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Fluoride Concentration in Dunedin (New Zealand) Drinking Water

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Abstract

Background and objectives: It is important that the fluoride concentration of water received by households in an urban area such as Dunedin (New Zealand) should fall consistently within the recommended range of 0.7 to 1.0 mg/L. Dunedin's water fluoridation concentration is monitored routinely by the Dunedin City Council at the point of water treatment (the Mount Grand and Southern water treatment plants) but not at the point of water delivery to households. **Methods:** This study investigated the fluoride concentration in water received by households located over a wide area of Dunedin City. Over a period of 20 weeks, water samples were collected from 19 sites receiving fully-fluoridated water, 1 site receiving partially/part-time fluoridated water, and 3 sites for which the water was not fluoridated at all. The concentration of fluoride in each of these samples was determined using a standard water analysis procedure involving a fluoride ion-sensitive electrode. **Results:** Observed fluoride concentrations at sites receiving fluoridated water ranged from 0.63 to 0.85 mg/L, with a mean of 0.74 mg/L. Average fluoride concentrations of samples from sites supplied primarily from the Southern water treatment plant were significantly lower than those from Mt. Grand, but the difference was only 0.02 mg/L. No statistically significant association was found between fluoride concentration and distance from the treatment plants or the number of reservoirs.

Conclusions: The level of fluoride in Dunedin water is reasonably constant over time and across the city.

Introduction

Human consumption of water containing low levels of fluoride in the range of 0.7 to 1.0 mg/L is recommended by the New Zealand Ministry of Health for the prevention of dental caries. However, levels of fluoride in New Zealand natural waters are generally less than 0.2 mg/L (National Fluoridation Information Service, 2011). Fluoride-containing compounds are therefore often added to these natural waters during the water treatment stage to increase fluoride levels to within the above recommended range, with a maximum allowed level of 1.5 mg/L. Community water fluoridation is implemented at the discretion of local government authorities (such as city and district councils) pursuant to the Local Government Act 2002 and the Health Act 1956 (New Zealand High Court, 2014). According to the 2012-2013

Annual Report on Drinking-Water Quality, 56% of the New Zealand population resides in areas with fluoridated drinking water (Ministry of Health, 2014).

In accordance with the Ministry of Health recommendation, the Dunedin City Council (DCC) has fluoridated its natural water since 1967 as part of its water treatment protocols, through the controlled addition of sodium silicofluoride powder to the water at the Mt. Grand and Southern water treatment plants that supply most of metropolitan Dunedin. In May 2013, the DCC reduced its target concentration of fluoride in the final treated water from 0.85 mg/L to 0.75 mg/L but this is still within the 0.7 to 1.0 mg/L range recommended by the Ministry of Health. The DCC routinely monitors the water fluoride concentration in the city, immediately after the fluoride is added to the water at either treatment station. However, there has been no determination of fluoride concentrations at more distal points in the city to determine whether the water received at households consistently contains optimal concentrations of fluoride within the recommended 0.7 to 1.0 mg/L range.

Findings from a recent study of water fluoride levels in Aracatuba, Brazil, (Moimaz et al., 2012) suggested little attenuation of fluoride concentration given the inertness of the materials used in a reticulation system. However, there is the potential for fluoride ions to be taken up by calcareous deposits on the inside of the water pipes, possibly reducing their concentration to levels which are no longer caries-preventive. Accordingly, the aim of this study was to investigate spatial and temporal variations in the fluoride concentration in Dunedin drinking water with distance from the two water treatment plants.

Methods

Water samples were collected from 23 locations widely distributed across Dunedin City (Figure 1) as determined by the residential locations of a convenience sample of University of Otago staff members and postgraduate students. The sampling sites included 21 residential taps and 2 naturally-occurring springs. One site received water that was fluoridated for only part of the time; three received non-fluoridated water (including the two springs), and the remainder received continuously fluoridated water. Weekly samples were collected over a four-month period starting the week commencing 10/2/2014 and concluding during the week beginning 23/6/2014. Samples were collected in 100 mL polyethylene bottles which had been pre-cleaned by



Figure 1. Distribution of sample sites receiving fluoridated water, excluding Seacliff.

soaking in soapy tap water, rinsed thoroughly with deionised water, and left to air dry overnight. The bottles were labelled with a code representing the collection site, and the date and time of sample collection.

The concentration of dissolved fluoride in each sample was determined using the standard American Public Health Association (APHA) method 4500-F for fluoride analysis in water using a fluoride ion sensitive electrode (American Public Health Association 1992)

The measurement procedure was as follows. A 10 mL volume of sample solution was placed in a clean 25 mL beaker and a small magnetic “flea” added to ensure moderate stirring at a uniform rate. The fluoride ion selective electrode was carefully lowered into the solution until the membrane end of the electrode was approximately 3 mm above the rotating magnetic flea. The meter reading of potential difference in units of mV was recorded once the reading had stabilised (typically within 2 min). The electrode was removed from the solution, rinsed with deionised water, and carefully wiped dry with soft tissue paper. This measurement procedure was used for both the direct calibration method and the low level calibration method (described below).

A series of solutions containing fluoride in the concentration range of 0.5 to 1.0 mg/L (known as “secondary fluoride standards”) was prepared by mixing different volumes of a primary standard fluoride solution (10.0 mg/L) with deionised water to make up a total volume of 100 mL (Table 2). For each secondary fluoride standard solution made, 10.0 mL was added to 10.0 mL of buffer solution in a 25 mL beaker. Use of the buffer solution (Total Ionic Strength Adjustment Buffer; TISAB) ensured that all samples and standards had similar ionic strength; this is a necessary requirement for consistent electrode responses (Mettler-Toledo, 2011). Using the measurement procedure outlined above, the potential difference readings for each of the secondary standard solutions were recorded.¹

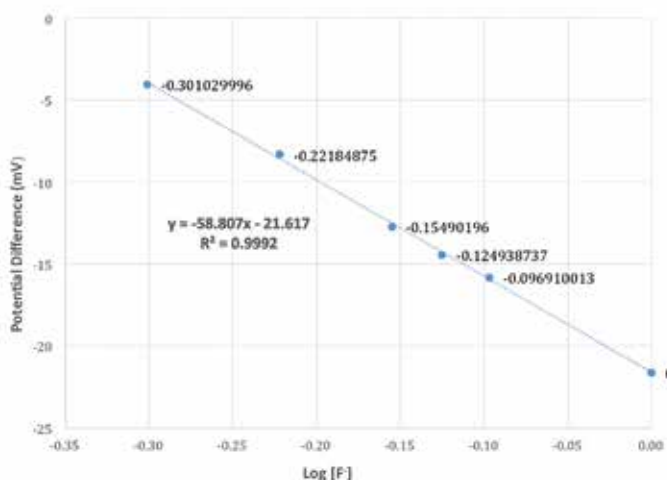


Figure 2. Example calibration graph of fluoride standards.

To create a calibration graph for direct calibration, the measured potential differences (E) recorded for the secondary standard fluoride solutions were plotted on the y-axis against the log of their concentration values on the x-axis. The Nernst equation, which relates E to concentration, predicts that the resulting graph should be linear, with an expected gradient range of -54 to -60 mV when the solution temperature is 20–25 °C.

Samples collected from the sites receiving partially fluoridated water (Port Chalmers) and non-fluoridated water (Mosgiel, Saddle Hill, and the Rattray Street ‘Speights’ tap) were expected to have very low fluoride concentrations, and so these were analysed using the low-level calibration graph method recommended for when fluoride concentrations are likely to be lower than 0.38 mg/L (Mettler-Toledo, 2011). A 10.0 mg/L primary standard fluoride solution was made up using the stock fluoride solution (1.00 g/L). 100.00 mL of this primary standard was added to 100.00 mL of the TISAB solution in a beaker to give a secondary standard fluoride solution of concentration 5.00 mg/L. 50.00 mL of distilled water and 50.00 mL of TISAB were then added to a beaker. After placing the electrode in the beaker, increments of the secondary standard fluoride solution were progressively added. A stable potential difference reading was recorded after each increment, following the measurement procedure outlined above. As with the direct calibration method, the measured potential difference was plotted against the log of the corresponding fluoride concentration. The resulting graph was also predicted from the Nernst equation to be linear. It should be noted that fluoride concentrations below 0.10 mg/L cannot be reported with confidence due to the inaccuracies of the calibration curve at such low concentrations (Clesceri et al., 1998). Therefore, any values calculated from the calibration graph to less than 0.10 mg/L are reported as “<0.10 mg/L”.

A calibration graph created from measurements made on 06/05/2014 is shown in Figure 2. Linear regression analysis was used to calculate the regression equation, together with the variances of the slope and intercept. This calibration graph and linear equation was then used to obtain the concentrations of fluoride ion in

¹ Since electrode potentials are affected by changes in temperature, measurements of the standard solutions and unknown samples should be made within ± 1.0 °C of each other. All measurements in this study were undertaken at a temperature of 19.0 ± 0.5 °C.

the unknown water samples. A calibration graph was prepared from fresh standard solutions before measuring each batch of unknown samples to eliminate possible instrumental variations such as those arising from temperature variations, electronic noise and sensor drift. According to the product manual for the electrode, "Reproducibility is limited by factors such as temperature fluctuations, drift, and noise. Within the operating range of the electrode, reproducibility is independent of concentration. With hourly calibrations, direct electrode measurements reproducible to +/- 2% can be obtained." (Mettler-Toledo 2011). Some measurements were taken in triplicate, and excellent replicability of measurements was achieved.

The distance from the treatment plants to the sampling sites was obtained by measuring the length of the water pipe mains network, using the DCC's combined services web-map², in conjunction with Quantum Geographic Information System 2.4.0. Additionally, the number of small reservoirs between either treatment plant or sampling site was noted in order to investigate their possible influence on the fluoride concentration data. All statistical analyses were conducted in Intercooled Stata 13.1, using general linear models.

Results

Between February and June 2014, 395 water samples from 23 sites in Dunedin (19 sites receiving fluoridated water, 3 sites receiving non-fluoridated and 1 site receiving partially-fluoridated water) were collected and analyzed. The mean fluoride concentration of all samples

of fluoridated water was 0.74 mg/L. The average, lowest, and highest fluoride concentrations for each fluoridated sampling site are presented in Table 1, together with the distance from the water treatment plants and the number of small reservoirs between the sampling sites and treatment plants. No samples from fluoridated areas exceeded a fluoride concentration of 0.84 mg/L. Approximately one in three samples (n=122, 33.1%) had fluoride concentrations ranging from 0.76 to 1.00 mg/L, while one in five (n=77, 20.8%) had concentrations below 0.70 mg/L; the remainder were between 0.70 and 0.75 mg/L (n=170, 46.1%). The lowest observed fluoride concentration was 0.63 mg/L.

One site received partially-fluoridated water (Port Chalmers), and an average fluoride concentration at the threshold of reliable estimation (0.10 mg/L) was observed with peaks on the 4th and the 10th week at that site. All non-fluoridated samples (Mosgiel tap water, Saddle Hill spring water, and the Rattray Street/"Speights" spring water) gave fluoride concentrations below the threshold for valid estimation (<0.10mg/L). Figure 3 shows the variations in fluoride concentration in all water samples collected during the 20-week period.

The DCC conducts weekly monitoring of fluoride concentration in the Mt. Grand and Southern water reservoirs that store water after fluoride addition and before distribution around the city. Table 2 compares the fluoride concentrations of the Mt. Grand and Southern samples, between February and June 2014, with the DCC's weekly data during the same period. On average, samples from sites primarily supplied by Mt Grand had a higher fluoride concentration than samples from sites primarily supplied by the Southern treatment station. The values obtained in this research project are comparable to those obtained by the DCC at the point of fluoridation, albeit slightly higher. A slightly lower average fluoride concentration at sites receiving fully-fluoridated water was observed toward the end of the 20-week sampling period, of the order of 0.04 mg/L. A similar trend of a decline in fluoride concentration with time was observed when the treatment plant data were examined separately (Table 2).

Lower concentrations of fluoride were noted at Seacliff, the most distal sampling point, some 30 km from the relevant treatment plant. Because of this, a further three samples were collected on 04/10/2014 at Seacliff, Waitati and Warrington (sites along the water pipe network between Mt. Grand and Seacliff), but no decline in fluoride concentration with distance along this pipe route was observed (Table 3).

Multivariate analyses (including and excluding Seacliff) showed no statistically significant association between fluoride concentration and distance from the water treatment plant (Table 4).

No statistically significant association was found between fluoride concentration and either distance from the treatment plants, or the number of reservoirs. Samples from sites supplied primarily from the Southern water treatment plant had significantly lower fluoride concentration than samples supplied primarily by Mt. Grand, but the absolute difference was only 0.02 mg/L.

² <http://www.dunedin.govt.nz/councilonline/webmaps/waterservices> (accessed 24/09/2014)

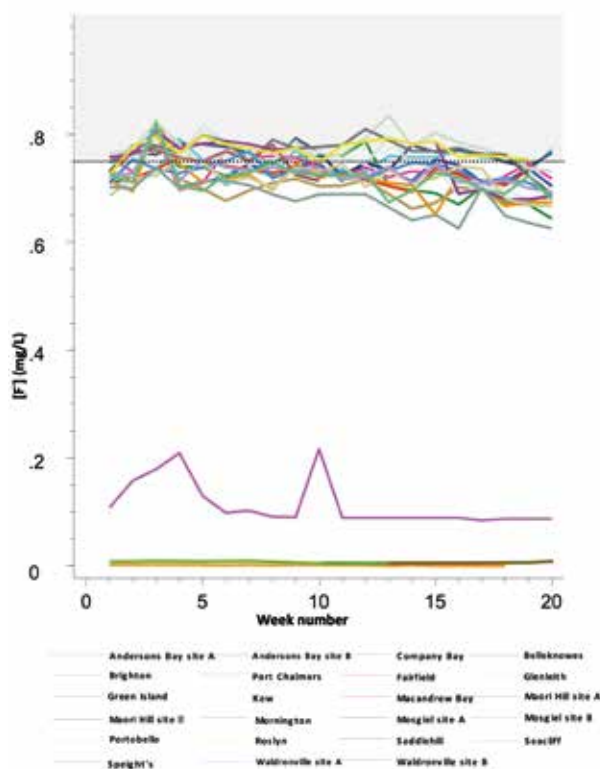


Figure 3: Fluoride concentration variation of all samples collected during the 20-week sampling period

**Table 1.** Fluoride concentrations by sampling site

Suburb	Treatment Plant	Distance (km)	Number of reservoirs	[F ⁻] (mg/L)		
				Average	Lowest	Highest
Andersons Bay site A	Southern	6.9	0	0.723	0.644	0.787
Andersons Bay site B	Southern	8.2	0	0.731	0.703	0.825
Company Bay	Southern	17.3	3	0.745	0.706	0.792
Belleknowes	Mt. Grand	4.4	0	0.761	0.722	0.793
Brighton	Southern	13.3	2	0.713	0.651	0.825
Fairfield	Southern	5.9	0	0.737	0.697	0.805
Glenleith	Mt. Grand	6.1	1	0.774	0.732	0.835
Green Island	Southern	4.1	0	0.704	0.662	0.806
Kew	Mt. Grand	3.2	0	0.744	0.680	0.816
Macandrew Bay	Southern	14.8	2	0.725	0.693	0.756
Maori Hill site A	Mt. Grand	6.3	1	0.767	0.690	0.810
Maori Hill site B	Mt. Grand	4.8	0	0.752	0.714	0.781
Mornington	Mt. Grand	3.8	1	0.730	0.689	0.769
Mosgiel	Southern	6.9	1	0.756	0.680	0.808
Portobello	Southern	20.6	3	0.712	0.667	0.753
Roslyn	Southern	4.7	1	0.773	0.725	0.797
Seacliff	Mt. Grand	30.7	5	0.681	0.626	0.739
Waldronville site A	Southern	7.4	2	0.729	0.693	0.818
Waldronville site B	Southern	7.6	2	0.719	0.674	0.821

Table 2. Comparison of fluoride concentration in this study and that determined by the DCC at the sampling point, by week of study

Week number	[F ⁻] of Mt. Grand samples (mg/L)		[F ⁻] of Southern samples (mg/L)	
	Study data	DCC data	Study data	DCC data
1	0.733	0.710	0.725	0.650
2	0.755	0.710	0.732	0.690
3	0.769	0.710	0.791	0.800
4	0.754	0.730	0.737	0.680
5	0.762	0.760	0.736	0.660
6	0.764	0.760	0.733	0.730
7	0.748	0.780	0.739	0.680
8	0.747	0.740	0.735	0.710
9	0.753	0.740	0.748	0.680
10	0.737	0.740	0.733	0.720
11	0.737	0.690	0.737	0.720
12	0.751	0.730	0.743	0.690
13	0.788	0.80	0.736	0.660
14	0.743	0.720	0.720	0.690
15	0.746	0.730	0.730	0.700
16	0.730	0.710	0.723	0.590
17	0.736	0.760	0.717	0.640
18	0.723	0.740	0.699	0.660
19	0.700	0.720	0.705	0.680
20	0.698	0.680	0.697	0.600
Average	0.744	0.735	0.732	0.682
	0.579		0.714	
	0.723			
Correlation	0.032			

Table 3. Fluoride concentration in water samples collected from Waitati, Warrington and Seacliff and the distance from the Mt. Grand treatment plant

Site	[F-] (mg/L)	Distance from Mt. Grand (km)
Waitati	0.735	20.4
Warrington	0.723	26.5
Seacliff	0.747	30.7

The fluoride concentration of sites supplied by Southern and Mt. Grand each followed a normal (Gaussian) distribution curve.

Discussion

The findings of this study suggest that fluoride concentrations in the water in fluoridated regions of Dunedin mostly fall within the acceptable range (0.70–1.00 mg/L), with minimal temporal or geographical variation. Fluoride concentration does not attenuate with distance from the plant.

It is important to consider the weaknesses and strengths of the study. First, the samples were collected from various sites that were essentially convenience samples. Ideally, the sampling sites should have been determined across the distribution network in such a way that they represented specific distances from the treatment plants and covered all areas of the city. Despite this, however, a reasonably even distribution of sampling sites was achieved, with most areas of the city covered. There were also unequal numbers of collection sites corresponding to the two treatment plants, with the majority of the sites being supplied by water from the Southern treatment plant. The weekly samples were collected from residential taps and relied upon the volunteers remembering to draw them. This manner of collection resulted in some loss of samples due to some participants' inability to collect weekly samples continuously for 20 weeks. Moimaz et al. (2012), who undertook a similar project in Aracatuba (Brazil), recommended collecting samples from public places in order to avoid loss of samples and to facilitate access to the site. Second, time constraints meant that the collection period was limited to 20 weeks. Among the study's strengths, all fluoride measurements were conducted using a fluoride ion-selective electrode—which was calibrated daily—in order to minimise any instrumental variations.

Our findings show a lower range (0.63 mg/L to 0.84 mg/L) of fluoride concentrations in areas of Dunedin

receiving fluoridated water than the range of 0.70 to 1.2 mg/L reported for the Brazilian city of Aracatuba during the period November 2004 to October 2010 (Moimaz et al., 2012). That study found variations in fluoride concentration at the same site in different periods, but spatial variations in fluoride concentration were not investigated. In Dunedin, around eight out of every ten samples from fluoridated areas were within the optimal range, while, in Aracatuba, only around two-thirds were.

Other than Seacliff, all sampled sites supplied with water primarily from Mt. Grand were located within 8 km of that plant. In order to further investigate any possibility of decreasing fluoride concentration with increasing distance from the Mt. Grand water treatment plant, more samples were subsequently collected from sites between Mt. Grand and Seacliff. The lower fluoride concentration observed at Seacliff could be due to measurement error or a small degree of mixing with non-fluoridated water from the non-fluoridated Waikouaiti water treatment plant. Pipes from the Waikouaiti water treatment plant feed into the Seacliff reservoir, but they are typically not used and the Seacliff reservoir is generally fed from Mt. Grand; this mixing of water from the two sources was unlikely to be the cause of the low fluoride concentration observed.

The slight decline in average fluoride concentration observed towards the end of the 20-week sampling period in water from both the Mt. Grand and Southern treatment stations—and in the DCC's weekly measurement of fluoride concentration at the reservoirs—requires explanation. During the period of the study, the treatment chemical appeared to have absorbed moisture from the air, rendering the chemical feeders more likely to have product 'hang up' and 'cake', rather than feed out smoothly. This caused some difficulty in maintaining the target concentration, which may explain the slightly lower fluoride concentrations observed.

The DCC data showed that the water fluoride concentration at the Southern treatment plant reservoir was consistently lower than the fluoride concentration measured for water samples from the Mt. Grand treatment plant. This was reflected in the lower average fluoride concentration of the Southern samples (Table 2). The water distribution system in Dunedin is a dynamic one, with water being moved about the network to meet changing patterns of demand. This can lead to changing sources of water for given areas, as well as mixing from more than one source³. This mixing might explain the

³ Personal communication, DCC geographic information system officer Mr Nathan Stubbs, 10/09/2014

Table 4. Fluoride concentration variation according to distance, treatment plant and number of reservoirs

[F-] (mg/L)	Coefficient	Standard error	z	p> z	95% Confidence Interval	
Distance (km)	-0.00117	0.00156	-0.75	0.453	-0.00424	0.00189
Southern Treatment Plant	-0.02110	0.01000	-2.11	0.035	-0.04070	-0.00146
Number of reservoirs	0.00407	0.00695	0.59	0.558	-0.00955	0.01770

*Outlier data for Seacliff excluded from analysis



higher fluoride concentration observed at sites receiving water nominally sourced from the Southern treatment station than in the water sampled at the Southern reservoir. The fluoride concentration in water sampled at households receiving water from Mt. Grand was also higher (on average) than that measured at the reservoir. The DCC collected and analysed one sample each week, while this research project obtained an average of 19 samples collected at different days each week. This could explain the difference between our measurements and those of the DCC.

A good example of mixing of water can be observed at Port Chalmers, which is a site that we have classified as receiving partially-fluoridated water. It is supplied with fluoridated water from the Mt. Grand treatment plant for some periods of the year, and with non-fluoridated water from its own treatment plant for the remainder. There is also mixing of the fluoridated and non-fluoridated water from time to time, due to the inability of either source to fully cater for the demand at any one time. The Port Chalmers samples had a generally low fluoride concentration during the 20-week sampling period, with peaks on the 4th week and the 10th week. The findings suggest that Port Chalmers was predominantly supplied during that period with water that had been treated at its own treatment plant with no addition of fluoride, and that the observed peaks in fluoride level resulted from an increase in supply of

fluoridated water from Mt. Grand at those times, with the mixing of fluoridated and non-fluoridated water increasing the levels. The Port Chalmers treatment plant was taken off-line in early March and April, which meant that Port Chalmers was supplied by Mt. Grand at those times⁴. This explains the higher fluoride concentration observed in week 4 and week 10, with mixing of fluoridated and non-fluoridated water. These findings also suggest that the measurement of fluoride levels in water from a mixed source may be useful as an approximate marker of the degree of mixing, providing the levels of fluoride in the two end members (that is, fully fluoridated and non-fluoridated water) can be determined.

In summary, we investigated fluoride levels in reticulated water in Dunedin over a 20-week period and found no association between fluoride concentration and distance from the treatment plant, suggesting no attenuation of the preventive properties of the fluoridated water with distance from the treatment points. The level of fluoride in Dunedin water is reasonably constant over time and across the city. Future surveillance and monitoring are important to ensure that optimal fluoride concentrations continue to be maintained for water delivered to Dunedin's fluoridated areas.

⁴ Personal communication, DCC water treatment employee, 06/10/2014

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