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RESEARCH ARTICLE

Hardness of tap water samples in Manila City, Philippines through complexometric titration

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ABSTRACT

Background: Water hardness varies depending on the source, treatment procedures, and pipeline conditions among others, though not of immediate concern in water quality control but may have significant health, infrastructural, or industrial effects. **Aims and Objectives:** This study quantified, classified, analyzed, and compared hardness of tap water samples from household and commercial faucets across the six legislative districts of Manila City, Philippines through complexometric titration. **Materials and Methods:** Tap water samples were collected through stratified random sampling, and the hardness was subsequently measured through complexometric titration. **Results:** Using the United States Geological Survey Water Quality Information ordinal classification scheme, tap water samples have fluctuating values from “soft” to “very hard” qualitative description of the water hardness. **Conclusion:** Despite fluctuations in values, water hardness nonetheless passed the 2007 Philippine National Standards for Drinking Water.

KEY WORDS: Water Hardness; Complexometric Titration; Manila City, Philippines; Water Quality

INTRODUCTION

Water hardness is the measure of the number of polyvalent cations (Ca^{2+}, Mg^{2+}, and Fe^{3+}) present in a water sample[1] and is usually expressed in terms of parts per million calcium carbonate (ppm $CaCO_3$). Separate quantification of these individual cations is possible often with health-related or nutrition-related purposes in mineral water samples. Different types of water sources have different average levels of total hardness.[2] Information regarding the total hardness of water in the Philippines is not published or not made readily available. The determination of these values may give an overall perspective of the water profile and quality of water sources here in the Philippines. Although not of severe concern to any portion of the society, hard water nevertheless has mostly negative effects, especially to the infrastructural frameworks. Hard water precipitates soap because of the reaction of excess cations with esters present in soap.[3] In the health sciences perspective, these polyvalent cations present in water may cause osteoporosis, nephrolithiasis, colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance, and obesity when taken inadequately or hypercalcemia when taken in excess.[4] Many studies have tried to correlate these effects to hard water, but none have been widely accepted, so far. Some studies correlate the protective effects of hard water against the development of cardiovascular diseases while other studies suggest otherwise.[5] Eczema is commonly argued to be an adverse

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effect caused by hard water, especially among children due to soap and metallic residues that are not washed off easily during bath.[6] It has also been suggested that hard water can be used as dietary supplement for the necessary calcium and magnesium minerals or that drinking hard water can be advantageous in reducing the activity of other toxic metals in the body. Nonetheless, very hard water often affects turbidity and taste of water which can decrease quality and satisfaction.

Although many other factors such as microbial content and heavy metal contamination should also be considered, the results of this study can help in the formulation of recommendations for the use of Manila City tap water systems as a suitable source for dietary contents. This research determined and assessed the quality of tap water sources in Manila City, Philippines in terms of water hardness measured in ppm $CaCO_3$. This evaluation of the quality of tap water in Manila was in accordance with a set of pre-existing guidelines for classification, established by external organizations, or agencies. Specifically, the study employed complexometric titration technique in the analytical quantification of dissolved polyvalent cation concentration, compared total hardness of water from the six legislative districts of Manila City, performed statistical calculations to the data gathered for acceptable summaries and inferences, reported and assessed the total hardness of water in Manila City and evaluated with respect to a selected standard reference for classification, and proposed the necessary recommendations to concerned parties for improvement of the status quo.

MATERIALS AND METHODS

Materials and Equipment

For the complexometric titration, reagents, glassware, and various other pieces of equipment were used. An analytical balance precise up to 10,000 of a gram was used in the weighing of standard reagents. Beakers, graduated cylinders, and volumetric flasks were used for the accurate preparation of the titrant, indicator, and buffers. Erlenmeyer flasks were used as the vessel for the analyte, and burets calibrated to tenths of a milliliter were used for the titrant, suspended in an iron stand by a universal clamp. An electric stove was used for heating processes. Wash bottles were also used during the titration process for careful control of the drops of the titrant.

Solid reagents used were sodium hydroxide pellets, standard grade calcium carbonate, ethylenediaminetetraacetic acid (EDTA) crystals, magnesium chloride hexahydrate crystals, solid ammonium chloride, and Eriochrome Black T (EBT) indicator. The liquid reagents used were 25% ammonium hydroxide solution, concentrated hydrochloric acid, distilled water, and 95% ethanol. All reagents were stored at room temperature (approximately 30°C).

Specific handling techniques employed are listed as follows: Washed, uncalibrated glassware was dried in an oven while calibrated glassware was air dried. During the cleaning of the glassware, chromic acid was not employed due to the possible interference of chromium (III) ions; instead, distilled water was used for the last two rinsing processes. pH measurements were taken through the use of pH paper. Parafilms were used in the mixing of prepared solutions in volumetric flasks. The distilled water used was also pre-boiled and cooled to room temperature before the use for the removal of dissolved carbon dioxide contents.

Sampling Method

A two-level sampling scheme was employed in this study. Initially, stratified sampling with equal allocation was used. Manila City is legislatively divided into 6 districts, and each district was used in this study as one of the 6 individual strata for data collection. These 6 districts are defined in the 1987 Constitution of the Republic of the Philippines (ordinance apportioning the seats of the House of Representatives of the Congress of the Philippines to the different legislative districts in provinces and cities and the Metropolitan Manila Area). Within these districts, simple random sampling was employed to gather three samples per district, for a total of 18 samples. Three replicates were recorded for the measurement of total hardness. Samples were retrieved and tested within 24 h; hence, these samples may only be representative of the date of collection May 15, 2013.

Sample Collection and Handling

Samples were stored in 500-ml plastic bottles (high-density polyethylene bottles recycled from similar, bottled distilled water products), cleaned with liquid detergent, and rinsed with distilled water and air dried.

Direct collection into sample bottle was employed from mid-stream tap water sources. A "control wash" was employed by prerinsing the collection bottle 3 times with 20 ml of the sample water before final collection. Bottles were filled completely to the brim to avoid inclusion of air. Air bubbles were also eliminated, and bottles were capped tightly and appropriately labeled.

Samples were stored overnight in the refrigerator, not cooler than 4°C, and were tested within 24 h. No additional filtration or purification techniques were employed before total hardness measurements.

Protocol for water collection and handling was derived from the surface water sampling methods and analysis-technical appendices, published by the Government of Australia Department of Water.[7]

Preparation of Reagents

All reagents were prepared on the same day they were used. Ammonia buffer was prepared by mixing approximately 6.40 g solid ammonium chloride crystals and 42.80 ml of

25% ammonium hydroxide. This solution was diluted to 1.00 L with carbon dioxide-free water in a volumetric flask. The resulting solution's pH was adjusted to 10 with the drop-wise addition of concentrated ammonium hydroxide solution.

EBT which served as the indicator was prepared by dissolving approximately 250.0 mg of powdered EBT in 50.00 ml of 95% ethanol.

The EDTA solution which was used as the titrant was prepared by dissolving approximately 500.0 mg sodium hydroxide pellets, 50.0 mg magnesium chloride hexahydrate, and 1.0000 g solid disodium salt of ethylenediaminetetraacetate in 100.00 ml of carbon dioxide-free distilled water. This solution was then analytically transferred and diluted to a final volume of 2.00 L in a volumetric flask.

Establishment of Blanks and Standardization

A 50-ml distilled water sample was added with ammonia buffer to adjust the pH to 10 and with two drops of EBT. The distilled water sample immediately resulted to a blue color which served as the reference end point for the succeeding titrimetric procedures.

A standard solution was prepared by dissolving 105.4 mg primary-grade calcium carbonate. A 5.00 ml hydrochloric acid was added, and evolution of gas (carbon dioxide) was observed. A 5.00 ml of distilled water was added and the solution was boiled to remove excess carbon dioxide from the carbonate anion dissociation product. The solution was cooled and then diluted to 500.00 ml. Subsequently, 5 ml of this solution was added with the ammonia buffer in an Erlenmeyer flask to adjust the pH to 10. Finally, three drops of EBT indicator were added, and the final aliquot was titrated with the prepared EDTA solution. This was done in triplicate and the average volume of titrant needed (in L) allowed for the confirmation of the actual concentration of the EDTA solution using Equation 1.

Measurements and Calculations

Ten milliliters of each water sample were diluted with distilled water, adjusted to pH 10 with the ammonia buffer, and added with three drops of the EBT indicator solution. This aliquot was titrated with the EDTA solution to the blue end point set by the distilled water blank. Three replicate measurements were recorded for each water sample.

The total hardness of the water sample is obtained using Equation 2. The needed information for the calculation is the volume of EDTA titrant used and the molarity of the EDTA established in the standardization process.

A total of 54 measurements for the samples and 3 measurements for the standardization process were recorded. All values were recorded and reported as ppm $CaCO_3$ (also mg/L), up to 10,000 place.

Standard Ordinal Classification of Water Based on Total Hardness

There are many different conventions in the expression of total hardness content in water samples. Aside from the metric system and hereby adapted ppm $CaCO_3$ system, other standards use either other combinations of metric and imperial units or the system of degrees of hardness (dH). However, the definition for the dH system varies largely, especially among European countries, and was therefore not employed for the purposes of this research.

Similarly, the classification of certain water samples as "hard" or "soft" is highly arbitrary, often depending not only on the country of use but also depending on the government agency, organization, or entity that imposes the classification. In the 2007 Philippine National Standards for Drinking Water, a maximum amount of 300 ppm $CaCO_3$ is imposed, but no classification scheme was proposed.[8] This maximum limit was used in this research as a reference for the maximum acceptable level of hardness. Other entities do not merely propose a maximum hardness level but present an ordinal classification scheme of water samples. For qualitative descriptions of results in this experimental study, the classification of the United States Geological Survey (USGS) was employed (Table 1).[9]

$$\text{Molarity}_{\text{EDTA}} = \frac{0.1054\ \text{g CaCO}_3 \times \dfrac{1\ \text{mole CaCO}_3}{100.0872\ \text{g CaCO}_3} \times \dfrac{5\ \text{ml}}{500\ \text{ml}}}{\text{L}_{\text{titrant}}}$$

Equation 1: Computational formula for the molarity of ethylenediaminetetraacetic acid

$$\text{Total hardness} = \frac{\text{Volume in L}_{\text{titrant, EDTA}} \times \text{Molarity}_{\text{EDTA}} \times \dfrac{1\ \text{mol CaCO}_3}{1\ \text{mol EDTA}} \times \dfrac{100.0872\ \text{g}}{1\ \text{mol CaCO}_3} \times \dfrac{1000\ \text{mg}}{\text{g}}}{10.00\ \text{ml water sample} \times \dfrac{1.00\ \text{L}}{1000.00\ \text{ml}}}$$

Equation 2: Computational formula for the total hardness

Standardization of the EDTA Titrant Solution

The standardization process for the EDTA solution allows for the valid expression of total hardness as calcium carbonate. Using a standard grade calcium carbonate solution, the amount of the EDTA present in the solution that can be effectively used to chelate calcium ions was initially determined in this process.

The three 5.00 ml aliquots of the 200 ppm $CaCO_3$ standard solution needed a mean volume of 12.29 ml of the prepared EDTA titrant solution (standard deviation [SD] = 0.26 ml). Using the presented Equation 1, this corresponded to a mean molarity of 8.5725×10^{-4} M (SD = 0.1823×10^{-4} M). This molarity value was then substituted to Equation 2, for the succeeding calculations of total hardness, which can consequently be validly expressed as parts per million calcium carbonate (the standard reagent to which the titrant is analytically cross-quantified). The recorded values of the volumes of titrant needed for the three runs of standardization are presented in Table 2.

Statistical Analysis

Measurements were reported as means with SD. One-way analysis of variance was employed in comparing water hardness means across different districts. A *post hoc* Tukey's honestly significant difference test was employed to determine which of the district means significantly differed. Statistical analysis was carried out at 5% level of significance using Bill Miller's Open Stat software.

Table 1: The United States Geological Survey classification scheme for water hardness

Classification	Hardness in ppm $CaCO_3$
Soft	0-60
Moderately hard	61-120
Hard	121-180
Very hard	>180

Table 2: Volumetric measurements for the standardization of the EDTA titrant solution

Replicate	EDTA needed (ml)	Molarity EDTA, calculated
1	12.29	8.5686E-4
2	12.61	8.3512E-4
3	11.97	8.7977E-4

EDTA: Ethylenediaminetetraacetic acid

RESULTS

The water hardness values obtained from the titrimetric measurement procedures ranged from 10.6563 ppm $CaCO_3$ to 224.7954 ppm $CaCO_3$. The overall mean of the water hardness data values is 102.7713 ppm $CaCO_3$ with SD of 66.1967 ppm $CaCO_3$. This value is classified as "moderately hard" in the USGS-Water-Quality Information (WQI) classification scheme and passes the 2007 Philippine National Standards maximum limit of 300 ppm $CaCO_3$. To compare the values and variability across different districts, relevant descriptive statistics were calculated, tabulated, and presented in Table 3. Classifications per district per USGS-WQI are also included.

Among the 6 districts, district 2 has the lowest mean water hardness (classified as "soft") while District 4 has the highest mean water hardness (classified as "very hard"). All the districts passed the Philippine National Standards for maximum water hardness limit of 300 ppm $CaCO_3$. However, districts 3 and 4 both have classifications beyond the range of "soft" to "moderately hard" hypothesized by this study. The means of districts 1, 2, 5, and 6 did not significantly vary ($P > 0.05$). The pairings of districts 1, 2, 5, and 6 against districts 3 and 4 all yielded $P < 0.05$ suggesting unequal means (Table 4).

It is a notable observation from Table 4 that Grouping A, apart from satisfying the study's hypothesis of having equal means, also satisfies the hypothesized acceptable ordinal classification range of "soft" to "moderately hard." On the other hand, Group B has districts with equal means, but the water hardness values are beyond the hypothesized acceptable range.

DISCUSSION

Water hardness, or the presence of Ca^{2+} and Mg^{2+} ions in water, is not a new concept to those who utilize tap or running water on a regular basis to clean dishes, cook food, flush the toilet, or take shower. It is expressed as absolute hardness which is given by adding the temporary (carbonate) and permanent (non-carbonate) hardness.[4] Since most waters contain more calcium than magnesium, water hardness is usually reported as milligrams of calcium carbonate per liter of solution.[10] Natural sources of water hardness are primarily dissolved polyvalent metallic ions from sedimentary rocks that seep and runoff through soils toward the water table. The two main ions,

Table 3: Descriptive measures and USGS-WQI classification for calculated total hardness across different districts

Water Hardness	District					
	1	2	3	4	5	6
Mean (ppm $CaCO_3$)	57.9224	56.9233	156.0451	203.4620	66.7808	75.4943
SD (ppm $CaCO_3$)	51.9622	1.3877	67.9063	9.3345	2.5238	10.1631
Classification	Soft	Soft	Hard	Very hard	Moderately hard	Moderately hard

SD: Standard deviation, USGS-WQI: United States Geological Survey-Water Quality Information

Table 4: Groupings of districts with equal means, based on Tukey's HSD test results

Grouping	Districts	Hardness classification
A	1	Soft
	2	Soft
	5	Moderately hard
	6	Moderately hard
B	3	Hard
	4	Very hard

HSD: Honestly significant difference

calcium and magnesium, are present in many of these sedimentary rocks, such as limestone and chalk. Chemicals such as fertilizers applied to plants may also seep and affect the groundwater, increasing the total hardness, especially if it contains some of the contributing metals. Minor contributors to the total hardness of water include other polyvalent ions, such as aluminum, barium, iron, manganese, strontium, and zinc.[4]

The fluctuations in the total water hardness are mostly observable when studying groundwater sources.[11] The presence of these sedimentary rocks and other factors that contribute to total hardness is not constant through time and locations, thus producing variability in the levels of total hardness in different places, at different points in time. This justifies this study's purpose of instantaneous measurement of total hardness since it has been established that measurements made in the past, even if available, are not necessarily constant. Although the fluctuations are hereby justified only for groundwater sources, this can consequently affect the total hardness of tap water, mineral water, and other non-pure forms or sources (i.e., distilled) of water because eventually these other forms of water are derived from groundwater as well but only with the application of treatment methods.[4] Some of these treatment methods include chlorination, aeration (removal of iron and manganese), coagulation, sedimentation, filtration, desalination, and disinfections. These methods target or eliminate microorganisms, heavy metals, suspended solids, and other chemical pollutants.[12] Naturally available dissolved ions that are nonetheless harmless at set concentrations are left in household tap water, including essential minerals such as calcium and magnesium.

Although water-softening methods that eliminate these contributors to total hardness are easily applicable, most water treatment programs regard this as an optional treatment method only for increasing the quality of taste of water. Water-softening methods are also often avoided since the softening process increases sodium or potassium content in water, two elements that have been related to organ defects such as kidney malfunction, cardiac arrythmia, and other cardiovascular diseases.[13]

CONCLUSION

The mean water hardness values from the six legislative districts of Manila City, Philippines passed the 2007 Philippine National Standards for Drinking Water, while the USGS-WQI ordinal classification system found "soft" to "very hard" water classifications. Although no direct health effects are pointed to water hardness, citizens living in these districts can still benefit from the improvement in the industrial and household applications of tap water.

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