the probable fluoride content in water and hence the potential effect of drinking water on human health. Undoubtedly, such kind of estimation it's not a substitute for correct fluoride determinations, but knowing the geology of aquifer forming rocks and the main ions in groundwater, we can make some first conclusions on fluoride content in groundwater.

5. Conclusions
Fluoride concentration in 4404 groundwater samples ranges from 0 to 6.71 mg/l in Estonia. Values higher than 1.5 mg/l were detected in 8 % of samples, mostly in Silurian-Ordovician aquifer system, composed of limestones and dolomites. Low fluoride area in southern Estonia coincides with the outcrop of Devonian sedimentary rocks, where the major source of drinking water is terrigenous Middle-Devonian aquifer system. 37 % of the water samples contained fluoride less than 0.5 mg/l. The occurrence of fluorides is correlated to variations in groundwater chemical type, which is the function of the proportional content of main cations and anions. The highest F values prevail in wells, which produce the water with low Ca\(^{2+}\) content and vice versa. Thus, the content of calcium ions in
groundwater has an important effect on fluoride concentration, insofar as Ca is an element that removes F from water through CaF₂ formation and precipitation. Generally, in terrigenous aquifer systems consisting of sand- and siltstones the optimal fluoride content (0.7-1.2 mg/l) is achieved at the calcium concentration within 30-120 mg/l, in carbonaceous Silurian-Ordovician aquifer calcium content which provides the optimal fluoride amount in carbonaceous aquifer system is 150-340 mg/l. The Ca²⁺ content determined within routine water quality analyses is a simple indicator to assess the probable fluoride content in water and hence the potential effect of drinking water on human health.

Acknowledgments
This study has been carried out with the financial support of Estonian Research Council grant IUT20-34. The authors thank the staff of the Estonian Environment Agency for providing the long-term groundwater monitoring data.

References
[1] WHO, “Guidelines for drinking-water quality,” 3rd edn., Geneva: World Health Organization, 2008.
[2] V. K. Saxena, and S. Ahmed, “Dissolution of fluoride in groundwater: a water-rock interaction study,” Environmental Geology, vol. 40(9), pp. 1084-1087, 2001.
[3] S. Naseem, T. Rafique, E. Bashir, M. I. Bhanger, A. Laghari, and T. H. Usmani, “Lithological influences on occurrence of high-fluoride groundwater in Nagar Parkar area, Thar Desert, Pakistan,” Chemosphere, vol. 78, pp. 1313-1321, 2010.
[4] Y. Kim, J.Y. Kim, and K. Kim, “Geochemical characteristics of fluoride in groundwater of Gimcheon, Korea: lithogenic and agricultural origins,” Environmental Earth Sciences, vol. 63, pp. 1139-1148, 2011.
[5] J. Hem, “Study and interpretation of the chemical characteristics of natural water.” U.S. Geological Survey, Water-Supply Paper 2254, 1985.
[6] M. Edmunds, and P. Smedley, “Fluoride in natural waters - occurrence, controls and health aspects.” In: O. Selinus (Ed.). Essentials of Medical Geology, Amsterdam, Elsevier, pp. 301-329, 2005.
[7] G. T. Chae, S. T. Yun, B. Mayer, K. H. Kim, S. Y. Kim, and J. S. Kwon, “Fluorine geochemistry in bedrock groundwater of South Korea,” The Science of the Total Environment, vol. 385, pp. 272-283, 2007.
[8] E. Karro, and M. Uppin, “The occurrence and hydrochemistry of fluoride and boron in carbonate aquifer system, central and western Estonia,” Environmental Monitoring and Assessment, vol. 185(5), pp. 3735-3748, 2013.
[9] M. Uppin, and E. Karro, “Geological sources of boron and fluoride anomalies in Silurian-Ordovician aquifer system, Estonia,” Environmental Earth Sciences, vol. 65(4), pp. 1147-1156, 2012.
[10] A. Raukas, and A. Teedumäe, “Geology and mineral resources of Estonia.” Tallinn: Estonian Academy Publishers, 1997.
[11] R. Perens, and L. Vallner, “Water-bearing formation.” In A. Raukas, & A. Teedumäe (Eds.), Geology and mineral resources of Estonia, Tallinn, Estonian Academy Publishers, pp. 137-145, 1997.
[12] R. Perens, V. Savva, M. Lelgus, and T. Parm, The Hydrogeochemical Atlas of Estonia (CD version). Tallinn, Geological Survey of Estonia, 2001.
[13] E. Indermitte, A.Saava, E. Karro, “Exposure to high fluoride drinking water and risk of dental fluorosis in Estonia,” International Journal of Environmental Research and Public Health, vol. 6, pp. 710-721, 2009.
[14] P. Lahermo, H. Sandström, and E. Malisa, “The occurrence and geochemistry of fluorides in natural waters in Finland and East Africa with reference to their geomedical implications,” Journal of Geochemical Exploration, vol. 41, pp. 65-79, 1991.