IDŐJÁRÁS

QUARTERLY JOURNAL
OF THE HUNGARIAN METEOROLOGICAL SERVICE

CONTENTS

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Quarterly Journal of the Hungarian Meteorological Service

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EDITORIAL

Dear Reader,
On April 1, 1999 there was a change in the position of the Editor-in-Chief of IDŐJÁRÁS. *Prof. G. Major,* Member of the Hungarian Academy of Sciences, who has been the Editor-in-Chief in the last four years, retired from this position due to several other obligations he has to fulfil. From January 1999 he was appointed to serve as the Chairman of the Scientific Council of Hungarian Meteorological Service (HMS), and, of course, he continues to be the Head of the Satellite Research Laboratory.

The President of the HMS, the organization which owns the IDŐJÁRÁS, has nominated me as Editor-in-Chief. It is a great honour for me to greet you in my new position, and, please allow me to introduce myself shortly and also to say some words about my ideas concerning the journal.

I graduated from mathematics and meteorology at the Eötvös Loránd University in Budapest in 1974, and begin my scientific work at the HMS. After one year work in the field of numerical weather prediction I obtained a Ph. D. (or more exactly C. Sc.) fellowship in Moscow at the Hydrometeorological Scientific Research Centre of the previous Soviet Union, one of the leading scientific institutions in meteorology at that time. I spent three years in Moscow working on my thesis, the subject of which was the development of a limited area nested grid NWP model. There I had opportunity to meet and learn from famous scientists, like *Prof. L. S. Gandin*, *Prof. G. I. Marchuk* and others.

After successfully defending my C. Sc. thesis I returned home and began to work at the Department of Meteorology of the Eötvös Loránd University as associate professor. Here I worked out the training plan of some new subjects in meteorologists' training, like Dynamical Models of the Atmosphere and Numerical Weather Prediction, and also participated in writing of university textbooks. From 1987, keeping my position at the university in half-stage, I returned to the HMS and began to work as the head of Section for Atmospheric Dynamics at the Institute for Atmospheric Physics under the directorship of *Prof. E. Mészáros*. The scientific profile of the section was climate modeling, in which we got special support and valuable scientific supervision from *Dr. G. Götz*, deputy director of the Institute at that time.

In 1989 I was granted a one year postdoctoral position at the National Center for Atmospheric Research (Boulder, U.S.A.). Here my research work was concentrated on the sensitivity analysis of some climate and NWP models with the application of the adjoint technique. During this time I had scientific cooperation with outstanding scientists like *Dr. D. Williamson*, *Dr. E. Kalnay* and others, whom I owe a debt of gratitude for supporting my work. My scientific cooperation with scientists working in the field of adjoint applications and variational data assimilation continued after my returning home in 1990. In 1994 I headed the local organizing committee of the Second Workshop on Adjoint Applications in Meteorology.

Unfortunately the political change which took place in Hungary in 1989 has found the Meteorological Service in a rather bad shape concerning its ability to adapt itself to the new economic circumstances. In this situation a new leadership was nominated and I took the position of the head of Department for Atmospheric Observations. In this capacity my task was to supervise the countrywide meteorological observation network, including upper-air and meteorological radar observatories, and environmental measuring sites. In the period 1991–1997 with the substantial help of my colleagues we succeeded in reconstructing the main components of the observing system, enhancing both their quality and cost-efficiency.

In the beginning of this year research and development activities of the HMS, that were largely hindered in the past years by financial restrictions were brought together in the frame of a Research and Development Department, and I was nominated as its head. As you can see, I have already tried almost every possible field of activity which is given inside our science and dare hope, that wide-range experience will help me in the editorial work.

Now, some words about my intended editorial policy. I do not plan significant changes in the profile of the journal. Repeating the words from the editorial comments written by my predecessor, *Prof. Major* four years ago: "the basic purpose of the journal is to publish high quality articles from any field of the atmospheric sciences written in English", and — in my view — both he and *Prof. Mészáros* before him did an excellent job to fulfil this task. While encouraging and highly appreciating papers from the "traditional" fields of the journal in the future, I try to put more stress in its profile on meteorological scientific subjects, which — in my judgment — were somehow under-represented in the journal until now, like weather forecasting including NWP or scientific results with new observational techniques, etc.

The regions from which we especially intend to attract publications are countries with economies in transition and developing countries, where, in our thinking, significant scientific potential not always matches the possibilities of publication, or, in other words, it is not always an easy task for scientists from this regions to make their high level results available for the global scientific community. Of course, absolutely no formal geographical limitation exists when choosing our authors. Another baseline of our publishing strategy is to choose reviewers for the papers from the circle of the most widely known and recognized experts of the field in question. I am absolutely convinced that the above goals can be met only with a high level Editorial Board, where good balance of geographical representation and uniform scientific excellence are both present. Since the previous Editorial Board well exhibited these features, we plan only a few changes, mainly in the direction to include outstanding young scientists in its rows.

Closing my comments I wish to express my sincere thanks to authors, readers and all who contributed in the past and hopefully will continue to contribute in the future in the publication of the 103 years old IDŐJÁRÁS. I will try to serve in accordance with the traditions of the journal.

Sincerely,

Dr. Tamás Práger
Editor-in-Chief

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Energy budget components in a forest clearcut: analysis of measurement results

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Abstract—Energy budget components were measured over a big forest clearcut during a 2 week period in June and July, 1995 in the framework of NOPEX (**No**rthern Hemisphere Land Surface Climate **P**rocesses **Ex**periment) CFE-2 (Second Concentrated Field Effort) to analyze the energy budget residue and its relation to energy budget components. The energy budget residue can be interpreted as the uncertainty of energy budget calculation, which consists of the measurement error, the differences between the source areas of radiation and energy balance components, the effects of advection, surface inhomogeneity, etc. It was determined as the residual of land-surface energy balance equation. The energy budget components were measured independently of each other. The values of turbulent fluxes were determined using eddy correlation technique.

The main measurement results are as follows: the daily mean values of the energy budget residue are between 2–28 W m^{-2}; the 2 week average value is 15 W m^{-2}, the corresponding standard deviation is 40 W m^{-2}. The order of magnitude of the energy budget residue is as great as the total soil heat exchange. The investigation has shown that the residuum is mainly not caused by instrumental problems.

Modellers always find closure of the energy balance because they use the energy balance equation to determine the soil temperature. Closure is obtained by iterating while allowing the soil temperature to vary. This method can result poor soil and surface temperature forecasts in case of significant energy budget residue.

Key-words: NOPEX, clearcut, surface energy budget, energy budget residue, eddy correlation technique.

1. Introduction

The basic object of NOPEX (**No**rthern Hemisphere Land Surface Climate **P**rocesses **Ex**periment) is to estimate the regional scale surface fluxes for boreal ecosystems (*Lundin,* 1995). The project has started in 1991 by long-term and

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special measurements performed in different areas of NOPEX-region (Central-Eastern Sweden). The long-term measurements were extended by special observations in CFE1 and CFE2 (Concentrated Field Efforts). The dataset is completed with remote sensing, hydrological and climatological observations. Field experiments with specific biophysical observations representative for patch scale have a special role in NOPEX (*Halldin et al.,* 1995). They provide both specific and basic information for scaling up the fluxes from patch to region (*Chehbouni et al.,* 1995). A specific surface type of NOPEX region is the forest clearcut. To know the daily variation and uncertainty of energy budget components above the different surface types is important for upscaling the fluxes from local to regional scale.

There are a few reasons why the energy budget studies above forest clearcuts are important.

(1) Clearcut and its microclimate completely differ from the surrounding forest (*Ghuman* and *Lal.,* 1986; *Chen et al.*, 1993). Its characteristics are studied by measurements and/or modelling. During the growing season the daily averages of air and soil temperatures, wind velocity and solar radiation are consequently smaller, air and soil moisture are larger inside a forest than in a clearcut (*Chen et al.*, 1993). The clearcut's albedo parameter is larger than the albedo in a forest area. The runoff is faster, the soil heat flux is larger. As the microclimate of a clearcut differs from the microclimate of a forest thus the turbulent exchange also alters over clearcuts. These effects are important for planning of reforestation.

(2) The basic energy balance characteristics of forest clearcuts are not known well. The surface energy and water budgets completely differ in a clearcut and inside a forest; they are influenced by the differences between the source areas of radiation and energy balance components (*Schmid*, 1997), by surface inhomogeneities (vegetation, soil and water content heterogeneities, direction dependent fetch), local advection and many other edge-caused effects.

(3) Model experiments and field observations are necessary to describe the properties of evapotranspiration, diurnal and seasonal variations of the surface and soil parameters, and to predict their values. Most of the studies are based on the energy balance equation describing one or more specific properties of a clearcut. However, most of the measurements performed have difficulties in the closure of the energy budget; they only deal with some of its components. Evapotranspiration and surface conductance above a clearcut were considered by *Adams et al.* (1991), where the analysis was based on eddy correlation measurements of sensible heat flux and additional measurements of soil heat flux and net radiation. Our measuring concept is similar to that of described by *Adams et al.* (1991). Unlike in *Adams et al.* (1991) study we measure the latent heat flux separately instead of calculating it from the energy balance equation. In order to estimate evapotranspiration in a forest clearcut *Flint* and *Childs*

(1991) have used the Priestley-Taylor equation. This method also requires the measurement of all terms of the energy budget. They have estimated their components with Bowen-ratio technique. Some microclimatic elements (soil and air temperature, soil moisture and saturation deficit) were also analyzed by *Groot* and *King* (1993) using soil-atmospheric model and field observation of energy budget components together with the use of the Bowen-ratio method. It was found that the prediction of atmospheric variables over a clearcut is more erroneous than the prediction of soil state variables due to the surface heterogeneities. *Stathers et al.* (1985) have shown that over clearcuts the soil temperature is quite sensitive to solar radiation, wind speed and surface roughness, but relatively insensitive to air temperature, lower boundary soil temperature and soil thermal properties. All these studies concentrate on one or few components of the energy balance equation; that is one component is always determined as a residual in the energy balance equation. Thus, there is no energy budget error estimate whatsoever represented in these studies.

The aim of this study is therefore twofold: first of all, the determination of daily courses of the energy balance components, and the investigation of some aspects of energy budget closure.

First, we review the measurement of energy balance components over a large forest clearcut near Siggefora during a two week period in summer 1995 in the frame of NOPEX CFE2 (Second Concentrated Field Effort). The results obtained are important because the surface type is very specific and there are only a few similar measurements published in the literature. Compared to former studies we performed more detailed measurements; each energy balance component has been measured independently, which made it possible to evaluate the energy budget residue (Δ). This term can be interpreted as

$$R_n - LE - H - G_{st} - G_c = \Delta \neq 0 \,, \tag{1}$$

where R_n is the net radiation, LE and H is the latent and sensible heat flux, respectively; G_{st} is the heat storage of 8 cm depth surface soil layer and G_c is the heat conductance into the deeper soil. The total soil heat exchange (G) is the sum of the heat storage and the heat conductance term ($G = G_{st} + G_c$).

Second, we analyze the relationship between the energy budget residue (Δ) and energy balance components to prove the reliability of measurement results. Energy must be conserved at the earth's surface. This statement of the first law of thermodynamics is used in all weather and climate models as one of the basic equations. The discrepancy between the available energy ($R_n - G$) at the surface and the consumption of energy by turbulent fluxes ($H + LE$) is well-known for about 10 years and widely accepted in recent years. The "unclosure" of about 10–30% of the available energy is presently a "number" to characterise and to compare field experiments (*Foken* and *Oncley*, 1995). In most cases the absolute values of available energy (R_n - G) have exceeded the turbulent fluxes (H + LE) (*Panin* and *Tetzlaff*, 1999).

In the 1980s, significant progress was made in methods to measure sensible and latent heat fluxes so it was no longer necessary to determine one part of the energy balance equation (mostly the latent heat flux) as the residuum of all the other parts. However, using these measurements, many land surface experiments were unable to demonstrate that the sum of all terms of the energy balance equation is zero. In fact, differences of 50 W m^{-2} were common and values even up to 200 W m^{-2} were observed. Fundamental problems may exist in our understanding of the energy exchange between atmosphere and surface (*Foken* and *Oncley*, 1995; *Oncley*, 1999).

Nevertheless, the closure problem did not result in significant effort to determine its cause. There are two reasons for this lack of research effort.

(1) Many experimentalist use the so-called Bowen-ratio method to measure fluxes. With this method, a surrogate for the ratio H/LE (Bowen ratio) is measured and the sum $H + LE$ is determined from measurements of R_n, G_{st}, G_c and the energy balance equation. With the sum and ratio of H and LE, it is trivial to determine their values.

(2) Even if both fluxes were measured, the energy budget residue (Δ) is sometimes used to correct their values.

Of course, modellers always find closure of the energy balance because they use the energy balance equation to determine the soil temperature. Closure is obtained by iterating while allowing the soil temperature to vary. This method can result in poor soil and surface temperature forecasts. This problem can also affect the fluxes of chemical species, such as carbon dioxide, since similarity relations are often used to compute these fluxes from the turbulent energy fluxes (*Oncley*, 1999).

Recently, the problems of Global Climate Change focused our interest on the water cycle (GEWEX, IGBP) and the carbon cycle (EUROFLUX, AMERIFLUX, JAPANNET and others) not for a qualitative overview but for a highly accurate quantitative determination (*Hutjes*, 1998). Therefore the discussion of the residuum of closure of energy balance is important above different surface types.

In the present study site description is presented first and methodology of measurement is demonstrated. Next, the calculation of momentum, latent and sensible heat flux is reported. Then properties of surface heterogeneity in the source region, the daily courses of all energy budget components and the energy budget residue (Δ) are discussed. Finally, a section for conclusions is provided.

2. *Micrometeorological measurements*

2.1 *Site description*

The experimental site is located in a large clearcut of a boreal pine forest within the NOPEX area, about 40 km far from Uppsala, Sweden. The forest was cut over a few years ago, therefore direct forest degradation effect is already not visible in the site. The shape of the clearcut and the meteorological conditions (precipitation, temperature, wind direction, momentum flux and frontal overpasses) during the measuring period are presented in *Fig. 1*. The characteristic size of the clearcut is 0.5 km × 1.5 km. The mean slope angle is approximately 1.5°.

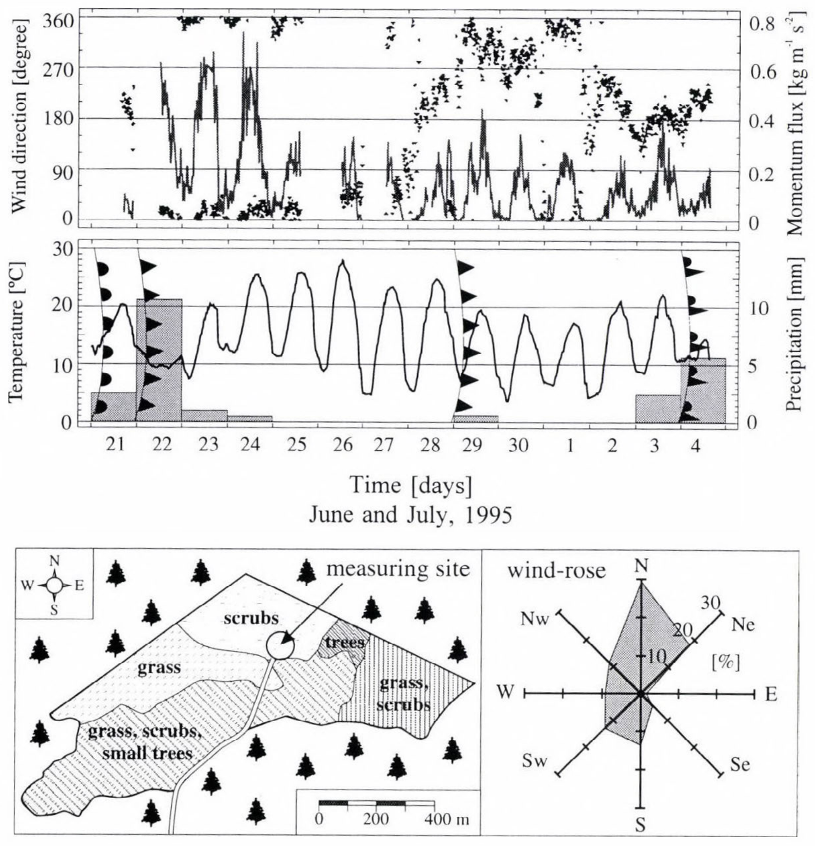

Fig. 1. Site characteristics and meteorological conditions during the measurement period.

The measuring equipment were mounted in the middle, slightly sloping part of the field. The fetch was approximately 200 m long at the beginning of the expedition for mainly northern wind (June 22–26, 1995) and on July 3–4 for mainly southern wind. In other cases the fetch was about 300–800 m long. About 80% of the field was covered by shrub and grass with 0.2–0.6 m height, by stumps of the cut trees and sparsely by young pines and some other type of trees. Among vegetation different size granite stones were scattered in grant numbers, which modified the surface albedo and roughness of the area. The wet soil surface was partly covered by smaller or greater puddles. At the beginning of the expedition there was frontal precipitation (Fig. 1). Then the soil was saturated. In that time about 3–5% of the surface was covered by puddles. The water disappeared from the pits at the end of June. Site values of soil moisture content is obtained by interpolation of measurements performed at different locations every 3 days. Precipitation was taken from *in situ* measurements. The soil water table was approximately at 0.6 m depth near the measurement tower. The average density of the upper 8 cm soil was 1.65×10^3 kg m^{-3}. Values of soil moisture content were obtained by gravimetric measurements; it was 0.35×10^3 and 0.26×10^3 kg m^{-3} at saturation and under dry conditions, respectively. The specific heat capacity of wet soil varied between 1400 and 1580 J kg^{-1} K^{-1} depending on soil moisture content. During the measurement period the soil heat capacity change was greater than 10% of the initial value. The estimated leaf area index (LAI) and roughness length was 1.3–1.8 m^2 m^{-2} and 5 cm, respectively.

2.2 Measurements of state variables and fluxes

Air temperature, dew point temperature and the temperature of the upper 8 cm soil layer were measured in every 20 minutes. The soil heat storage term was calculated from the averaged soil temperature values obtained by 4 sensors installed on wet and dry soil surfaces using the spatially averaged soil density. Soil heat flux was measured in 8 cm depth at two locations on 0.5 m distance. The heat flux plates were situated in a dry and a wet location. The solar radiation was measured by Schenk pyranometer, the photosynthetically active radiation (PAR) by LI-COR sensor, and the net radiation by REBS Q-6 net radiometer. The radiation components together with other meteorological elements were collected by a Campbell 21X datalogger. The solar radiation and PAR sensors were calibrated in Hungary. In other cases the manufacturing calibration was used. The measurement error of net radiation, caused by neglecting wind speed corrections for REBS Q-6 net radiometer, were between 2–4% according to the manual of new type REBS Q-7 net radiometer.

Wind speed, wind direction, momentum, sensible and latent heat fluxes were determined, using the eddy-correlation measurement technique applying a Solent three-axis research ultrasonic anemometer (GILL-1012) and a KH-20

Krypton Hygrometer (Campbell Scientific, Ltd) using 20 minute averaging periods. This equipment was mounted on a 5.5 m height mast. Data were sampled at 21 Hz. The reference moisture for the determination of moisture fluctuations was given by the dew point temperature measurement. In cool nights (e.g., on the 27th of June and the 2nd of July) the condensed dew at the iron body of the KH-20 Krypton Hygrometer could cause errors in the latent heat flux estimation.

When eddy correlation measurements are missing, the sum of sensible and latent heat flux ($H + LE$) are calculated using the correlation between R_n and ($H + LE$). Missing 20 minute average wind speed data (U) is estimated from its daily average courses.

2.3 Determination of turbulent fluxes

The turbulent fluxes are determined after *McMillen's* methodology (1988) using 20 minute averaging time. The coordinate system is rotated to the main wind direction. The wind speed, temperature and moisture datasets are detrended for calculation of the time series of fluctuations (actual value – mean value) by moving averages technique using 400 s time window for the estimation of mean values.

The sonic temperature was calculated according to *Kaimal* and *Gaynor* (1991) as:

$$T_s = T(1 + 0.32\,e/p) = \frac{c_{vm}}{c_{pm} R_m} c^2, \tag{2}$$

where c_{vm}, c_{pm} are the specific heat capacities of moist air at constant volume and pressure, respectively; R_m is the specific gas constant of moist air; c, T, T_s are the measured sound speed, air temperature and the sonic temperature, respectively; p and e are air pressure and the water vapor pressure, respectively. The sensible heat flux (H) was calculated from

$$H = c_{pm} \rho_m \overline{w'T'} = c_{pm} \rho_m (\overline{w'T_s'} + 0.1\,\overline{w'e'}), \tag{3}$$

where ρ_m is the density of moist air, w', T_s', T', e' are the fluctuation of vertical wind speed, sonic temperature, air temperature and water vapor pressure (in hPa), respectively.

Flow distortion by sonic anemometer is eliminated by applying the manufacturer's wind speed calibration (Gill calibration). This seemed to be an adequate available tool for our measurements. The matrix calibration method proposed by *Grelle* and *Lindroth* (1994) is more precise than Gill's one, but the deviation between them in the case of latent and sensible heat fluxes is only up to 2–4%. This deviation produces slight underestimation of H and LE. The matrix calibration was not applied because the rough dataset from sonic anemometer was collected using the option of manufactory calibration.

On the other hand, the calculation error of temperature fluctuation may cause a few percent overestimation of sensible heat fluxes after *Kaimal* and *Gaynor*, 1991. They have suggested a wind speed correction for sonic anemometers with three pairs of sensors that are orthogonal to each other. Since the sensors of Gill sonic anemometer are not orthogonal, we did not apply this correction. Negligence of the above mentioned two corrections partly compensated each other.

The latent heat flux is calculated according to *Tanner et al.* (1993) using both the equipment-dependent oxygen-correction and the corrections of latent and sensible heat fluxes (*Webb et al.,* 1980):

$$LE = LE_m (1 + K_0)(1 + K_E + K_H), \tag{4}$$

where L is the latent heat of vaporization, E_m is the measured water vapor density flux; K_0, K_E and K_H are the correction terms of oxygen, latent and sensible heat flux, respectively.

The KH-20 Krypton Hygrometer works on both 123.58 nm and 116.49 nm wavelengths. The absorption of energy due to the presence of oxygen has also to be taken into account. The voltage output of the hygrometer depends upon fluctuations of the two gases and can be approximated by

$$V = V_0 e^{-x k_w \rho_v} e^{-x k_0 \rho_0}, \tag{5}$$

where ρ_v and ρ_0 are the densities of water vapor and oxygen in g m^{-3}, respectively; x is the path length between source and detector (x = 1.32 cm), k_w and k_0 are the extinction coefficients of water vapor and oxygen respectively, while V_0 and V are the base and the output voltages in mV, respectively.

Using the logarithmic form of Eq. (5) combined with Eq. (4) the uncorrected latent heat flux is:

$$LE_m = -\frac{L}{x k_w} \overline{(\ln V)' w'}, \tag{6}$$

where $(\ln V)'$ is the deviation of logarithmic voltage from its average. The extinction coefficient k_w is found to be 0.138 m^3 g^{-1} cm^{-1} < k_w < 0.152 m^3 g^{-1} cm^{-1} using the factory calibration based on 20 minute average of water vapor density.

Neglecting pressure fluctuations with respect to the fluctuations of temperature, the oxygen fluctuation corrections implemented into the Bowen-ratio (β) can be expressed as:

$$K_0 = 0.23 \frac{k_0}{k_w} \frac{L}{T} \beta , \tag{7}$$

where k_0 is 8.5×10^{-3} m^3 g^{-1} cm^{-1} according to *Tanner et al.* (1993). The oxygen correction (K_0) of the rough latent heat flux is 10% of the value of LE_m for $\beta = 1$, which is a relatively large value. K_E and K_H in Eq. (4) were calculated after *Webb et al.* (1980) from

$$LE = LE_m (1 + K_0)\,(1 + rm)(1 + s \frac{\beta}{c_{pm} T}) , \tag{8}$$

where r is the average mixing ratio, s is the specific moisture and $m = 1.607$ is the ratio of dry air molecule weight to water molecule weight. After *Tanner et al.* (1993) $K_H/K_E \approx 5$ and typical values of K_E are between 0.01 and 0.02.

3. Results

First, the surface homogeneity of the measurement site is considered. Further, the effect of soil wetness variations upon soil heat conductance term (G_c) is analyzed. At last, daily courses of energy budget components and the energy budget residue (Δ) are analyzed with more attention.

The effect of local surface heterogeneity in the source region can be characterized by a correction factor k (*Panin et al.,* 1996) as:

$$k = \frac{\sum_i ((R_n)_i - G_i)}{\sum_i (H_i + LE_i)} , \tag{9}$$

where $G_i = (G_{st})_i + (G_c)_i$ is the total soil heat exchange. The factor k is determined for the 10 day measurement period between June 24–July 3, 1995. The ratio of available energy ($R_{ni} - G_i$) and the turbulent fluxes ($H_i + LE_i$) is calculated for every 20 minutes ($i = 1, 2, \ldots 10 \times 24 \times 3$). The mean value of k is 1.24 which is practically equal with LINEX experiment ($k_{LINEX} = 1.25$; *Foken,* 1997). According to *Foken's* (1997) criterion, the experimental location can be classified as slightly heterogeneous.

Daily courses of turbulent fluxes (*H*, *LE*) with the energy budget residue (Δ) in measuring period are presented in *Fig. 2*. According to the convention used the turbulent fluxes are positive upwards.

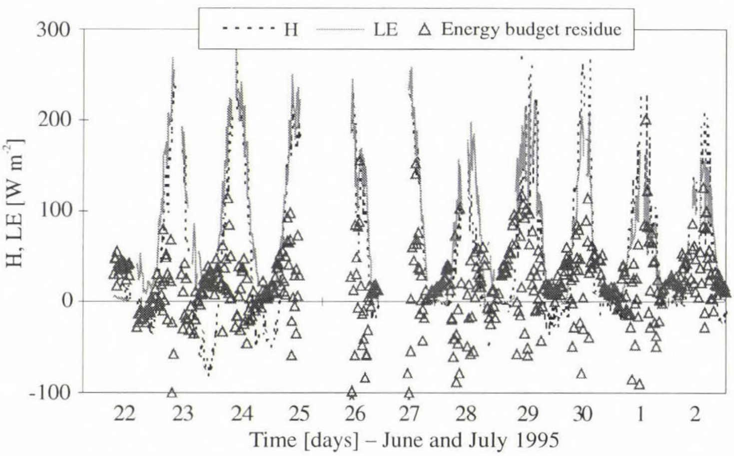

Fig. 2. Daily variation of turbulent fluxes and closure term in the measuring period.

At the beginning of the measuring period *H* and *LE* are approximately equal; their maximum values are between 250 and 300 W m^{-2}. The absolute value of Δ is usually – excepting some rare situations – below 100–150 W m^{-2}. In the last days of the measuring period – when the soil surface layer was much more dry – *H* exceeds *LE* and the scatter of Δ is somewhat larger.

Mean values (m) and standard deviations (σ) of net radiation (R_n), sensible (H) and latent (LE) heat flux and the soil heat conductance at 8 cm depth (G_c) are presented in *Table 1* for 9 days, when the eddy covariance system worked well (594 measurement periods for 9 days).

Table 1. Main values (m) and standard deviations (σ) of net radiation (R_n), sensible (H) and latent heat flux, and the soil heat conductance at 8 cm depth (G_c) for 9 days, when the eddy covariance system worked well (W m^{-2})

	R_n	H	LE	G_c
m	151	48	63	6.5
σ	187	78	59	14

The mean values and standard deviations of energy budget components for this period are not deviate considerably from the values for the whole measurement period (not presented here). The values of standard deviations are grater than the means. It is clear because the daily variation of energy budget components is higher than the mean values. For instance, the difference between the minimal and maximal net radiation is approximately 650 W m^{-2} (-55 W m^{-2}< R_n < 590 W m^{-2}).

The daily course of soil heat conductance at 8 cm depth, measured by REBS heat flux plates located on wet (plate I.) and dry (plate II.) areas, are shown in *Fig. 3*. The accuracy of the soil heat plates is good because their registrations are the same during the frontal precipitation time period of 22 June. There is an expressed deviation between the amplitudes measured in wet and dry locations; they exceeded 25 W m^{-2} in the afternoon of 25 June, when the areal mean value is close to 40–45 W m^{-2}. In the second half of the measuring period the deviations were smaller due to soil water content decrease. The greatest G_c values appeared in wet soil at about 15 LT (Local Time); in dry soil between 17 and 18 LT. In the energy budget analysis areally averaged soil heat conductance is used. Wet and dry areas are taken into account by 80% and 20%.

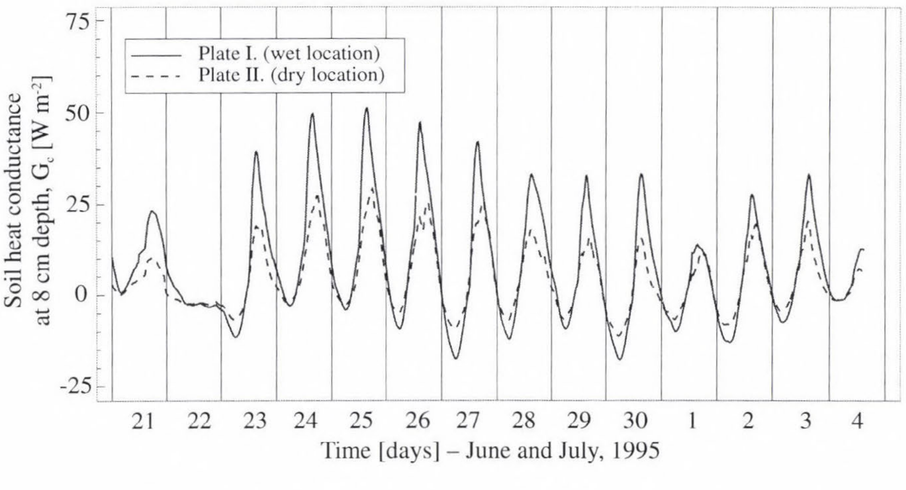

Fig. 3. Soil heat conductance (G_c) at 8 cm depth measured by plates on wet and dry locations.

Daily courses of all energy budget components for 30 June and 1 July are presented in *Fig. 4*. General features are as follows: all energy budget components show large fluctuations. The largest, medium and smallest terms are net radiation, turbulent fluxes and soil heat flux with the energy budget residue, respectively. The soil heat exchange and the energy budget residue are smaller than the turbulent fluxes but the difference is not irrelevant.

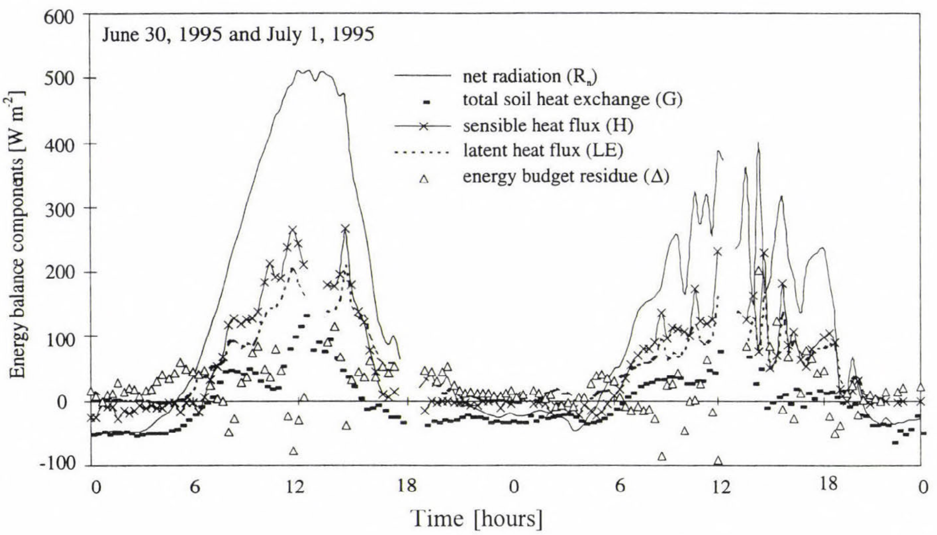

Fig. 4. Daily variation of energy budget components and closure term on 30 June and 1 July.

The two days chosen are different. 30 June is a sunny day with much insolation while 1 July is cloudy with weaker insolation. On 30 June the daily average of net radiation and the energy budget residue is 148 W m^{-2} and 22 W m^{-2}, respectively. On 1 July the averages are 109 W m^{-2} and 8 W m^{-2}, respectively. Δ shows large fluctuations similarly to all energy budget components. Δ is mostly positive in both days. It depends largely upon net radiation fluctuations. Inspecting Fig. 4 we see that the order of magnitude of G is as great as that of Δ. The standard deviation of Δ is about 30 W m^{-2} and 50 W m^{-2} on 30 June and 1 July, respectively.

The day-time ($R_n > 0$) and night-time ($R_n < 0$) averages of the energy budget residue (Δ) are presented in *Fig. 5*. The main characteristics are as follows:

(i) The energy budget residue (Δ) differs from zero but it is always smaller than 35 W m^{-2}.

(ii) $\Delta > 0$ except of the night-time period of 22–23 June. 11 and 1 mm precipitation is observed in day- and night-time period, respectively.

(iii) At night (from 22 to 06 LT) Δ is between −12 W m^{-2} and 13 W m^{-2}, which is a relatively large value as compared to energy budget components. The corresponding standard deviation of Δ is 15 W m^{-2}.

(iv) The larger the day-time mean net radiation is, the greater the Δ is and vice versa. For instance Δ is smaller than 10 W m^{-2} on 28 June, 1 July and on 3 July when average day-time net radiation is between 190 W m^{-2} and 210 W m^{-2}. Reversed Δ is about 30 W m^{-2} on 29 and 30 June and on 2 July when average day-time net radiation is between 250 W m^{-2} and 275 W m^{-2}. The standard deviation of the energy budget residue for day-time during the whole measurement period is about 45 W m^{-2}.

(v) The energy budget residue depends on wind speed and wind direction. For instance $|\frac{\Delta}{R_n}| < 0.2$ for $U > 2$ m s^{-1} and $-0.2 < \frac{\Delta}{R_n} < 0.4$ for $U < 2$ m s^{-1} when $R_n > 100$ W m^{-2} and the wind direction is between north and northeast (see Fig. 1).

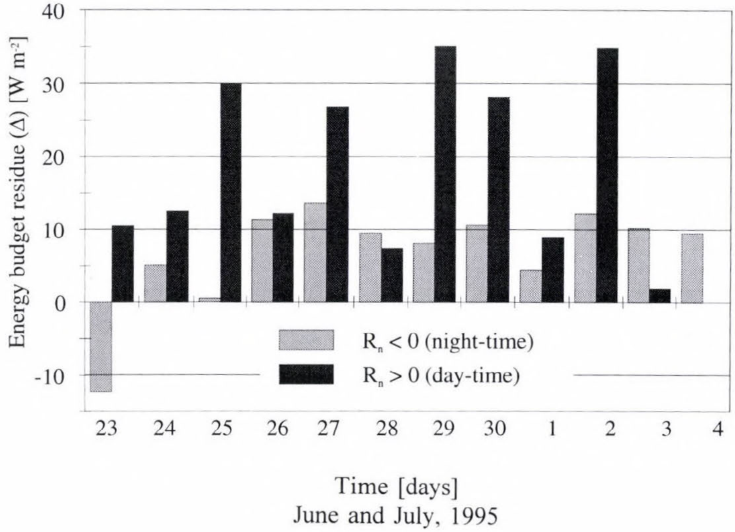

Fig. 5. Day-time (R_n>0) and night-time (R_n<0) averages of energy budget residue.

4. Conclusions

Daily variations of energy budget components over a big forest clearcut have been estimated by measurements to analyze the energy budget residue (Δ) and its relation to energy budget components. The energy budget components were independently measured from each other as accurately as possible. Turbulent fluxes were determined using the eddy correlation technique.

An energy deficit was observed, which means that the sum of turbulent fluxes were less than the available energy. Those are experienced by many field experiments (e.g., *Foken*, 1997; *Panin et al.*, 1998). The accuracy of our measurements for energy budget components (as *H, LE*, R_n, G_c) was below 5–10% and there was not any detected systematic error. Recent investigation has shown that the energy budget residue, which in the day-time period may grow up to 150 W m^{-2} is not caused mainly by instrumental problems but

(i) by methodological problems associated with uncertainties of estimation of flux time series (*Foken* and *Wichura*, 1996; *Weidinger* and *Matyasovszky*, 1998),

(ii) by neglecting the effect of density fluctuations for calculation of turbulent fluxes and

(iii) by differences between the source areas of radiation and energy balance components (*Schmid*, 1997),

(iv) by effect of surface heterogeneity, since the standard method to describe the turbulent fluxes requires stationarity and horizontal homogeneity which are not realised between the horizontally inhomogeneous land surface and atmosphere (*Panin* and *Tetzlaff*, 1999),

(v) by horizontal advection (*McNaughton*, 1976),

(vi) by effect of convective-scale flux components (*Laubach* and *Teichmann*, 1999), and

(vii) by effects of the additional terms of energy budget like the photosynthetic heat flux density, the heat storage for the vegetation and for the air, etc.

The energy budget residue is quantified and the possible reasons are qualified in this paper. The results are as follows:

(1) The maximum values of turbulent fluxes change between 150 and 300 W m^{-2}. At the beginning of the measurement period *H* and *LE* are close to each other, while at the end of the measurement period *H* usually exceeds *LE*.

(2) The deviations between the soil heat conductance measured at two different locations at 8 cm depth can exceed 25 W m^{-2} in the afternoon; this is considerably large with respect to the areal mean of G_c, which is up to 40–45 W m^{-2}.

(3) The daily mean of the energy budget residue is between 2–28 W m^{-2}. Its average value in the measurement period is 15 W m^{-2}. It shows large fluctuations which are governed by changes of net radiation. Therefore the time averaged value of standard deviation is more than 40 W m^{-2}. The order of magnitude of Δ is as large as *G*. In extreme cases their values can exceed 150 W m^{-2}. The energy budget residue depends on net radiation, wind speed and wind direction.

(4) The surface heterogeneity factor k introduced by *Panin et al.* (1996) is 1.24 for the experimental site chosen. According to *Foken's* (1997) criterion, the site can be characterized as slightly heterogeneous.

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Connection between vine production and meteorological variables on the Great Hungarian Plain

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Abstract—The effect of the weather type of different years on the production of two varieties of vine grape has been investigated. One of the varieties (*Zenit*) has short growing period, the other (*Jubileum 75*) has long growing period. Phenological and production data altogether with meteorological ones were collected in 1982–1987 at Kecskemét-Miklóstelep, the centre of the Great Hungarian Plain. Statistical relationships has been looked for between the characteristics of the grape and vine at one side and the yearly temperature and precipitation characteristics at the other side. It is found, that the effect of the weather type is much smaller on the phenology and the production of the short growing grape variety than on that of the long growing one.

Key words: growing period, cluster yield and weight, berry weight and diameter, sugar degree and acid content, mean temperature, amount of precipitation.

1. Introduction

Extreme meteorological elements of the continental climate represent stress effect on the life of vine, and influence the effectiveness of its cultivation. Besides the producing area and varieties, year is a quite important factor. Effect of the year is basically determined by sunshine duration and precipitation. Production of vine highly depends on the year because it is a plant requiring much light and warmth. However, depending on their genotype, the different vine varieties respond to environmental effects (such as year) in different ways.

In the Research Institute for Viticulture and Enology, Kecskemét-Miklóstelep (Hungary), wine-grape varieties of short and long growing period were chosen for our study. The purpose was to attempt to reveal the role of temperature and precipitation as meteorological elements determining their production. This kind of study was performed in connection with a breeding experiment with new variety candidates (*Füri et al.*, 1991).

2. Experimental conditions, variety characteristics

On the basis of meteorological and experimental data from the period 1982-1987, the varieties *Zenit* of short growing period and *Jubileum 75* of long growing period were studied. According to *Csepregi* and *Zilai* (1988) they can be described as follow:

Zenit (Ezerjó×Bouvier) has early maturity. It ripens in early September with a sugar degree above 17 Mm°. The cluster is middle large (100 g), the berries are little (1.7 g). This variety is not too susceptible to rot, however, it is sensitive to frost and drought. It produces well (11-14 t ha^{-1}). Its wine has excellent quality.

Jubileum 75 (Ezerjó×Szürkebarát) is a slowly ripening variety; it ripens in early October. The cluster is middle large (150 g), the berries are little (2.4 g), and they are not susceptible to rot. It tolerates frost as low as -21°C. It requires high nutritive supply. Yield is moderate (10-12 t ha^{-1}). Its wine is fine: a table wine that is poor in extracts.

The experimental plantation is on sand, in arid environment and lives on its own root. The vine-stocks are cultivated by high cordon with Sylvoz dressing. The vegetation area is big, in a twin-stock design.

3. Aim of the study

On the basis of the six years of observations, notices and measures, the following features of the above mentioned vine varieties were available: *sprouting day, harvest day, length of the growing period, cluster yield, cluster weight, berry weight, berry diameter, sugar degree and titrated acid content of the must and sugar free solids content of the wine.*

The following features were obtained from daily mean temperatures and daily amounts of precipitation: *annual mean temperature and precipitation amount, annual accumulated temperature above 10°C, annual number of wet days, annual intensity of precipitation,* as well as *mean temperature, precipitation amount, accumulated temperature above 10°C, number of wet days and intensity of precipitation in the growing period.*

Aim of our study was to determine the main statistical characteristics of above mentioned features, and to reveal the stochastic connection between the selected meteorological elements and the two vine varieties.

4. Results

As it will be seen from the detailed results, the extreme climate of the Great Hungarian Plain is well represented by the selected six years.

4.1 Meteorology of the area in the studied period

First, the main characteristics of observed temperature and precipitation amounts measured in Katonatelep and Miklóstelep during 1982–87 were compared to the longer-term climate conditions in Katonatelep. Since the meteorological measurements are not continuously available in Miklóstelep, the observed values of the two variables were compared to the climate of Katonatelep. Miklóstelep lies 18 km to the SW of Katonatelep. In Katonatelep a 35 year long dataset is available from 1962 to 1996. Measured values suggest that Miklóstelep was slightly warmer and wetter than Katonatelep during the given period (1982–87): annual mean temperature was 0.6°C higher and annual mean precipitation was 30 mm more in Miklóstelep. The highest temperature differences occurred in January and July, while maximum precipitation differences were observed in August. These results permit an assumption that the simplified Walter-Lieth climate diagram (*Justyák*, 1995) for Katonatelep (*Fig. 1*) can be applied to Miklóstelep as characteristic climate of the period 1962–96. According to the diagram all the months are humid. *Fig. 2* shows annual climate diagrams derived from monthly mean temperature and precipitation amounts during the six year long observation period. This figure suggests that climate of the tentative area is favourable for vineyard; spring and two summer months are wet, autumn is dry. Annual climate diagrams result in the following wet-dry relation. During the 1982–87 period 18 months were arid, that is 25% of all possible months, while 42% of all the summer and autumn months were arid (15). The period between March and October is the most important part of the year (for vineyards); humid conditions occurred in 28 months, that is 58% of all possible cases.

Table 1 shows the annual values, their mean and standard deviation and the variation coefficient (relative standard deviation = standard deviation/mean). The values of the table show, that 1983 and 1985 were the warmest and the coldest years, respectively. The coldest year was the most humid one and 1986 was the most arid year (as Fig. 1 also suggests). The highest number of wet days occurred in the most humid year, while the number of them was the lowest in 1983. Consequently, the highest and the lowest precipitation intensity happened in 1985 and in the most arid year (1986), respectively. However, the difference is only 1 mm day^{-1}. Values of the variation coefficient show that the annual precipitation amount and number of wet days have the highest, and the annual mean temperature has the lowest variation in the experimental plantation which represents the wine districts of the Great Hungarian Plain well.

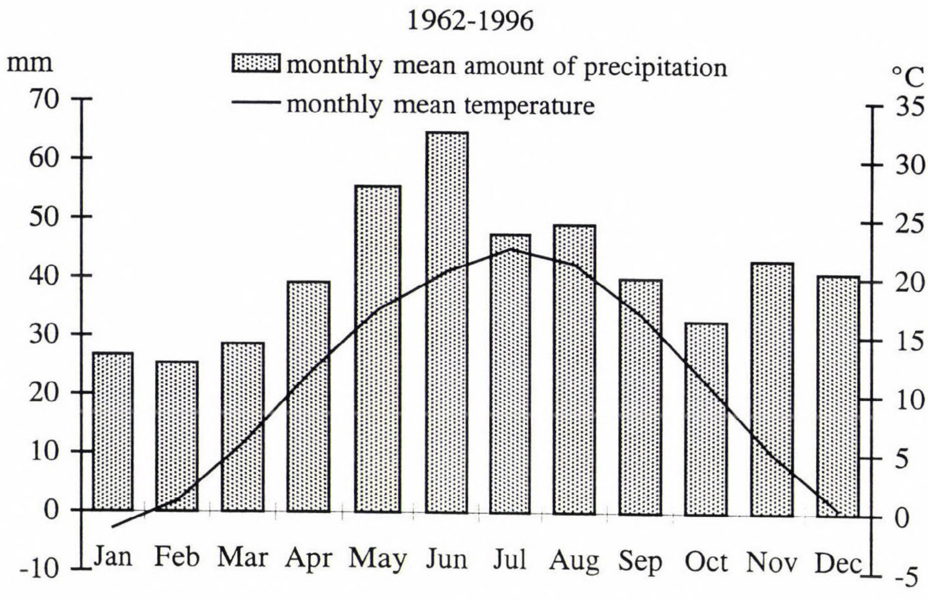


Fig. 1. Climate diagram of Kecskemét-Katonatelep on average of 35 years.

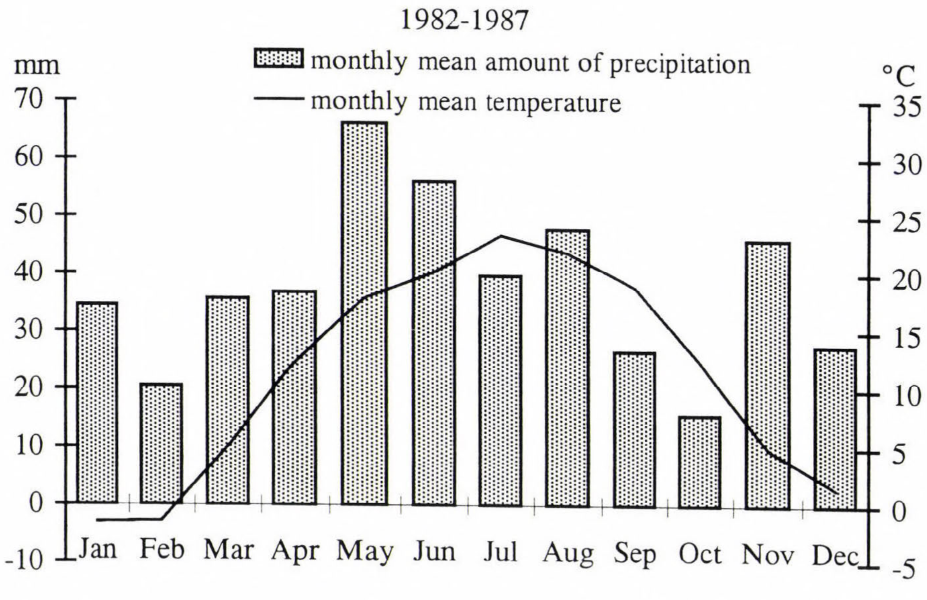


Fig. 2. Climate diagram of Kecskemét-Miklóstelep on the average of six years.

Table 1. Annual values and most important statistical parameters of meteorological elements of the study (Kecskemét-Miklóstelep)

Year	Yearly				
	mean temperature (MTY, °C)	accumulated temp. > 10°C (TSY, °C)	amount of precipitation (PSY, mm)	number of wet days (PDY)	intensity of precipitation (mm day^{-1})
1982	11.7	1854.0	406.9	81	5.0
1983	12.3	1950.2	405.4	78	5.2
1984	11.2	1651.8	462.6	101	4.6
1985	10.6	1685.5	540.8	110	4.9
1986	11.6	1944.5	369.5	89	4.2
1987	10.8	1723.2	532.0	109	4.9
Mean	**11.4**	**1801.5**	**452.9**	**94.7**	**4.8**
Standard deviation	0.6	132.1	71.3	14.0	0.4
Coeff. of variation	0.055	0.073	0.157	0.148	0.078

Table 2 contains sprouting and harvest days and the length of the growing period (difference of sprouting and harvest days) of the two vine varieties as well as some meteorological features of this period for each year. Some statistical parameters were also calculated.

The growing period of *Jubileum 75* is generally 23 days longer than that of *Zenit*. The highest difference (40 days) was in 1985, and the lowest (3 days) in 1986, in the most arid year. Variation around the mean value (standard deviation) of the length of the growing period is 14 in the case of *Jubileum 75*, and it is higher by half than that of *Zenit*. Difference between the mean temperatures of their growing periods does not dramatically differ: it ranges from 0.5°C (1984) to 0.1°C (1983, 1987). Therefore, there is no characteristic difference between the mean values and standard deviations of the six years. Maximum values of the accumulated temperature above 10°C can be found in 1983 (the warmest year) for both varieties. In the case of *Jubileum 75*, however, the minimum values happened in 1983, the second coldest year, and not in the coldest one. In general, the growing period of this variety begins six days later and takes almost 30 days longer. This fact can explain that the accumulated temperature above 10°C is higher by 200°C on an average than that of *Zenit*. On the other hand, the late sprouting is advantageous for it to survive late spring frosts. Precipitation amount of the growing period is also higher (by 25 mm on an average) for this variety except 1986, the most arid year. Maximum of the precipitation amount was in 1985, the most humid year, for both varieties. However, its minimum was in the most arid year for *Jubileum 75* only. In the case of *Zenit*, the minimum occurred in 1983, the warmest year. That year the low amount of precipitation had a negative effect on acid content of the must and extract content of the wine in *Zenit*. Number of wet days of the growing period follows the same pattern for this variety. However, in the case of *Jubileum 75*, the maximum is in 1984, a year when the temperature and the precipitation were more or less normal. On the other hand, mean temperature of the growing period of this variety is the lowest in this year. Contrary to the annual precipitation intensity, the precipitation intensity in the growing period is always over 5 mm day^{-1} for both varieties. It must be noticed that in the case of *Jubileum 75* the maximum is in the warmest year, while the minimum occurred in 1984 for both varieties.

Table 2. Yearly values and most important statistical parameters of the growing period and phenological features of the vine varieties

Year	The growing period's							
	beginning	end	length	meteorological features				
	(sprouting day)	(harvest day)	(day)	mean temperature (MTV, °C)	accumulated temp. > 10°C (TSV, °C)	amount of precip. (PSV, mm)	number of wet days (PDV)	intensity of precip. (mm day^{-1})
				Zenit				
1982	122	245	123	21.4	1417.3	204.5	31	6.6
1983	102	251	149	20.9	1646.4	187.1	30	6.2
1984	110	249	139	19.1	1285.8	209.7	42	5.0
1985	112	241	129	19.7	1266.7	266.3	45	5.9
1986	112	251	139	21.3	1575.7	205.8	31	6.6
1987	120	251	131	20.2	1345.8	241.2	35	6.9
Mean	**113**	**248**	**135**	**20.4**	**1423.0**	**219.1**	**36**	**6.2**
Standard deviation	7.2	4.1	9.2	0.9	156.5	29.0	6.4	0.7
Coeff. of variation	0.064	0.017	0.068	0.046	0.110	0.133	0.179	0.111
				Jubileum 75				
1982	127	284	157	21.0	1733.5	231.7	38	6.1
1983	110	271	161	21.0	1777.5	239.9	32	7.5
1984	118	296	178	18.6	1550.5	261.2	52	5.0
1985	120	289	169	19.4	1599.8	288.1	50	5.8
1986	118	260	142	21.3	1617.7	205.8	31	6.6
1987	121	264	143	20.3	1488.0	242.7	36	6.7
Mean	**119**	**277**	**158**	**20.3**	**1627.8**	**244.9**	**40**	**6.3**
Standard deviation	5.5	14.5	14.2	1.1	109.5	27.8	9.0	0.9
Coeff. of variation	0.046	0.052	0.090	0.053	0.067	0.114	0.227	0.137

According to the variation coefficients concerning meteorological features, the number of wet days in the growing period shows the highest, while mean temperature the lowest variation for both varieties. The order between these values, however, depends on the varieties. As the standard deviation shows, distribution of the sprouting day is more uniform for *Jubileum 75* and the two other phenological parameters for *Zenit*, respectively. The time of ripening of *Zenit* is in a period of the year when the climate is generally not too extreme and fluctuating.

In *Table 3* annual meteorological elements and meteorological elements in the growing period are compared: difference of the mean temperatures (MTV-MTY), ratio of accumulated temperatures above 10°C, precipitation amount and number of wet days (TSV/TSY, PSV/PSY, PDV/PDY) are calculated. Mean temperatures of the growing period are higher by 9.1 and 8.9°C on an average than the annual mean temperature for *Zenit* and *Jubileum 75*, respectively. The difference between the mean temperatures of the two periods is the lowest in 1984 and the highest in 1986 (the most arid year) for both varieties. The growing period represents 79 and 90% of the annual accumulated temperature above 10°C in the cases of *Zenit* and *Jubileum 75*, respectively, obviously because of the longer growing period of the latter variety. It can also be noticed that the minimum of these ratios was in 1985 (the coldest and the most humid year) for *Zenit*, however, the maximum of them was in the same year for *Jubileum 75*. Values of the variation coefficients are always higher in the case of *Jubileum 75*.

Table 3. Parameters containing the annual and the growing period meteorological elements (symbol as in Table 1 and 2)

Year	MTV-MTY (°C)	TSV/TSY (%)	PSV/PSY (%)	PDV/PDY (%)
		Zenit		
1982	9.8	76.4	50.3	38.3
1983	8.6	84.4	46.2	38.5
1984	7.8	77.8	45.3	41.6
1985	9.1	75.2	49.2	40.9
1986	9.7	81.0	55.7	34.8
1987	9.4	78.1	45.3	32.1
Mean	**9.1**	**78.8**	**48.7**	**37.7**
Standard deviation	0.7	3.4	4.0	3.6
Coeff. of variation	0.080	0.043	0.083	0.096
		Jubileum 75		
1982	9.3	93.5	56.9	46.9
1983	8.7	91.1	59.2	41.0
1984	7.3	93.9	56.5	51.5
1985	8.8	94.9	53.3	45.5
1986	9.7	83.2	55.7	34.8
1987	9.5	86.4	45.6	33.0
Mean	**8.9**	**90.5**	**54.5**	**42.1**
Standard deviation	0.9	4.7	4.8	7.2
Coeff. of variation	0.097	0.052	0.087	0.171

4.2 *Production of the vine varieties in the studied period*

Differences were studied in the harvest values of these two varieties at the meteorological conditions characterised above. *Table 4* lists features concerning production, must and wine of these varieties as well as their most important statistical indices for each year.

Table 4. Annual values and most important statistical parameters of production features of the vine varieties.

Year	Cluster yield (kg stock^{-1})	Cluster weight (g)	Berry weight (g)	Berry diameter (mm)	Sugar degree of the must (Mm°)	Acid content of the must (g l^{-1})	Solids content of the must (g l^{-1})
				Zenit			
1982	2.13	132	1.80	13.85	17.2	8.1	-
1983	2.60	148	2.30	14.00	17.6	6.6	17.8
1984	2.29	96	1.20	12.75	19.6	8.5	18.7
1985	4.16	112	1.30	12.85	17.3	8.4	18.0
1986	2.70	88	1.40	13.95	21.8	8.0	24.7
1987	0.68	100	1.50	13.85	19.2	9.5	21.6
Mean	**2.43**	**112.7**	**1.58**	**13.54**	**18.8**	**8.2**	**20.2**
Standard deviation	1.1	23.1	0.4	0.6	1.8	0.9	3.0
Coefficient of variation	0.462	0.205	0.257	0.043	0.095	0.115	0.147
				Jubileum 75			
1982	5.46	188	2.00	15.70	17.6	6.1	16.7
1983	4.89	190	2.20	15.70	19.5	6.0	22.0
1984	3.69	76	2.20	14.95	19.8	7.2	19.3
1985	3.54	148	1.80	13.60	18.8	8.3	18.5
1986	2.65	120	2.10	15.05	20.6	5.1	17.4
1987	0.31	80	1.70	14.70	18.3	7.0	-
Mean	**3.42**	**133.7**	**2.00**	**14.95**	**19.1**	**6.6**	**18.8**
Standard deviation	1.8	50.4	0.2	0.8	1.1	1.1	2.0
Coefficient of variation	0.533	0.377	0.105	0.052	0.057	0.169	0.104

Maximum of the cluster yield was in 1985 (the coldest and most humid year) and 1982, for *Zenit* and *Jubileum 75*, respectively. The secondary maximum, however, is in 1983 (the warmest year) for the latter variety. The maximum is in 1987 (the second coldest and most humid year having the most wet days) for both varieties. It can be noticed, however, that 1986/87 winter was extremely cold (with an absolute radiation minimum temperature of -29,6°C), and both varieties suffered significant frost damage. The mean value, the standard deviation and the variation coefficient are higher for *Jubileum 75*.

Maximum of the cluster weight was in the warmest year for both varieties, however the minimum value was in the most arid year for *Zenit*; this suggests that this variety is susceptible to the lack of water. The minimum was in 1984 for *Jubileum 75*. Accumulated temperature above 10°C was the lowest in this year. This experience supports observations that this variety requires much warmth. Mean, standard deviation and variation coefficients are also higher for this variety.

Berry weight of *Zenit* is extremely high in the warmest year (1983). In the case of *Jubileum 75*, however, there are the same maximum values in this year and in 1984 (the year having the lowest accumulated temperature above 10°C). At the same time, the maximum value of berry weight of *Zenit* was obtained in this year, too. *Jubileum 75* also had a high value in 1986, the most arid year. In the case of this variety mean value is higher but standard deviation and variation coefficient is lower than those of *Zenit*. Time pattern of the berry weight well shows the susceptibility of *Zenit* and tolerance of *Jubileum 75* to drought.

Time pattern of berry *diameter* is similar to that of berry weight. Values of the statistical parameters are higher for *Jubileum 75*.

Sugar degree of the must was the highest in 1986 (the most arid year with a minimum precipitation intensity and with an accumulated temperature above 10°C near the maximum), and the lowest in 1982. It is interesting that in 1982 mean temperature in the growing period of *Zenit* was maximum, and that of *Jubileum 75* also was high. The mean value was also higher, however, the two other parameters were lower for this variety.

Time pattern of the *acid content of the must* is also characteristic for the given varieties. The minimum content was in the warmest and in the most arid year for *Zenit* and *Jubileum 75*, respectively. *Jubileum 75* has its maximum in the coldest and most humid year. However, *Zenit* reaches the maximum value in the second coldest and most humid year. Mean value is higher, standard deviation and variation coefficient is lower in the case of *Zenit*.

Because of lacking data, statistical parameters for *solids content of the wine* can be compared only. These are higher for *Zenit*.

According to the variation coefficient, the cluster yield shows the highest, and berry diameter the lowest variation. The order between these limits depends on the varieties.

4.3 Connection between the features of the vine varieties and meteorological elements

The above mentioned analyses and comparisons show that different features of the must and wine of these two varieties are in stochastic relationship with the studied meteorological elements. If this relationship is supposed to be linear, then in the $y = bx + a$ regression equation y means the different production features of the vine varieties and x means the meteorological elements. Closeness of the relationship is shown by the linear correlation coefficient. Its value is theoretically zero if there is no (even a stochastic) connection between the studied random variables. Therefore, a statistical test calculated from a sample of random variables is necessary to decide when its value can be regarded to be significantly different from zero. The point is that an r_p critical value depending on the element number of the sample and the significance level can be determined, and r correlation coefficients of absolute value higher than r_p significantly differ from zero. In our case at $p = 0.05$ significance level $r_{0.05} = 0.814$, and at $p = 0.10$ significance level $r_{0.10} = 0.7239$. Regarding the solid content of the wine, the correct values are $r_{0.05} = 0.8783$ and $r_{0.10} = 0.8054$ since the number of elements is less by one.

Table 5 lists linear correlation coefficients between phenological features and production of the vine varieties as well as meteorological elements, that are suitable for the above mentioned test and can be evaluated (they are higher than 0.6, but are not significant at the above mentioned levels).

The table shows that the number of the correlation coefficients suitable for above mentioned criteria are 32 and 26 for *Jubileum 75* and *Zenit*, respectively. Number of significant cases of $p = 0.05$ probability providing a very close connection is 11 and 7, that of $p = 0.10$ probability is 9 and 6 for the above mentioned varieties. The numbers of the coefficients, which are valuable but not significant, are almost equal (13 and 12). Therefore, production of *Jubileum 75* is more climate dependent than that of *Zenit*.

The number of correlation coefficients, which are significant at the probability levels 0.05 and 0.10, is 13 and 20 for *Zenit* and *Jubileum 75*, respectively. About 50% (6 and 11) coincides with meteorological elements of the growing period. Therefore, the climate of a year influences production and phenological features of the given vine varieties as much as the climate of the growing period.

There is no significant relation between the phenological features and the meteorological elements for *Zenit*. Length of the growing season of *Jubileum 75* seems to be in relation with wet days, mean temperature and amount of precipitation of this season. It is strange that length and mean temperature of the growing period does not show strong negative correlation (increase in one implies decrease in other). This can be explained by the growing period being prolonged by autumnal days of lower mean temperature. Of course,

Table 5. Values of linear correlation coefficients between phenological and production features of vine varieties and meteorological elements.

Meteorological elements	Phenological features									
	Lenght of growing period	Sprouting day	Harvest day	Cluster yield	Clusree weight	Berry weight	Berry diameter	Sugar degree of the must	Acid content of the must	Solids content of the wine
Zenit										
Annual mean temperature						*0.7844*			**-0.8483**	
Annual accumulated temperature >10°C						0.7009	**0.8305**		-0.7103	
Mean temp. of growing period						0.6117	**0.8773**			
Accumulated temp. >10°C of growing period	0.6251					*0.7353*	*0.7865*		*-0.7607*	
Annual amount of precipitation									0.6577	
Annual number of wet days					-0.6257	*-0.7674*	-0.6275		*0.8021*	
Annual intensity of precipitation					**0.8564**	0.6540		**-0.9270**		-0.7854
Growing period amount of precipitation			-0.6070						0.6634	
Growing period number of wet days						-0.7115	**-0.9554**			
Growing period intensity of precipitation							**0.8460**			0.6021
Jubileum 75										
Annual mean temperature				0.6092		*0.7839*	**0.8816**		*-0.7664*	
Annual accumulated temperature >10°C			-0.6456		0.6135		0.6648		**-0.8763**	
Mean temp. of growing period	*-0.7810*		*-0.7787*						*-0.8086*	
Accumulated temp. >10°C of growing period					**0.9365**		0.6186			
Annual amount of precipitation				**0.8538**		*-0.7652*	*-0.7831*		**0.9109**	
Annual number of wet days					-0.7142	-0.6820	**-0.8762**		*0.7785*	
Annual intensity of precipitation				-0.6979				-0.6930		
Growing period amount of precipitation	*0.7375*		0.7252				-0.6973		**0.9675**	
Growing period number of wet days	**0.8279**		**0.8976**						**0.8280**	
Growing period intensity of precipitation	-0.6486		**-0.8158**							

(It is significant on **p = 0.05** or *p = 0.10* sigificance level.)

date of the harvest day shows similar connection with meteorological elements since it is one (partly subjective) of the determinative factors. Its strong negative correlation with precipitation intensity in the growing period can be explained by the fact that prior to the late date of harvest there are early autumnal days of low precipitation. Of course, these results are not surprising, but, strangely enough, *Zenit* does not show them.

Cluster yield is not correlated with any meteorological element in the case of *Zenit*. It has very strong positive relation with the accumulated temperature above 10°C in the growing period in the case of *Jubileum 75*. Correlation of the *average cluster weight* is in similar connection with the accumulated temperature above 10°C in the growing period. The average cluster weight is in the closest connection with the annual precipitation intensity in *Zenit*. Probably, this variety can utilise water when there is higher precipitation. The berry weight has the strongest correlation with the annual mean temperature for both varieties; it is followed by negative correlation with the number of wet days and the annual accumulated precipitation for *Zenit* and *Jubileum 75*, respectively. Berry diameter significantly depends on four meteorological elements in *Zenit*, first of all on the number of wet days in the growing period. This connection, however, is negative similarly to the annual wet days for *Jubileum 75*.

Sugar degree of the must is in significant and valuable negative correlation with annual precipitation intensity for *Zenit* and *Jubileum 75*, respectively. It is obvious that correlation of sugar degree with precipitation is negative. The fact that this was experienced only at precipitation intensity can be explained that it represents both accumulation of precipitation and length of the humid period. *Acid content of the must* is in negative connection with temperature variables, and shows positive correlation with precipitation ones for both varieties. The closest negative correlation is found with the annual mean temperature and the annual accumulated temperature above 10°C for *Zenit* and *Jubileum 75*, respectively. The latter variety shows a very close positive correlation with the annual accumulated temperature and the accumulated temperature in the growing period. It is not so close with the number of wet days in the growing period.

According to above mentioned data, there is no significant correlation between the same variables at the level $p = 0.05$ at the same time for both varieties. If both levels are allowed, the common combinations are the following: berry weight–annual mean temperature, acid content of the must–annual mean temperature, acid content of the must–annual number of wet days. This is less than 10% of the total events (33), consequently, features of the varieties have a significant effect on the closeness of the studied connections.

When correlation is significant (i.e., can be considered real) at the level $p = 0.05$, it is reasonable to calculate constants of the regression line.

Knowing the meteorological elements, approximate values of a given limit of error for the phenological and production feature can be calculated by the equation $y = bx + a$. Perhaps, it is more important that b regression coefficient represents susceptibility of these features to the given meteorological element: it shows how a unit change of the latter modifies values of the phenological and production features on an average.

Fig. 3 and *Fig. 4* show the observed values and regression lines at the level $p = 0.05$ in cases that are interesting from a viticultural point of view on the basis of Table 5. Therefore, susceptibility can be concluded from the equation of the lines. For instance, 1 mm/day increase in annual precipitation intensity results in 53 g increase in cluster weight on an average according to the equation $y = 53.03\ x - 141.44$ giving the connection between cluster weight and annual precipitation intensity in the case of *Zenit*. Another example: 1°C increase in accumulated temperature above 10°C in the growing period results in an increase of 0.4 g in the cluster weight of *Jubileum 75*. The other figures can be analyzed similarly.

Connection of the phenological and production features with the parameters representing annual and vegetation seasonal meteorological elements listed in Table 3 was also studied. In the case of *Zenit*, only a negative significant correlation between berry diameter and the PDV/PDY ratio can be obtained at the level $p = 0.10$: $r = -0.7309$. In the case of *Jubileum 75*, correlations of the PSV/PSY ratio with cluster yield and berry weight proved to be significant at the level $p = 0.05$: $r = 0.8953$ and $r = 0.8720$, respectively. The adequate regression lines are shown in *Fig. 5*.

5. Conclusions

(1) The effect of the yearly weather is different on the two varieties of the investigated vine grape.
(2) The phenological and production parameters of the long growing grape are more weather dependent than those of the short growing grape.
(3) The berry diameter and acidity are the most weather dependent characteristics of the grape varieties.
(4) The extract content of the vine seems to be independent of the yearly weather.
(5) To obtain good production, the long growing grape requires warm year, the short growing grape requires wet year.

Fig. 3. Regression between production feature of Zenit vine variety and the meteorological elements.

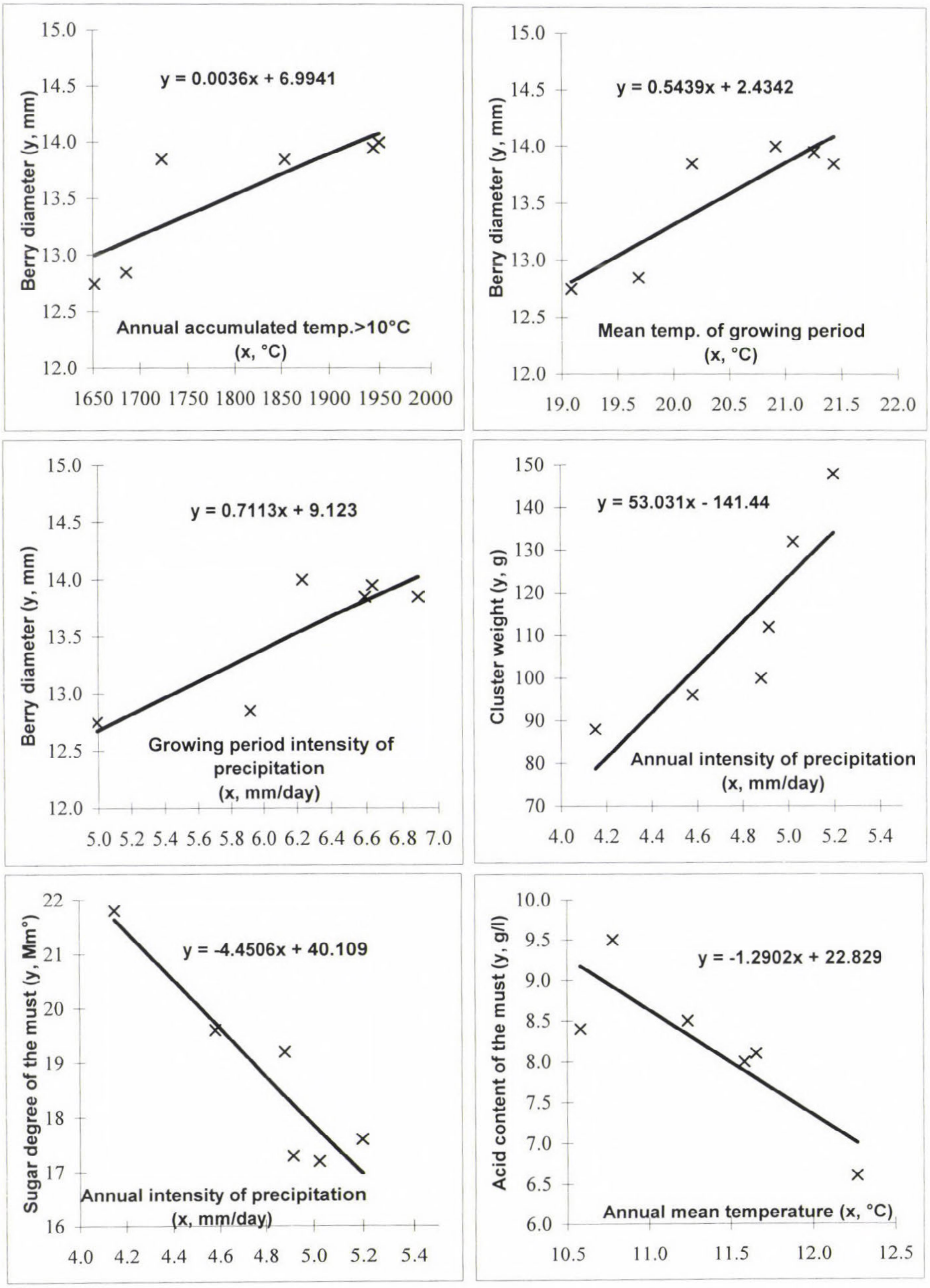
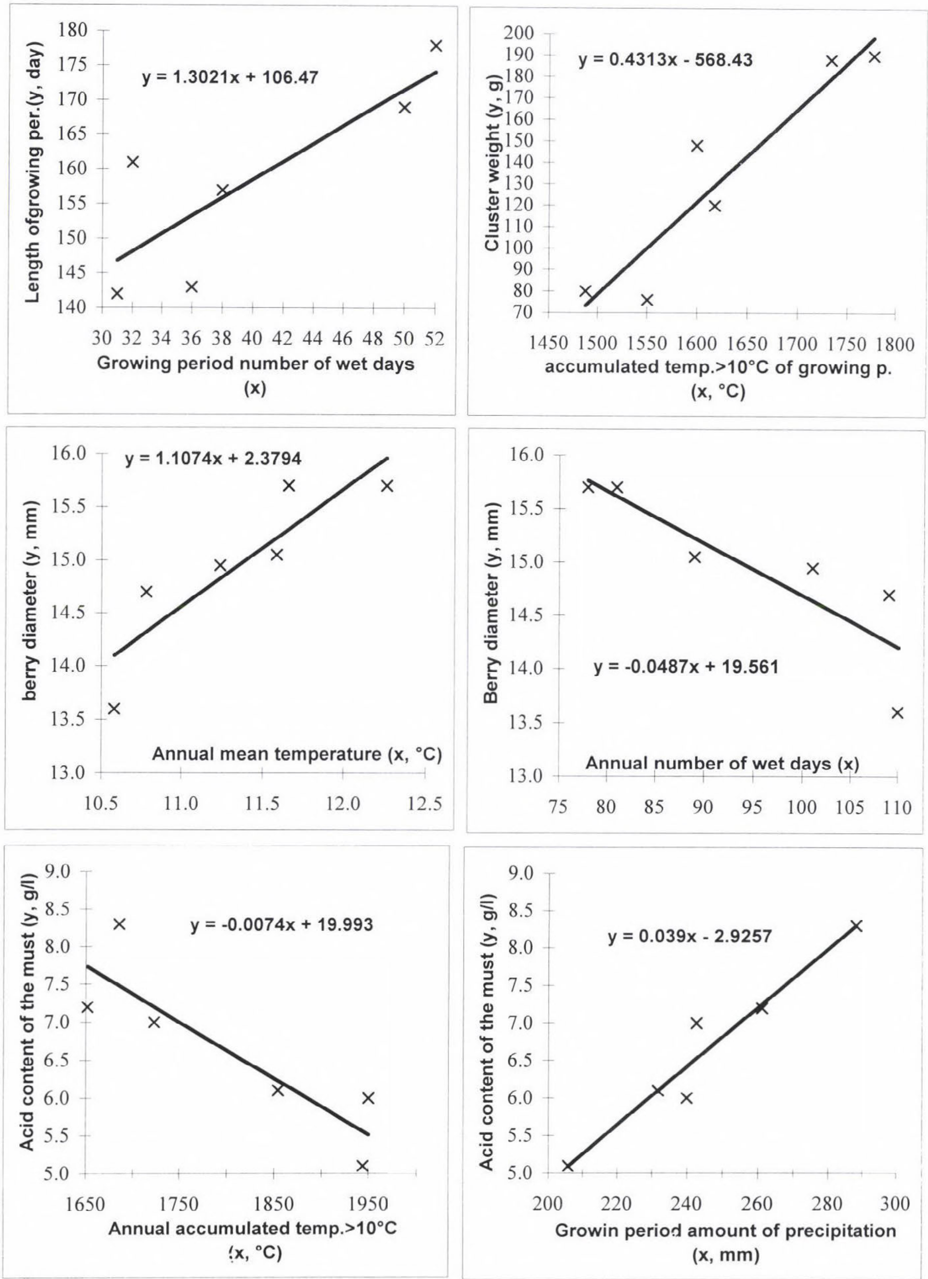


Fig. 4. Regression between production feature of Jubileum 75 vine variety and the meteorological elements.



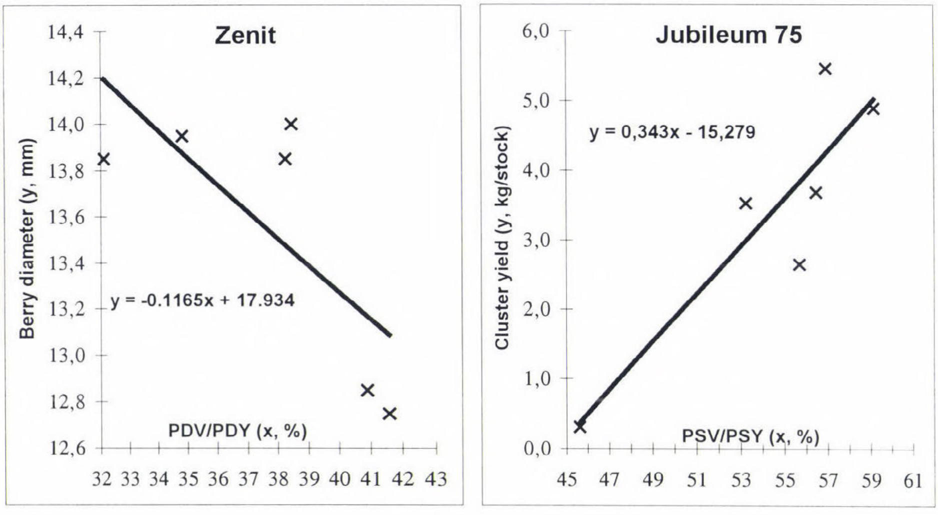


Fig. 5. Regression between production features of vine varieties and parameters containing the annual and vegetation seasonal meteorological elements (see Table 3).

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A climatological study of soil moisture and irrigation water requirement in Paraiba State (NE Brazil)

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Abstract—Results of a study of soil moisture conditions in Paraiba state (NE Brazil) are presented in this paper. Paraiba is one of the several states in NE Brazil which is frequently affected by droughts. Considerable parts of the state have a semiarid climate and the highly irregular nature of rainfall makes the practice of agriculture a risky proposition. Information on soil moisture conditions is hence a matter of importance.

The study is based on the estimation of daiiy soil moisture values for a minimum period of 25 years at twenty seven locations representing different parts of the state. A simple water balance model using daily precipitation and monthly mean temperature data is used for the estimation of soil moisture content. A first order Markov chain model is applied to the soil moisture data and the initial and conditional probabilities of days with dry and wet soil are computed for each decade of the year. Soil moisture averages and probabilities are used to evaluate the crop growing periods at the stations. The amounts of supplementary irrigation necessary to maintain the soil moisture content above selected levels during the crop growing periods are determined.

Key-words: soil moisture, Markov chain probabilities, crop growing periods, irrigation needs.

1. Introduction

The semiarid zone of Northeast Brazil is 860,000 km^2 in extent and contains nearly 10% of the country's population. The main climatic characteristics are: annual rainfall of 400–800 mm with a coefficient of variability of up to 80%, high air temperatures and high potential evapotranspiration rates (on average 2000 mm).

The frequent appearance of droughts in the region is responsible for the extreme poverty that affects the majority of the population. Various attempts are being made to reduce the impact of droughts on the region's economy.

In the semiarid zone the main constraint to crop production is the rainfall and it's extreme variability. The explanation and prediction of the rainfall fluctuations in this region is one of the challenging issues of tropical meteorology.

Agroclimatic studies based on long-term soil moisture information would be superior to those using rainfall averages and probabilities, since soil moisture information can be related to crop growth and production. Long-term soil moisture records are not often available. Models of varying degrees of complexity had been developed in the past for the evaluation of soil moisture conditions.

A simple water balance using long-term averages of monthly rainfall and potential evapotranspiration gives some indication of the availability of soil water and of water surplus (*Thornthwaite*, 1948). The simplicity of the model renders the results somewhat questionable. On the other hand, models such as the versatile soil moisture budget (*Baier* and *Robertson*, 1966; *Dyer* and *Mack*, 1984) involve several soil layers, information on the crop rooting depth, knowledge of the water holding and water releasing characteristics of the soil layers, etc.

Considering the large uncertainty in even the best measurement of soil moisture over a large area (*Robertson*, 1973), its estimation by models involving many parameters of unknown certainty may not be a very realistic approach. For agroclimatic purposes it seems preferable to use models and techniques which are simpler than the complex mathematical models, and still yield better results than those based on long-term averages of rainfall and temperature.

In the present study simple techniques are used to convert historical rainfall information to soil moisture data. These techniques integrate the knowledge of potential evapotranspiration, available moisture capacity as well as daily rainfall data and provide an estimate of available soil water on a daily basis.

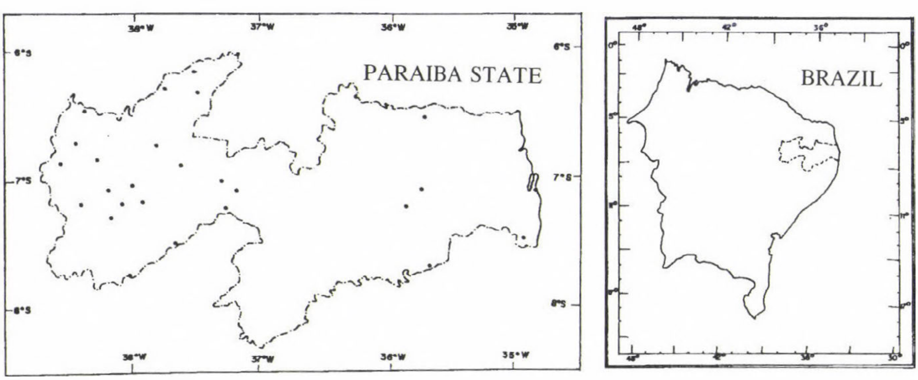

Fig. 1. Location of the stations.

The estimated daily soil moisture data are subjected to various types of analysis. Evaluation of crop growing periods and irrigation needs at the stations is the main objective of the study. *Fig. 1* shows the locations of the stations selected for this study.

2. *Methodology*

The evaluation of daily values of available soil moisture at the stations is based on the procedure suggested by *Thornthwaite* and *Mather* (1957). Mean monthly potential evapotranspiration (PE) values are computed using long-term mean monthly temperature data. The variation of PE during the year is used to obtain the PE values for each decade of the year. Each month is divided into three decades for this purpose; the last decade has 8, 9, 10 or 11 days depending on the month. The daily values are obtained from the decadal PE values and these together with the daily precipitation values are used to evaluate the daily soil moisture values. At each station the daily soil moisture content values are evaluated for the entire study period for each of five assumed available moisture capacity (AWC) values (25, 100, 150, 200 and 250 mm). The term 'available moisture capacity' represents the difference between the field capacity and the permanent wilting point.

A first order Markov chain model is applied to the estimated soil moisture data. Using the daily soil moisture values, the initial and conditional probabilities P(D), P(W), P(D/D) and P(W/W) are determined for each decade of the year. Here P(D) is the probability of soil being dry on a given day, P(W) is the probability of soil being wet, P(D/D) is the probability of soil being dry given that soil on the previous day is also dry and P(W/W) is the probability of soil being wet on a day given that on the previous day it was wet too. The threshold moisture content (VC) separating a dry day from a wet one is 50% of the AWC value adopted.

Mean soil moisture contents in individual decades and the corresponding probabilities for different AWC values are used to evaluate the growing periods at the stations.

In the simplified water balance studies the soil moisture fluctuation is regarded as the difference between the gain due to precipitation and the loss due to evaporation and transpiration. This method of computing soil moisture suggests a simple climatological approach to irrigation planning. One can set up limits below which soil moisture will not be allowed to decrease for a crop with a given root depth. Then, by means of daily water balance computations, it would be possible to know when the predetermined level of soil moisture is reached and how much to irrigate to bring the moisture back to a safe level.

The two important parameters in this study are the available moisture capacity and the critical soil moisture level (CV). The available moisture capacity depends on the soil characteristics and the crop rooting depth. Each crop has its own critical moisture level below which a reduction in yield will occur. Also for same crop the critical moisture level may vary with the phenological phase.

Due to lack of reliable soil and crop data, two AWC values (100 and 200 mm) and three critical moisture levels (55%, 70% and 85% of the AWC) are adopted in this investigation.

For a given station with a chosen AWC value, daily soil moisture values are evaluated for all the years of the study period. However, in each year during the crop growing season, whenever the soil moisture content decreases to a preselected level, the value on that day is replaced with that of corresponding to 95% of the AWC. In practical terms this means that each time soil moisture is depleted to a predetermined level, irrigation is applied to bring it back near to its maximum value.

The number of irrigation applications and the mean interval between irrigations are computed for each year and mean values for the study periods are derived from the results.

3. Results and discussion

Decadal mean values of soil moisture at Cathole de Rocha for different AWC values are averaged over all the years of the study period (*Fig. 2*). The period with the maximum soil moisture content seems to vary with variation in the AWC value. For example for AWC_{25} the three decades with the highest moisture content are the 8th, 9th and 10th decades while for AWC_{250} the three corresponding decades are the 11th, 12th and 13th, respectively.

A preliminary estimate of the growing season at Cathole de Rocha can be obtained from Fig. 2 on the assumption that the moisture content must be at least 50% of the maximum for favourable crop growth. Fig. 2 shows that the growing season at Cathole de Rocha has a duration of 140 days for AWC_{100} and 150 days for the other three AWC values.

The above information is based on mean soil moisture patterns. A better understanding of the soil moisture conditions can be obtained from the probabilities of sequences of days with dry and wet soil.

The probability of occurrence of five consecutive days with wet soil in each decade of the year is shown in *Fig. 3* for different AWC values. We now assume that a five day wet spell in each decade is sufficient for productive crop growth, and that successful agriculture is based on good crops being produced in at least seven out of ten years. From Fig. 3 we notice that the growing season at Cathole de Rocha extends from the 7th to 15th decades for AWC_{100} and from the 6th to 16th decades for AWC_{150}. For AWC values of 200 and 250 mm, the period starts at the 8th and 9th decades and ends at the 18th, respectively.

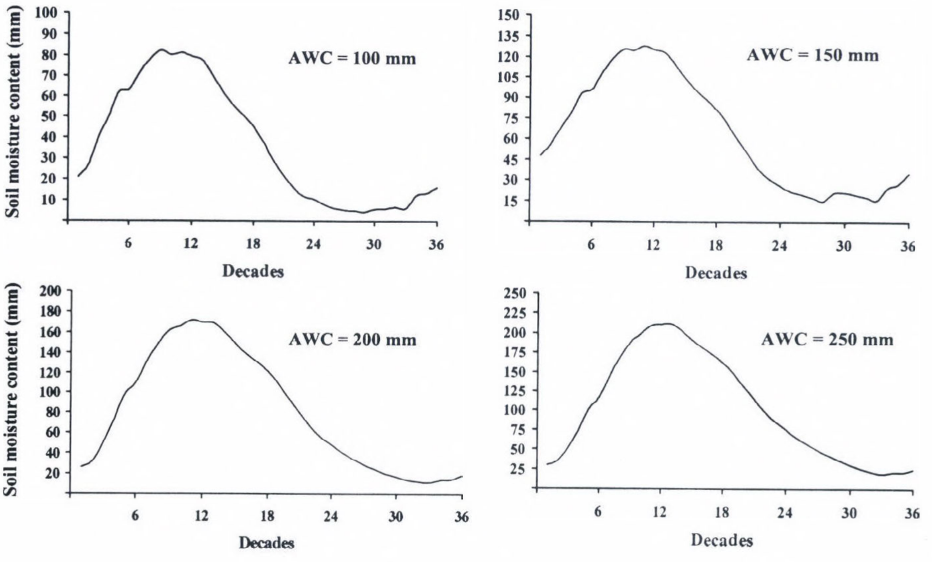

Fig. 2. Mean values of available soil moisture content at Catole do Rocha.

We assume that the seedbed holds 25 mm of moisture and that germination and early seedling growth require half of this amount for at least five days after sowing. We further assume that sowing is normally done after rain has sufficiently moistened the soil. From the mean decadal soil moisture content for AWC_{25} it is seen that for decades 5–13 the mean moisture content is more than half of the maximum value. The probability of occurrence of at least one wet day and of five consecutive wet days after a wet day is computed for decades 5–8, and it is found that the 6th decade is the most suitable for sowing purposes. If sowing is done in this decade, the growing seedling will enter a period when the expanding root system can tap moisture from greater depths (AWC values varying between 100 and 250 mm). The length of the growing season will be 100, 110, 150 and 150 days for AWC values 100, 150, 200 and 250 mm, respectively.

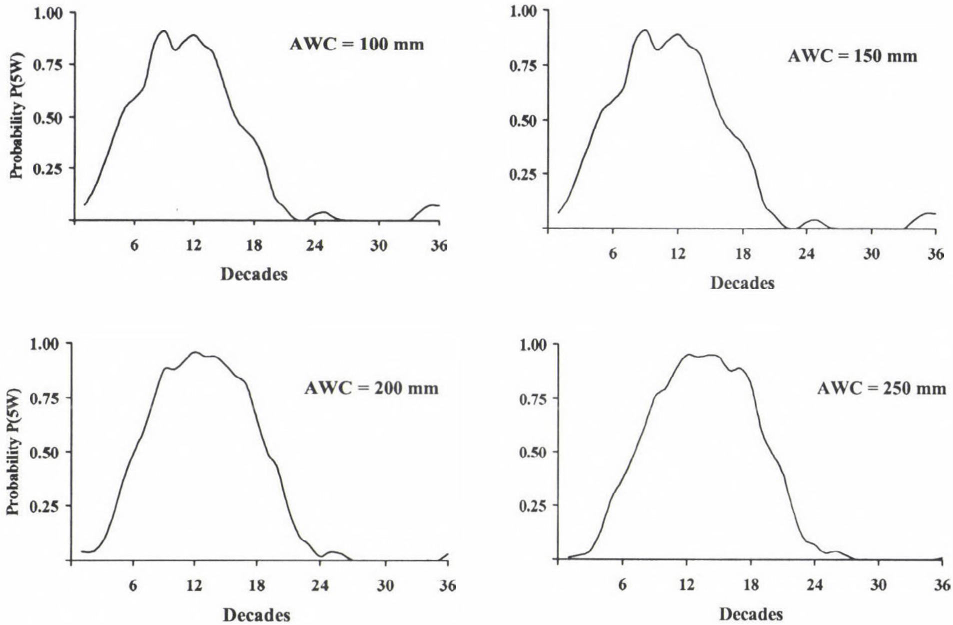

Fig. 3. Probability of occurrence of five consecutive wet days in each decade at Catole de Rocha.

Crop growing periods at the selected stations evaluated as discussed above are given in *Table 1* for two AWC values. Based on the results for all the stations, the following conclusions are arrived at:

(i) There is a significant phase postponement between the variation during the year of mean decadal values of precipitation and soil moisture content. This suggests that crop growing periods evaluated on the basis of precipitation data alone may not yield reliable results.

(ii) The period of the year with the maximum moisture content varies with the AWC value assumed. Also the ratio between soil moisture content and AWC varies with the AWC value considered.

(iii) Length of the growing season increases with increase in the AWC value adopted. This implies that at a given station with a given soil type the growing period for deep rooted crops will be longer than for shallow rooted crops.

Results of irrigation water requirement computations for São Gonçalo are discussed below and a summary of the results for all the stations is presented in *Table 2*.

Table 1. Crop growing periods in Paraiba State

Station	Available moisture capacity (mm)	Crop growing period		
		Start	End	Durations (days)
Barra de Jua	100/250	10 Mar	31 MAY/30 JUNE	80/110
Antenor Navarro	100/250	20 Feb	20 MAY/20 JUNE	90/120
Nova Olinda	100/250	10 Feb	10 MAY/10 JUNE	90/120
Serra Grande	100/250	01 Mar	20 MAY/10 JULY	80/130
Pianco	100/250	01 Mar	10 MAY/20 JUNE	70/110
Porcos	100/250	10 Feb	10 MAY/20 JUNE	90/130
Catole do Rocha	100/250	20 Feb	31 MAY/30 JUNE	100/130
Alhandra	100/250	10 Apr	20 SEPT/31 OCT	160/200
Joao Pessoa	100/250	10 Apr	30 SEPT/30 OCT	170/200
Imaculada	100/250	20 Mar	20 MAY/10 AUG	60/140
Belem do Brejo do Cruz	100/250	20 Feb	10 MAY/10 JUNE	80/110
Bom Jesus	100/250	10 Mar	20 MAY/30 JUNE	70/110
Itaporanga	100/250	10 Mar	20 MAY/20 JUNE	70/100
Princesa Isabel	100/250	01 Mar	31 MAY/20 JULY	90/140
Aguiar	100/250	01 Mar	10 MAY/10 JUNE	70/100
Araruna	100/250	01 Apr	30 SEPT/30 OCT	180/210
Sao Goncalo	100/250	20 Feb	20 MAY/20 JUNE	90/120
Agua Branca	100/250	20 Feb	20 MAY/31 JULY	90/160
Cajazeiras	100/250	10 Feb	10 MAY/20 JUNE	90/130
Piloes	100/250	10 Mar	20 MAY/20 JUNE	70/100
Condado	100/250	10 Mar	20 MAY/20 JUNE	70/100
Patos	100/250	10 Mar	20 APR/10 JUNE	40/90
Teixeira	100/250	10 Mar	10 MAY/20 JUNE	60/100
Umbuzeiro	100/250	10 Jun	31 AUG/30 SEPT	80/110
Pombal	100/250	20 Mar	20 MAY/20 JUNE	60/90
Alagoa Nova	100/250	01 Mar	10 OCT/20 NOV	220/260
Campina Grande	100/250	01 May	31 SEPT/30 OCT	150/180

Table 2. Irrigation needs at the stations

Station	Period	Available moisture capacity (mm)	Irrigation need (mm)
Barra de Jua	MAR – JUN	100 / 200	108 / 104
Antenor Navarro	MAR – JUN	100 / 200	148 / 112
Nova Olinda	MAR – JUN	100 / 200	168 / 144
Serra Grande	MAR – JUN	100 / 200	92 / 88
Pianco	MAR – JUN	100 / 200	152 / 120
Porcos	MAR - JUN	100 / 200	144 / 128
Catole do Rocha	MAR – JUN	100 / 200	108 / 96
Alhandra	MAR – OCT	100 / 200	176 / 160
Joao Pessoa	APR – OCT	100 / 200	96 / 80
Imaculada	MAR – JULY	100 / 200	120 / 104
Belem do Brejo do Cruz	MAR – MAY	100 / 200	124 / 104
Bom Jesus	MAR – JUN	100 / 200	112 / 104
Itaporanga	MAR – JUN	100 / 200	132 / 88
Princesa Isabel	MAR – JUN	100 / 200	108 / 88
Aguiar	MAR – MAY	100 / 200	96 / 88
Araruna	APR – OCT	100 / 200	124 / 104
Sao Goncalo	FEB – JUN	100 / 200	168 / 160
Agua Branca	APR - JULY	100 / 200	88 / 72
Cajazeiras	FEB – JUN	100 / 200	168 / 144
Piloes	MAR – JUN	100 / 200	144 / 120
Condado	MAR – JUN	100 / 200	148 / 128
Patos	MAR – JUN	100 / 200	168 / 144
Teixeira	MAR – JUN	100 / 200	120 / 104
Umbuzeiro	JUN – SEP	100 / 200	48 / 88
Pombal	APR – JUN	100 / 200	108 / 88
Alagoa Nova	MAR – NOV	100 / 200	160 / 128
Campina Grande	MAY – OCT	100 / 200	104 / 96

Limiting soil moisture value is 55% AWC

Irrigation requirements at São Gonçalo for AWC_{100} and limiting moisture level of 55% are shown in *Table 3*. In this case irrigation is applied whenever the soil moisture content decreases to 55 mm and thus the soil moisture content is maintained between 55 mm and 100 mm. It is seen that irrigation is needed in all years of the study period ranging from one application in 1974 to nine in 1958 and 1976. The mean interval between irrigations is 31 days and the mean irrigation water requirement during the five month crop growing period is 204 mm. It is noticed that in 15 out of 37 years the soil moisture deficit (difference between the AWC and the available moisture content) is more than 30 mm on at least 25% of the days.

A summary of the results for two AWC values and three limiting moisture levels is shown in *Table 4*. As it is to be expected, the number of irrigations increases and the mean interval between successive irrigations decreases as the limiting moisture level increases. However, the change in the total water need is not very pronounced since at higher moisture levels less water is applied in each irrigation.

For both AWC values, adoption of 70% level results in the soil moisture content remaining above 80% of the AWC on 70% of the days. Table 4 also suggests that to maintain similar moisture levels in the soil, less irrigation water seems necessary for AWC_{200} than for AWC_{100}. Similar result was obtained by *De Jong* (1985).

Long-term mean values of precipitation and potential evapotranspiration at Umbuzeiro during the six month wet season (May–October) are 468 mm and 463 mm, respectively. However, it is seen from Table 2 that even to maintain the soil moisture above 55% of the AWC, nearly 140 mm of irrigation is necessary. During the period February–May Terezina receives, on the average, 967 mm of precipitation. Potential evapotranspiration during the four month period is much less: 504 mm. Significant amount of supplementary irrigation is, however, necessary during the period to maintain the soil moisture content above half of the available moisture capacity.

This feature, also observed at the other stations, suggests that use of long-term mean monthly values of precipitation and potential evapotranspiration for the identification of crop growing periods may lead to erroneous conclusions in this region.

The crop growing periods shown in Table 1 are based on Markov chain probabilities of dry and wet days and represent the optimum months for crop growth at the stations. Results shown in Table 2 suggest that significant amounts of irrigation water are necessary even to maintain the soil moisture content near half of the available moisture capacity which is often considered as the minimum moisture level for plant growth (*Robertson*, 1985). In the case of corn and rice, the soil moisture levels are much higher and the irrigation needs increase correspondingly.

Table 3. Irrigation schedule for São Gonçalo. Available moisture capacity is 100 mm and minimum moisture content is 55 mm

Period: Feb–Jun

Year	Number of irrigations	Mean interval between irrigations	Number of days with soil moisture content between		
			55–70 mm	70–85 mm	85–100 mm
1944	4	43	44	46	54
45	5	36	30	43	77
46	4	22	55	47	48
47	3	15	21	42	87
48	5	35	28	44	79
49	6	27	26	49	75
50	6	28	31	45	74
51	8	17	31	59	60
52	5	33	38	57	56
53	6	27	39	53	58
54	6	28	38	44	68
55	4	19	25	53	62
56	7	22	34	47	70
57	8	19	42	46	62
58	9	16	59	50	41
59	5	29	48	46	56
60	6	28	34	49	68
61	4	32	25	56	69
62	6	27	29	49	72
63	6	27	33	40	77
64	4	43	31	47	73
65	4	40	27	35	88
66	5	26	35	53	62
67	4	49	19	23	108
68	6	29	28	43	80
69	3	27	38	46	66
70	8	18	48	44	58
71	2	21	16	45	89
72	2	82	38	60	53
73	3	58	25	55	70
74	1	0	14	25	111
75	4	44	39	38	73
76	9	16	39	39	73
77	2	52	30	55	65
78	5	18	40	40	70
79	7	22	34	52	64
80	7	23	45	52	54

Table 4. Water requirements at São Gonçalo during the period February-June

Available moisture capacity (mm)	Limiting soil moisture value (mm)	Number of irrigations	Mean interval between irrigations (days)	Number of days with soil moisture content between			Irrigation need (mm)
	55	5	31	55-70	70-85	85-100 mm	204
				34	46	69	
100	70	11	14	70-80	80-90	90-100 mm	270
				33	49	67	
	85	30	4	85-90	90-95	95-100 mm	299
				39	42	68	
	110	2	83	110-140	140-170	170-200 mm	195
				26	44	80	
200	140	5	39	140-160	160-180	180-200 mm	239
				31	45	72	
	170	14	11	170-180	180-190	190-200 mm	272
				41	49	58	

Irrigation needs evaluated from easily available climatological information by means of simple models such as that used in this study can be of use in land use and irrigation system planning. A detailed study along these lines has been carried out by *Robertson* (1970).

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Chemistry of rain in central India

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Abstract—The south-western Arabian summer monsoon loaded with local and distant pollutants causes heavy rainfalls in the central region of the Indian continent. The chemistry of summer rain water of the country (lies between 17° and 24°N latitudes, and 80°17' and 84°11'E longitudes at altitude >300 m) during hydrological years 1995 to 1997 is described. A total of 800 rain events at twelve sites, i.e., Raipur (during 1995–1997), Korba, Bilaspur, Kanker, Janjgir, Raigarh, Chirmiri, Bhatapara, Pithora, Gariyaband, Dallirajhara and Ambikapur of central India (during 1995) were occurred, from which 477 rain water events were collected in a polyethylene bucket kept over the roof of the houses. The chemical composition for ions, i.e., H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_2^- + NO_3^-, Cl^-, F^-, I^-, ionic balance, pH and conductivity of the rain water samples were determined. The concentration, flux, deposition patterns and trends of the ions and their sources in the monsoon rain water are described. The sulphate is a predominating ion and primary source of acid rain in central India. Most of the rain storms of India occur on its central areas. The rain water of these storms is mostly acid, especially in the monsoon season, probably due to blown of less amount of soil dust and higher humidity.

Key-words: pH, rainfall, acidity, chemical composition of rain water, concentration, flux and distribution of the ions, sources.

1. Introduction

Precipitation is a natural phenomenon through which pollutants from the atmosphere are scavenged out by natural processes, i.e., rain, fog, dew, snow, etc. Rain is the main source for getting large quantities of water to change the ground water aquifers and supporting the forest vegetation in the tropical countries. The rain water is not pure but contaminated with a variety of pollutants due to increased human activities. Acidic precipitation to the earth's surface is well known serious phenomenon due to adverse environmental

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impacts (*Pitelka* and *Raynal*, 1989; *Longhurst et al.*, 1993; *Tuovinen et al.*, 1993). Acid rain is blamed for tree damage, acidification of water reservoirs, deterioration of marble structures and ancient monuments, etc. (*O'Sullivan*, 1985; *Cheng et al.*, 1987; *Vocom*, 1979; *Skoulikidis*, 1983). Much work have been carried out in the western countries in order to define the sources, causes, extent and consequences of acid precipitation (*Kasina*, 1980; *Hansen* and *Hidy*, 1982; *Kallend et al.*, 1983; *O'Sullivan,* 1985; *Blanchard* and *Stromberg*, 1987; *Lacaux et al.*, 1987; *Moldan*, 1988; *Goreham*, 1989; *Cowling*, 1989; *Falkengren-Grerup*, 1989; *Likens*, 1989; *Porteous* and *Barratt*, 1989; *Bowersox et al.*, 1990; *Udisti et al.*, 1991; *Cerceo*, 1983; *Atteia*, 1994; *Lynch et al.*, 1995; *Sanusi et al.*, 1996). The activities, i.e., generation of electricity by burning of coal, combustion of gasoline by automobile and smelting/refinement of metals and non-metals are major sources of the oxides of nitrogen and sulphur that are involved (*Mohnen*, 1988; *Galloway*, 1989; *Schwartz*, 1989; *Khemani et al.*, 1987; *Irwin* and *Williams*, 1988; *Khemani et al.*, 1994). The question of the extent of acidification in the tropical globe has received little scientific attention until recently, so the answers are unsatisfactory or unavailable. For this region, the scope project "acidification in tropical countries" was initiated in 1984, culminating in a workshop in Caracas, 1986 (*Nollor* and *Chadha*, 1990). It is a clear that the question of acidification is very relevant to the tropics. Some identified areas of acidification such as South-Western China, Thailand, Japan, etc. are probably occurring due to increased combustion of fossil fuel, smelting of sulphide minerals as well as poor buffering capacity of soil present (*Zhao et al.*, 1988; *Saylor et al.*, 1992; *Environment Agency*, 1996). The tropical region has large population and it is the area of the globe where changes in population, energy usage, industrial capacity and agricultural practices are the fastest (*Nollor* and *Chadha*, 1990). Another geographical feature is that about 40 percent of acid sulphate soil of the world occurs naturally in the tropics of Asian region (*Singh*, 1982). About half of the globe population resides in the Asian region and the use of fertilizers is increasing too fast due to multiple crop yields in the agriculture. Tropical regions are characterized by rice forming and biomass burning which provides sources for green house gases like CH_4, NMHC, CO, NO_x and NO_2 (*Clairac et al.*, 1988; *Suman*, 1988; *Talbot et al.*, 1988). The industrialization and production of energy in the tropics are mainly based on burning of fossil fuel such as coal with emission of an enormous amount of the acidic gases, SO_x, NO_x into the atmosphere. The expected emitted amount of SO_2 alone by 2000 AD in South Asia is 76 million tons, more than projected for the whole of Europe and North America (*Hordijk*, 1993). These anthropogenic pressures on atmospheric composition and chemistry are likely to be increased with time in this region.

The data on the atmospheric precipitation of India is fragmentary and even less data exist on the acidity of precipitation in particular. Some authors reported the acidity and ion composition of rain water of the northern and western part of the Indian continent in isolated pattern (*Mukherjee*, 1978; *Das et al.*, 1981; *Khemani et al.*, 1989; *Verma*, 1989; *Ravichandran* and *Padmanabhamurty*, 1994).

There is rapid industrialization and urbanization in the central region of the country (lies between 17° and 24°N latitudes and 80°17' and 84°11'E longitudes) due to availability of vast natural resourced materials, i.e., coal and minerals of Fe, Al, Cu, Mn, Sn, Nb, Ca, etc. More than 2000 small and more than 200 large scale industrial works and thermal power plants, mostly based on burning of coal, are operating in this region. Heavy rainfalls occur in this region by breaking of the south-west (SW) summer monsoon. The most of tropical rain forests of the country lie in this region where active exchange of gases and aerosol between the atmosphere and the biosphere takes place as a natural process. In this work, the chemistry of precipitation in central India has been investigated to define the concentration, amount, distribution pattern and sources of major ions, i.e., H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, F^-, I^- in rain water.

2. *Experiments*

2.1 Sampling sites

The choice of sampling network and location of sampling equipment were made according to internationally accepted specifications (*WMO GAW* No. 85; *Khemani et al.*, 1989). Twelve sampling sites were established in the central India: Raipur, Korba, Bilaspur, Kanker, Janjgir, Raigarh, Chirmiri, Bhatapara, Pithora, Gariyaband, Dallirajhara and Ambikapur (see *Fig. 1*). These sites were chosen as representatives of different geographical, geological and meteorological effects, and their summary descriptions are given in *Table 1*.

2.2 Sampling of precipitation water

Wet (rain water) samples were collected on an event basis. The sampling period was extended from January 1995 to December 1997 and the total number of rain water samples collected during these period were 477. The instrument consists of a bucket system covered with a lid which exposed and closed manually. A cylindrical polyethylene bucket (diameter = 30.5 cm and height = 32 cm) was fixed on a wooden stand mounted over the roof of a house (height = 4 m). The depth of rain amount was measured with a graduated scale. The rain water samples were filtered with Whatmann filter paper No. 42 and transferred into a one liter polyethylene bottle. Each collector was washed out from the container with 500 ml deionized double distilled water. Each collected sample was identified with a site identification code and sample collection data.

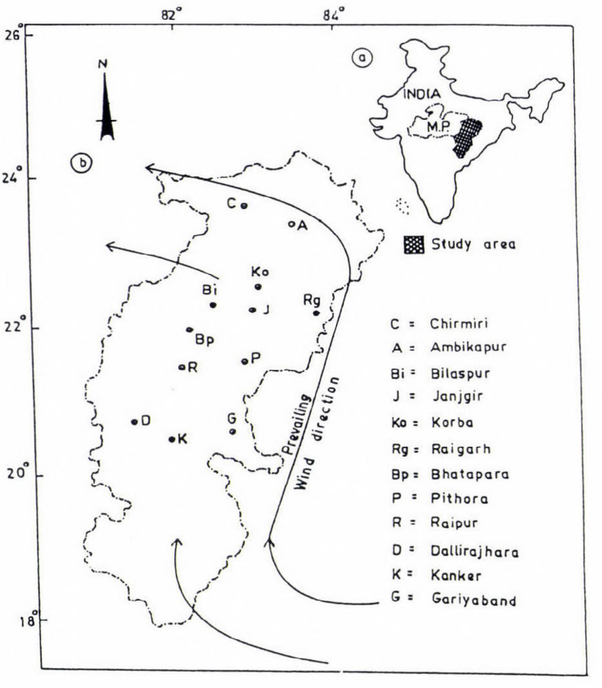

Fig. 1. Geographical map of (*a*) India, (*b*) central India.

2.3 Shipment and storage of samples

Sample bottles were packed with foam in wooden-board boxes and shipped to the laboratory by bus or train. The time between field sampling and receipt of samples was typically 3 to 4 days whereas between receipt of samples and subsequent chemical analysis ranged between 1 to 30 days. The samples were stored at 4 °C in the refrigerator and no preservatives were added to the samples at any time during shipping or storage. Interaction between sample solutions and storage bottle, effect of ambient gases and potential losses by evaporation were not studied.

2.4 Measurements and chemical analysis

All plastic equipments used in experiments were acid washed prior to use. They were soaked overnight in 1 N HNO_3 which was rised 3 times with distilled water. A Systronic μ-pH meter (type–361) and a Systronic conductivity-meter (type–304) were used to measure pH and conductivity values. A GBC flame AAS (type–932AA) equipped with air-acetylene and nitrous oxide-acetylene flames was used for monitoring of elements, i.e., Na, K, Ca, Mg. A Tecator flow injection analyzer (type–5012) equipped with ALPKEM UV–VIS spectrophotometer detector (type–510) with a 5.5 mm flow cell, and two peristaltic pumps of constant speed (48 cycle min^{-1}) were used for monitoring of ions F^-, Cl^-, I^-, NO_2^-, NO_3^-, and NH_4^+. A Systronic turbidimeter (type–131) was used for monitoring of SO_4^{2-}.

Table 1. Study site location and description

Site No.	Location	Type	Description
1.	Raipur	UA	Steel and cement industries and urban pollution source area
2.	Korba	UA	Thermal power plants, aluminum industry, coal mines and urban pollution
3.	Bilaspur	UA	Cement industries and urban pollution source
4.	Kanker	RUA	Forest area with deposition of iron ore
5.	Janjgir	SUA	Cement industry and agricultural land
6.	Raigarh	SUA	Ferro-alloy industry, agricultural land and forest area
7.	Chirmiri	SUA	Coal mines and urban pollution
8.	Bhatapara	SUA	Cement industry and agricultural land
9.	Pithora	RUA	Agricultural land
10.	Gariyaband	REA	Forest area with deposition of pyrites
11.	Dallirajhara	SUA	Iron ore processing industry and forest area
12.	Ambikapur	RE - SUA	Remote and forest area with deposition of coal

UA = urban area; RUA = rural area; SUA = suburban area; REA = remote area;

RE - SUA = remote suburban area

The pH of the solution was measured in the laboratory using μ-pH meter equipped with glass and calomel electrode calibrating with buffer 4 and 7.25 ml. The solution was taken into a plastic beaker, and the meter was allowed to equilibrants for 5 minutes before the pH value was recorded. Electrical conductivity of the solution was also recorded by using conductivity meter. The used 25 ml solution was discarded. The ions were analyzed with techniques AAS, FIA, turbidimetry. Their optimal analytical parameters are summarized in *Table 2*. For the analysis of the metals with AAS, a 25 ml aliquot of filtered rain water sample was treated with 0.2 ml concentrated HNO_3 (ultrapure, E. Merck) in a polyethylene tube covered with lid. A reagent blank was prepared using de-ionized distilled water in a similar way. Cations Na^+, K^+, Ca^{2+}, Mg^{2+} were analyzed with the flame-AAS as described in the literature. Filtered rain water samples were used for the analysis of the anions NO_2^-, NO_3^-, Cl^-, F^-, I^-, NH_4^+ with the flow injection analysis (FIA) technique by measuring the colour change as described in the literatures (*Tecator*, 1992b; *Tecator*, 1991; *Chandrawanshi et al.*, 1996; *Chandrawanshi* and *Patel*, 1998; *Tecator*, 1992a). Sulphate ions were analyzed turbidimetrically using $BaCl_2$ as reagent (*Vogel*, 1978).

3. Results and discussion

3.1 Geography and geology

The study area (central India) is situated between 17° and 24°N latitudes, and 80°17' and 84°11'E longitudes at altitude of $\geq$300 m a.s.l. Tropics of cancer passes through this region and the total area is about 1.4×10^5 km^2 (4.1% of the area of India). It is based on igneous and metamorphic rocks with heavy deposition of minerals like iron/copper/manganese pyrites, bauxite, dolomite, coal, etc. The soil is red-yellow or red in colour and it is low in silica with high levels of iron and aluminium. Both tropical moist and dry deciduous forests are present in this region. The area of the forest is about 6.0×10^4 km^2 and the tree, *Shore Robust* is the predominant species in this area. Other important trees found are *Terminals arjuna, Terminals belerica, Terminals chabula, Amblica officinales, Dalbergia sissoo, Tectona grandis, Acaccia catechu, Butea monosperma, Madhulica officinales,* etc. Rice is the main food crop of this region includes 60% of the total cropped area. The total of 1.2×10^6 tons yr^{-1} of rice grain is produced on this part of the country.

This part of the country has the highest summer temperature and the lowest summer atmospheric pressure profiles, probably due to emission of huge amount of green house gases by forest vegetation, rice field, combustion of fossil fuels, biomass burning, etc. Temperature rises steadily from January to May which is usually the hottest month of the year. The mean maximum

Table 2. Details of techniques used for rain water analysis

Species	Techniques	Wave length (nm)	Detection limit (mg ℓ^{-1})	Optimum con-centration range (mg ℓ^{-1})
Na^+	AAS, air - C_2H_2 flame	589.0	0.004	0.18 - 0.7
K^+	AAS, air - C_2H_2 flame	766.5	0.008	0.40 - 1.5
Ca^{2+}	AAS, N_2O - C_2H_2 flame	422.7	0.02	1.00 - 4.0
Mg^{2+}	AAS, N_2O - C_2H_2 flame	285.2	0.003	0.10 - 0.4
NH_4^+	Colorimetric FIA gas-diffusion technique using dye as colour developing agent	590.0	-	0.10 - 1.0
SO_4^{2-}	Turbidimetric method using reaction SO_4^{2-} + $BaCl_2$	420.0	-	-
NO_2^- + NO_3^-	Colorimetric FIA technique using on line Cd-reductor and sulphanili-amide + N-(-1-Naphty1)-ethylenediamine dihydrochloride as colour developing agent	540.0	-	0.20 - 100
Cl^-	Colorimetric FIA technique based on destruction of the colour of $Hg(SCN)_2$ + Cl^- + Fe^{3+}	470.0	-	1.0 - 150
F^-	Colorimetric FIA technique based on destruction of the colour of Zr-SPADNS complex with F^-	580.0	0.01	0.05 - 0.7
I^-	Colorimetric FIA technique based on catalytic destruction of the colour of Fe(III)-SCN^--CP^- complex with NO_2^- and NO_3^-	470.0	0.0001	0.005 - 0.1

temperature in May 1995 was ranged from 26.5 to 46.5°C. The period of May and the early June prior to the arrival of south-western monsoon is rather hot. Towards the close of the monsoon season in September, the day temperature increases slightly, and the rise is maintained in October after the withdrawal of monsoon. December is usually the coolest with the mean daily temperature in the range of 7.0°C to 27°C. A decreasing trend of the atmospheric temperature at a rate of 1°C to 2°C from, 1995 to 1997 was observed. The mean monthly (from January to December) relative humidity (morning & evening) and evaporation in site Raipur during hydrological years from 1995 to 1997 are 88 & 41% and 4.1 mm, 75 & 33% and 5.2 mm, 60 &20% and 7.0 mm, 55 & 25% and 9.9 mm, 40 & 15% and 12.6 mm, 72 & 48% and 11.1 mm, 85 & 71% and 5.3 mm, 91 & 78% and 4.2 mm, 92 & 77% and 3.9 mm, 88 & 60% and 3.5 mm, 89 & 40% and 3.0 mm, 82 & 25% and 2.5 mm, respectively. The highest relative humidity was recorded during the south-west monsoon season. After the monsoon season, humidity decreases during the winter season and the air is fairly dry with lowest evaporation rate. The dry part of the year is the summer season when the evening relative humidity is rather low (12%) in May. The rate of evaporation increases steadily from January to May and decreases steadily from June to December. The evaporation rate is lowest in December whereas highest in May.

3.2 Air quality

Air pollution is considered to be any atmospheric substances that are foreign to the "natural" atmosphere. Before the independence in 1947 the whole central region of the country was covered with dense tropical rain forest. After 1960 a rapid industrialization and urbanization of this region started. Nowadays the most of the metal and non-metal industries and coal based thermal power plants of the country are operating in this region. An enormous increase in population, industries, thermal power plants and agriculture production intensified the environmental problems, which already are plaguing the area. The total population of this area according to 1991 census was 18 millions with growth rate of $\pm$ 2.5% and at present the population expected is about 21 millions. The average population density is 130 persons km^{-2}. The number of both two and four wheeler vehicles are about 0.5 millions. There are 200 large scale and 2000 small scale (i.e., agro, building, chemical, engineering, forest, leather, paper, polymer, textile, etc. based) industries and thermal power plants of high capacity operating in this region. The amount of fossil fuel and coal consumed by various sources in this region are estimated to be 8 million tons yr^{-1}. In addition, every year, a huge amount of minerals like copper, iron and manganese pyrites (13 million tons yr^{-1}), aluminium (0.21 million tons yr^{-1}), dolomite (0.75 million tons yr^{-1}) and coal (31 million tons yr^{-1}) are mined out from various open and under ground mines. The level of NO_x, SO_x and SPM in the Raipur city during the years 1995 to 1997 were determined by the pollution department and their mean concentration ranged between 13–14, 8-25, and 128–381 $\mu g\ m^{-3}$ with increasing rate of 15, 17 and 10% in the ambient air, respectively. The highest reported level of NO_x, SO_x and SPM in the ambient air of the Korba city during January 1997 was 55, 73 and 500 $\mu g\ m^{-3}$, respectively. The relatively higher level of NO_x, SO_x and SPM in this region of the country is probably due to rapid industrialization, transportation of distant pollutants from other parts of the country and the globe, etc.

3.3 Rainfall

The central part of the country receives the highest rainfall excluding Himalayan and eastern regions of the country. Rainfall with a maximum of 1650 mm was recorded in this region due to raining of both south-west (SW) and south-east (SE) monsoons. The SW summer monsoon comes with high wind speed probably due to high temperature above 40°C and causes a heavy rainfall. The average annual rainfall at 12 sites of central India during the hydrological year 1995, is 1300 mm varied from 1176 mm at Bilaspur in the south-east to 1376 mm at Gariyaband in the north-east. The amount of rainfall is not the same at different sites and the excess rain causes floods. The period between June and October receives about 88.5% of the annual rainfall. Decreasing of the rainfall starts in September and shrinks to less than 50 mm. In October, SW monsoon returns and substitutes by SE monsoon. The period between November and May receives only about 110 mm and it is 8.5% of the total annual rainfall. The rainfall during the hydrological years 1995 to 1997 at site Raipur is 1283, 1123 and 1214 mm, respectively. A decreasing trend in the rainfall height with lower frequency and rainfall duration from 1995 to 1997 was observed.

3.4 Mean concentration and quality assurance of data

The details of rainfall chemistry at twelve sites of central India occurred in the hydrological year 1995 are summarized in Table 3. The overall mean rainfall amount, duration and events or storms were 1300 mm, 224 hr and 58, respectively.

The sampling precision was checked by collecting 2×10 rain water samples from two sites of Raipur city: Daganiya (R_1) and Tikarapara (R_2) during 1995 by analyzing their physical parameters and ionic concentrations. Their analytical precision was checked by using Eq. (1).

$$S_i = \left(\frac{\sum d_i^2}{2N_i} \right)^{\frac{1}{2}}, \tag{1}$$

where d_i = difference between two analyses of the same sample, N_i = number of sample pairs used, i = 1,2. The value of S_i for rainfall amount, pH, conductivity, H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, F^- and I^- for the 2×10 rain water samples collected at two sites of Raipur city in 1995 were 1.3, 0.4, 9.6, 2.0, 5.4, 1.8, 8.1, 20.7, 10.7, 19.8 and 3.5, respectively. Good sampling precisions for the most parameters were obtained except for the F^- and NO_3^-, probably because of the variation in rate of evaporation and reaction with the other materials of F^-, and biodegradation of NO_3^-.

The accuracy of the chemical analysis in the proposed results was checked by ion and conductivity balance of the rain water samples. The rain water samples with pH ≤ 5.8 and the concentration of HCO_3^- were considered to be negligible in the tropics, whereas for the samples with pH > 5.8 the bicarbonate concentration was not considered. A linear correlation between measured anion and cation equivalent concentrations was determined and found to be significantly excellent: r = 0.996 for n = 373 (see *Table 3*). The ratio of the sum of anionic concentrations $\Sigma(\text{anions}) = \{[F^-] + [Cl^-] + [I^-] + [NO_3^-] + 2[SO_4]^{2-}\}$ to sum of cationic concentrations $\Sigma(\text{cations}) = \{[H^+] + [NH_4^+] + [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}]\}$ in 12 sites during the hydrological year 1995 was calculated and ranged between 0.97 to 1.00. The agreement between measured and calculated conductivity was determined. The calculated conductivity of the rain water samples was evaluated by using Eq. (2), where the concentrations are expressed in n mol ℓ^{-1}, the conductivity in μS cm^{-1}.

$$\text{Conductivity}_{\text{calc.}} = 10^{(3-\text{pH})} \times 350 + 2(SO_4^{2-})79.6 + (NO_3^-)70.6 + (Cl^-)75.5 + (NH_4^+)74.5 + (Na^+)50.9 + (K^+)74.5 + 2(Ca^{2+})60.0 + 2(Mg^{2+})53.1, \quad (2)$$

where concentrations are expressed in m mol ℓ^{-1}, conductivity is expressed in μS cm^{-1} units. The correlation coefficient (r) between measured and calculated conductivity was found to be +0.80 (n = 5).

3.5 Rain water acidity

Table 4 shows the pH distribution (from 4.9 to 6.7) of samples over the period January to November 1995. About 32% of rain water samples appeared with pH ≤ 5.8 and only 8% of samples appeared with < 5.0 which could be considered as the lower pH of natural rain water (*Charlson* and *Rodhe*, 1982). Acid pH values revealed the presence of strong acid in rain water, while neutral and alkaline pH values occur because of the neutralized acids by soil dust and sea salt. High concentration of soil dust in small samples of rain water are responsible for the neutral pH values.

Table 3. The volume weighed mean physical and chemical parameters of rain water in central India in the hydrological year 1995

Sampling site	No. of site	Total rainfall events	Total rainfall height (mm)	Total rainfall duration (hour)	No. of sample analysis	Ave. pH	Ave. cond. ($\mu S\ cm^{-1}$)	Volume weighed mean contcentration ($\mu eq\ \ell^{-1}$)											$\frac{\Sigma[\text{anions}]}{\Sigma[\text{cations}]}$	$\frac{\Sigma[SO_4^{2-}]}{\Sigma[NO_3^-]}$	$\frac{\Sigma[H^+]\text{obs.}}{\Sigma[H^+]\text{cal.}}$
								H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^-	SO_4^{2-}	NO_3^-	Cl^-	F^-	I^-			
Raipur	3	57	1283	225	115	5.8	65	2.0	25.6	4.4	136	45.5	9.5	166	21.7	32.7	2.7	0.02	0.97	7.6	0.8
Korba	2	55	1198	230	31	4.9	42	16.8	20.7	3.7	183	42.8	15.3	213	25.1	31.8	11.6	0.04	0.99	8.5	0.7
Bilaspur	2	55	1176	227	60	5.9	65	1.6	50.1	6.1	112	35.4	12.3	138	17.5	59.0	2.8	0.02	1.00	7.9	0.8
Kanker	1	70	1518	221	25	6.7	97	0.3	54.7	6.8	140	33.8	2.8	149	21.5	62.0	7.5	0.04	1.00	6.9	0.7
Janjgir	1	59	1320	226	18	6.4	75	1.5	33.3	4.5	153	78.4	1.3	170	60.0	35.5	5.9	0.02	0.99	2.8	0.3
Raigarh	1	62	1376	231	20	5.8	46	2.7	39.7	5.8	101	32.2	9.3	123	15.5	49.9	2.5	0.04	1.00	7.9	0.6
Chirmiri	1	51	1297	223	15	5.7	33	5.7	47.8	5.9	117	25.3	18.9	153	12.7	53.0	2.3	0.02	1.00	12.0	0.4
Bhatapara	1	53	1252	219	13	6.7	84	0.9	60.2	8.4	147	34.8	12.1	170	16.6	73.0	3.7	0.02	1.00	10.2	0.2
Pithora	1	54	1191	217	12	6.6	90	1.2	46.2	7.0	114	63.0	8.6	163	19.6	52.0	3.2	0.02	0.98	8.3	0.3
Gariyaband	1	65	1376	224	30	5.8	66	3.5	30.6	2.3	121	44.9	21.6	156	21.9	34.2	3.9	0.02	0.97	7.1	0.5
Dallirajhara	1	58	1312	227	20	5.6	61	5.0	50.4	6.8	132	33.0	2.9	146	20.2	61.0	3.1	0.03	0.99	7.2	0.5
Ambikapur	1	60	1270	219	14	5.8	63	2.2	30.0	2.6	131	42.6	2.3	144	23.5	35.1	3.6	0.03	0.97	6.1	0.7
Overall mean con-centration			1297	224		5.9	74	3.6	40.7	5.3	132	42.7	9.7	158	22.9	48.4	4.4	0.03			

obs. = observed; cal. = calculated

Table 4. pH distribution of event samples and volume weighed percentage acids in rain water at 12 sites of central India during the hydrological year 1995

Site No.	Sampling site	pH of rain water events (%)			Acid (%)		
		pH > 5.65	pH < 5.65	pH < 5.0	H_2SO_4	HNO_3	HCl + HF
1.	Raipur	75.5	24.5	–	74.4	9.7	15.8
2.	Korba	–	22.3	77.7	75.6	8.9	15.4
3.	Bilaspur	69.1	30.9	–	63.4	8.0	28.5
4.	Kanker	95.6	4.4	–	61.9	8.9	29.1
5.	Janjgir	88.3	11.7	–	62.7	22.1	15.2
6.	Raigarh	66.7	27.7	5.5	64.5	8.1	27.4
7.	Chirmiri	23.1	61.5	15.4	69.2	5.7	25.1
8.	Bhatapara	91.6	8.4	–	64.3	6.3	29.4
9.	Pithora	90.0	10.0	–	68.5	8.2	23.2
10.	Gariyaband	55.2	44.8	–	72.3	10.1	10.1
11.	Dallirajhara	68.4	26.3	5.3	63.4	8.7	27.8
12.	Ambikapur	66.6	66.6	–	69.8	11.4	18.7
Overall volume weighed mean % concentration of acid					67.5	9.8	22.6

Detailed statistics of the rain water acidity during the hydrological year 1995 is summarized in *Tables 4–5*. It is obvious that "acid rain" commonly occurred in central India specially in the monsoon periods. Korba was the site with the lowest volume weighed mean pH value (4.9) of the event samples and the lowest pH value (4.1) of the event samples. Other seven locations: Raipur, Bilaspur, Raigarh, Chirmiri, Gariyaband, Dallirajhara, Ambikapur were the sites where the overall volume weighed mean pH values of rain water was 5.8. Thus, these eight sites commonly faced acid rain problems with pH values well below the neutral pH, 5.8, specially in the monsoon season as shown Table 4. In the sites: Janjgir, Pithora, Kanker and Bhatapara, relatively higher volume weighed mean pH values were recorded (6.4, 6.6, 6.7 and 6.7, respectively). The high pH values were probably due to neutralization of acids with alkaline particulates emitted from the cement factories and soil dust.

The effect of meteorological parameters, i.e., rainfall amount, frequency, rainfall duration on the pH value of rain water was examined. Results are shown on *Fig. 2*. The pH values decrease as the number of frequency of rainfall amount and the duration of rainfall increase, probably due to blown of lower amount of soil dust. Similarly, the pH values of rain water decrease as the relative humidity increase, probably due to relatively more absorption and hydrolysis of the acidic oxides, i.e., NO_2 and SO_3 from distant area. However, no exact trend was observed with variation in atmospheric temperature and wind speed.

The monthly and annual variations in pH values of rain water samples at site Raipur were studied. The pH values of the rain water decreased from May to August probably due to blown of lower amount of soil dust and higher humidity. From August the pH values gradually increased probably due to lower rainfall amounts. The pH of the rain water samples decreased in hydrological years 1995–1997 during the monsoon period probably duo to either increase in emission rate of acidic gases or decrease in soil buffering capacity or both.

3.6 Ionic species relationship

The pair correlation coefficient dataset of 11 ions in the rain water of 1995 is computed for entire central India. The highest correlations appear for the ion pairs: Na^+ and Cl^- (r = 0.97), K^+ and Cl^- (r = 0.91), Na^+ and K^+ (r = 0.87), Ca^{2+} and SO_4^{2-} (r = 0.8), Ca^{2+} and F^- (r = 0.84), Mg^{2+} and NO_3^- (r = 0.8), F^- and SO_4^{2-} (r = 0.74), Ca^{2+} and F^- (r = 0.72), H^+ and SO_4^{2-} (r = 0.67), H^+ and F^- (r = 0.66), H^+ and Ca^{2+} (r = 0.58), NH_4^+ and NO_3^- (r = 0.57), F^- and I^- (r = 0.55). Most of these well correlating pairs have either common sources, (they occur in precipitation as a result of a common source) or they exist in the form of compounds like NaCl, KCl, $CaSO_4$, CaF_2, $Mg(NO_3)_2$, NH_4NO_3, etc. The ion-pair Na^+ and K^+ has good correlation due to common occurrence in

Table 5. Statistical descriptions of the chemical composition of precipitation at each sampling station

Site No.	Sampling site	Statistical parameter	pH	Cond. ($\mu S\ cm^{-1}$)	Ions ($\mu eq\ \ell^{-1}$)										
					H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	F^-	I–
1.	Raipur	V. M. Mean	5.8	65	2.0	25.6	4.4	135.9	45.5	9.5	165.8	21.7	32.7	2.7	0.02
		A. Mean	–	–	4.0	30.8	9.5	145.8	52.6	11.4	175.9	26.9	38.6	5.5	0.08
		Median	6.1	39	0.7	29.7	3.1	144.0	18.3	6.1	18.7	18.5	42.5	2.1	0.40
		Minimum	5.0	13	0.01	4.3	0.5	75.0	12.1	0.0	81.0	1.7	1.8	1.0	0.02
		Maximum	7.9	476	7.1	265.0	71.8	800.0	136.6	272.2	745.8	224.2	352.1	54.3	2.15
		Sd (±)			1.9	46.8	11.9	149.7	25.7	48.0	118.9	39.2	71.6	8.5	0.02
2.	Korba	V. M. Mean	4.9	42	16.8	20.7	3.7	182.7	42.8	15.3	213.1	25.1	31.8	11.6	0.04
		A. Mean	–	–	19.7	26.1	6.9	197.6	49.3	19.8	226.2	35.4	38.5	19.2	0.06
		Median	4.9	41	18.5	19.2	2.6	73.7	19 9	14.7	81.2	23.9	26.5	12.4	0.60
		Minimum	4.4	13	0.5	6.5	1.3	25.0	7.2	0.8	42.3	10.1	11.8	4.2	0.08
		Maximum	5.6	80	40.6	89.4	23.1	290.0	64.0	158.9	278.2	53.0	128.3	42.1	5.40
		Sd (±)			11.7	26.1	5.3	69.7	18.1	36.6	75.9	12.0	34.7	7.6	0.03
3.	Bilaspur	V. M. Mean	5.9	65	1.6	50.1	6.1	111.8	35.4	12.3	138.4	17.5	59.5	2.8	0.02
		A. Mean	–	–	3.8	58.2	12.3	131.7	42.8	21.4	167.1	29.2	68.4	5.4	0.05
		Median	6.0	31	0.8	21.7	6.9	75.0	66.7	1.6	287.4	22.5	28.2	1.8	0.30
		Minimum	5.4	7	0.1	0.0	0.0	0.0	7.4	0.0	15.0	0.6	4.2	0.5	0.03
		Maximum	7.0	490	4.4	180.4	669.2	130.0	135.8	67.3	1120.8	214.5	701.4	62.1	1.70
		Sd (±)			1.2	41.7	17.9	159.3	29.3	21.6	154.1	51.1	108.9	9.5	0.02
4.	Kanker	V. M. Mean	6.7	97	0.3	54.7	6.8	140.5	33.8	2.8	148.8	25.5	62.4	7.5	0.04
		A. Mean	-	-	1.1	59.5	10.8	155.2	41.5	5.4	159.7	33.8	68.2	11.8	0.07
		Median	6.7	59	0.2	25.2	8.5	161.0	63.4	1.7	304.2	32.2	29.6	3.7	0.50
		Minimum	5.8	8	0.03	0.0	0.7	0.0	7.4	0.0	133.4	0.8	8.4	1.1	0.14
		Maximum	7.5	380	0.7	652.2	127.5	925.2	127.6	15.0	650.0	417.7	971.8	33.7	2.90
		Sd (±)			0.3	276.8	78.8	270.4	42.6	6.5	160.3	120.8	262.4	9.3	0.02

Continued Table 5

Site No.	Sampling site	Statistical parameter	pH	Cond. (μS cm^{-1})	Ions (μeq ℓ^{-1})										
					H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	F^-	I^-
5.	Janjgir	V. M. Mean	6.4	75	1.5	33.3	4.5	152.8	78.4	1.3	170.3	60.0	35.5	5.9	0.02
		A. Mean	-	-	2.6	38.4	7.8	159.1	84.5	5.1	179.5	68.5	42.7	8.1	0.07
		Median	6.5	59	0.3	25.2	33.3	135.0	51.8	1.7	245.8	39.3	34.1	3.7	0.40
		Minimum	6.2	17	0.1	0.0	0.0	30.0	9.0	0.0	175.0	8.2	9.8	2.1	0.01
		Maximum	7.2	210	5.5	221.7	405.1	1125.0	224.6	20.5	408.4	227.4	112.8	18.9	1.60
		Sd (±)			1.5	54.9	82.6	321.9	55.2	5.1	61.5	57.5	24.9	5.2	0.01
6.	Raigarh	V. M. Mean	5.8	46	2.7	39.7	5.8	101.5	32.2	9.3	123.2	15.5	49.9	2.5	0.04
		A. Mean	-	-	5.8	44.8	12.0	110.1	36.8	12.5	134.5	26.2	55.1	6.2	0.08
		Median	6.1	40	0.7	9.8	5.1	105.0	73.6	1.7	260.5	14.1	13.4	2.1	0.50
		Minimum	5.0	9	0.1	0.0	0.0	0.0	7.4	0.0	62.4	0.6	7.0	0.5	0.10
		Maximum	6.9	128	9.7	47.8	38.5	385.0	132.4	60.5	825.0	237.1	59.7	17.9	7.50
		Sd (±)			2.6	14.8	11.1	123.1	37.0	15.6	173.7	69.7	16.3	4.2	0.03
7.	Chirmiri	V. M. Mean	6.6	90	1.2	46.2	7.0	114.2	63.6	8.6	163.0	19.6	52.0	3.2	0.02
		A. Mean	-	-	3.4	52.4	12.8	126.9	71.2	11.8	185.2	25.8	60.3	7.1	0.06
		Median	6.8	58	0.2	30.9	12.8	110.0	79.7	1.7	229.1	19.4	35.0	2.1	0.30
		Minimum	5.5	6.0	0.02	3.5	5.1	5.0	14.2	0.0	150.0	0.8	12.7	1.1	0.02
		Maximum	7.8	144	3.3	320.8	58.9	2063.4	773.6	27.7	1120.8	83.4	1135.2	12.6	1.30
		Sd (±)			4.5	31.1	4.1	28.0	10.9	16.2	32.9	8.6	80.9	1.3	0.02
8.	Bhatapara	V. M. Mean	6.7	84	0.9	60.2	8.4	147.2	34.8	12.1	169.6	16.6	73.7	3.7	0.02
		A. Mean	-	-	2.8	67.5	13.5	157.5	41.2	15.4	175.1	19.8	77.2	5.5	0.06
		Median	6.9	90	0.1	71.7	5.2	36.2	81.5	1.7	272.2	33.0	98.7	4.2	0.40
		Minimum	5.5	17	0.03	0.0	1.0	10.0	22.2	0.0	170.8	2.7	7.0	1.6	0.02
		Maximum	7.5	106	3.1	369.6	112.8	330.0	138.2	577.7	637.4	674.2	300.0	19.5	2.10
		Sd (±)			0.8	130.9	199.6	245.6	34.2	165.5	144.5	104.5	107.5	5.7	0.03

Continued Table 5

Site No.	Sampling site	Statistical parameter	pH	Cond. (μS cm^{-1})	Ions (μeq ℓ^{-1})										
					H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	F^-	I^-
9.	Pithora	V. M. Mean	6.6	90	1.2	46.2	7.0	114.2	63.6	8.6	163.0	19.6	52.0	3.2	0.02
		A. Mean	-	-	2.5	52.2	13.0	122.2	68.7	12.1	175.2	26.8	61.0	7.1	0.08
		Median	6.8	58	0.2	30.9	12.8	110.0	79.7	1.7	229.1	19.4	35.0	2.1	0.30
		Minimum	5.5	6	0.02	3.5	5.1	5.0	14.2	0.0	150.0	0.8	12.7	1.1	0.02
		Maximum	7.8	144	3.3	320.8	58.9	2063.4	773.6	27.7	1120.8	83.4	1135.2	12.6	1.30
		Sd (±)			1.0	124.2	20.5	631.3	226.8	3.8	289.6	22.5	349.2	18.8	0.03
10.	Gariyaband	V. M. Mean	5.8	66	3.5	30.6	2.3	120.6	44.9	20.6	156.5	21.9	34.2	3.9	0.02
		A. Mean	-	-	5.8	36.8	4.5	131.7	51.0	27.1	167.9	29.1	43.2	7.9	0.06
		Median	6.1	32	0.7	43.5	1.8	136.0	36.2	20.0	173.4	20.9	48.7	2.1	0.20
		Minimum	5.1	4	0.02	10.0	0.4	0.0	12.2	0.0	92.4	0.9	11.3	0.6	0.01
		Maximum	7.7	583	7.4	161.7	16.7	542.4	138.6	213.9	786.4	202.9	202.2	23.7	2.20
		Sd (±)			2.3	39.0	4.2	98.7	35.1	57.8	126.8	42.9	49.1	4.6	0.02
11.	Dallirajhara	V. M. Mean	5.6	161	5.0	50.4	6.8	132.4	33.0	2.9	146.0	20.2	60.9	3.1	0.03
		A. Mean	-	-	7.5	59.5	12.9	143.6	39.0	6.1	162.0	30.3	68.0	7.8	0.06
		Median	5.9	72	1.1	18.3	7.7	254.4	76.6	0.0	300.0	14.0	547.0	2.6	0.30
		Minimum	5.0	8	0.3	0.0	1.3	0.0	26.4	0.0	116.6	0.6	8.4	0.5	0.02
		Maximum	6.5	735	9.7	303.9	230.7	1175.0	888.8	66.1	787.4	529.1	2642.2	17.0	2.40
		Sd (±)			2.9	89.5	51.6	344.5	295.5	15.2	201.5	123.4	592.7	14.1	2.80
12.	Ambikapur	V. M. Mean	-	63	2.2	30.0	2.6	130.8	42.6	2.3	143.9	23.5	35.1	3.6	0.03
		A. Mean	55.8	-	5.5	38.0	6.8	135.8	50.5	5.4	156.1	34.6	43.2	7.8	0.07
		Median	0.9	44	1.0	43.9	21.8	145.0	63.8	0.0	224.9	48.0	33.9	2.1	0.40
		Minimum	5.2	12	0.2	3.5	4.1	15.0	27.2	0.0	62.4	2.7	5.6	1.1	0.06
		Maximum	6.5	166	5.6	200.0	195.4	1125.0	157.8	27.8	454.2	109.2	126.8	12.1	2.30
		Sd (±)			2.3	57.9	52.2	211.1	36.3	7.9	163.8	35.0	35.1	3.5	0.02

V. M. Mean = Volume Weighed Mean; A. Mean = Arithmetic Mean the sea water and in soil dust, while other pairs, e.g., H^+ and SO_4^{2-}/F^-, F^- and SO_4^{2-}, Ca^{2+} and F^-/SO_4^{2-} have good correlationship probably due to their similar way of emission from burning of coal, smelting of pyrite minerals and dolomite, etc. The relatively high correlation of Mg^{2+} and NO_3^-, Ca^{2+} and SO_4^{2-}, Ca^{2+} and F^-, H^+ and Ca^{2+}, NH_4^+ and NO_3^- are probably due to either their occurrence in the rain water or reaction of acids with the alkaline metals and NH_3. The relatively high correlation of Ca^{2+} and F^- and F^- and I^- show that they apparently steam from a common source, i.e., burning of coal, smelting of pyrite minerals and dolomite, etc.

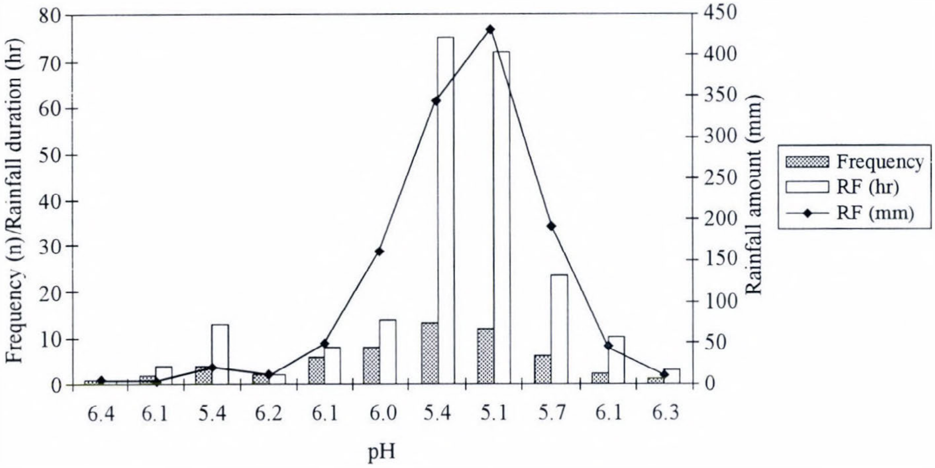

Fig. 2. The effect of frequency (n), rainfall duration (hr) and rainfall amount (mm) on monthly pH of rain water at site Raipur city in hydrological year 1995.

3.7 General relationship

The statistical analytical data base of 11 ions in the total of 373 rain water samples, collected during hydrological year 1995, has been established. Arithmetic and volume weighed means, range and median values have been calculated for each species of each site and for entire data set of 12 sites during hydrological year 1995 as shown in Tables 3 and 5. The average relieve magnitude of ionic species concentrations shows the following decreasing order: $SO_4^{2-} > Ca^{2+} > Cl^- > Mg^{2+} > Na^+ > NO_3^- > NH_4^+ > K^+ > F^- > H^+ > I^-$. This relative abundance relationship holds for both arithmetic and volume weighed mean concentration.

Fig. 3 shows a typical plot of SO_4^{2-} concentration versus amount of precipitation. It is observed that the highest SO_4^{2-} concentration generally occurred in samples of the smallest amount of precipitation, whereas lower concentration occurred with higher amount of precipitation. Generally, similar trends have been observed for other ions, Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^-, F^-, I^-. However, a reverse trend has been noticed for concentration of H^+ and NH_4^+.

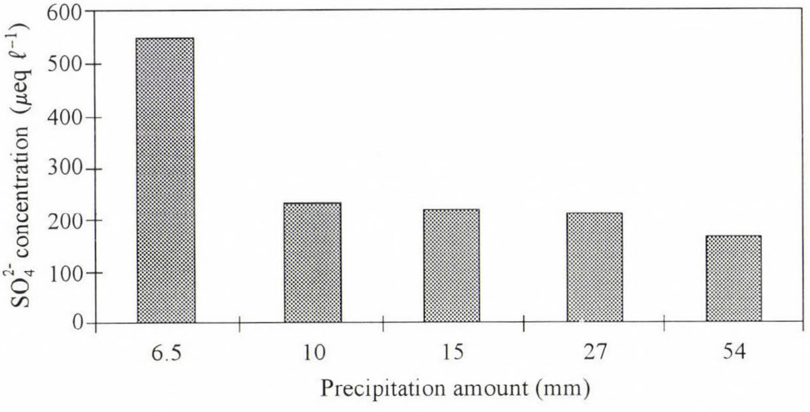

Fig. 3. Variation of SO_4^{2-} concentration with respect to the amount of precipitation in July 1995 at site Raipur.

3.8 Seasonal, temporal and spatial variations

Monthly and annual volume weighed mean concentration of H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^-, F^-, I^- and values of pH and conductivity were calculated over the entire operating interval of 1995–1997, see *Figs. 4* and *5*. The concentration of Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, Cl^- and F^- was in top during the period from March to June probably due to dusty air. In the rainy season, from July to October, the concentration of seven ions, Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^- and F^- in rain water was decreased due to higher amount of precipitation or blown of lower amount of dust or both. However, the concentration of H^+, NH_4^+, I^- and SO_4^{2-} have different trends. The concentration of free acid, H^+ was the highest during August probably due to blown of lower amount of alkaline soil dust. Similarly, the concentration of NH_4^+ was the highest in the rainy season from July to August probably due to more rapid biodegradation of the forest biomass and municipal waste, wide cropping of rice plants, etc. The concentration of SO_4^{2-} was the highest from April to August probably due to high amounts of dust in the dry season (April to June) and formation of more sulphuric acid in the rainy season (July to

August). I^- ion has no exact variation trend. The annual variation in concentration of H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, Cl^-, F^-, I^- in rain water samples of the period 1995–1997 was found to be increasing probably due to increased emission rates of the ions and other factors, see Fig. 5.

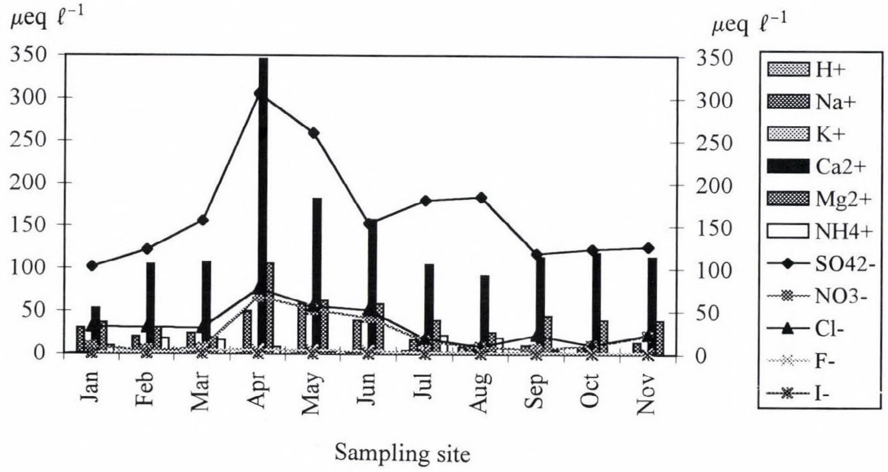

Fig. 4. Seasonal variation of concentration of major ions at Raipur during hydrological year 1995.

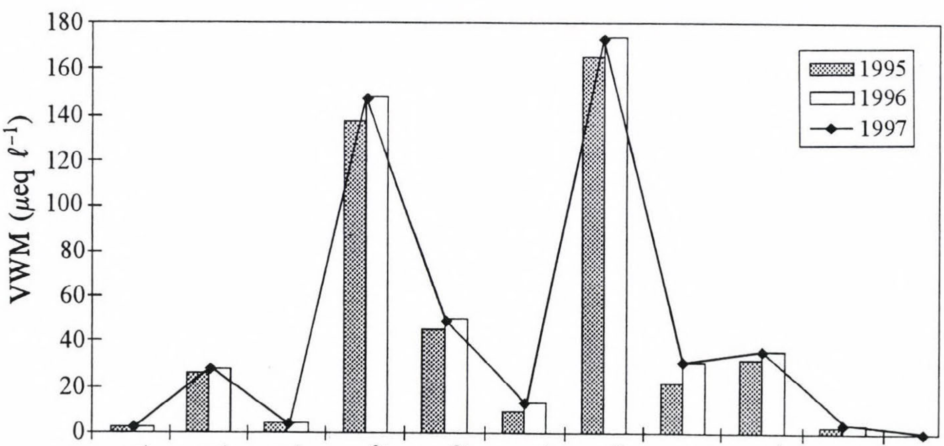

Fig. 5. Temporal variation of volume weighed mean (VWM) concentration at Raipur during hydrological year 1995–1997.

Spatial variations of the volume weighed annual mean concentrations of H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, Cl^-, F^- and I^- in rain water of central India were examined in detail. Among them, the concentration of H^+, NH_4^+, F^- shows high spatial variations. The rain water acidity (concentration of free H^+) was the highest at site Korba, whereas the lowest at site Kanker. The concentration of SO_4^{2-} was also the highest at Korba but almost the same in the other eleven sites. Ammonium concentration was the higher in coal and pyrite mineral sites, Korba, Chirmiri, Gariyaband. The concentration of free H^+, NH_4^+ and SO_4^{2-} have positive correlation. NO_3^- and Mg^{2+} ions had the highest concentration at rice growing site Janjgir and almost the same in the other sites. The concentration of Cl^- was higher in sub-urban, rice growing and forest areas than in urban and industrial areas, i.e., Raipur, Korba. Fluoride was the highest in sites Korba, Janjgir and Kanker due to operation of an aluminum plant (capacity about 0.2 million tons yr^{-1}) or cement plant (capacity about 0.4 million tons yr^{-1}) and contamination of soil with fluorite minerals, respectively. Iodide was present at higher levels in the remote and forest sites probably due to atmospheric temperature and more evaporation from the forest sites. The concentration variation of alkali and alkaline metals was higher in sub-urban and urban sites.

3.9 Annual deposition

The overall mean fluxes of H^+, I^-, F^-, NH_4^+, K^+, Mg^{2+}, Na^+, NO_3^-, Cl^-, Ca^{2+} and SO_4^{2-} were 5, 5, 146, 221, 267, 657, 1203, 1830, 2550, 3399 and 9781 kg km^{-2} yr^{-1} in 1995 with median and standard deviation of 2.7, 4.0, 111, 219, 290, 603, 1266, 1680, 2437, 3357, 9805 and $\pm$ 5.7, 1.4, 110, 156, 99, 232, 381, 1005, 1167, 566, 1232, respectively. H^+, I^-, F^-, NH_4^+, K^+, Mg^{2+}, Na^+, NO_3^-, Cl^-, Ca^{2+} and SO_4^{2-} ions were precipitated with weighted ratio of 1, 1, 29, 44, 131, 240, 366, 510, 680 and 1956, respectively. Very high amounts (>99%) of acids like HF, HCl, HNO_3, H_2SO_4 are neutralized by alkaline particulates. Their standard deviation ranges from $\pm$ 1.4 to 1232 showing high variation in the nature, the strength of emission sources as well as the loading of distant pollutants. We analysed the spatial variations in the flux of ions at 12 sites of central India. The flux of free acid (H^+) was the highest in the sites where large amount of coal is burnt (Korba), several coal mines are in operation (Korba, Chirmiri, Raigarh) or pyrite minerals are deposited or processed (Gariyaband, Dallirajhara). The flux of SO_4^{2-} was the highest in site Korba where large amount of coal is burnt. Deposition trend of SO_4^{2-} in central India in decreasing order is Korba > Janjgir > Kanker > Gariyaband > Raipur > Bhatapara > Chirmiri > Pithora > Dallirajhara > Ambikapur > Raigarh > Bilaspur. The fluxes of NO_3^- and Cl^- were in top in rice cropping site Janjgir with different deposition patterns. The fluoride flux was the highest in sites where either aluminum industry (Korba) or soil is loaded with fluorite mineral (Kanker). The iodide flux was the highest in the forest areas (Kanker, Raigarh, Dallirajhara, Ambikapur) probably due to lower atmospheric temperature, higher emission rate from the forest vegetation, higher rainfall, etc. Similarly, the ammonia has some sort of similarity with I^- in deposition pattern and found to be the highest in the forest areas Gariyaband and Chirmiri. The deposition patterns of alkali and alkaline elements have some similarity, and the alkali metal fluxes were in top in sites Bhatapara and Kanker, however, the alkaline metal fluxes were in top in sites Korba, Kanker and Bhatapara.

Deposition trends, rainfall amount, pH, conductivity and ionic concentration H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, F^-, I^- at site Raipur during hydrological years from 1995 to 1997 were determined and shown in *Table 6*. The precipitation amount decreased in the hydrological period 1995–1997, whereas their pH values were almost the same. The value of conductivity and ionic concentrations of H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, F^- and I^- showed increasing trends but fluxes of some ions were the lowest in 1996.

3.10 Sources

Gases like NO_x, SO_x, hydrocarbon, etc. are emitted into the atmosphere by both natural and anthropogenic sources, rice paddy, biodegradation of forest vegetation and municipal waste, burning of coal and forest biomass, combustion of gasoline, smelting of pyrite minerals and dolomite, etc. The production and consumption of fossil fuels like coal, pyrites (Cu, Fe, Mn), aluminum and dolomite in this region are 31.0 and 8.0, 13.0 and 10.0, 0.2 and 0.16, 0.75 and 0.60 million tons yr^{-1}, respectively. In summer the Arabian SW monsoon causes heavy rainfall in central India. The air masses while crossing the Arabian sea proportionally enriched with sea salt particles which are incorporated with cloud droplets. The monsoon generally breaks into central India on the 2nd or 3rd week of June. During this long travel (about 1500 km), the cloud profiles are contaminated with soil dusts, acids, gases, metals, non-metals, etc. The monsoon loaded with both local and distant pollutants breaks in the central India. The main ions associated with sea salt are Na^+ with Cl^- with smaller amounts of Mg^{2+}, Ca^{2+}, K^+ and SO_4^{2-}. The ratio is modified when the air masses move inland due to presence of calcite, clay minerals, soil components and ions emitted from anthropogenic sources in the air. Various authors used Na^+ as tracer and claimed the ionic ratio of Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, Cl^- and NO_3^- to Na^+ in sea water to be 1.17, 0.12, 0.22, 0.044, 0.021, 0.0008, and 0.0006, respectively (*Mamane*, 1987). Thus, sea salts account the most of Cl^-, partially K^+ and Mg^{2+}, very less amount of SO_4^{2-} and Ca^{2+} and negligible amount of other ions (F^- and NO_3^-). The ionic ratio of Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, F^- and NO_3^- to Na^+ in the rain water of central India were found to be 1.2, 4.4, 1.2, 3.7, 0.14, 0.11 and 0.56, respectively. The contribution of the natural and anthropogenic sources in the rain water of central India accounts to be 2.5, 97.3, 81.7, 98.8, 85.0, 99.3 and 99.9% for the ions Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, F^- and NO_3^-, respectively.

Table 6. Trend of rainfall height, pH, conductivity and major ion concentrations at site Raipur during hydrological years from 1995 to 1997

Station No.	Parameters	Volume weighted mean concentration (µeq ℓ^{-1})			Flux (kg km^{-2} yr^{-1})		
		1995	1996	1997	1995	1996	1997
1.	Rainfall (mm)	1283	1123	1214	1283	1123	1214
2.	pH	5.8	5.9	5.8	5.8	5.9	5.8
3.	Cond. (µS cm^{-1})	65	70	72	65	70	72
4.	H^+ (µeq ℓ^{-1})	2.0	1.2	2.0	2.6	1.3	2.4
5.	Na^+ (µeq ℓ^{-1})	25.6	24.4	28.2	770	630	787
6.	K^+ (µeq ℓ^{-1})	4.4	3.8	4.2	218	166	199
7.	Ca^+ (µeq ℓ^{-1})	138	145	148	3464	3733	3589
8.	Mg^+ (µeq ℓ^{-1})	45.5	47.2	49.5	706	699	733
9.	NH_4^+ (µeq ℓ^{-1})	9.5	12.3	13.9	218	249	303
10.	SO_4^{2-} (µeq ℓ^{-1})	166	171	174	10211	9207	10163
11.	NO_3^- (µeq ℓ^{-1})	21.7	25.6	31.5	1719	1782	2371
12.	CL^- (µeq ℓ^{-1})	32.7	34.6	35.8	1488	1379	1543
13.	F^- (µeq ℓ^{-1})	2.7	3.4	3.9	110	121	150
14.	I^- (µeq ℓ^{-1})	0.02	0.03	0.03	3.8	4.3	4.6

4. Conclusion

(1) Acid rain occurs in central India specially in the monsoon period. Mean pH of storms in 1995 at the twelve sampling sites varied from 4.9 at Korba to 6.7 at Bhatapara, and the lowest pH of any storm was 4.1 at Korba. Thus, rain water was about 10–100 times more acidic than unpolluted rain which has a theoretical pH of 5.8 at the tropics.

(2) On chemical-equivalent basis, more sulphate is present in the precipitation than nitrate. Sulphate is the anion most closely correlated with H^+ at eight of the twelve sampling sites, thus air pollution by SO_2 forming sulphuric acid (H_2SO_4) is presumed to be the primary cause of the acidity of rain; NO_x forming nitric acid (HNO_3) appears to be the secondary cause at the present time.

(3) Total deposition of ionic constituents of rain precipitation is a function of both ionic concentration and total volume of rain. Total weighted deposition of both sulphate and H^+ ions were the highest at sites Korba and Gariyaband. These sites are about 150 km apart from Raipur in opposite directions. It is concluded that acid rain is widely distributed from pollution source areas to sub-urban, receptor areas. The ecological effect may be expected in the urban and sub-urban area where soil has poor buffering capacity.

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