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**CHEMICAL CHARACTERISTICS  
OF RAINWATER IN CENTRAL INDIA**

*K.S. Patel* \*, *B. Ambade* \*,  
*J. Nicolás* \*\*, *E. Yubero* \*\*

\* *School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur-492010, CG, India;* \*\* *Atmospheric Pollution Laboratory, Applied Physics Department, Miguel Hernandez University, Avda de la Universidad S/N, 03202 Elche, Spain*

In the present work, the rainwater chemistry in the most industrialized area of central India, Raipur city (capital, Chhattisgarh state) is described. The volume weighted mean value (n=31) of pH, conductivity and TDS of the rainwater during monsoon season, May – October, 2008 was 6.42, 483  $\mu\text{S}$  and 237  $\text{mg l}^{-1}$ , respectively. The volume weighted mean content of ions i.e.  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  was 2.83, 2.71, 7.64, 0.73, 1.00, 0.92, 1.1 and 2.53  $\text{mg l}^{-1}$ , respectively. The variations, scavenging and enrichment, correlations and sources of the ions in the rainwater are discussed.

В данной работе описаны химические особенности дождевой воды в наиболее индустриальной местности центральной Индии, город Райпур (столица штата Шаттигарф). Показатели измерений (n=31) рН, проводности (ионы) и TDS в дождевой воде во время сезона муссона, май – октябрь, 2008 года были 6.42, 483  $\mu\text{S}$  и 237  $\text{mg l}^{-1}$  соответственно. Состав ионов представлен  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  та  $\text{Ca}^{2+}$  с показателями 2.83, 2.71, 7.64, 0.73, 1.00, 0.92, 1.1 и 2.53  $\text{mg l}^{-1}$ . Также обсуждаются вопросы вариативности показателей, их ошибки, связи и источники ионов в дождевой воде.

**Introduction**

Air quality in India is depleting tremendously due to a huge vehicular and industrial emissions. Rain is formed due to condensation of the cloud droplets in the upper troposphere and scavenges the atmospheric air pollution. The rain chemistry is indicator of the atmospheric pollution in a particular area. The rain chemistry in the various locations of the World has been reported [1-30]. The Asian rainwater was contaminated with higher levels of ions due to increased human and industrial activities [8-30]. The rain chemistry of some locations of India i.e.

Delhi, Mumbai, Dhanbad, Osansol, Bhubaneswar, Tirupati, etc. has been investigated [22-30].

The rain chemistry of the most industrialized location of central India has been not reported. In the present work, the rainwater chemistry of Raipur city (capital, Chhattisgarh state, central India) during period, May – October, 2008 is described. The content, variations, sources, enrichment and fluxes of ions i.e.  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are discussed.

**Materials and methods**

**Site Description**

Raipur city (21° 13' 48" N, 81° 37' 48" E) capital, Chhattisgarh state, central India was selected for the proposed studies due to running of several industries and thermal power plants, Figure 1. The population of city is  $\approx$  2 million and exposed with severe air pollution [31].

**Collection of samples**

The rain gauze was used for collection of rain samples on the event basis. The collector was installed at roof of building,  $\approx$  10 m from the ground level in Dagania, Rohinipuram, Raipur. The collector was washed with deionized double distilled water after collection of each event samples. Total amount of rain precipitated in Raipur during period, May – October, 2008 was 67 cm in 42 events. Of them, 31 event samples

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was collected, filtered and transferred into 1-lit cleaned polyethylene bottle. They were refrigerated at 4 °C to avoid the degradation.

**Analysis**

The pH, conductivity and TDS values of the samples were measured immediately after collection by using the Checkmate (E – 58902) analyzer. The content of ions i.e. Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and

Ca<sup>2+</sup> was analyzed by using technique i.e. ion chromatography (Dionex Corporation, Sunnyvale, CA, USA) equipped with anion (AS9-HC, 250x4 mm) and cation (CS12A, 250x4 mm) equipped with separation columns and conductivity detector.

The E. Merck standard was used for preparation of the calibration curves. The laboratory blank was used to assess the contamination.

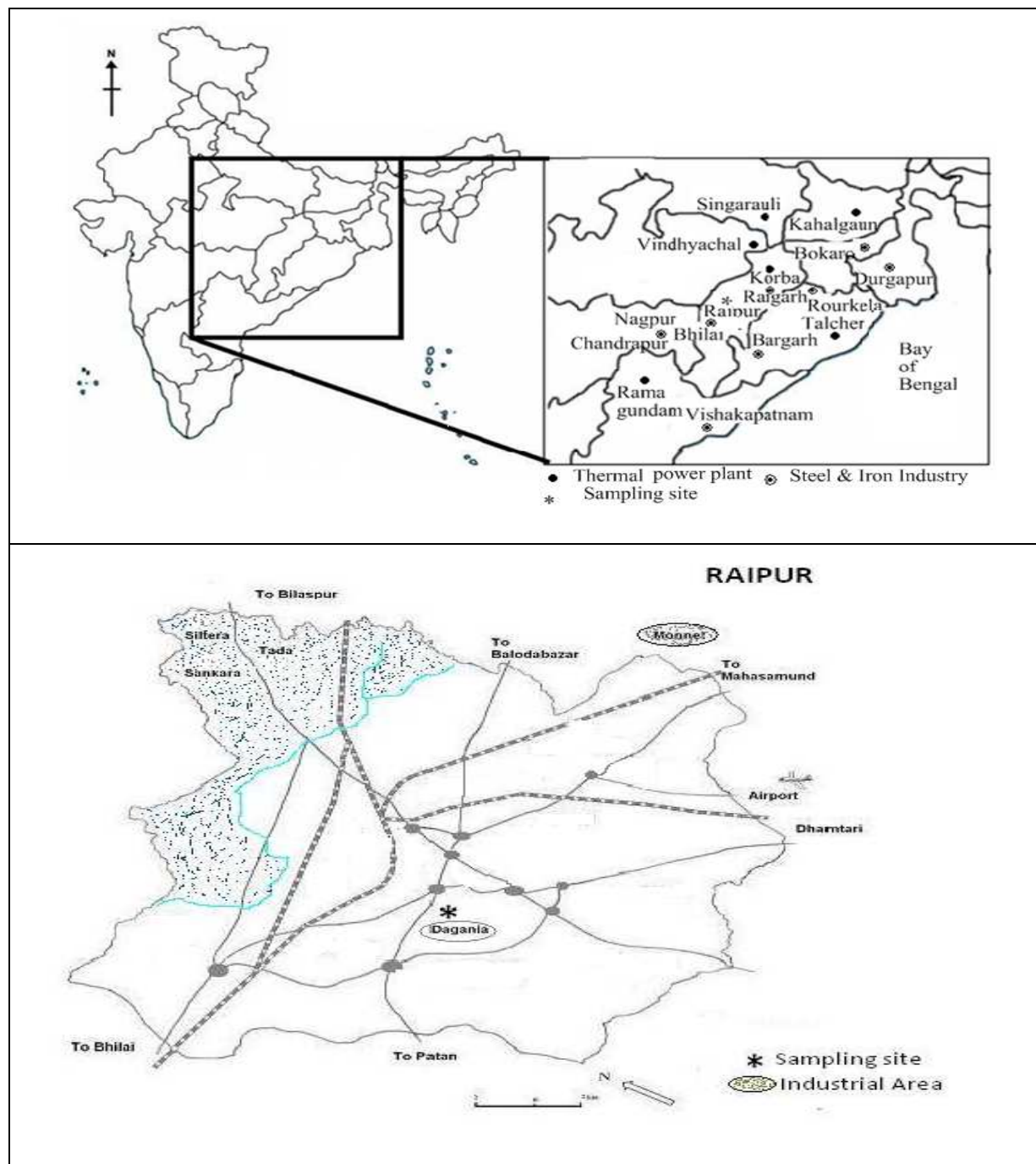


Figure 1 - Location of Raipur in India and sampling description

**Results and discussion**

**Meteorology**

The monthly mean values of meteorology i.e. rainfall (RF), ambient temperature (T), relative humidity (RH), vapor pressure (VP) and wind speed (WS) of Raipur during the study period are summarized in Figure 2. The mean value of T, RH and VP during the rainy season, July – September was found to 28 °C, 83% and 23 mm of Hg, respectively. The 98% (66 cm) of the total rain was precipitated in four months, June – September, 2008 with the highest precipitation in month of September, 2008.

The value of wind speed was decreased sharply from June to September, 2008. The correlation matrix of the meteorology with the rain

composition is shown in Table 1. The meteorology remarkably influenced the rain content of three ions i.e. Na<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>. The RF value had negative correlation with the content of ions i.e. Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup> or Ca<sup>2+</sup>, and they become diluted when the precipitation of rain amount was increased.

The T value had good positive correlation with the content of two ions i.e. Na<sup>+</sup> and Ca<sup>2+</sup> unlikely to other ions i.e. Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>. Increase in value of RH and VP remarkably decreased the rain content of Na<sup>+</sup> unlikely to Mg<sup>2+</sup>. The rain content of the most of the ions was diluted with increase in WS value, may be due to their large emission by the local emission sources.

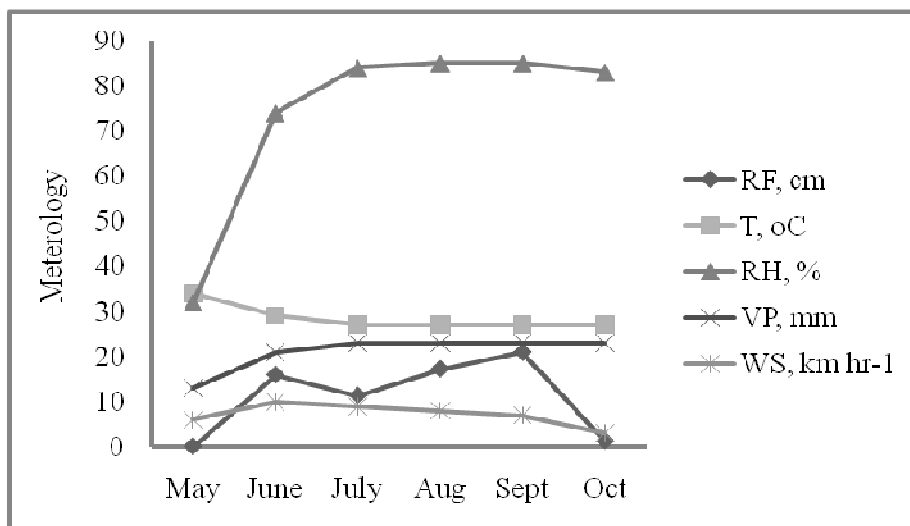


Figure 2 - Meteorology 2008 for study period

Table 1- Correlation matrix of ions with meteorology

Ion	RF	T	RH	VP	WS
Cl <sup>-</sup>	-0.61	-0.45	0.11	0.11	-0.81
NO <sub>3</sub> <sup>-</sup>	-0.36	-0.17	0.17	0.22	-0.48
SO <sub>4</sub> <sup>2-</sup>	-0.36	-0.14	0.17	0.20	-0.25
NH <sub>4</sub> <sup>+</sup>	0.00	-0.11	0.17	0.17	0.00
Na <sup>+</sup>	-0.45	0.70	-0.69	-0.69	-0.39
K <sup>+</sup>	0.00	0.14	0.00	0.00	0.24
Mg <sup>2+</sup>	0.42	0.53	0.56	0.59	-0.14
Ca <sup>2+</sup>	-0.50	-0.28	-0.30	-0.28	-0.79

**Physical characteristics**

The volume weighted mean value (n=31) of pH, conductivity and TDS of the summer monsoon rain at Raipur was 6.42, 483 μS and 237 mg l<sup>-1</sup>, respectively. The lowest pH

value was observed in month of July, probably due to the highest wind speed, Figure 3. However, the value of conductivity and TDS was found to be increased from July to September, 2008, Figure 4.

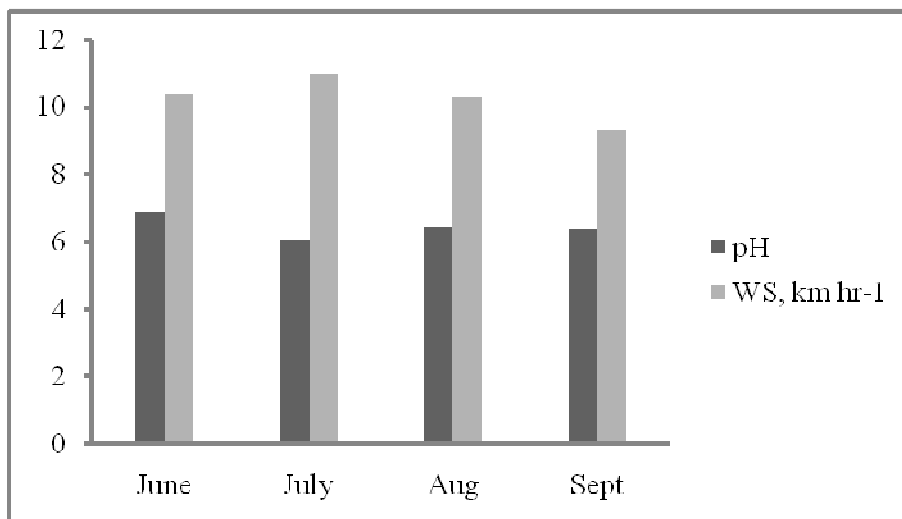


Figure 3 - Volume weighted monthly pH and WS (km hr<sup>-1</sup>) for year 2008

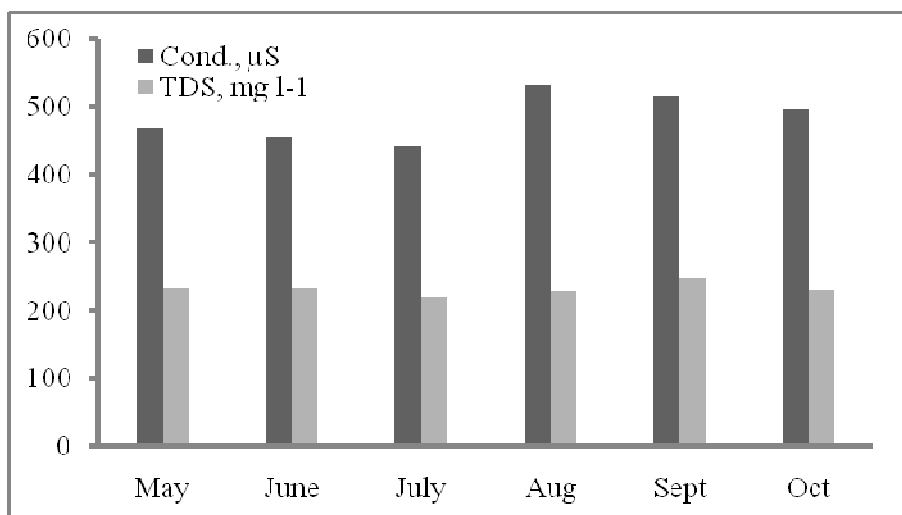


Figure 4 - Volume weighted monthly conductivity and TDS value for year 2008

#### Chemical characteristics

The volume weighted mean content of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , was 2.83, 2.71, 7.64, 0.73, 1.00, 0.92, 1.1 and 2.53, mg l<sup>-1</sup>, respectively. The relative abundance of ions i.e.,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  was 4, 5, 5, 6, 13, 13, 14 and 39%, respectively. The sum of ratio of equivalent content of the  $[\Sigma\text{anion}]/[\Sigma\text{cation}]$  at Raipur was found to be 1.02 with coefficient (r) value of 0.35.

#### Scavenging ratio

The annual mean content of species i.e.  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  associated to the  $\text{PM}_{10}$  in the air of Raipur was 4.8, 6.4, 9.5, 1.6, 2.2, 2.1, 0.7 and 7.1  $\mu\text{g m}^{-3}$ ,

respectively. The scavenging (SR) value for  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  was found to be 590, 423, 804, 456, 455, 438, 1571 and 356, respectively. Among them,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  exhibited relatively higher SR value, due to the most effectively scavenging out [29].

#### Variations

The volume weighted monthly mean content of the ions in rain of Raipur is shown in Figure 5. The highest content of almost all species during month of June, 2008 at Raipur was observed due to first flush out of monsoon water. No exact seasonal variations in other three months: July, August and September was noticed. The highest content of  $\text{SO}_4^{2-}$  was observed in the rain water.

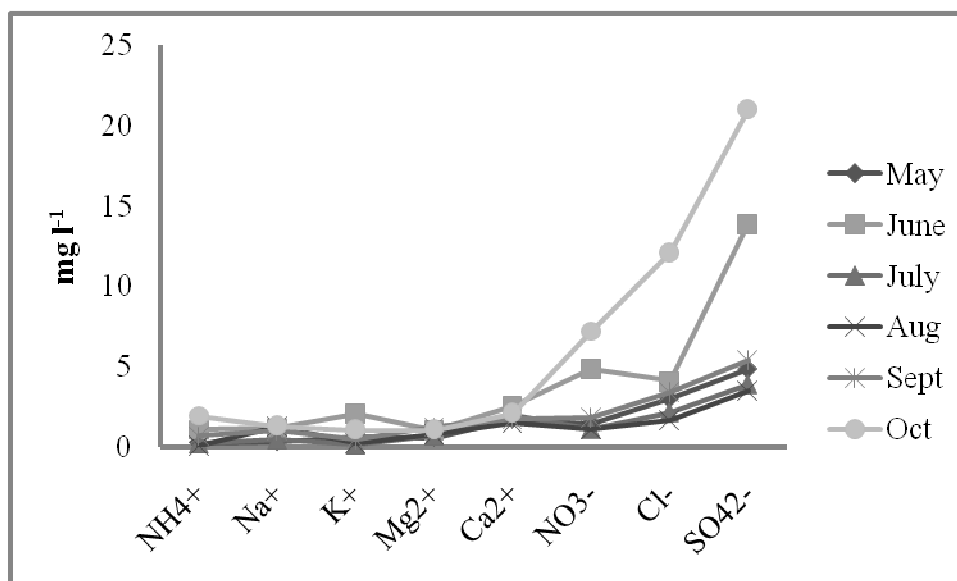


Figure 5 - Volume weighted monthly of ions for year 2008

### Correlation and Sources

The correlation matrix of ions is summarized in Table 2. Anions (i.e.  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) and cations (i.e.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) among themselves have good correlation, suggesting their common origin in the rain water. All ions among themselves (except  $\text{Cl}^-$  and  $\text{NO}_3^-$ ) had fair to good correlation. They are contributed by the anthropogenic and natural sources. The following approach [33] is used to estimate

the marine contribution of ions in the rain.

$$EF_{\text{marine}} = ([x]/[\text{Na}])_{\text{rain}} / ([x]/[\text{Na}])_{\text{marine}}$$

Where, x denotes the concentration of the species of interest in the rain and sea. The  $EF_{\text{marine}}$  values for ions i.e.  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  was ranged 1.6, 31, 25, 29 and 21, respectively when Na was used as marine indicator. It means that ions i.e.  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in the rain was largely contributed by anthropogenic and crustal sources.

Table 2 - Correlation matrix of ions

	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_4^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
$\text{Cl}^-$	1							
$\text{NO}_3^-$	0.80	1						
$\text{SO}_4^{2-}$	0.69	0.64	1					
$\text{NH}_4^+$	0.00	0.41	0.14	1				
$\text{Na}^+$	0.24	0.42	0.50	0.26	1			
$\text{K}^+$	0.00	0.41	0.52	0.46	0.44	1		
$\text{Mg}^{2+}$	0.00	0.00	0.22	0.51	0.50	0.50	1	
$\text{Ca}^{2+}$	0.33	0.20	0.55	0.35	0.48	0.45	0.75	1

### Comparison of rain composition

The ionic composition of rain of various locations of the World is presented in Table 3. The highest rain content of the ions i.e.  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  were observed in the locations (i.e. Mumbai, Nanjing, Eshidiya, Shanghai, etc.) lie near sea due to marine contribution. Whereas, the highest rain content of ions i.e.  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Mg}^{2+}$  were

seen in the industrial and mega cities i.e. Tokyo, Nanjing, Shanghai, Esidiya, Mumbai, Delhi, Asansol, Raipur, etc., due to anthropogenic contribution. Significant rain content of  $\text{NH}_4^+$  was observed in the Chinese cities i.e. Nanjing, Zhejiang, etc. The rain content of ions of Raipur is found to be higher than the rain ion content value of many locations, Table 3.

Table 3 - Comparison of rain acidity and ionic contents,  $\mu\text{eq}$ 

Location	pH	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{NH}_4^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	Ref.
Guaiba, Brazil	5.7	7	13	2	28	11	3	4	8	1
Mexico City	5.1	10	62	43	92	7	2	2	26	4
Anatolia, Turkey	6.1	18	56	28	64	16	8	11	74	8
Eshidiya, Jordon	6.6	122	122	64	43	85	51	134	192	11
Tokyo	4.5	55	50	31	40	37	3	12	25	13
Shanghai	4.5	58	200	50	81	50	15	30	204	16
Korea	4.7	38	19	47	33	19	4	11	26	18
Zhejiang	4.5	10	117	37	97	7	5	4	56	19
Nanjing	5.5	143	242	40	193	23	12	32	295	21
Mumbai	5.7	275	175	17	51	221	10	70	351	22
Dhanbad	5.3	28	63	11	35	18	13	156	129	23
Asansol	6.1	63	44	16	33	20	4	37	107	24
Tirupati	6.8	34	128	41	20	33	34	51	151	25
Delhi	6.3	43	131	109	82	44	20	44	181	26
Bhubaneswar	6.2	18	19	10	19	15	2	5	20	27
Raipur	6.4	80	149	44	41	26	24	92	127	PW

PW = Present work

### Conclusion

The acid rain is halting in Asia due to increased industrial and vehicular emission of acidic oxides i.e.  $\text{NO}_x$  and  $\text{SO}_x$ . The two acids i.e.  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  have major contribution in the Asian rain. Increase in rain amount and wind speed influence adversely

the rain content of ions i.e.  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$ . The atmospheric humidity and vapor pressure has positive correlation with the atmospheric acidity. In central India, the rain ions are largely contributed by the anthropogenic sources.

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*Хагешвар Сінгх Пател \**, **ХІМІЧНІ ХАРАКТЕРИСТИКИ ДОЩОВОЇ**  
*Балрам Амбаде \**, **ВОДИ У ЦЕНТРАЛЬНІЙ ІНДІЇ**  
*Джозе Ніколас \*\**,  
*Едуардо Юберо \*\**

\* Школа вивчення хімії, Університет Пт. Равішакар Шукла, Райпур – 492010, Індія; \*\* Лабораторія атмосферного забруднення, Факультет прикладної фізики, Університет Мігеля Хернандеза, Avda de la Universidad S/N, 03202 Елч, Іспанія.

В даній роботі описані хімічні особливості дощової води в найбільш індустріальній місцевості центральної Індії, місто Райпур (столиця штату Шаттігарф). Показники вимірювань (n=31) рН, провідності (іони) та TDS у дощовій воді під час сезону мусону, травень – жовтень, 2008 року були 6.42, 483  $\mu\text{S}$  та 237  $\text{mg l}^{-1}$  відповідно. Склад іонів представлений  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  та  $\text{Ca}^{2+}$  з показниками 2.83, 2.71, 7.64, 0.73, 1.00, 0.92, 1.1 та 2.53  $\text{mg l}^{-1}$ . Також обговорюються питання варіативності значень, їх похибок, зв'язків та джерел іонів у дощовій воді.

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