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# IDENTIFICATION AND QUANTIFICATION OF THE SOURCE TERMS FOR SODIUM, CALCIUM AND FLUORIDE IONS IN SOILS AND SURFACE WATER OF SIL RIVER WATERSHED

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## Abstract

This preliminary study identifies and quantifies selected ions in Sil river watershed. The selected ions were Sodium, Calcium and Fluoride alongwith pH of each sample. There were 256 samples (128 of soil and 128 of water) collected from 32 different sites in four seasonal times of the year 2013, from Sil river watershed. Selected ions detected approximately in sufficient amount in the entire Sil river watershed. Comparison of these ions availability and pH with WHO guidelines showed that, pH, Sodium and Fluoride ions are within permissible level at all sites of Sil river watershed. Calcium availability in the entire watershed is very high, except at sites S6, S7 and S8 having zero level of calcium availability. Spatial variability of these selected ions was also considered. Fig. 7 shows the altitudinal variation of selected ions in Sil river watershed. There was no significant variation found in all three major intervals of 41 meter. This work is believed to serve as a baseline data for further studies in Sil river watershed as well as to inform decision makers on the possible sources of ions in the study area.

**Keywords:** Ions, Watershed, Comparison, Spatial variability.

## Introduction

Ions detection is one of the most important tools to validate the environmental research of any area for future planning and management. Ions detection provides the level of vulnerability of water and soil, to the area and people. The flow in the interest of vulnerability study in the 1990s has been determined in a large part by the worldwide environmental change communities, where there were distinct changes in the concepts from the opinions of impacts to an evaluation of all the methods, conditions, and distinctiveness of approaches that increases sensitivity and reduce adaptive reactions (Jalil and Khan, 2013). The importance of water quality of both surface and ground water is the main issue in the world and leads mainly towards the social and economic loss. Similarly, importance of water quality for ecosystem and biophysical systems management is evident. The focus of these studies was always centered on the human welfare and benefits. Water quality plays a major role in the health related issues and influences the social development. Water quality provides current information on concentration of various parameters at a given place at certain time (Jalil and Khan, 2012). Sil river is also a river having a significant impact on the areas related to it.

Sil river lies in the Potohar region and is the major tributary of Soan river, Islamabad (Fig. 1). Similarly, Soan is one of the left bank tributary of Indus River Jehanzeb (2004). Sil river has the watershed with most critical climatic conditions with respect to low rainfalls and high temperatures, compared to the entire region of Potohar. Sil river watershed has very high erodibility and siltation ratio due to its existing geological conditions. Sil river watershed contains small barren hills with relatively moderate slopes with high erosion rates. The information collected from local people of the community of Sil river watershed provides the information that is nearly 10 to 15 years earlier when there was a significant amount of the natural flows available throughout the year in Sil river. However, presently it has became a nullah with very low or sometimes with no natural flow (at some sites) during a year. The peak runoff generation occurs during the Monsoonal rainfalls, which causes flooding in low-lying areas of the watershed and damages the relatively fertile lands of downstream areas.

### Sil river watershed area (SRWA)

Sil river watershed area is relatively a neglected area for research and development. Therefore, there is very small amount of data available (or not) for case studies. It is the first ever report of its kind on the initial status of Sil river watershed. Due to unfavourable environmental conditions and low per capita production, people mainly rely on nature-based products, which is the major cause of deforestation and deterioration of natural environment of the area.

Following are the tributaries entering into Sil river (Fig. 2):

- Ratrian Kas tributary

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- Khaur village tributary
- Ikhlas tributary
- Shahbazpur dam tributary
- Hariwala tributary
- Upper Naushera tributary
- Lower Nowshehra tributary 1
- Lower Nowshehra tributary 2

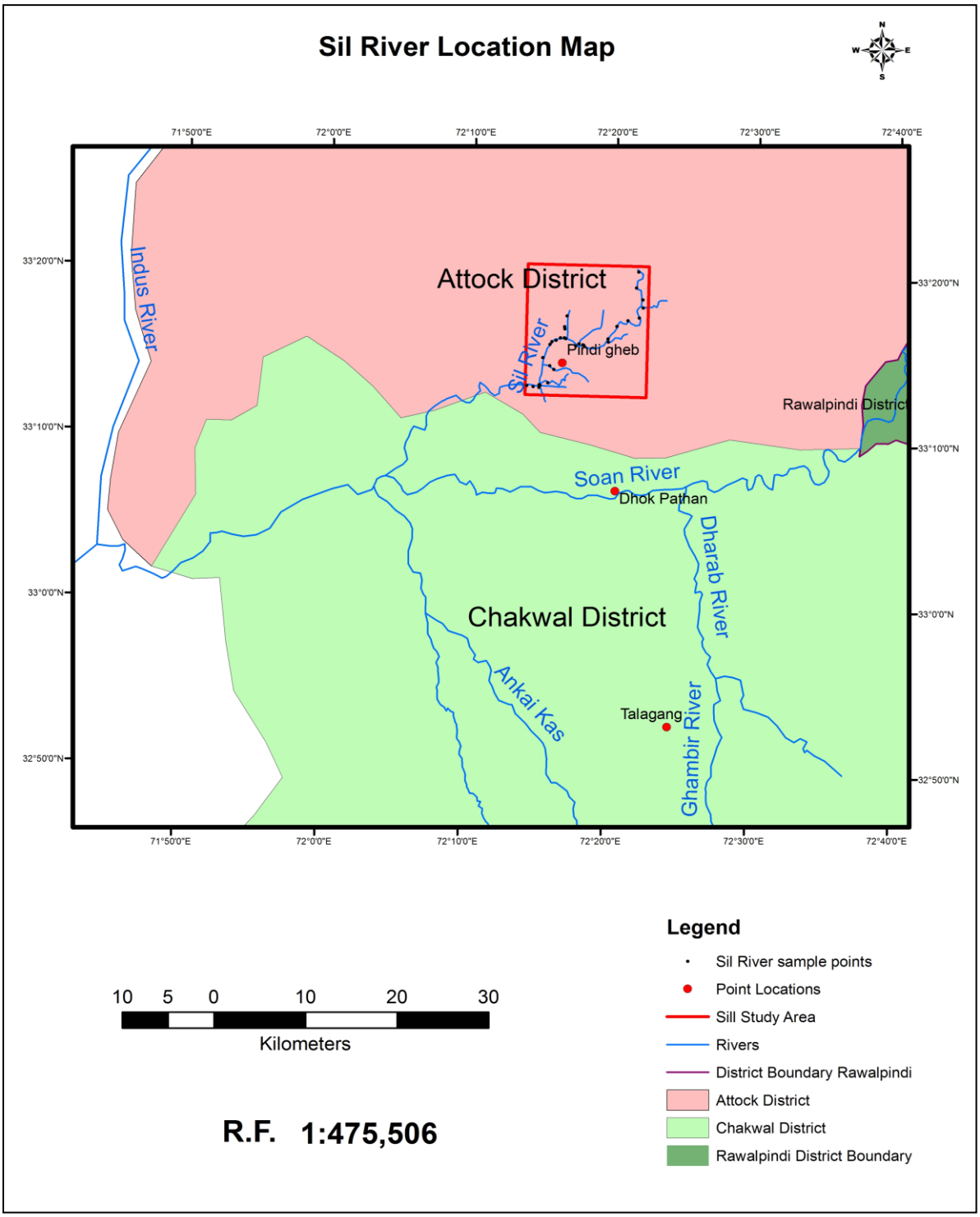



**Fig. 1. Sil river location map.**

In this entirely 49 km long river, major tributaries which are entering in Sil river: firstly, start from a Kas (small valley) called Ratriyan kas, just 2 kilometers below from start. After crossing the area of Ratriyan, the river enters into a deep valley called Saghar Kas and runs in semi circular arc shape. Just below the Saghar kas, two tributaries enter into Sil river, first from the catchment of Khaur village and second from the Ikhlas village. After crossing the bridge of Pindi Gheb Tehsil, another tributary coming from Shahbazpur dam downstream joins the river. Sil river flows through Tehsil Pindi Gheb from North to North-west direction. Hariwala tributary enters from the downstream of Pindi Gheb city. Hariwala tributary contains highly contaminated waters of Pindi Gheb

city. Two tributaries starting from small dams from above and downstream of village Nowshehra enters into the river next to the Hariwala tributary.

The above-discussed area contains the whole distributions of Sil river watershed. Sil river just below the village Toot (a small village of Tehsil Pindi Gheb), enters into the river Soan (Left Bank tributary of River Indus).

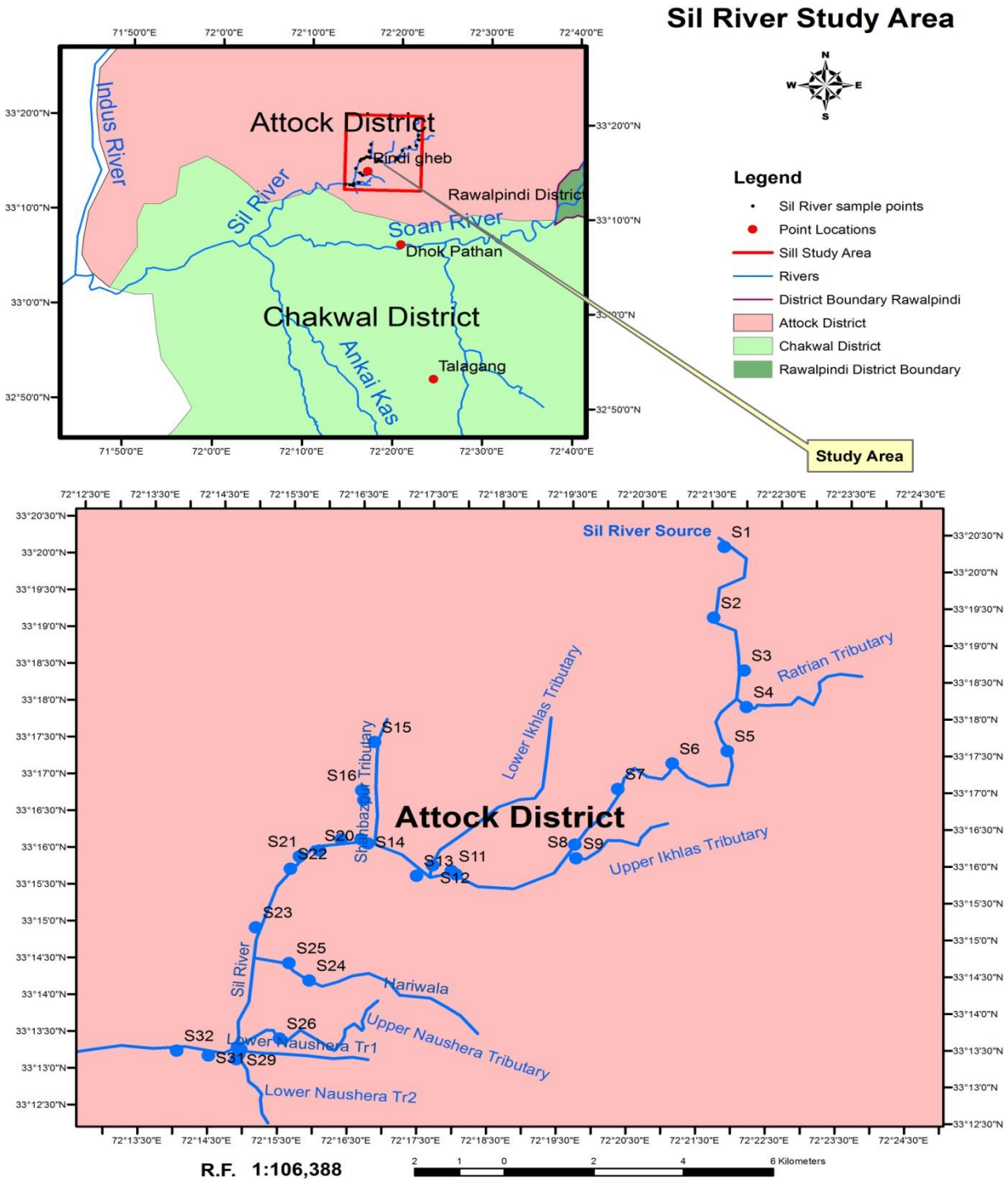



**Fig. 2. Study area of Sil river.**

## Materials and Methods

Sil river watershed is one of the most vulnerable areas in Potohar region having very high erodibility, which is the reason for the leaching of major minerals from the top soils causing the deficiency of those mineral contents.

This preliminary study contains the information and analytical justification of basic important ions, which includes Fluoride, Sodium and Calcium along with the values of pH of each sample. Because Sil river watershed contains different types of drainage with respect to nature and physical conditions, the sampling sites were divided into the following categories:

- Natural flow samples
- Landfill site (dumping of solid waste in watershed) samples
- Municipal drainage samples

- Fertilised field drainage samples
- Mini dams downstream flow samples.

**Sample collection**

Sil river samples were collected at the interval of four months in 2013. Selected intervals were adjusted according to the variations of base flows of the river at different times of winter and summer. There were 32 sites selected for sampling in all seasons, categorised accordingly as discussed above.

Two samples from each site were collected in each interval of time. Water sampling points were selected carefully (near to bank in case of river) to avoid any kind of debris in water. Considerable variations like seasonal stratification, runoff, rainfall and wind were also documented while collecting water sample. Plastic bottles were used to collect water samples and were stored at normal temperature.

Similarly, soil samples were collected from the selected sites after careful observation of each site (near the bank of river), such that the collected sample could be able to represent the actual status of the soils of that area. Each soil sample was collected in polythene bags, which were sealed and tagged accordingly.

**Samples preparation and testing**

Samples were tested in the Laboratory of the Center for Integrated Mountain Research, University of the Punjab, Lahore. Digital water quality meter (Model: 930 single parameter Meter) with electrodes was used to test samples. pH of each sample was tested with all other parameters.

Water samples were examined at room temperature and each sample was tested with two electrodes (one for temperature and one for desired parameter) while testing any parameter.

Soil samples were prepared using the following steps:

- Each soil sample was dried in oven at 150°C for half an hour.
- Each soil sample was meshed, using the sieves of different pore sizes, to get the smallest proportion of soil particles (0.002 mm sized particles).
- 100 gram of the smallest particles, used in distilled water for preparing the desired sample.

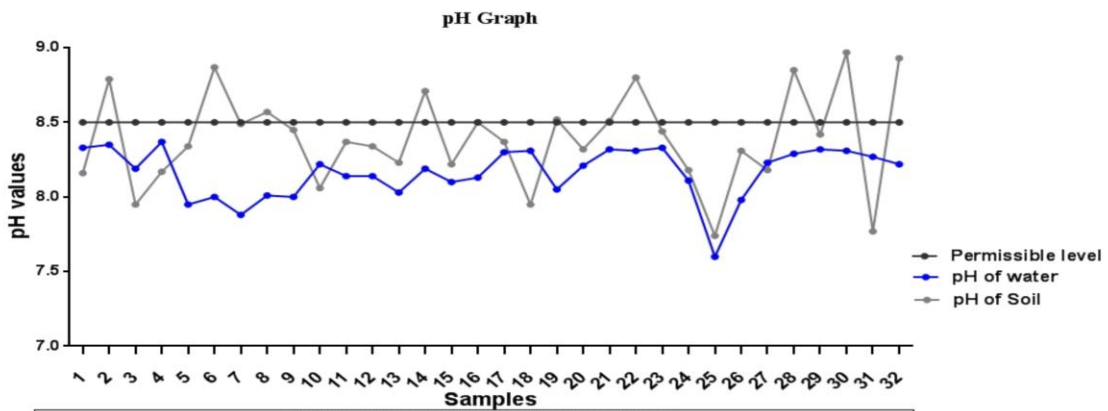
The prepared samples were tested accordingly, using the same technique, which was used for water samples.

**Sodium**

**Statistical analysis:** The data expressed as mean ± SD was compared with the control group using student paired t-test with one way ANOVA non-parametric test and Dunn's multiple comparison test. $P < 0.05$ was considered statistically significant. WHO standards were used as control parameters for pH of sodium, calcium and fluoride ions and each sample was compared with control parameter to get the significance of the data provided.

**Results and Discussion**

pH of water was within usual permissible level of 6.5-8.5 (WHO, 2011), in Sil river watershed as shown in Fig. 3. However, in soils of S2, S6, S14, S22, S28, S30 and S32, the values are more than the permissible level.

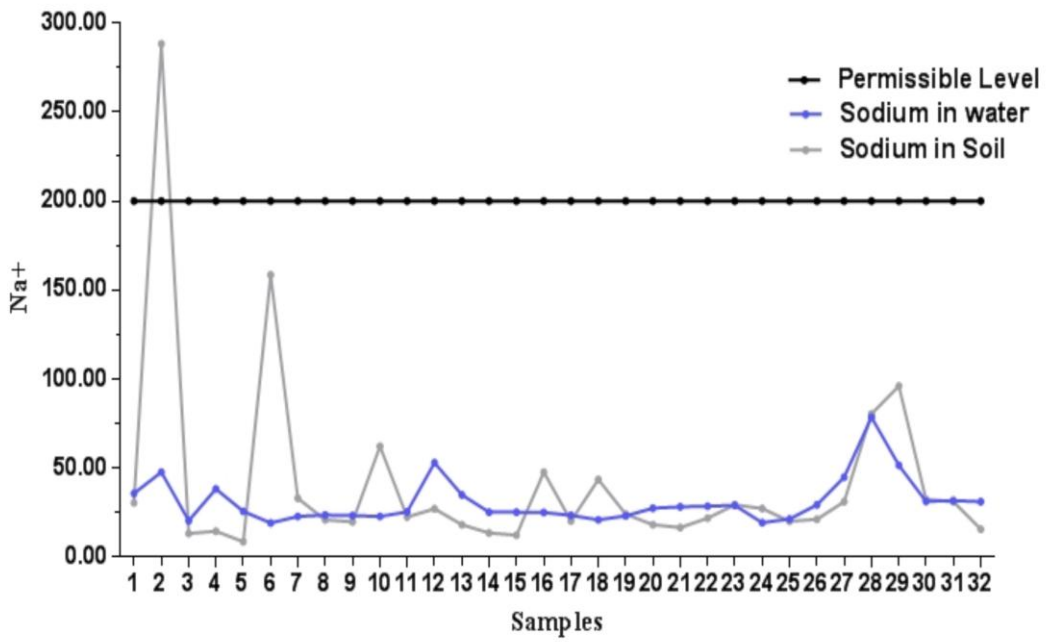



| One Way ANOVA Nonparametric (paired t-test) | | | | |
|---|---|---|---|---|
| Friedman test | Approximate P value | < 0.0001 | | |
| | P value summary | **** | | |
| | Are means signif. different? (P < 0.05) | Yes | | |
| Dunn's multiple comparisons test | | Rank sum diff. | Significant? | Summary |
| Treated water vs. Control | | -46.50 | Yes | **** |
| Treated Soil vs. Control | | -18.00 | No | ns |
| Treated Soil vs. Treated water | | 28.50 | Yes | ** |

**Fig. 3. Change of pH of different water samples.**

Hence, it may be concluded that Sil river watershed soils of these points have the characteristics of more alkaline properties, as a comparison of pH shows a significant difference between soil data of those points and control parameter. The higher pH values indicate that soils of this watershed have more alkalinity and less infiltration rates. This reflects the condition of soils is arid and leaching of minerals occurs frequently. These soils are comparatively less fertile and the hardness of upper layer of these soils is due to large amount of salts, which is the major issue.

Sodium is the most abundant element among alkali metals group, and a graphical representation of sodium ion reflects that S2, have slightly more value than that of control parameter. Fig. 4 provides a complete comparison of all subject data of sodium for Sil river watershed. Sodium ion ($Na^+$) combines with a variety of anions to form a number of different salts. Common sodium salts are chloride, carbonate, bicarbonate, hypochlorite, silicate, phosphate, and sulfate (Sax, 1975; Clayton and Clayton, 1981; Sittig, 1981; Sax and Lewis, 1987; Budavari, 1996; HSDB, 2000). Desirable limit of sodium in drinking water is 200 mg/L (WHO, 1996).



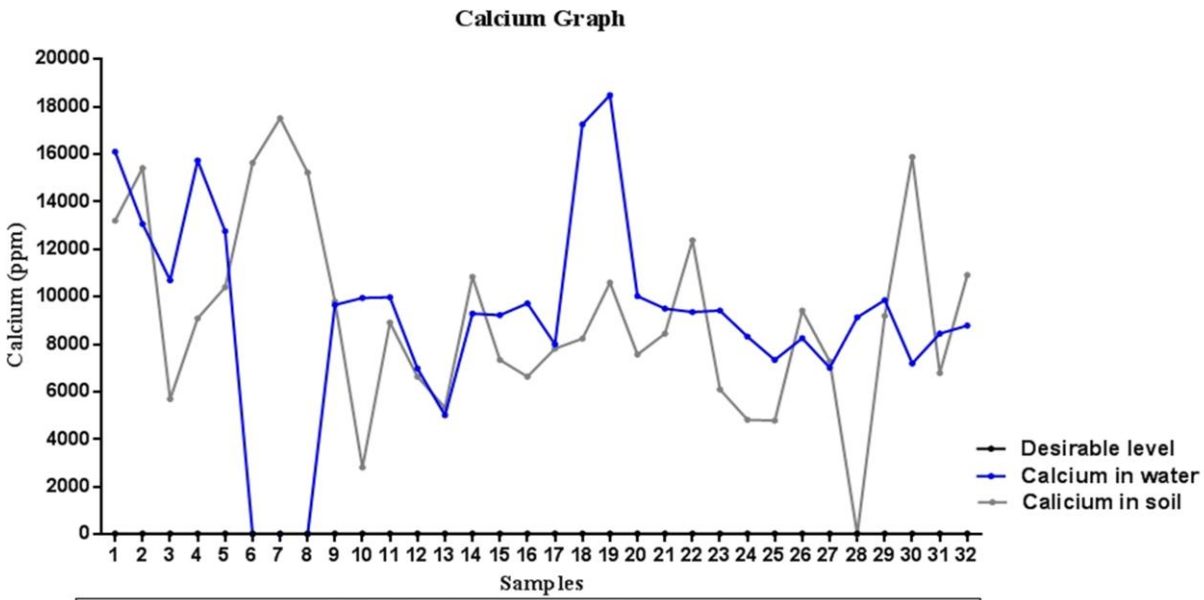

| One Way ANOVA Nonparametric (paired t -test) | | | | |
|---|---|---|---|---|
| Friedman test | Approximate P value | < 0.0001 | | |
| | P value summary | **** | | |
| | Are means signif. different? (P < 0.05) | Yes | | |
| Dunn's multiple comparisons test | | Rank sum diff. | Significant? | Summary |
| Treated water vs. Control | | -43.00 | Yes | **** |
| Treated Soil vs. Control | | -50.00 | Yes | **** |
| Treated Soil vs. Treated water | | -7.000 | No | ns |

**Fig. 4. Concentration of Na+ in different samples.**

In Sil river watershed, results of sampling site S2 indicate that in soil, this site has value is slightly more than the level of sodium availability throughout watershed.

Calcium availability in Sil river watershed has very irregular pattern, ranging from 0 to 17514 ppm in soils and 0 to 18489 ppm in water. It indicates that the availability of calcium in the entire Sil river watershed is very high. Minimum desirable limit described by WHO is 30 ppm.

There are only three sites having values below the permissible level of 30-50 ppm as discussed above (WHO, 1980). In Fig. 5, 50 ppm has been considered as control parameter for optimum outcome, which shows great variation of calcium availability throughout Sil river watershed.




| One Way ANOVA Nonparametric (paired t-test) | | | | |
|---|---|---|---|---|
| Friedman test | Approximate P value | < 0.0001 | | |
| | P value summary | **** | | |
| | Are means signif. different? (P < 0.05) | Yes | | |
| Dunn's multiple comparisons test | | Rank sum diff. | Significant? | Summary |
| Treated water vs. Control | | 45.00 | Yes | **** |
| Treated Soil vs. Control | | 39.00 | Yes | **** |
| Treated Soil vs. Treated water | | -6.000 | No | ns |

**Fig. 5. Concentration of calcium ions in different samples.**

Fluoride has a regular pattern in Sil river watershed soils and waters, as shown in Fig. 6 Sampling site S2 has a value higher than the permissible level as mentioned in WHO, 0.5 to 1.5 (WHO, 1993).

There is no harmful level of fluoride ions found in the entire Sil river watershed except site S2. There is a need of fluoridation, if it is considered having local use of water for drinking purpose.

If we study the availability of the above discussed ions at different altitudes of Sil river watershed, then it can be seen that;

(i) Between the altitudes of 379-420 there was one site (S1),

(ii) Between 338-379 there were 9 sites (S2, S3, S4, S5, S6, S7, S15, S16 and S17), and

(iii) Between 297-338, there were 22 sites (S8, S9, S10, S11, S12, S13, S14, S18, S19, S20, S21, S22, S23, S24, S25, S26, S27, S28, S29, S30, S31 and S32).

The above three were the intervals considered because of sampling sites location. Altitude interval was selected by dividing upper and lower values of altitudes into equal interval of 41 meters.

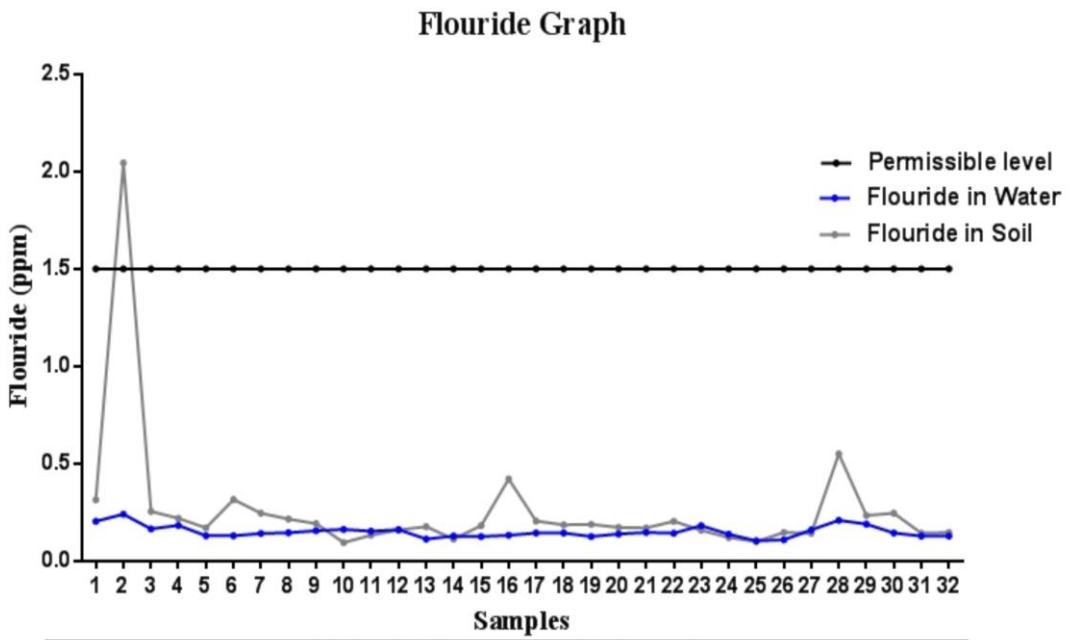
After matching the results at these intervals it can be seen that;

- pH values were nearly same in all intervals.
- Sodium has the highest value at S2 site soil of 2$^{nd}$ interval.
- Calcium has the highest values at S1 of 1$^{st}$ interval & S18, S19 of 2$^{nd}$ interval, and lowest at S6, S7 of 2$^{nd}$ interval and S8 of 3$^{rd}$ interval.
- Fluoride values were nearly same in all intervals, except S2 value of soil in 1$^{st}$ interval.

## Conclusions

Digital water quality meter with ion selective electrodes seems to be the most popular and convenient method to calculate ions in the desired samples. The advantages of this study include a short analysis time, elimination of sample pretreatment, simplicity of the measuring system and relatively low instrument cost. The

concentration of Sodium, Calcium and Fluoride ions was determined in 32 sites of Sil river watershed. There were two samples, which include, soil and water samples, at each site at one season. All these samples were analysed, using direct reading method. By our experimental data, we can conclude that the concentration of Sodium in water is within permissible level, and in soil, it slightly more than permissible limits at sites S2 and S6. Calcium level is very high at all sites of Sil river watershed except S6, S7, and S8 having values below the permissible level in soil samples. Fluoride ions have values within the permissible level as defined by World Health Organization, except S2 site soil having value slightly more than WHO guidelines. Altitudinal variation also has been considered in this study, which shows different values of sodium and calcium ions at different altitudes. There is no considerable difference of pH and fluoride ion values at different altitudes of Sil river watershed (Fig. 7). Therefore, results obtained reveal that the selected ions are at sufficient level of availability in the entire watershed of Sil river.




| One Way ANOVA Nonparametric (paired t-test) | | | | |
|---|---|---|---|---|
| Friedman test | Approximate P value | < 0.0001 | | |
| | P value summary | **** | | |
| | Are means signif. different? (P < 0.05) | Yes | | |
| Dunn's multiple comparisons test | | Rank sum diff. | Significant? | Summary |
| Treated water vs. Control | | -55.00 | Yes | **** |
| Treated Soil vs. Control | | -38.00 | Yes | **** |
| Treated Soil vs. Treated water | | 17.00 | No | ns |

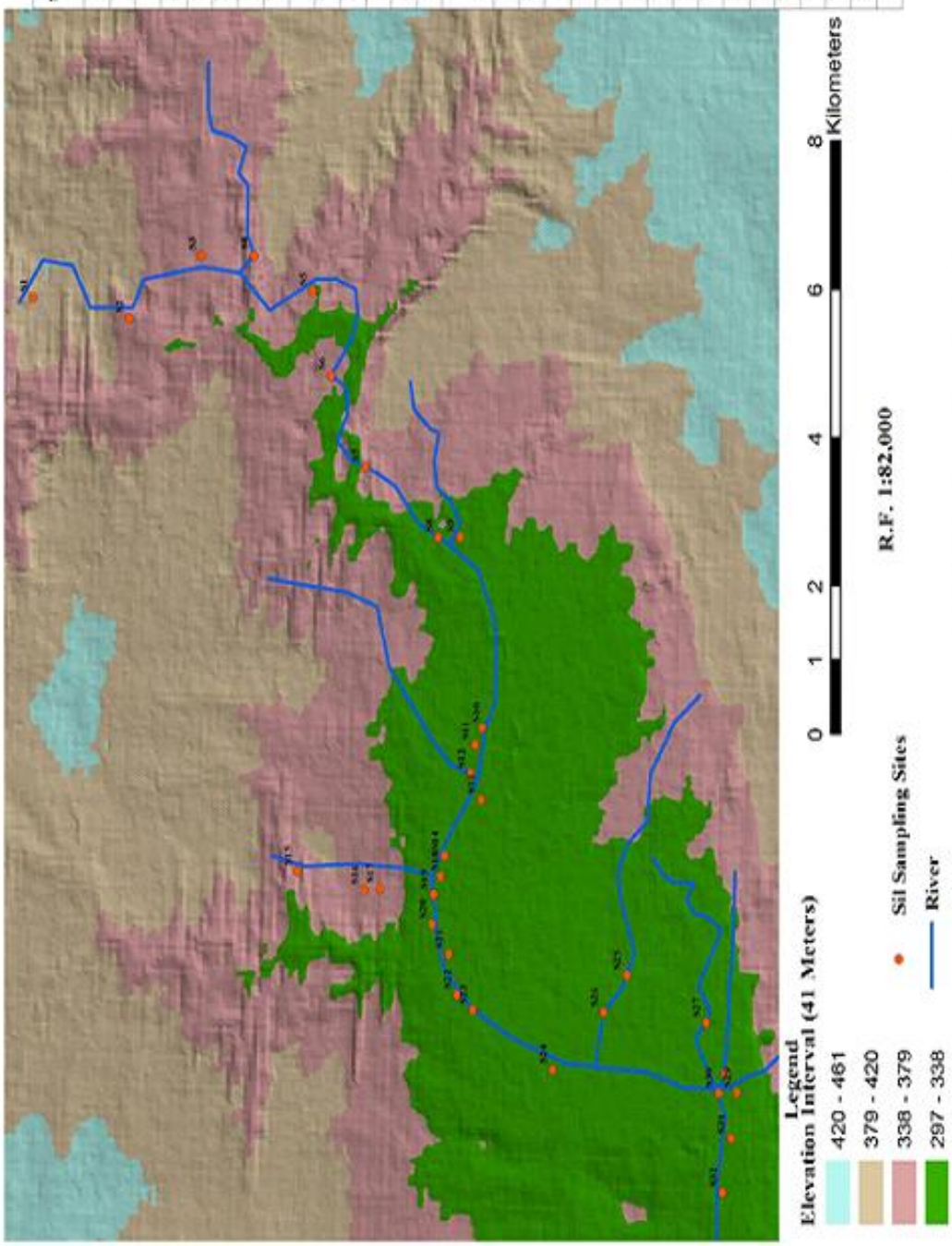
**Fig. 6. Concentration of fluoride ions in different samples.**

Availability of these ions in soil and water determines the health status of that soil and water for different uses. Selective ion of this study will provide:

- The baseline for the assessment of current condition of soil and water of study area
- For domestic use of water for drinking and irrigation purpose
- Agricultural capability of soils of different zones of study area
- Comparative study of the area for resource conservation and future planning

**Acknowledgement:**

We would like to pay special thanks to Miss Rehana Jamal for helping us in developing GIS based maps of this study area.




**Results of Water & Soil samples.**

| Sample | Pb | | Na⁺ | | Ca⁺⁺ | | F⁻ | |
|---|---|---|---|---|---|---|---|---|
| | Water | Soil | Water | Soil | Water | Soil | Water | Soil |
| S-01 | 8.33 | 8.16 | 35.37 | 30.44 | 16103 | 13197 | 0.202 | 0.318 |
| S-02 | 8.35 | 8.79 | 47.70 | 208.4 | 13099 | 15417 | 0.240 | 2.045 |
| S-03 | 8.19 | 7.95 | 20.44 | 13.20 | 10688 | 5693 | 0.165 | 0.255 |
| S-04 | 8.37 | 8.17 | 38.33 | 14.50 | 13737 | 5993 | 0.183 | 0.219 |
| S-05 | 7.95 | 8.34 | 25.67 | 68.50 | 17362 | 10195 | 0.179 | 0.136 |
| S-06 | 8.0 | 8.37 | 19.16 | 156.5 | — | 15656 | 0.129 | 0.316 |
| S-07 | 7.88 | 8.49 | 22.75 | 37.92 | — | 17414 | 0.141 | 0.246 |
| S-08 | 8.01 | 8.37 | 23.32 | 20.88 | — | 15226 | 0.145 | 0.216 |
| S-09 | 8.09 | 8.45 | 27.40 | 19.72 | 09658 | 9601 | 0.156 | 0.192 |
| S-10 | 8.22 | 8.06 | 22.72 | 62.16 | 09952 | 2819 | 0.162 | 0.094 |
| S-11 | 8.14 | 8.37 | 23.32 | 22.41 | 09973 | 8911 | 0.153 | 0.132 |
| S-12 | 8.14 | 8.38 | 33.03 | 27.01 | 06081 | 6636 | 0.161 | 0.168 |
| S-13 | 8.03 | 8.23 | 34.87 | 18.09 | 09013 | 5332 | 0.133 | 0.177 |
| S-14 | 8.19 | 8.71 | 23.15 | 13.50 | 09288 | 10837 | 0.128 | 0.112 |
| S-15 | 8.10 | 8.22 | 23.15 | 12.17 | 09224 | 7343 | 0.126 | 0.182 |
| S-16 | 8.13 | 8.50 | 23.03 | 47.70 | 09723 | 6636 | 0.132 | 0.421 |
| S-17 | 8.30 | 8.37 | 23.36 | 20.25 | 08000 | 7818 | 0.141 | 0.265 |
| S-18 | 8.31 | 7.95 | 20.91 | 43.60 | 17253 | 8289 | 0.134 | 0.183 |
| S-19 | 8.03 | 8.52 | 23.11 | 24.05 | 18889 | 10590 | 0.125 | 0.188 |
| S-20 | 8.21 | 8.32 | 23.36 | 18.15 | 10621 | 7562 | 0.139 | 0.172 |
| S-21 | 8.32 | 8.51 | 24.19 | 16.61 | 09504 | 8151 | 0.147 | 0.170 |
| S-22 | 8.31 | 8.80 | 28.44 | 28.80 | 09552 | 12375 | 0.143 | 0.204 |
| S-23 | 8.33 | 8.11 | 28.94 | 29.31 | 09817 | 6694 | 0.181 | 0.158 |
| S-24 | 8.11 | 8.18 | 19.17 | 27.26 | 08816 | 4818 | 0.138 | 0.121 |
| S-25 | 7.60 | 7.74 | 21.40 | 20.08 | 07343 | 4785 | 0.104 | 0.100 |
| S-26 | 7.98 | 8.31 | 29.27 | 21.20 | 08759 | 9417 | 0.105 | 0.146 |
| S-27 | 8.23 | 8.18 | 44.82 | 31.15 | 07018 | 7276 | 0.166 | 0.142 |
| S-28 | 8.29 | 8.85 | 78.44 | 80.45 | 09139 | — | 0.209 | 0.550 |
| S-29 | 8.32 | 8.42 | 51.46 | 56.05 | 09661 | 9202 | 0.189 | 0.234 |
| S-30 | 8.31 | 8.97 | 31.79 | 32.32 | 07909 | 15682 | 0.184 | 0.245 |
| S-31 | 8.27 | 7.77 | 31.73 | 31.08 | 08451 | 6799 | 0.129 | 0.142 |
| S-32 | 8.32 | 8.91 | 31.61 | 19.54 | 08788 | 10912 | 0.129 | 0.146 |

**Fig. 7. Selected ions detected at different altitudes.**

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