

COMPARATIVE STUDY UPON THE QUALITATIVE AND QUANTITATIVE ANALYSIS OF METAL IONS OF VARIOUS WATER SAMPLES OF DOON VALLEY

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Abstract

Water is the basic requirement for the continuity of life upon this planet. The concerned study upon the metal analysis and the physicochemical parameters were taken into consideration. The water samples so far collected from various places of Dehradun are being consumed on large scale. The water samples so far collected showed different types of metal content concentrations. The results are being shown in the below given tables. Among the three sites the water of NAGAL NALA seems to be more portable for consumption because the metal contents are within the range of acceptability. Also the water collected from the SONG RIVER was found to be more suitable than the SAHASTDHARA RIVER, as per their metal content and the physicochemical properties concerned.

Key Words: Metal Analysis, water samples, Nagal Nala, Sahastradhara and Song River

INTRODUCTION

Aquatic systems such as the seawater, inland water etc. is important stages in the biogeochemical cycle. Although dissolved levels are usually in the trace range of 10^{-6} - 10^{-9} Ml⁻¹ they remain significant, because they entry into the food chain and interactions with suspended particulate and sediments largely occur via the dissolve state. Today, there is a strong and necessary trend toward instrumental techniques, as opposed to the classical methods, especially when assaying very small amounts of materials. The first analyses of seawater were performed just prior the beginning to the 19th century in laboratories. However, problems arising from changes in chemical composition through evaporation, biological activity, or chemical interactions with the containing vessel, forced the marine chemist to transfer his laboratory from land to ships.

According to World Health Organization (WHO), (1) nearly 1.8 million deaths, due to diarrhea and cholera per year, are attributed to unsafe water supply in conjunction with inadequate sanitation and hygiene whereas improvement in water supply can help reduce morbidity by 6 to 25%. In spite of the fact that chemical contaminants health effects are generally linked with long term exposures, in contrast

to immediate effects of biological/bacteriological contamination, yet these chemicals may result in serious adverse effects (2).

In environmental research and protection toxic metal, particularly Cd, Pb, Hg, As, Ni, Cr, etc. are becoming increasingly significant owing their biological non degradability and chronic toxicity resulting from their accumulation in vital organs of man. As part of the SEAFDEC Cooperative Program in the Study of Fisheries Oceanography of the South China Sea, a Research on trace heavy metals in seawater was made. General comparative considerations like visible spectroscopy and modern flame photometric methods, with high sensitivity, precision, and accuracy also a simple sample preparation and treatment to be the most promising chose for the determination and characterization of metal traces in different water samples.

ifferent species of human pathogens (*Salmonella*, *Yersinia enterocolitica*, *Shigella*, *Campylobacter* including various viruses such as Rota virus, Hepatitis A and E virus and parasites like *Giardia lamblia* and *Entamoeba histolytica*) (3-5), when present in drinking water causes serious risk of ailment like gastroenteritis (6), diarrhea, dehydration etc. To determine bacteriological contamination, (7) coli form group of organisms are considered best indicators as

they are easily detectable in water. Analyses revealed that arsenic, selenium, strontium and total dissolved solids (TDS) exceeded the Environmental Protection Agency's Drinking Water Maximum Contaminant Limit (MCL) in some samples from private water wells located within 3 km of active natural gas wells (8). The (9) Study described the water quality parameters for human consumption being kept stored in tanks by its Physical, Water Quality in Terms of Physico-chemical parameters and showed that the water is safe for consumption.

MATERIAL AND METHODS

Study area and water sampling

The water samples were collected from different regions of Dehradun. The water samples were collected early morning in air tight bottles and were stored in shade at a temperature range of 25^o-30^oC.

Experimental

The water samples so far collected were analysed for their physicochemical characteristics.

Estimation of inorganic elements

Qualitative analysis

Calcium: One drop of dil. ammonium hydroxide and saturated ammonium oxalate solution was added to 10ml of the above filtrate. White precipitates of calcium oxalate, soluble in hydrochloric acid but insoluble in acetic acid, were formed.

Magnesium: White calcium oxalate precipitate was separated by filtering the above solution. The filtrate was heated and cooled. Solution of sodium phosphate in dilute ammonia solution was added. White crystalline precipitate was observed.

Sodium: Little uranyl magnesium acetate reagent was added to 2ml of the test solution, shaken well and kept for few minutes. Yellow crystalline precipitate of sodium magnesium uranyl acetate was observed.

Potassium: Few drops sodium cobalt nitrite solution was added to 2-3ml of the test solution. Yellow precipitate of potassium cobalt nitrite was observed.

Iron: Few drops of 2% potassium ferrocyanide were added to 5ml of the test solution. Dark blue coloration was observed.

Sulphate: To 5ml of the test solution, lead acetate

reagent was added. A white precipitate, soluble in sodium hydroxide, was formed.

Phosphate: 5ml of test solution was prepared in nitric acid and a few drops of ammonium molybdate solution were added. It was heated for about 10 minutes and left to be cooled. A yellow crystalline precipitate of ammonium molybdate was observed.

Chloride: 3 to 5ml of lead acetate solution was added to about 5 to 7ml of the filtrate. A white precipitate soluble in hot water was observed. **Carbonate:** To 5ml of the test solution, dilute acid was added. Carbon dioxide was liberated from the solution.

Nitrates: Ferrous sulphate solution was added to 5ml of the test solution. No brown colour was produced, but when sulphuric acid was added (slowly from the side of the test tube), a brown colored ring was produced at the junction of two liquids.

Barium: Take a sample at the tip of a charred match stick and introduce into a colourless Bunsen flame near the base. The flame is coloured an apple green, indicating Ba.

Lithium: To 1 cm³ of the solution in a test tube, add NH₃ solution drop wise till smell persists. Add 1 cm³ ammonium carbonate solution. A white precipitate of Li₂CO₃ is formed.

Quantitative analysis

Sulphate: Sulphate was estimated by Turbidimetric method based upon the precipitation of Sulphate ion in an acetic acid medium with barium chloride so as to form barium sulphate crystals of uniform size. A suitable portion of sample was taken in a 250ml Erlenmeyer flask. Then 20ml of buffer solution was added to the sample and mixed in stirring apparatus. A spoonful of barium chloride crystals was added while stirring, and timing was begun immediately. It was stirred for 60±2s at constant speed. After stirring period has ended, the solution was poured into the absorption cell of spectrophotometer and turbidity was measured at 420nm. Light absorbance of the barium sulphate suspension was measured and the sulphate concentration was determined by comparison of the reading with a standard curve using Chemito 2100 scanning spectrometer.

Chloride: Chloride was estimated by Argentometric method. In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the

silver nitrate titration of chloride. Silver chloride will be precipitated quantitatively before red silver chromate is formed. A suitable portion of sample was diluted to 100ml and 3ml of aluminium hydroxide suspension was added if and only if the sample was highly colored. Mixed, let aside to get settled and filtered. pH was adjusted to 7 to 10 and the samples in the pH range 7 to 10 were directly titrated. 1ml of potassium chromate indicator solution was added and titrated with standard silver nitrate titrant up to a pinkish yellow end point.

Phosphate: A series of 10ml volumetric flasks are taken to each 10 ml volumetric flasks, add 0.5 ml of NH_4 molybdate and 3ml of 0.25 N of H_2SO_4 and 0.1 , 0.2 , 0.3 , 0.4 , 1 ml Na_2HPO_4 were added. Finally to each flask 1ml of Sodium Sulphite solution was added ($2.0 \times 10^{-3}\text{M}$) and make up to 10ml. Then each solution is kept for 20 min at room temperature. The absorbance of solution was measured at 715 nm using water as a blank.

Nitrate: Pipette an aliquot (0.25 ml) of sample or Standard into a 50 ml of volumetric flask. Mix thoroughly, with 0.8 ml of 5 % salicylic acid in H_2SO_4 . After 20 min at room temperature, add 19 ml of 2N NaOH to raise pH about 12. Cool samples to room temperature and measure absorbance at 410 nm.

Sulphate: Run 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 cm cube of the standard potassium sulphate solution from calibrated burette into separated 100 cm cube graduated flasks. To each flask add 10 cm cube of the NaCl-HCl reagents and 20 cm cube of the glycerol ethanol solution and dilute to 100 cm cube with distilled water. Add 0.3g Or the sieved BaCl_2 to each flask , stopper each flask and shake for one minute by inverting each flask to stand for 2 -3 minute and measure the turbidity in the EEL Nephelometer : take care to avoid small bubbles adhering to the walls of the test tube .Use the most conc. Solution as standard solution by means of sensitivity . Control, adjust the galvanometer reading to 100 divisions. Prepare a blank solution repeat the above sequence of operations but do not add. Place the blank solution in Nephelometer and adjust to 0 reading of galvanometer scale by means of the zero controls above the galvanometer suspension. Check the reading of the most turbid solution and adjust any deviation from 100 by means of the sensitivity control. Repeat the measurement with 5 other standard sulphate ions and determine the sulphate ion content of an unknown solution by using calibration curve.

Potassium: Preparation of standard solutions for **calibration curve:** Dissolve exactly 1.090gm of potassium chloride in water and make up to 1 liter. This contains 1mg per ml (1000 ppm).

Estimation of potassium by flame photometer

First, switch on the digital flame photometer followed by the air compressor with the required value (10 bars). Open the gas from the gas cylinder (after the instrument is warmed up for 10 minutes). Initially allow the ion-free water (distilled water) to aspirate in to the flame and set the digital value as 100. Now the instrument is said to be calibrated. After this calibration of the instrument, no adjustment should be made. Introduce the solutions containing different concentrations of potassium chloride (2, 4, 6, 8, 10 μg) to the flame and find out the intensity of emitted light of each solution. Plot a calibration graph between concentration and intensity of KCl solution which passes through the origin. Finally, introduce the sample of unknown solution containing sodium into the flame and find out the intensity of emitted radiation. From the intensity, the concentration of unknown solution can be determined.

Sodium, lithium barium and calcium: The estimation of these metals was carried out by flame photometry by setting up of the flame photometer with their usual standards and rest of procedure was as same as for potassium ion determination.

Observation

Colour Determination

The water sample collected from the Nagal region was colourless, and the sample collected from the Sahastradhara river was little greenish, which could due the accumulation of various types of bryophytes. The water sample collected from the Song River was colourless.

Table 1 Qualitative analysis of various metal ions

S. No	Sample Name	Metal Ions											
		Ca	Mg	Na	K	Fe	SO_4^{2-}	PO_4^{3-}	Cl^-	CO_3^{2-}	NO_3^-	Li	Ba
1	Nagal Nala Water	+	+	+	+	+	+	+	+	+	+	+	+
2	Sahastradhara River	+	+	+	+	+	+	+	+	+	+	+	+
3	Song River	+	+	+	+	+	+	+	+	+	+	+	+

pH Determination

The pH value was determined by using electronic pH-meter. The pH was standardized at its three level of standardization using buffers (4, 7, 9 pH buffers). Then directly the pH of the concerned 3 samples was determined.

Table 2

S. No	Sample Name	pH-Value
1	Nagal Nala Water	7.08
2	Sahastradhara River	8.45
3	Song River	7.48

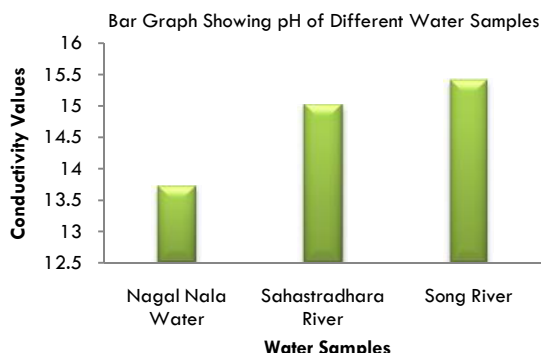


Figure 1

Conductivity Determination

The conductivity of the solution was determined by using electronic conductivity meter. The standardization of instrument was done by setting the cell constant of instrument at its known value with reference to water. Then by inserting the electrochemical in the sample its conductivity was noted.

Table 3

S. No	Sample Name	Conductivity- Value at 20 ms
1	Nagal Nala Water	0.126
2	Sahastradhara River	1.69
3	Song River	0.63

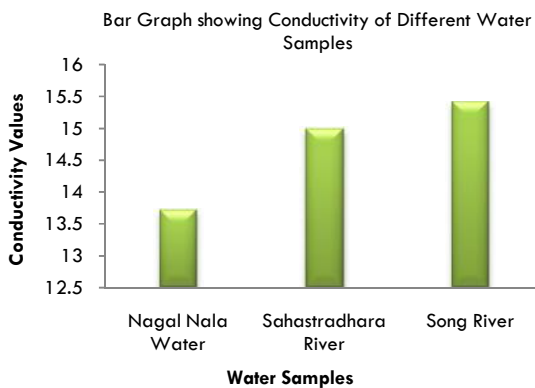


Figure 2

Turbidity value Determination

The turbidity of the water samples was recorded by using electronic turbidimeter. The turbidity meter was standardized by using 400 and 40NTU standards of SO₄⁻ ion. Turdity values are tabulated as below.

Table 3

S. No	Sample Name	Sulphate ion Conc. In ppm
1	Nagal Nala Water	30
2	Sahastradhara River	28
3	Song River	004

Bar Graph Showing Sulphate Ion Conc. in Different Water Samples

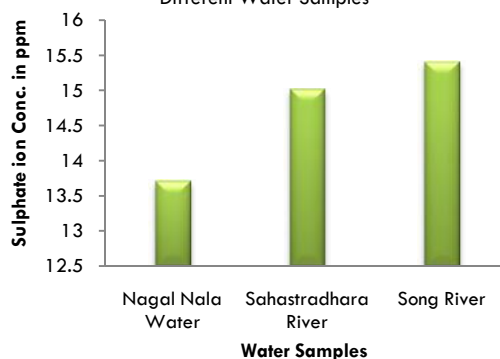


Figure 3

Calcium ion Determination

The calcium ion was determined by complexometric titration and the concentration of calcium in different water samples is tabulated as under.

Table 4

S. No	Sample Name	Calcium ion Conc. In ppm
1	Nagal Nala Water	17.3
2	Sahastradhara River	142
3	Song River	138

Bar Graph Showing Calcium Ion Conc. in Different Water Samples

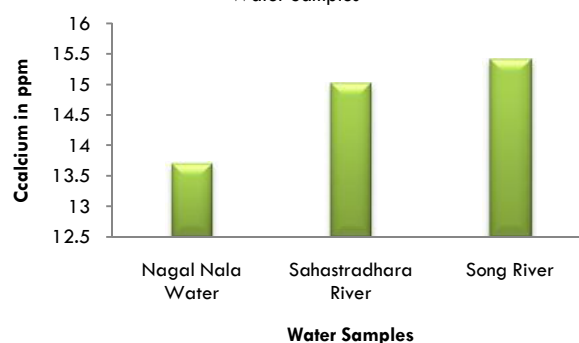


Figure 4

Magnesium ion Determination

The calcium ion was determined by complexometric titration and the concentration of magnesium in different water samples is tabulated as under.

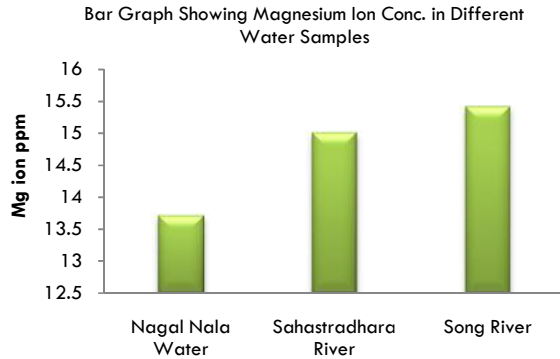
Table 5

S. No	Sample Name	Magnesium ion Conc. In ppm
1	Nagal Nala Water	5.1
2	Sahastradhara River	82.7
3	Song River	71.2

Flame photometric analysis of Sodium, Potassium, Calcium, Lithium, Barium, ions

Sodium, Potassium, Calcium, Lithium, Barium were

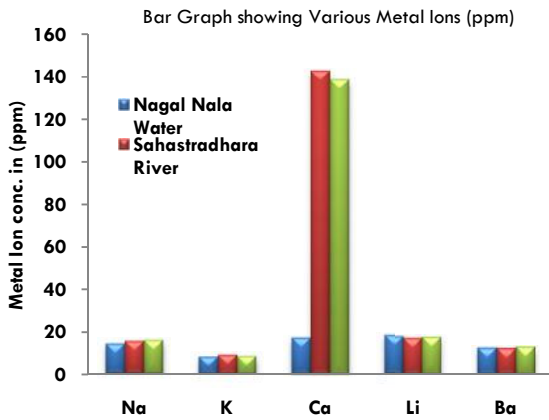
analysed by flame photometry, using their respective standards. Every time the instrument was set up with a particular standard of a respective ion. For calcium 20, 40 and 100 ppm standard solution was used in increasing order. Similarly other types of metals were analysed using their respective standards in increasing order. The data sheet for various metal ions is as under.



Water Samples
Figure 5

Table 6

S. No	Sample Name	Metal Ions (ppm)				
		Na	K	Ca	Li	Ba
1	Nagal Nala Water	13.7	8.2	17.3	17.8	12.2
2	Sahastradhara River	15.0	9.1	142	17.04	12.0
3	Song River	15.4	8.5	138	17.5	12.6

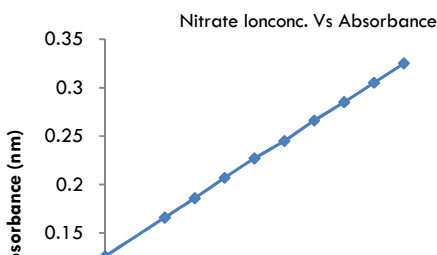


Water Samples
Figure 6

Standard Graph for the estimation of phosphate ion

Table 7

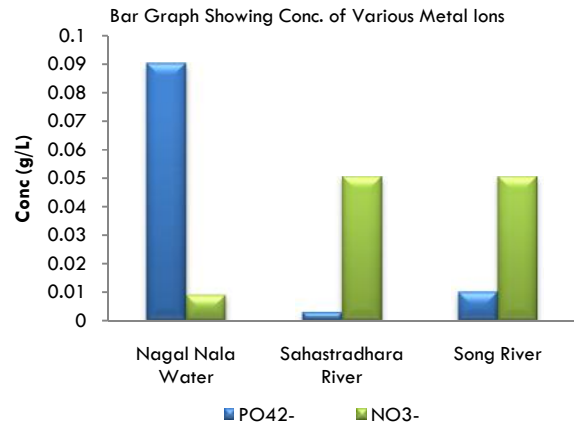
Conc.	Absorbance
0	0.001
0.5	0.008
1	0.014
1.5	0.021
2	0.027
2.5	0.033
3	0.039
3.5	0.045
4	0.051
4.5	0.058



From the Standard straight line graph the value of PO_4^{2-}/NO_2^- ion three concerned water samples was calculated and tabulate below

Table 7

S. No	Sample Name	Metal Ions (g/L)	
		PO_4^{2-}	NO_3^-
1	Nagal Nala Water	0.09	0.01
2	Sahastradhara River	0.12	0.1
3	Song River	0.009	0.05



Water Samples
Figure 8

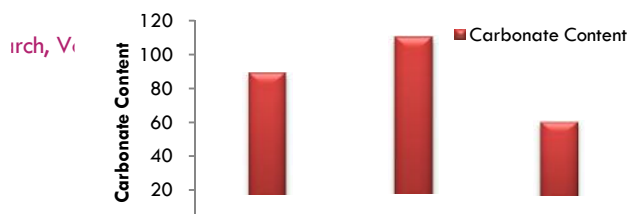
Oil and Grease content

The Carbonate and oil/grease content in different water samples are tabulated below.

Table 8

S. No.	Sample Name	Carbonate and Oil/Grease content (mg/L)	
		Carbonate content	Oil Grease Content
1	Nagal Nala Water	88	3
2	Sahastradhara River	110	1
3	Song River	59.4	0.1

Bar Graph showing Carbonate content in different water samples



RESULT AND DISCUSSION

- From the above results it had been found that all the three samples collected from different sites contain all the metal ions like (Ba, Li, Cl⁻, Fe, K, Na, Mg, Ca) and the salt ions in good concentration (NO₂⁻, CO₃²⁻, PO₄³⁻, SO₄²⁻).
- All types of salts and metal ions present these water samples show that water collected from these sites is portable and should be consumed in good quantity.
- Due to the presence of these chemical constituents the water samples show a good conductivity so the water consumed from these places act as good source of electrolyte, and full fills the bodily demand of minerals.
- As per the pH of water collected from these sites are taken into consideration it is within the consumptional range, because pH maintenance is very essential within the body. All type of blood circulation is under the control of bodily pH. All types of nutrient distribution between the cells because of potential difference between the cells which in turn is under the control of pH.
- All of water samples are colourless so possesses little suspended particles, except the water samples collected from Sahastradhara site which

is bluish in colour due to the presence of algae species.

- The sodium content in Nagal Nala was found to be (13.7ppm), Sahastradhara River (15.0 ppm) and that of Song River (15.4ppm)
- The potassium content in Nagal Nala, Sahastradhara and Song River was found to be 8.2, 9.1 and 8.5 ppm
- The lithium content in Nagal Nala, Sahastradhara and Song River was found to be (17.8, 17.01, 17.5 ppm) respectively.
- The barium content in Nagal Nala, Sahastradhara and Song River was found to be (12.2, 12.1, 12.6 ppm) respectively
- The magnesium content in Nagal Nala, Sahastradhara and Song River was found (5.1, 82.7, 71.2 ppm) respectively.
- The PO₄⁻, NO₃²⁻ content in Nagal Nala, Sahastradhara and Song River was found (0.09, 0.12, 0.009) and (0.01, 0.1, 0.05) ppm respectively.

CONCLUSION

From the results, all the values were within the acceptable limits of the WHO (2006)/NAFDAC (2001). The pH values ranged between 6.1- 6.5 which is in the normal range for irrigation water, and the conductivity of the water samples shows that the water is useful. As per the metal contents and the dissolved salts, are taken into consideration they within the guidelines so is consumptional. Among the all three types of sample the NAGAL NALA responded well towards the metal content concentration, dissolved salts and the pH and conductivity range. So the water from the NAGAL NALA should be consumed as much as possible.

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