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Long-term Changes of Rainwater Quality in the Industrial Corridor of Visakhapatnam, India

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Abstract: The industrial expansion during the twenty-year period of 1983 to 2003 had shown its impact on rainwaters of Visakhapatnam. The ionic contents of SO_4, NH_4, NO_3, Ca, Na and Cl along with pH and electrical conductivity are analysed for the rainwaters of Visakhapatnam industrial corridor during the period. The analysis shows that the atmospheric dust is more in summer rains than in the post-monsoon period, when the same had been washed down. However, unabated increase of air pollution over the two decades is indicated by the steady rise of conductivity of rainwater. The ratio between $Ca^+ + NH_4^+$ and $NO_3^- + SO_4^-$ shows values consistently less than one, indicating the rise of acidic nature, in spite of the neutralization due to alkaline agents like Ca and NH_4. Gradual decline of pH of rainwater forecasts an impending acidic rain in near-future.

Key words: Rainwater quality, industrial corridor.

Introduction

The study of rainfall chemistry assumed importance in hydrological assessment for two reasons: (a) dissolved ionic content in rainwater reflecting the industrial and urban activity on the surface and (b) possible transport of salinity into groundwater. During the last three decades, studies in rainwater chemistry brought out interesting results about the impact of surface human activity on the atmosphere in the cities of India (Singh et al., 2007).

The magnitude of net fall-out of pollutants during precipitation scattering is of considerable importance as it suggests the intensity and location of major pollutant sources. The data of chemical composition of precipitation samples, obtained from the main industrial corridor in Visakhapatnam (courtesy: India Meteorological Department, Pune), has been assessed over a period of two decades from 1983 to 2003. From the variability in concentrations of ions like Cl, Na, NO_3, SO_4, NH_4 and Ca and the magnitude of pH and electrical conductivity (Ec), efforts have been made to identify the predominant reasons. The corresponding increase in the ionic content and Ec with respect to the time of establishment of industries revealed the vulnerability of air quality due to rapid industrialization in Visakhapatnam.

Sarma and Subbarao (1972) registered the behaviour of Visakhapatnam rainwaters in 1970 itself, wherein they mentioned that the seasonal variation of ionic activity and wind movements together determine the chemical character of rains. However, industrial development and consequent population growth after 1970 could be observed to be tremendous (Table 1).

Giant industries like steel plant and thermal power plant came into existence during two-decade period and interestingly a dozen of them are packed within a space of 15 km from the coastline, barring all environmental regulations as shown in Figure 1.

Population, consequently, expanded from a total of 0.6 million in 1983 to around 2.0 million in 2003. About

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Table 1: Establishment of major industries and growth of population in Visakhapatnam

S. No.	*Name of the industry*	*Year*	*Population*
1	Visakhapatnam Port Trust (VPT)	1950	1,08,042
2	Hindustan Petroleum Corporation Limited (HPCL) - Crude Oil Refinery	1957	2,11,456
3	Coromandal Fertilizers Limited (CFL)	1967	-
4	Bharat Heavy Plates and Vessels Limited (BHPV)	1971	-
5	Union Carbide	1971	3,63,467
6	Hindustan Polymers Limited	1973	-
7	Hindustan Zinc Limited (HZL)	1977	-
8	Pragati Fertilizers	1982	6,03,631
9	Coastal Chemicals	1982	-
10	Andhra Cement Company	1983	-
11	Visakhapatnam Steel Plant	1989	10,51,918
12	Simhadri Thermal Power Station	2004	22,69,608 (approximately)

Courtesy: Census of India 1991, General population and Census of India 2001.

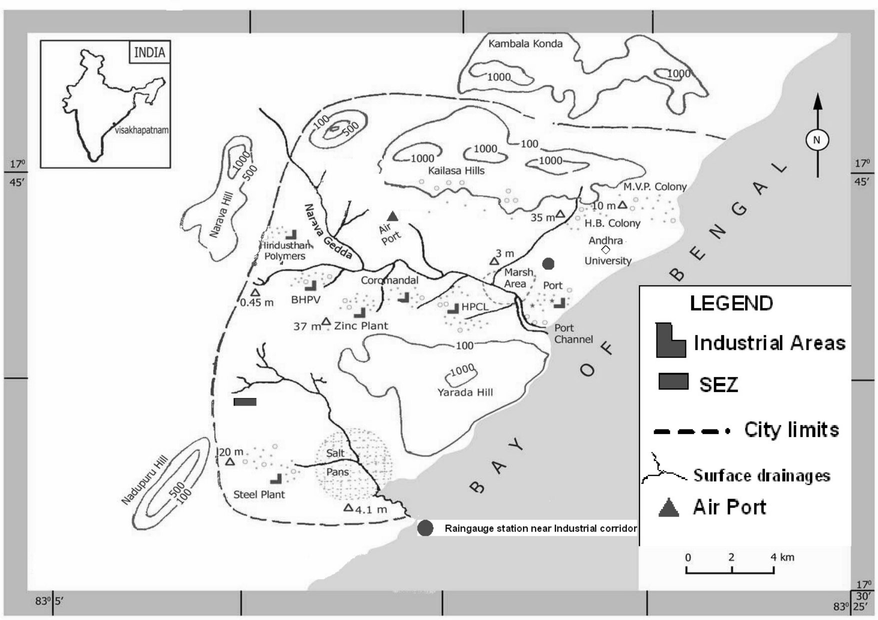

Figure 1: Location of major industries in Visakhapatnam.

two hundred ancillary units rose in the industrial corridor to feed the main giants, which made the corridor a hazardous air-polluting chimney (Subbarao and Subbarao, 1994).

Linkens et al. (1979) and Leonard et al. (1981) stressed the dust load in the sky to be high during the ‘dry’ periods which results in an increase of the ionic content in rainwater. The dust load is enormous in India during summer and for a city like Visakhapatnam, coastal spray adds ‘fuel’ to the industrial ‘fire’. Maske and Krishna Nand (1982) observed that Visakhapatnam is subjected to heavy air pollution when compared to other stations like Pune, Jodhpur, Kodai Kanal, Srinagar and Port Blair. The authors categorically stated that the industrial air-pollution is pushing higher amounts of salts into rainwater.

Present Work

The present work is an extended study of rainwater quality of Visakhapatnam, studded with industries like Hindustan Zinc, Coromandal Fertilizers, petroleum refinery, heavy plates and vessels, polymers, steel plant and thermal power plant. The industrial development, initiated after 1950, caused the ‘population explosion’ in Visakhapatnam (Table 1). Further, the industrial chimney is surrounded by hill-forestry on three sides and Bay of Bengal on the eastern side as shown in Figure 1. Combustion of large quantities of chemicals in industries like zinc, fertilizers (nitrogen, phosphate, potassium), polymers, cement manufacture, steel production and oil refinery release pipes of smoke into air which is full of pollutants, both gaseous and liquid. Number of studies exist in the past with reference to the wash-out of SO_2 (Postma, 1970; Dana et al., 1972; Barries, 1978; Davies, 1973) and NO_2 (Linkens and Borman, 1974). Such situations turned into 'HCl production' activity and resulted in acid-rains (Cogbill and Linkens, 1974). Sodium, chloride and sulphate could be emitted by sea spray as well (Granat, 1972). The sulphur and nitrogen are formed by fuel combustion and vehicular traffic of the urban population. Ammonia has two major pathways to atmospheric deposition (Warneck, 1998): bacterial nitrogen fixation and combustion from chemical and fertilizer plants and refrigeration systems.

IMD Data

The rainwater quality data comprising Ec, total monthly rainfall, pH and major ions—SO_4, NO_3, Ca, NH_4, Na and Cl—were obtained from National Data Centre, India Meteorological Department (IMD, Pune 2006) for the period of January 1983 to December 2005. Rainwater samples for each rainy day were collected by IMD, Visakhapatnam at its central station which is in the close vicinity of Industrial Corridor (Figure 1). The samples were analysed at the IMD Air Pollution Monitoring laboratory, Pune. IMD Air Pollution Monitoring laboratory, Pune is equipped with ion chromatograph and atomic absorption spectrophotometer to analyze for anions and cations respectively; and also the microprocessor based pH and conductivity meters.

Monthly averages for ionic concentrations, Ec and pH were calculated. Table 2 shows the rainwater quality data of Visakhapatnam for the years 1983, 1993 and 2003 to understand the long-time variation of the contents of the rainwater solution.

It can be observed that during the months of March to June, higher values of ionic contents are recorded as the accumulated dust from the industrial corridor and evaporated particulates of effluents from industries and vehicular smoke are lifted into the atmosphere. Electrical conductivity, an indicator of the total ionic activity, is increasing during the premonsoon months of March, April and May every year. However, the character of the rainwater solution, being a composite effect of many factors like coastal spray, industrial lift-up, agricultural dust (neighbouring areas) and forest fires of the surrounding hills, cannot be explained for individual ions for a city like Visakhapatnam.

The variation of ions Na and Cl in rainwater is shown separately in Figure 2a to observe the sea water influence for the years 1983, 1993 and 2003. The variations of non-sea salts (nss) like NH_4, NO_3, Ca and SO_4 are shown in Figure 2b for the same decadal values. The phenomenon of premonsoon lift is observed clearly for ions of SO_4, Cl, NH_4 and NO_3. Lesser values are recorded after the monsoonal 'washout' during September, October and November of 1983, December of 1993 and October, November of 2003. Further, values of observed ions and Ec are observed to be increasing steadily over decades. SO_4 in May, 1983 was 1.83 mg/l, 2.67 mg/l in May, 1993 and by 2003 reached a peak value of 15.39 gm/l. Cl in June, 1983 was 0.21 mg/l, 1.47 mg/l in June 1993 and attained a value of 36.0 mg/l by 2003. NO_3 in May, 1983 was 5.75 mg/l, 18.55 mg/l in May 1993 and was 3.76 mg/l in the same month of 2003. NH_4 in February, 1983 was 2.51 mg/l, 2.55 mg/l in June 1993 and 4.73 mg/l in May 2003. The values in 'September-October' period are lower than their respective pre-monsoon magnitudes. In addition, an upward trend is visible during the two-decade period from 1983 to 2003. The average premonsoon Na is almost equal during the premonsoon months for 1993 (5.007 mg/l) and 2003 (5.275 mg/l). As Na is mostly due to sea spray, the steady levels are possible. Chloride, however, has a double origin of sea spray and anthropogenic as well. The arrows in Figure 2a indicate almost a stable nature for this reason. In Figure 2b, the nss salts exhibit an upward trend. The characteristic is more apparent in Figure 3, where the monthly average pH values show a downward trend towards an 'acidic' pH value (pH values reaching 4).

The phenomenon with its 'two' characteristics is confirmed vigorously in Figures 4a and 4b, when the pictures are drawn for the consecutive years of 2003, 2004 and 2005 (data in Table 3). The increase of ionic contents in summer is extremely clear during the years, with their downfalls in postmonsoon. The upward suggesting arrows continue, indicating the hazardous air over Visakhapatnam. Banerjee (2008) used the ratio of $Ca^+ + NH_4^+$ and $NO_3^- + SO_4^-$ to indicate the alkaline nature of precipitation chemistry (ratio >1) in the industrial city of Asansol. The ratios are calculated for Visakhapatnam too (Tables 2 and 3). The values are consistently less than one, showing the growing acidic nature. A few ratio values (February 2004, November and December of 2005) are exceeding '1', may be due to two reasons. The first one is that, even though the anions like SO_4 and

Table 2: Variation of monthly rainfall, pH, Ec and other ionic contents for the years 1983, 1993 and 2003

Year	*Month*	*MRF*	*pH*	*Ec*	*Na*	*Cl*	NH_4	SO_4	NO_3	*Ca*	$(Ca^{+}+NH_4^{+})/(NO_3^{-}+SO_4^{-})$
		cm		*(µs/cm)*	*mg/l*		*mg/l*				
1983	Jan	0.4	7.3	62.3	-	0.86		10.06	4.96	-	
	Feb	1.1	6.6	73.8	-	1.52	2.51	1.5	0.4	-	
	Mar	1.6	6.62	212.5	-	0.72		4.4	9.07	-	
	Apr	21.4	6.1	36.2	-	2.55	0.06	1.44	4.43	-	
	May	19.7	6.2	48.4	-	3.02	0.26	1.83	5.75	-	
	Jun	11.4	6.5	49.4	-	0.21		1.14	3.79	-	
	July	8.9	6.7	21.6	-	2.56	0.08	2.19	2.35	-	
	Aug	39.4	6.6	108.1	-	6.7	0.04	1.86	3.05	-	
	Sep	1.3	6.2	32.9	-	1.92	0.46	0.72	0.44	-	
	Oct	1.4	7.08	93.5	-	3.13	0.1	3.3	7.4	-	
	Nov	0.1	7.03	24.6	-	2.29	0.55	8	7.46	-	
	Dec	8.8	7.96	34.7	-	22.75	0.15	15.88	0.41	-	
1993	Jan	0	0	0	-	0	0	0	0	-	
	Feb	9.3	7.44	128.2	0.49	13.48	1.5	7.44	27.92	11.41	0.365102
	Mar	0	0	0		0	0	0	0		
	Apr	11.2	6.28	66.2	6.04	6.63	1.4	0.21	20	12.58	0.691737
	May	6.6	6.45	33.4	9.56	5.99	0.34	2.67	18.55	3.86	0.197926
	Jun	21.5	6.94	22.9	3.94	1.47	2.55	0.59	7.74	3.52	0.728691
	Jul	18	5.13	20.1	1.05	1.49	0.27	0.5	19.84	0.64	0.044739
	Sep	0.2	7.55	390	0.67	14.6	0.11	1.78	4.46	1.01	0.179487
	Oct	1.7	5.32	144	0.93	4.56	3.52	17.61	39.28	1.15	0.082088
	Nov	0.6	6.63	156	10.9	27.58	0	20	25.29	9.32	0.205785
	Dec	0	0	0		0	0	0	0		
2003	Jan	0.3	6	66.4	1.34	5.83	0.3	2.96	8.21	1.57	0.167413
	Feb	0	0	0		0	0	0	0		
	Mar	6.2	5.89	49.4	2.66	13.14	0.9	3.9	2.02	3.04	0.665541
	Apr	0	0	0		0	0	0	0		
	May	3.4	6.73	282	1.6	13.64	4.73	15.39	3.76	0.15	0.25483
	Jun	1.7	6	156.7	15.5	22.5	0	32.8	0.77	6.14	0.182901
	Jul	27.7	6.23	81.1		0	4.52	8.87	5.91	5.06	0.648173
	Aug	8.3	5.28	71.5		0.82	3.87	10.81	5.74	4.59	0.511178
	Sep	15	6.38	99.3		0		8.77	1.81		0
	Oct	57.8	4.04	86.6	0.87	0	2.89	7.01	6.29	0.94	0.28797
	Nov	0	0	0		0	0	0	0		
	Dec	6.5	4.45	16.9		1.59	0.01	2.8	0.05		0.003509

*Data not available for Ca and Na during the year 1983

NO_3 which contribute acidity to rainwaters, increased to considerable levels (February 2004), the corresponding increase in the cationic concentrations of Ca and NH_4 are trying to neutralize the rainwaters. The second reason is the strong washout during the monsoon seasons (Sarma, 2003) may be scavenging the accumulated acidic anions and thus the ratio sometimes is exceeding '1'. But this can be seen to happen very rare.

Figure 5 brings out clearly that in the recent decade, the alarming trend of lower pH values is more.

Conclusions

Medha et al. (2002) observed the rainwater quality turning acidic in the industrial city of Mumbai. For Visakhapatnam the discussion could be summarized with the final tally of the 22-year data (annual average pH and annual average Ec) shown in Table 4. The same is picturised in Figure 6, where the two variables compliment each other to record the 'impending' disaster in the atmosphere of Visakhapatnam. The still-further

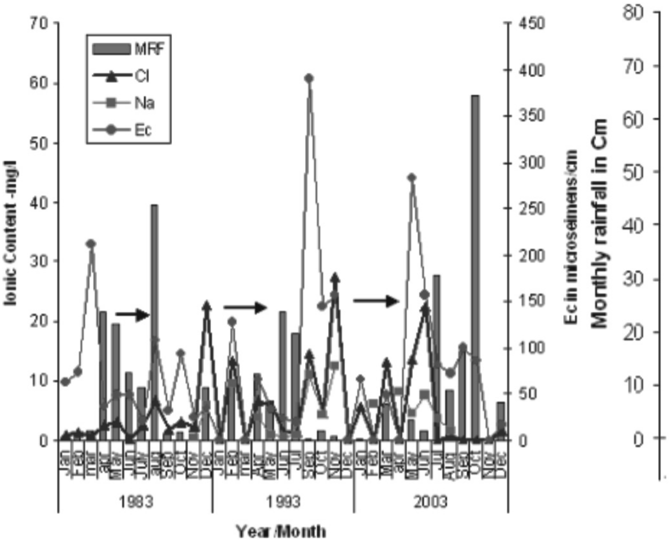

Figure 2a: Variation of Na, Cl and Ec of rainwaters and monthly rainfall amounts during the years 1983, 1993 and 2003.

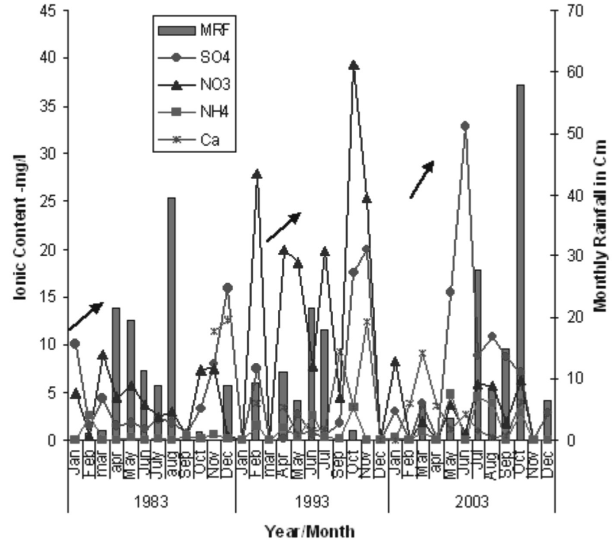

Figure 2b: Variation of SO_4, NO_3, NH_4 and Ca of Rainwaters and monthly rainfall amounts during the years 1983, 1993 and 2003.

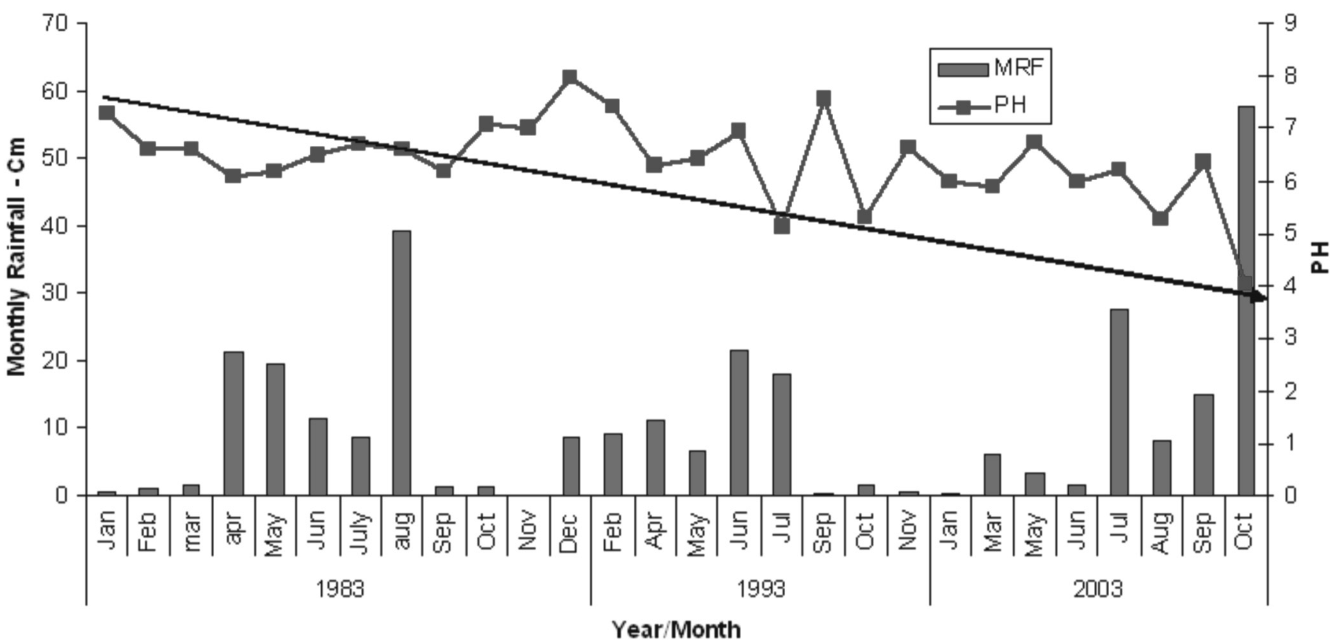

Figure 3: Variation of pH during the years 1983, 1993 and 2003.

industrial expansion in the city (Naidu 2006) leaves the atmospheric accumulation of particulate matter hazardously. The planners of development, willy-nilly, are unaware of the quality of rainwater that feeds the urban aquifers of Visakhapatnam. The just completed international air port and the proposed Special Economic Zone both in the neighbourhood of industrial corridor (Figure 1) are additional liabilities of future air quality. Budhhavant et al. (2009) observed the 'two-way' behaviour of rainwater in the monsoon and post-monsoon periods for the city of Sinhagad, India. Lower salt contents are observed in the post-monsoon, when nss ions are scavenged down due to monsoon rains. In spite of the cyclic behaviour of rise or salts in the dry periods and their wash-down in the following months, ceaseless action of industrial line-up is injecting more acidic salts to atmosphere.

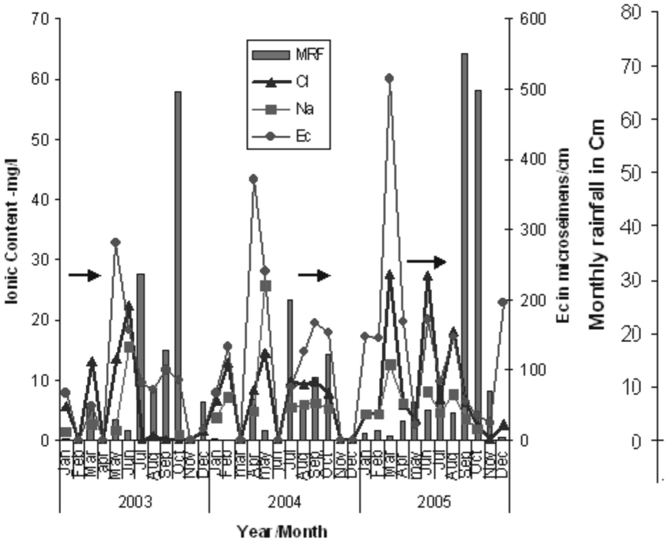

Figure 4a: Variation of Na, Cl and Ec of rainwaters and monthly rainfall amounts during the years 2003, 2004 and 2005.

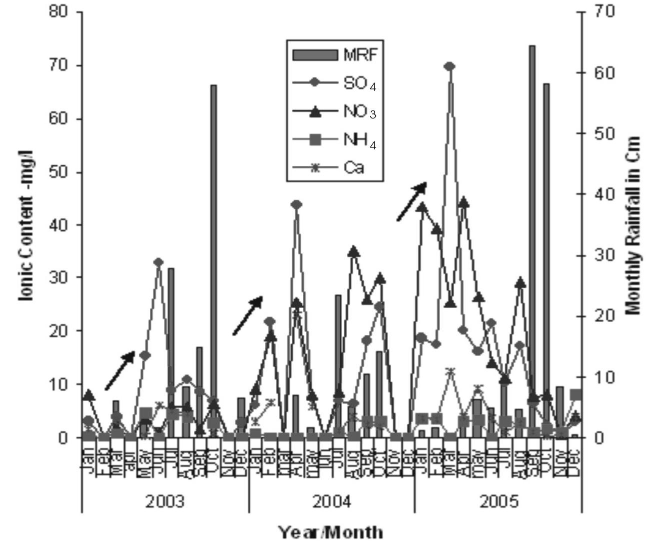

Figure 4b: Variation of SO_4, NO_3, NH_4 and Ca of rainwaters and monthly rainfall amounts during the years 2003, 2004 and 2005.

Table 3: Data of monthly rainfall pH, Ec and other ionic contents during the years 2003, 2004 and 2005

Year	*Month*	*MRF* mm	*Ec* (µs/cm)	*Na* mg/l	*Cl*	*NO_4* mg/l	*SO_4*	*NH_4*	*Ca*	*$(Ca^+ + NH_4^+)/(NO_3^- + SO_4^-)$*
2003	January	3	66.4	1.34	5.83	2.96	8.21	0.3	1.57	0.167413
2003	March	62	49.4	2.66	13.14	3.9	2.02	0.9	3.04	0.665541
2003	May	34	282	1.66	13.64	15.39	3.76	4.73	0.15	0.25483
2003	June	17	156.7	15.5	22.5	32.8	0.77	0	6.14	0.182901
2003	July	277	81.1	0	0	8.87	5.91	4.52	5.06	0.648173
2003	August	83	71.5	0	0.82	10.81	5.74	3.87	4.59	0.511178
2003	September	150	99.3	0	0	8.77	1.81	0	0.94	0.088847
2003	October	57	86.6	0.87	0	7.01	6.29	2.89	0	0.217293
2003	December	65	16.9		1.59	2.8	0.05	0.01	0	0.003509
2004	January	3	67.7	3.91	6.63	6.01	9.28	0.83	2.94	0.246566
2004	February	1	132.3	7.18	12.92	21.79	19.34	0.03	60.65	1.475322
2004	April	7	233	4.82	8.45	43.73	25.31	0	23.02	0.33343
2004	May	16	241	25.74	14.53	7.63	8.17	0	5.91	0.374051
2004	July	234	75.8	5.42	9.71	7.03	8.65	1.08	1.32	0.153061
2004	August	52	126.9	5.98	9.31	6.28	39.97	0.28	3.94	0.091243
2004	September	105	167.5	6.13	9.83	17.99	50.77	3.01	2.48	0.079843
2004	October	142	153	5.33	7.88	24.4	38.12	3.01	2.15	0.082534
2005	January	12	146	4.17	4.18	18.7	43.54	3.52	3.52	0.113111
2005	February	17	144	4.25	4.56	17.61	39.28	3.52	3.46	0.122693
2005	March	6	514	12.52	27.58	69.59	25.29	0	12.47	0.131429
2005	April	32	170	6.12	5.91	20.07	44.42	3.2	3.86	0.109474
2005	May	644	21.83	0	3.58	16.1	26.5	3.44	9.11	0.294601
2005	June	49	172	0	27.29	21.54	14.21	0.07	3.55	0.101259
2005	July	90	82.9	8.12	7	10.31	11.18	2.97	1.24	0.195905
2005	August	46	147	4.47	18.06	17.36	29.19	2.81	2.74	0.119227
2005	September	644	55.2	7.71	6.4	6.36	7.86	1	0.98	0.139241
2005	October	581	35	3.66	2.47	2.4	8.02	1.69	0.32	0.192898
2005	November	82	23.6	1.17	0.27	0.72	0.51	1.24	0.5	1.414634
2005	December	4	195	0	2.71	2.97	4.11	8.22	4.02	1.728814

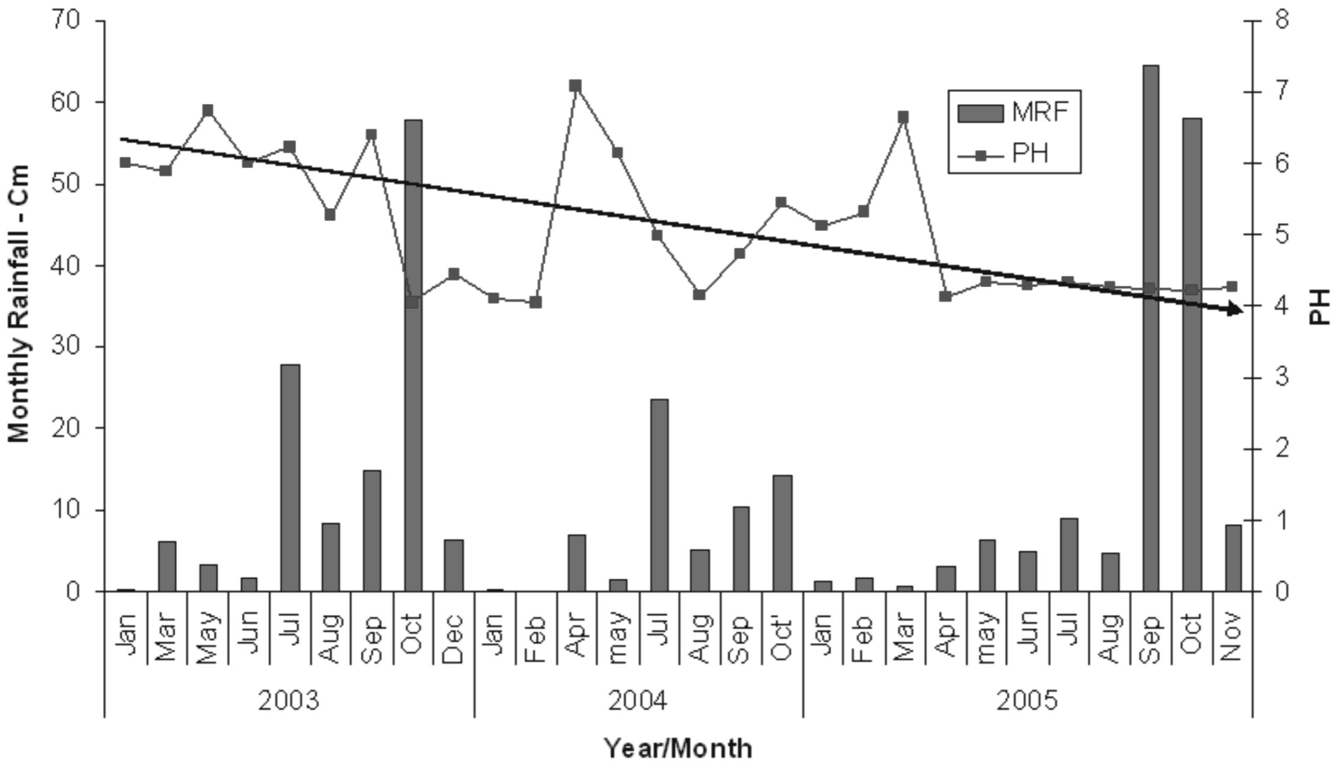

Figure 5: pH variations during the years 2003, 2004 and 2005.

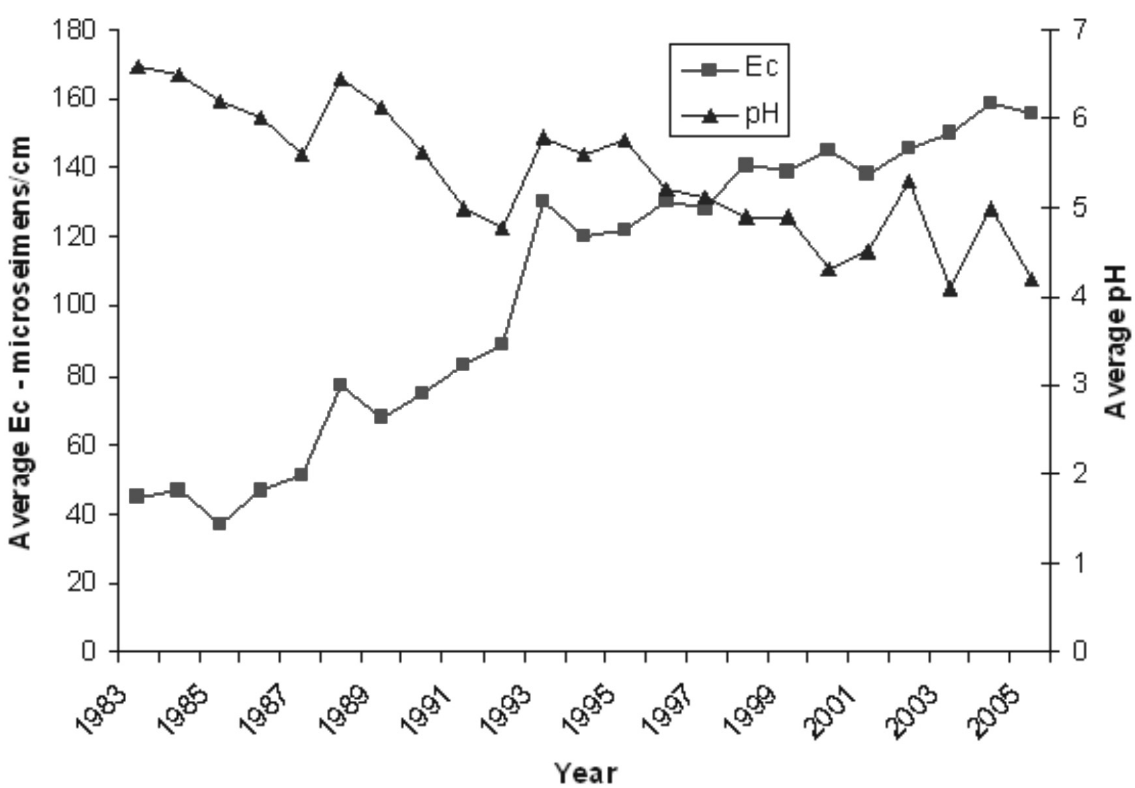

Figure 6: Long-time variations of annual average Ec and pH values during the period, 1983 to 2005.

Table 4: Annual average values of Ec and pH for the years 1983 to 2005

Year	*pH*	*Ec µs/cm*
1983	6.59	45
1984	6.482	47
1985	6.21	37
1986	6	47
1987	5.6	51
1988	6.45	77
1989	6.13	68
1990	5.61	75
1991	5	83
1992	4.77	89
1993	5.8	130
1994	5.6	120
1995	5.77	122
1996	5.2	130
1997	5.1	128
1998	4.9	141
1999	4.9	139
2000	4.3	145
2001	4.5	138
2002	5.3	146
2003	4.1	150
2004	5	159
2005	4.2	156

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