Comparative Analysis of Tap Water Chlorine Levels in Selected Southern Illinois Regions and Elimination of Variables between Water Quality Reports

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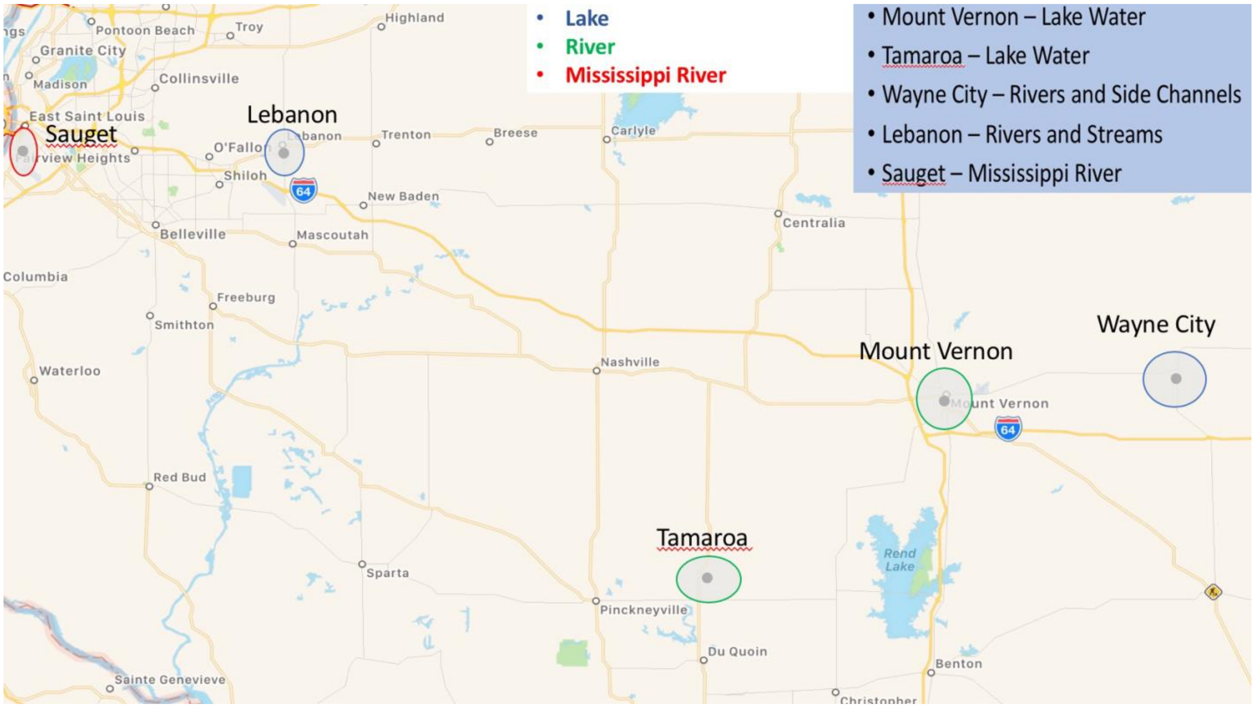
Abstract

The addition of chlorine to tap water is a necessary precaution that also can have detrimental effects if the concentration of chlorine is either above or below the mandated levels by the EPA. The addition of chlorine to water helps to ensure the public health by neutralizing dangerous bacteria and viruses that can be present in water. If insufficient amounts of chlorine were added, not all of the infectious organisms would be neutralized. If too much chlorine is added, the excess can be damaging to the public health. This project aims to quantify different chlorine species in tap water from various areas of Southern Illinois using the same method under identical conditions to test the validity of comparison (relative variation) of reported chlorine levels by the city water labs. Another goal of this project is to see if types of water sources and various environmental factors affect the species of chlorine present in water. Chlorine amounts are determined by microtitration which is known to be the most precise method for this type of analysis.

Introduction

The chlorine levels of water are highly-regulated by the EPA to ensure the safety of the populace. The EPA requires that water chlorination facilities regularly report the amounts of chlorine that is being added to the water supply. Added chlorine destroys bacteria and neutralizes metals that are present[18]. Water facilities use different chlorination methods which include the addition of chloramines, chlorine, or hypochlorite ions[9,10]. The amount of chlorine required to disinfect and neutralize metals for each source area of water is called the chlorine demand[18]. The chlorine demand is exceeded by the water chlorination systems because the water must also be protected from harmful bacteria while it is being stored or transported to the public for usage. The excess amount above a certain level can also be dangerous to the public however. The Environmental Protection Agency allows for total chlorine levels to be at a maximum of four parts per million[11]. Thus, it is necessary that the chlorine level is tested to determine that it is not in the amounts outside the safe range.

The excess chlorine is determined in this experiment and is referred to as "total chlorine". Total chlorine was determined by two separate titration methods, iodometric titration and DPD titration. Doing two separate titrations ensures that my determinations are accurate in the parts per millions (ppm) range levels. Total chlorine can be further divided into two separate categories, free and combined. The free chlorine is represented by hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) and combined represents free chlorine that has reacted with nitrogenous compounds present in the source water resulting in the formation of monochloramines (NH_2Cl), dichloramines ($NHCl_2$), and trichloramines (NCl_3). Currently there are water quality reports that are presented to the public annually, but the chlorine concentrations are not reported in the same units between different areas. For an example, Mount Vernon, Illinois has their chlorine units reported in ppm chloramine and Lebanon, Illinois, has their chlorine units reported in ppm chlorine. The first goal of this project is to quantify the different forms of chlorine accurately by keeping the same lab conditions ,performing the quantification titrations in an identical way and reporting the quantities in the same units for all water samples so that a realistic comparison can be made, eliminating the variables between water quality reports. The different areas that I have taken sample water from are Mount Vernon, Sauget, Tamaroa, Wayne City, and Lebanon. All of these towns are within Southern Illinois.



Experimental Methods

The iodometric method, which is used to determine total chlorine, involves the starch indicator with sodium thiosulfate titrant. The procedure starts with a set volume of tap water, preferably near five hundred milliliters because a very small amount (in the range of microliters) of titrant is required for large amount of water[8]. When excess (one gram), potassium iodide is added, it reacts with all of the chlorine present in the water by donating electrons at the pH of approximately 3 to 4[8]. The pH is adjusted using acetic acid.

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \qquad \text{Eq. 1}$$

Upon the addition of the starch solution, the iodine reacts with the amylose in starch giving off a dark blue color[1]. Then the dark blue color is titrated back to clear upon the addition of a necessary amount of standard sodium thiosulfate to reduce iodine back to iodide[8].

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \qquad \text{Eq. 2}$$

The DPD titration, an alternate method for "total chlorine" determination involves two consecutive titrations. The first titration gives the amount of free chlorine, while the second one is performed for the amount of combined chlorine. The free chlorine determination is based on the electron transfer reaction between the DPD indicator added to the water sample and hypochlorous acid present in water that changes the water sample color to red[7,8]. Phosphate buffer is also added to adjust the pH to 6.2-6.5[7,8].

$$2\ DPDH\ (colorless) + HOCl \rightarrow HCl + H_2O + 2\ DPD\ (red) \qquad \text{Eq. 3}$$

The magenta color is then titrated back to clear by reducing the indicator to its original colorless form with standard ferrous ammonium sulfate titrant.

$$DPD\ (red) + Fe^{2+} + H^+ \rightarrow DPDH\ (colorless) + Fe^{3+} \qquad \text{Eq. 4}$$

At the end of this titration, one gram of potassium iodide is added to the test sample which forces the combined chlorine to react with a portion of the excess iodide by accepting an electron from it and converting the left-over portion to triiodide (I_3^-)[7,8].

$$NH_2Cl + 3I^- + H_2O + H^+ \rightarrow NH_4OH + Cl^- + I_3^- \qquad \text{Eq. 5}$$

The DPDH that is already present in the solution after the first titration reacts with triiodide, forming its oxidized form[7].

$$2\ DPDH + I_3^- \rightarrow I^- + 2HI + 2\ DPD \qquad \text{Eq. 6}$$

After sitting in the dark for about five minutes, the second titration is performed to determine combined chlorine amount with the same titrant, ferrous ammonium sulfate used in the first titration (Eq. 4)[7]. The addition of the free and combined chlorine amounts result in the amount of total chlorine[7].

Data

Chlorine Amounts (Free, Combined, Total)	**Sauget, Illinois (Sample Taken on 3/18/18)**	**Lebanon, Illinois (Sample Taken on 3/21/18)**	**Mount Vernon, Illinois (Sample Taken on 3/25/18)**	**Tamaroa, Illinois (Sample Taken on 3/25/18)**	**Wayne City, Illinois (Sample Taken on 4/4/18)**
Total Chlorine (ppm Cl^-) (Iodometric)*	0.1416 0.1841 0.14868 Average: 0.1581± 0.0227	0.06372 0.07080 0.05664 Average: 0.0637± 0.0071	0.4602 0.4248 0.3894 Average: 0.4307± 0.0027	0.12744 0.12744 0.11328 Average: 0.12272±0.00818	0.15576 0.16284 0.16284 Average: 0.1604± 0.0041
Free Chlorine (ppm Cl^-) (DPD Ferrous)**	0.05 0.05 0.06 Average: 0.05333±0.00577	0.010 0.012 0.010 Average: 0.011± 0.00115	0.27 0.24 0.28 Average: 0.2634± 0.0208	0.021 0.02 0.02 Average: 0.0234± 0.00058	0.04 0.04 0.045 Average: 0.04167±0.0029
Combined (ppm Cl^-) (DPD Ferrous)**	0.10 0.10 0.07 Average: 0.09± 0.01732	0.05 0.04 0.04 Average: 0.0443± 0.00577	0.052 0.050 0.050 Average: 0.0506± 0.0012	0.050 0.040 0.040 Average: 0.0433± 0.00577	0.09 0.08 0.08 Average: 0.0833±0.00577
Total Chlorine (ppm Cl^-) (DPD Ferrous)	0.15 0.15 0.13 Average: 0.14333±0.01155	0.060 0.052 0.050 Average: 0.054± 0.00529	0.322 0.320 0.320 Average: 0.3207± 0.0012	0.071 0.060 0.060 Average: 0.06367±0.00635	0.13 0.12 0.125 Average: 0.125± 0.005
Difference (Total ppm Cl^-) between DPD and Iodometric	0.01477	0.0097	0.11	0.05905	0.0354

$$*\frac{mL\ of\ titration\ x\ N\ x\ molar\ mass\ Cl\ (mg)}{mL\ of\ sample}$$ *(N= normality)*

$$**\frac{mL\ of\ titant\ x\ FASSF}{2}$$ *(FASSF = Ferrous Ammonium Sulfate Standardization Factor which is equal to 1)* [7,8]

Discussion

The water quality reports depict chlorine concentrations in different units depending on the report that is in question. This makes it difficult to compare the values of chlorine between different municipal areas. Conversion of measured values to a common unit would allow for a comparison between different areas to determine by what quantity chlorine concentrations differ.

Municipal Water Districts	**Reported original values In arbitrary units**	**Reported values converted to the same unit (Cl^- ppm)**
Mount Vernon[4]	2-3 ppm chloramines	1.38-2.06 ppm chloride
Lebanon[4]	0.6-2 ppm chlorine	0.3-1 ppm chloride

Lebanon receives its water from the SLM Water Commission using river water or side channels of water[4]. Mount Vernon and Tamaroa use lake water from Rend Lake Inner-City Water system[4,6] . Wayne City provides their water through their own surface water from side channels[4]. Sauget receives water from the Mississippi River through American Water Company[5]. Lebanon, Mount Vernon, Wayne City, and Tamaroa all have comparable farming lands affecting their water. Mount Vernon and Sauget both have industrial factors, though Sauget has a greater effect from industry due to using the Mississippi River which harbors waste products from production plants.

Sauget presented the largest amount of combined chlorine. The Mississippi River has high amounts of nitrates due to farming areas and industrial production facilities located on the river. The Mississippi River feeds into the Gulf of Mexico and is the main reason that a large portion (8185 square miles) of the northern Gulf of Mexico now is considered a dead zone in which life will not survive[12]. This dead zone is due to the high amounts of nitrogen and phosphorus in water because farmers in the Mississippi Basin use nitrogen and phosphorus fertilizers for their crops[13]. This results in excess algal blooms. When bacteria consume the algal blooms, they use dissolved oxygen resulting in low amounts of oxygen for living organisms[13]. The amount of combined chlorine seems to be greater in industrial areas than the farming areas. The amounts in the farming areas seem to be comparable to one another. Mount Vernon is the outlier with its lower amount of free chlorine which may be due to less amount of chlorine being added initially to combat bacteria in the distribution system to Mount Vernon.

All of the total chlorine amounts are less than I expected. I initially expected to get values close to what is being reported by the water quality reports after conversion to consistent units, but my results were different.

Municipal Water Districts	**Reported values In arbitrary units**	**Reported values converted to the same unit (Cl^- ppm)**
Mount Vernon	2-3 ppm chloramines	1.38-2.06 ppm
Tamaroa	2-2.5 ppm chloramines	1.38-1.72 ppm
Lebanon	0.6-2 ppm chlorine	0.3-1 ppm
Wayne City	1.98-3.5 ppm chloramines	1.36-2.41 ppm
Sauget	2-3 ppm chloramines	1.38-2.06 ppm

After some investigation, I have found that the water quality reports showed the chlorine values as they leave the treatment plant whereas I measured the levels after distribution to the public. The variation between the reported and the measured values indicate that there is more consumption of chlorine during the storage and distribution processes due to bacterial contamination or heavy metal leakage by old water pipes. This shows that certain distribution systems need to be investigated and updated. The EPA could use these percent differences between the reported values (gathered right after chlorination process) and the experimental values (gathered as the water reaches the public) to establish that at a certain percent difference, the distribution system must be replaced. This would also be an important value to include within the water quality reports that are distributed annually because it would show the public that their distribution system is well-maintained or needs an upgrade. This would allow the public to have leverage over the water providers which would force an upgrade if necessary.

Areas / ppm Cl^-	Reported Values	Experimental Values	Percent Difference
Mount Vernon	1.93 ppm	0.437 ppm	77.4%
Tamaroa	1.58 ppm	0.1228 ppm	92.3%
Lebanon	0.7 ppm	0.0637 ppm	90.9%
Wayne City	2.13 ppm	0.1604 ppm	92.5%
Sauget	1.79 ppm	0.158 ppm	91.2%

Chloramines are used in some areas over chlorine because the chloramines last longer in the distribution system than the free chlorine does. Also, the chloramine disinfection has less dangerous by-products. The free chlorine is a more effective disinfectant than the monochloramines, thus in many cases there is a mixture of both being used[16]. If chlorine is used as a primary disinfectant to meet the initial demand then chloramines can be used as the secondary disinfectant to ensure safety of the water during distribution to minimize the formation of harmful chloromethanes from free chlorine[17]. The chloramines are dominantly produced over the free chlorine by adding ammonia if nitrogen is not present in the source water in a high enough concentration.

Chlorination is not the best technique to disinfect water in terms of the public health, but is still in use today because it is the cheapest way for a large population. Another popular way to disinfect water is through ozone addition, used by a few nations in Europe (France and the Netherlands) dominantly[15]. This process is more expensive and only a few cities in the United States have switched to ozone for public health considerations. Some advantages of ozone are that it is more effective at destroying bacteria and viruses than chlorine, it requires low contact time (only 10-30 minutes), and it does not produce any harmful residuals[14]. The disadvantages are the cost, the toxicity requiring workers be protected, and corrosiveness requiring special equipment[14].

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