

## Comparative Study of Wet Deposition at High Altitude Station

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**Abstract:** Comparative study of the wet deposition were carried out at high altitude station to find out the amount ionic compounds such as  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  and also the variation of pH and conductance with day to day for one month. Rain water samples were collected from day to day for one month of the station and different tests were conducted to measure wet deposition. Readings were contrasted and WMO division. It is demonstrated that the greater part of the examples qualified the gauges yet there is some recognizable pattern in contamination.

**Keywords:** Wed deposition, WMO, AAS, Ion Chromatography.

### 1. INTRODUCTION:

Acid deposition, an economic global environmental problem in many urban and rural areas. The deposition of potentially damaging chemicals from the atmosphere to ecosystems is precisely an undesirable consequence of local air pollution [16]. Acidification of soils, lakes, rivers, etc. can be the result of deposition of acid forming gases and acidic precipitation. Dry deposition represents the process where acidic gases and colloids are deposited directly from the atmosphere into soil and waters. Wet deposition represents the result of rain-out or wash-out by precipitation [2, 3]. Total deposition is the considerable sum of dry, wet and other deposition. The flux of an ion below the canopy in through fall provides information on the deposition to the soil. The term acid deposition represents the whole range of physical, chemical and biological processes [11]. The acidifying components which play a role in the acidification are gaseous sulphur dioxide ( $\text{SO}_2$ ), nitrogen oxides ( $\text{NO}$  and  $\text{NO}_2$ ), nitric acid ( $\text{HNO}_3$ ), nitrous acid ( $\text{HNO}_2$ ), hydrochloric acid ( $\text{HCl}$ ), Hydrofluoric acid ( $\text{HF}$ ), organic acids, ammonia ( $\text{NH}_3$ ) etc. These components are emitted mainly by various sources such as industry, refineries, traffic, livestock breeding, etc. [1]. Acid deposition, the direct effects of ambient acids to plants were reported the considerable influence of hydrochloric acid on trees and bushes. The negative effects to vegetation was found to be related to the size of the exposed area, but mostly to the wind direction. The relation of the sensitivity of species to hydrochloric acid was found for a list of species [17]. The direct effects of sulphur dioxide and sulphuric acid on vegetation were observed in various areas. The total nitrogen deposition can be estimated from the wet deposition the individual N-containing components [4]. The actual acid load from nitrogen, however, was found to be only about half the potential load. Furthermore, acids formed from gases in the atmosphere may be neutralised by basic substances before reaching the soil. Where is  $\text{SO}_x$  the wet deposition of sulphur compounds (one mole of  $\text{SO}_x$  forming two moles of acid),  $\text{NO}_y$  the wet deposition of oxidised nitrogen compounds and  $\text{NH}_x$  the wet deposition of reduced nitrogen compounds. The studies related to wet deposition were focused mainly on quantification of the inputs and origin of sulphur and nitrogen compounds to a remote and an urban areas [19]. The key ionic constituents like  $\text{Cl}$ ,  $\text{F}$ ,  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{NH}_4$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{Ca}$ , and  $\text{Mg}$  along with pH and conductivity of the samples were analysed. The results of the chemical composition of rain water were used to calculate acidic potential and neutralizing potential of the deposited materials. In addition, neutralization factors were also computed for major cations like  $\text{Ca}$ ,  $\text{NH}_4$ ,  $\text{K}$  and  $\text{Mg}$ .

### 2. MATERIALS:

#### 2.1 Location of sampling site

Rain water samples were collected at high altitude station, Sinhagad, District Pune in Maharashtra State. Which is located at about 40 km south west of Pune ( $18^\circ 21' \text{N}$  and  $73^\circ 45' \text{E}$ ) on a mountain top in the Western Ghats [1]. It's Top is flat with an area of about  $0.5 \text{ km}^2$ . This part of the Western Ghats is covered with vegetation, grass and trees. The noticeable sources of pollution are wood-burning for cooking, vehicle gases, etc. Winds are generally from west/southwest during the pre-monsoon and monsoon.

#### 2.2. Sampling of Rainwater

Rainwater samples were collected on a daily basis by using standard rain collection gadget consists of a polyethylene funnel with a 21-cm diameter fitted onto a 2-liter polyethylene bottle as shown in Fig. 1 during the year 2010. Rainwater collection instrument were kept about 2 m above the ground. Collecting bottles and funnels were cleaned daily with triple-distilled water. Samples were collected in polyethylene bottles rinsed with triple-distilled water. The present study represents the rain chemistry of the entire monsoon and post-monsoon seasons. In order to investigate



the sources of pollutants, the data of chemical species obtained in rainwater were compiled season-wise. During the period under study the rainfall at Sinhagad occurred only in monsoon and post-monsoon seasons.

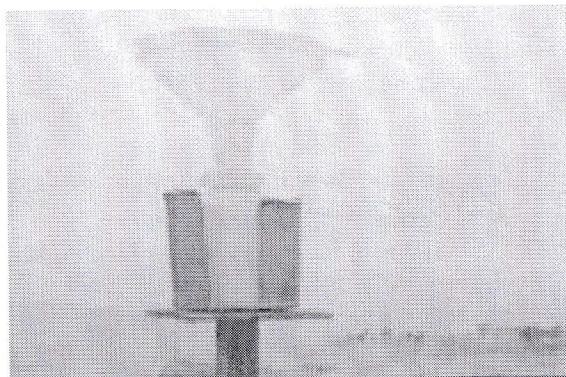


Fig 1. Rain water collection gadget.

### 2.3 Chemical analysis of rainwater

The collection of samples with their pH and conductivity were measured as immediate as possible. The pH was measured with the help of digital pH meter using glass electrodes. Conductivity of the rain water samples were measured with the help of digital conductivity meter calibrated against a reference KCl solution. A Pinch of (50-75 mg) Thymol was then added to the samples to prevent bio-degradation, and the samples were kept in a refrigerator at 4°C until the completion of all the analyses. Fig. 2 shows the methodology and techniques of the chemical analysis.

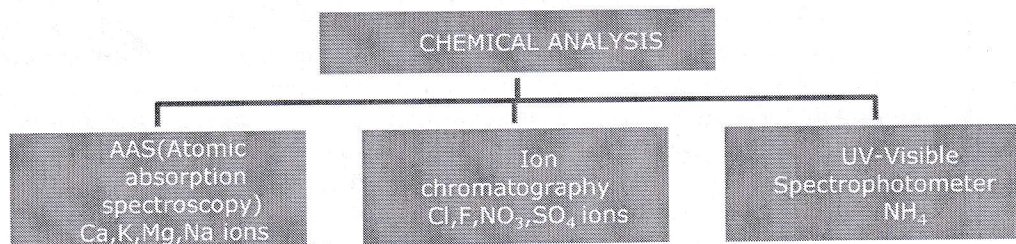


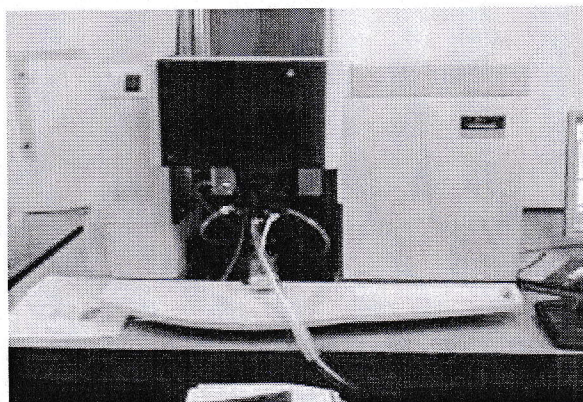
Fig. 2. Methodology and technique of analysis.

Concentrations of  $F^-$ ,  $Cl^-$ ,  $NO_3^-$  and  $SO_4^{2-}$  were measured by Ion Chromatograph (DIONEX-100, USA) using analytical columns Ion Pac-AS4A-SC (4 mm), anion micro-membrane suppressor ASRS-1, 1.8 mM sodium carbonate /1.7 mM sodium bicarbonate as eluent and triple distilled water as regenerate. Concentrations of  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  were measured by Atomic Absorption Spectrophotometer. The ion  $NH_4^+$  was measured by Indophenol method. Since no direct measurements of  $HCO_3^-$  were available, the concentration of  $HCO_3^-$  was estimated from the theoretical relationship between pH and  $HCO_3^-$ . When the pH of a sample is above 5.6 & the sample is in equilibrium with carbon dioxide, the concentration of  $HCO_3^-$  is given as  $[HCO_3^-] = 10^{-11.2 + pH}$ , with  $HCO_3^-$  concentration in mole /lit.

### 2.4. Instruments and Methods of Analysis:

#### 2.4.1 Atomic-Absorption Spectrophotometer (AAS)

Atomic-Absorption (AA) Spectroscopy as shown in Fig. 4 uses the absorption of light to measure the concentration of gas-phase atoms.





Ions	Slit setting (nm)	Light source	Flame type	Wavelength (nm)
Ca	0.7	Hollow Cathode Lamp (HCL)	Air-C <sub>2</sub> H <sub>2</sub>	423
Mg	0.7	Hollow Cathode Lamp (HCL)	Air-C <sub>2</sub> H <sub>2</sub>	285
Na	0.7	Hollow Cathode Lamp (HCL)	Air-C <sub>2</sub> H <sub>2</sub>	589
K	2.0	Hollow Cathode Lamp (HCL)	Air-C <sub>2</sub> H <sub>2</sub>	766

**Table 1.** The operating parameters of AAS

### 2.4.2 Analysis of Ammonium

A Milton Roy made Spectrophotometer (Spectronic-20D) as shown in table 2 is used for the measurement of ammonium concentrations. This is single beam, ratio indicating, manually operated UV visible range absorption spectrophotometer. Ammonium (NH<sub>4</sub>) reacts with phenol and hypochlorite in the presence of a catalyst (sodium nitroprusside) to produce a blue coloured indophenol dye. After the colour development the absorption was measured at 625 nm against the blank reagent. The concentration of NH<sub>4</sub> in µg ml<sup>-1</sup> was directly evaluated from the obtained calibration curve of ammonium.

**Estimation of Ammonium (NH<sub>4</sub>):** Estimation of ammonium is based on Berthelot's colour reaction procedure. Ammonium ion reacts with phenol and sodium hypochlorite in the presence of sodium nitroprusside as a catalyst to produce the blue coloured indophenol dye.

**AJ Standard Ammonium solution:** 100 µg ml<sup>-1</sup> standard solution of ammonium was prepared by weighing accurately 0.3666 gm of ammonium sulphate and dissolving it in deionised water. 1 ml of this solution contains 100 µg of NH<sub>4</sub><sup>+</sup>. Desired secondary standard solutions were prepared from this stock solution as shown table 4.

**BJ Analytical procedure:** Five ml sample was taken in a test tube and 2.5 ml of phenol-sodium nitroprusside solution was added to it. After shaking well, 2.5 ml of sodium hypochlorite solution (containing 5% sodium hydroxide) was added and again shaken well. After the solution was allowed to stand for 15 minutes, the absorbance of the blue coloured dye was measured at 625 nm wavelength against the blank. The concentration of ammonium in µg ml<sup>-1</sup> was evaluated from calibration curve of ammonium as shown in chart 2.

Ions	Techniques	Instruments	Precision (%)	Accuracy (%)
Na	Atomic absorption	AAS-Perkin Elmer AAnalyst-100	1.5	92.8
Ca	Atomic absorption	AAS-Perkin Elmer AAnalyst-100	0.5	97.5
Mg	Atomic absorption	AAS-Perkin Elmer AAnalyst-100	0.5	99.1
K	Atomic absorption	AAS-Perkin Elmer AAnalyst-100	0.5	98.9
F	Ion Chromatography Eluent- Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub>	Dionex -100	4.3	93.3
Cl	Ion Chromatography Eluent- Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub>	Dionex -100	6.4	85.8
NO <sub>3</sub>	Ion Chromatography Eluent- Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub>	Dionex -100	5.8	88.7
SO <sub>4</sub>	Ion Chromatography Eluent- Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub>	Dionex -100	2.2	97.7
NH <sub>4</sub>	Colorimetric using Indophenol blue method, 625 nm	Milton Roy- 20 D	10	95.0

**Table 2.** Analytical Protocol.

## 3. RESULTS AND DISCUSSION:

Chemical composition of rain water samples were presented in Table 3.3. The concentration of ions follows the pattern as Cl<sup>-</sup> > Na<sup>+</sup> > Ca<sup>2+</sup> > SO<sub>4</sub><sup>2-</sup> > Mg<sup>2+</sup> > HCO<sub>3</sub><sup>-</sup> > NH<sub>4</sub><sup>+</sup> > NO<sub>3</sub><sup>-</sup> > K<sup>+</sup>. The concentrations of Na<sup>+</sup> and Cl<sup>-</sup> were found to be more. The acidity of rain water depends on the concentration of anionic as well as cationic species. Acidic pH reveals the presence of strong acids in rain water while neutral or alkaline pH value indicates neutralization of acids by ammonia and soil dust. The pH of rainwater at this station ranges from 5.27 to 7.05, with an average value of 6.01.

### 3.1. Variation of pH and Conductance of the rain water sample:

Day	Time	pH	Conductance (per ohm)
1	12.30	6.46	15.80
2	11.00	6.63	20.50
3	11.30	6.23	9.00



4	11.00	6.16	9.20
5	11.00	6.45	19.00
6	11.30	6.98	52.80
7	11.00	6.97	62.90
8	11.30	6.74	28.10
9	11.00	6.38	14.10
10	11.00	6.06	12.50
11	11.00	6.38	29.50
12	11.00	6.27	27.90
13	11.00	5.26	5.70
14	2.00	5.82	2.40
15	2.00	5.82	2.40
16	3.00	5.44	5.40
17	3.00	5.86	12.70
18	11.00	6.28	19.80
19	11.00	6.78	56.30
20	11.30	6.45	20.90
21	11.30	6.14	8.60
22	11.00	6.22	16.40
23	11.00	5.89	2.30
24	10.30	6.78	76.50
25	12.00	6.31	32.70
26	11.30	6.43	71.00
27	11.30	7.04	43.90
28	11.00	6.43	16.80
29	11.00	6.04	7.20

Table 3. pH and Conductance of the rain water sample for one month.

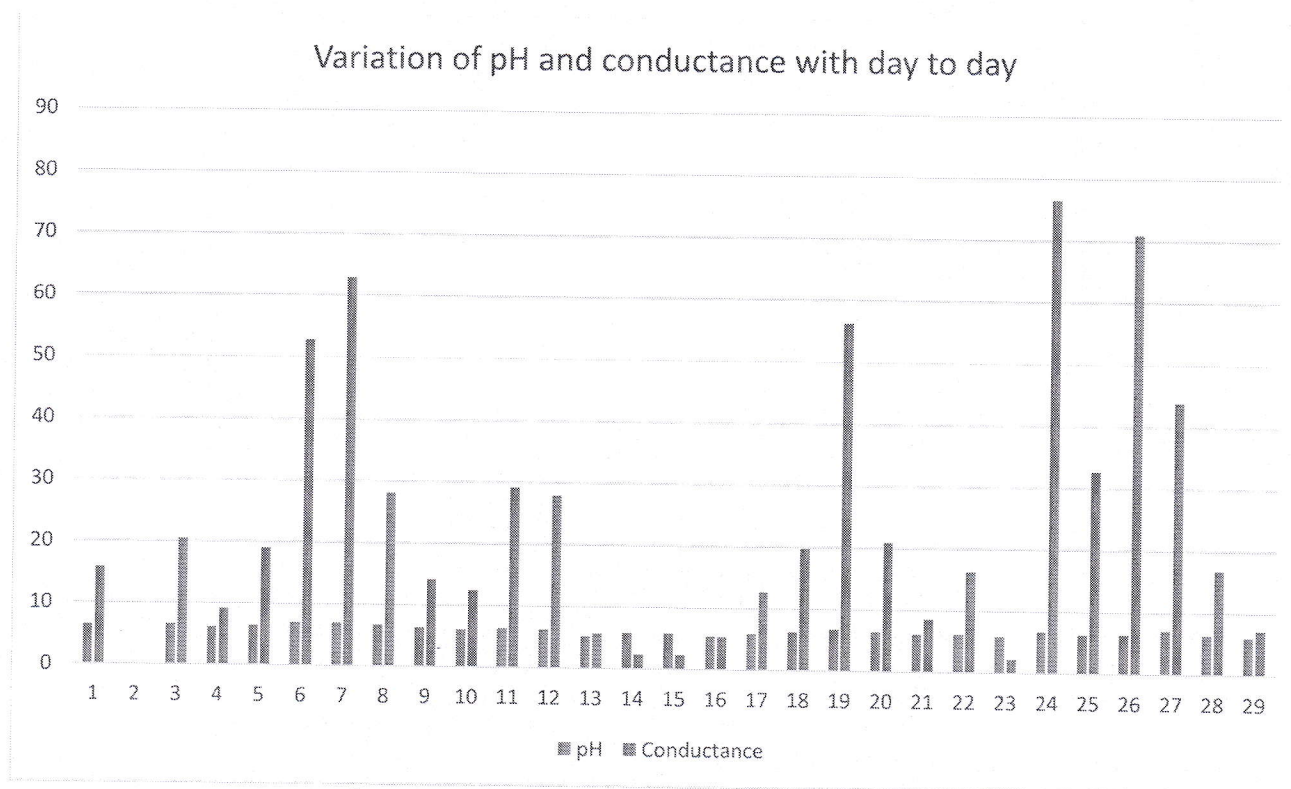


Chart 1. pH and Conductance of the rain water sample.

3.2. Analysis of ammonium ion: (Calibration of ion and graphical method)

Sr.no	Sample concentration (ppm)	Absorbance
1	Blank	0.033
2	0.2	0.099
3	0.4	0.182
4	0.6	0.315
5	0.8	0.400
6	1.0	0.504

Table 4. Absorbance of NH<sub>4</sub><sup>+</sup> ion solution.

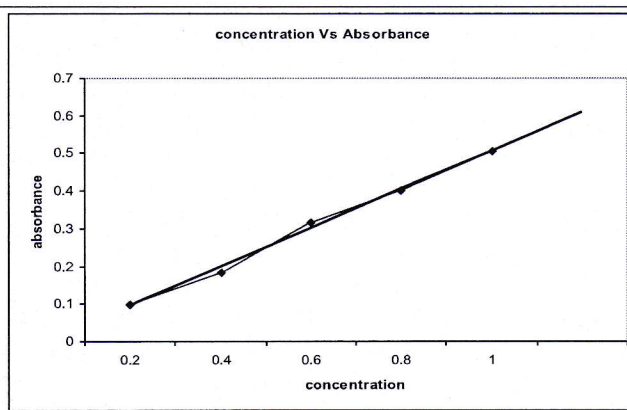


Chart 2. Calibration curve of NH<sub>4</sub><sup>+</sup> ion.

### 3.3. Average chemical composition of the rain water sample:

Ions	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	pH
Wt. Avg.	9.78	43.9	6.66	23.5	39.6	4.91	29.7	19.6	19.5	6.01
SD	± 19	± 53	± 14	± 35	± 47	± 4.2	± 36	± 26	± 23	± 0.5
Max.	100	225	56.1	141	193	14.5	141	111	99.8	7.05
Min.	0.12	5.13	0.02	2.55	4.37	0.18	0.63	1.98	1.66	5.27

Table 5. Chemical Composition of Rain water

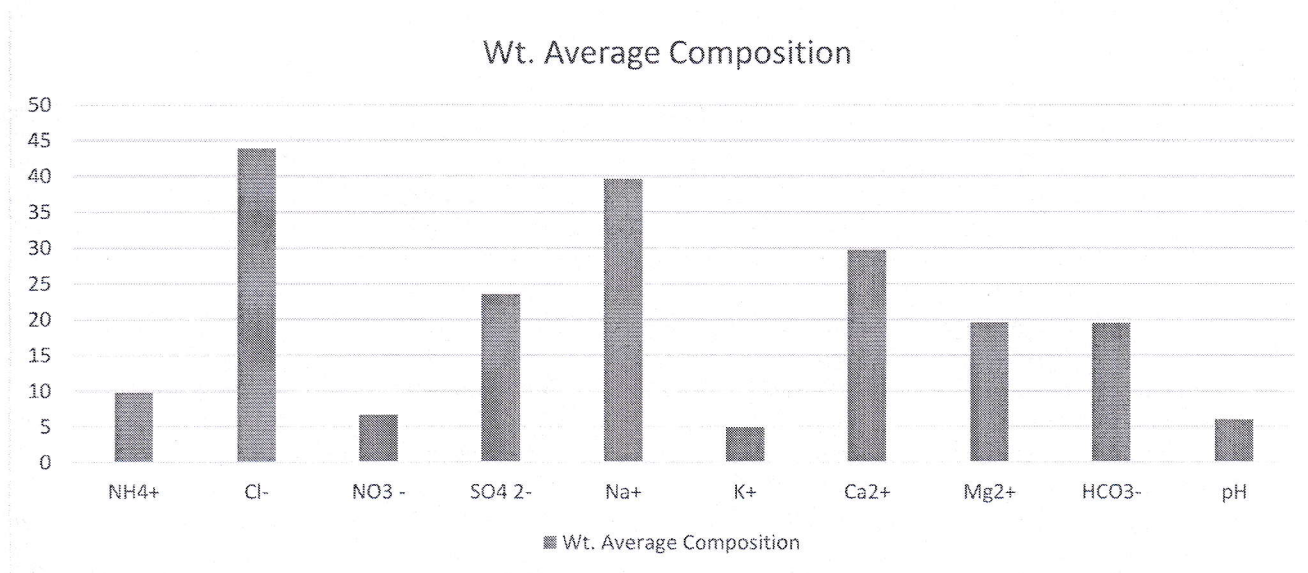


Chart 3. Weight Average Chemical composition of the Rain water sample.

### 3.4. Ion Balance [1].

Equivalent concentration of  $\sum$ anions and  $\sum$ cations as shown in table 5. Difference between them is an indicator of the completeness of the measured parameters. The sum of major anions (Cl, NO<sub>3</sub> and SO<sub>4</sub> is 74.06  $\mu\text{eq l}^{-1}$ , while the sum of major cations (Ca, Mg, Na, K and NH<sub>4</sub>) is 100.59  $\mu\text{eq l}^{-1}$  as shown in Chart 3. From these values the cations excess of 26.53  $\mu\text{eq l}^{-1}$  is observed. The significant anion deficiency in rain water samples may be due to the exclusion of some anions. Data points outside the range ( $m \pm 3\sigma$ ) were excluded as shown in table 5. (Where  $m$  = average and  $\sigma$  = standard deviation) The data obtained by the chemical analyses were then subjected to the quality check. It was done by ionic balance method [1]. A significant correlation ( $R=0.99$ ) was observed between the sum of anions and sum of cations as shown in chart 4 (a). Indicates the completeness of the analyses i.e., all the major ionic components were analysed. The second check was made through comparison between the measured and calculated conductivities of the individual samples as shown in chart 4 (b), this figure shows that there is a good agreement between the measured and calculated conductivities ( $R= 0.98$ ) in rain water samples.



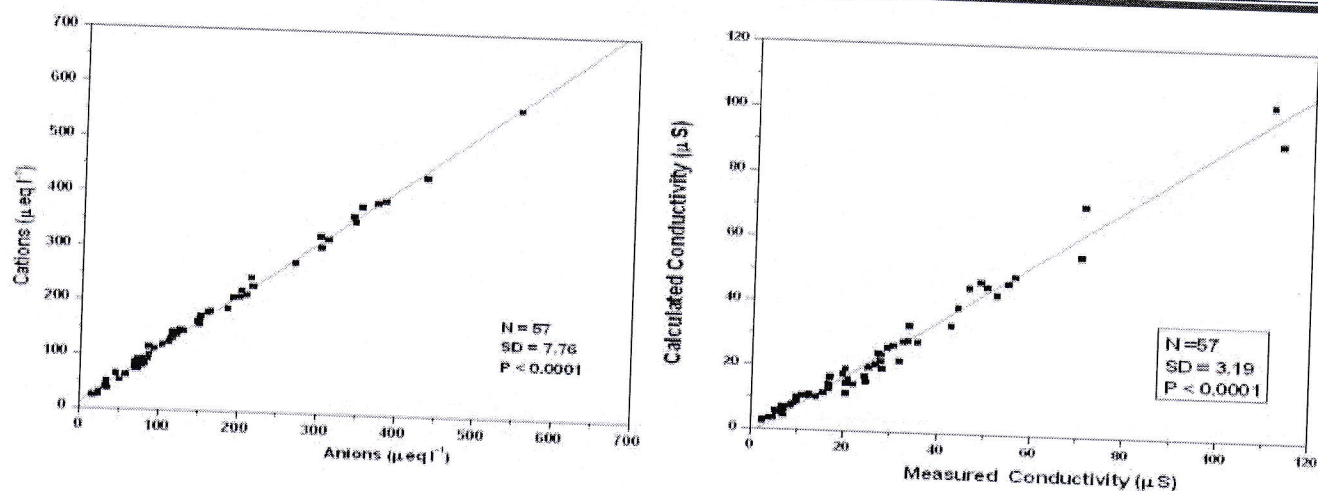


Chart 4. (a) Relation between cation and anions. (b) Calculated and Measured conductivity of the Rain water sample during the year 2010.

#### 4. CONCLUSION:

In present work, comparative study was made for amount of ionic compounds as well as pH and conductance of the rain water sample. The qualitative and quantitative study reveals that, the maximum average composition of Na<sup>+</sup> and Cl<sup>-</sup> ions were observed as agreed with view showing the increased rate of salt ions. The variation of pH and Conductance shows that the change of acidic and basic character in the rain water sample on daily basis this might be the presence of large amount of ionic compounds.

#### REFERENCES:

1. K. B. Budhavani, P. S. P. Rao, P. D. Safai, K. ali, 2009. Chemistry of Monsoon and Post-Monsoon Rains at high Altitude Location, Sinhgad. India. *Aerosol and Air Quality Research*, Vol. 9, No. 1, pp- 65-79, 2009.
2. K. B. Budhavani, P. S. P. Rao, P. D. Safai, R. D. Gawhane, M. P. Raju, C. M. Mahajan, P. G. Satsangi. Atmosphere Wet and Dry Deposition of Ions over an Urban Location in South-west India. *Aerosol and Air quality Research*, 12: 561-570, 2012.
3. Avila, A., Alarcon, M., 1999. Relationship between precipitation chemistry and meteorological situations at a rural site in NE Spain. *Atmos. Environ.* 33, 1663-1667
4. Buijmann, E., Mass, H. F. M and Asman, W. A. H (1987): Anthropogenic NH<sub>3</sub> emission in Europe. *Atmos. Environ.*, 21, 1009-102.
5. Dikaiakos, J. G., Tsitouris, C. G., Siskos, P. A., Meliossos, D. A., Nastos, P., 1990. Rainwater composition in Athens, Greece. *Atmospheric Environment* 24B, 171-176.
6. Galloway, J. N., Zhao, D., Xiong, J., Likens, G. E., 1987. Acid rain: China, United States, and a remote area. *Science* 236, 1559-1562.
7. Heuer, K., Tonnessen, K. A., Ingersill, G. P., 2000. Comparison of precipitation chemistry in the Central Rocky Mountains, Colorado, USA. *Atmos. Environ.* 34, 1713-1722.
8. Hu, G. P., Balasubramanian, R., Wu, C. D., 2003. Chemical characterization of rainwater at Singapore. *Chemosphere* 51, 747-755.
9. Kulshrestha, U. C., Sarkar, A. K., Srivastava, S. S., Parashar, D. C., 1996. Investigation into atmospheric deposition through precipitation studies at New Delhi (India). *Atmos. Environ* 30, 4149-4154.
10. Lee, B. K., Hong, S. H., Lee, D. S., 2000. Chemical composition of precipitation and wet deposition of major ions on the Korean peninsula. *Atmos. Environ.* 34, 563-575.
11. Marquardt, W., Bruggemann, E., Renate, A., et al., 2001. Trends of pollution in rain over East Germany caused by changing emissions. *Tellus* 53B (5), 529-545.
12. Migliavacca, D., Teixeira, E. C., Wiegand, F., Machado, A. C. M., Sanchez, J., 2005. Atmospheric precipitation and chemical composition of an urban site, Guaiba hydrographic basin, Brazil. *Atmos. Environ.* 39, 1829-1844.
13. Mouli, P. C., Mohan, S. V., Reddy, S. J., 2005. Rainwater Chemistry at a regional at a representative urban site: influence of terrestrial sources on ionic composition. *Atmospheric Environment* 39, 999-1008.

14. Parashar, D. C., Granat, L., Kulshreshta, U. C., Pillali, A. G., Naik, Momin, G. A., Rao, P. S. P., Safai, P. D., Khemani, L. T., Naqvi, S. W. A., Nargvekar, P. V., Thapa, K. B., Rodhe, H., 1996. A Preliminary Report on an Indo-Swedish and *International Meteorological Institute* in Stockholm, Report CM 90.
15. Praveen P. S., Rao P. S. P., Safai P. D., Devara P. C. S., Chate D. M., Ali K., Momin G. A. 2007 Study of Aerosol transport through precipitation Chemistry over Arabian Sea during winter and summer monsoon. *Atmospheric Environment* 41, 825-836.
16. Rao P. S. P., Momin, G. A. Naik, M. S. Safai, P. D., Pillai, A. G., Naik, A. G., Khemani, L. T., 1990. Impact of Ca and SO<sub>4</sub> on pH of rain water in rural environment in India. *Indian Journal of Environment Pollution*, 10(12), 941-943.
17. Safai, P. D., P. S. P., Momin, G. A., Ali, K., K., Chate, D. M., Praveen, P. S. ,2004. Chemical Composition of Precipitation during 1984-2002 at Pune, India. *Atmospheric Environment* 38, 1705-1714.
18. Satsangi, G. S., Lakhani, A., Khare, N., Kumari, K. M., Srivastawa, S. S., 1998. Composition of rainwater at semiarid rural site in india. *Atmospheric Environment* 32 (21), 3783-3793.
19. Topcu, S., Incecik, S. Atimtay, A., 2002. Chemical composition of rainwater at EMEP station in Ankara, Turkey. *Atmos. Res.* 65, 77-92.