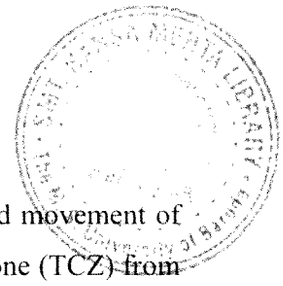
Chapter 2 Regional climate settings, materials and methods



2.1 Introduction

Monsoonal precipitation over India is caused by a periodic northward movement of east-west oriented precipitation belt named as tropical convergence zone (TCZ) from the southern (its winter position) to the northern hemisphere (its summer position) (Gadgil 2003). Some regions receive rains from both the summer/south-west (SW) (Jun to Sep) and winter/north-east (NE) (Oct-Dec) monsoons. The SW monsoon occurs throughout the country, while the NE monsoon prevails mainly over the southern part of the peninsula. The mean annual rainfall for India for the period 1813-2005 is 1166 mm with contributions of winter, summer, monsoon and post-monsoon rain of 3%, 9%, 78% and 11%, respectively (Sontakke et al., 2008).

Indian economy is largely dependent upon agricultural production. Positive relationship between monsoon precipitation and food grain production has been reported by Gadgil (2003). The winter monsoon rainfall over southern India and its effect on rabi (winter) food grain production is also reported (Kumar et al., 2007; Gunnell et al., 2007).

Indian summer monsoonal rainfall and El Niño-Southern oscillation (ENSO) are related (Sikka, 1980; Pant and Parthsarathy; 1981, Rasmusson and Carpenter, 1983; Krishna Kumar et al., 1995). Recent studies show that there could be potential impact of global climate change on the monsoonal precipitation. Goswami et al., (2006) showed for the period 1951-2000 that there was an increase in the frequency and magnitude of extreme rain events and a decrease in the frequency of moderate rain events. Increasing surface temperature trend over Eurasia and its effect on the relationship between ENSO and monsoonal rainfall is shown by Kumar et al., (1999). For the Indian region, IPCC (2007, Chap.11, page 850), in its fourth assessment report, has suggested a warming above the global mean, a likely increase in summer precipitation, very likely increase in frequency of intense precipitation events and a likely increase of extreme rainfall and winds associated with tropical cyclones. This makes it important to understand natural variability in the monsoonal rainfall.

To understand the effects of global climate change on monsoon precipitation, it is necessary to understand how monsoon precipitation varied in the past. Instrumental rainfall data collected by Indian Meteorological Department (IMD) dates back to 1813A.D. when the first rain gauge station was established in Chennai. By 1871 a fairly good network of rain gauge stations was established with a total of 312 meteorological stations. To know the variation of rainfall prior to 1871, it is necessary to use climate proxies. Long term monsoon rainfall reconstruction was done using speleothems (Yadava et al., 2004; and Yadava and Ramesh, 2005). However, such reconstructions are spatially limited and may not always give annual time resolution. Tree rings, in this context, can give valuable information as they are geographically wide spread and give annual to sub-annual resolution.

In India, the potential of trees in climate reconstruction has been demonstrated by Pant (1979), Pant and Borgaonkar (1983), Ramesh et al., (1985, 1989), Bhattacharyya et al., (1992), Hughes (1992), Bhattacharyya et al., (2007), Borgaonkar et al, (2007) and Sigh and Yadava (2007). Teak (*Tectona grandis*) is one of the few tropical species showing distinct and reliable growth rings and holds potential for reconstructing monsoonal precipitation over India. Teak has a widespread distribution in south-east Asia – Java, Sumatra, Burma and Thailand – a region important for tracking the history of El Nino- Southern Oscillation phenomenon. Bhattacharyya et al., (1992), Borgaonkar et al, (2007) and Shah et al., (2007), Somaru Ram et al., (2008) have shown that the variations in ring-widths of teak trees from India can be used in reconstruction of the past climate. However, the relationship between ring-width and climate is complicated by a variety of non-climatic parameters (Fritz, 1976). For example, in case of teak, attack by teak defoliator, *H. puera*, is shown (Sudheendrakuamr et al., 1993) to reduce tree growth (and hence ring width). In this context, isotope based tree ring studies are advantageous and their efficacy in rainfall reconstruction was shown by Ramesh et al., (1989).

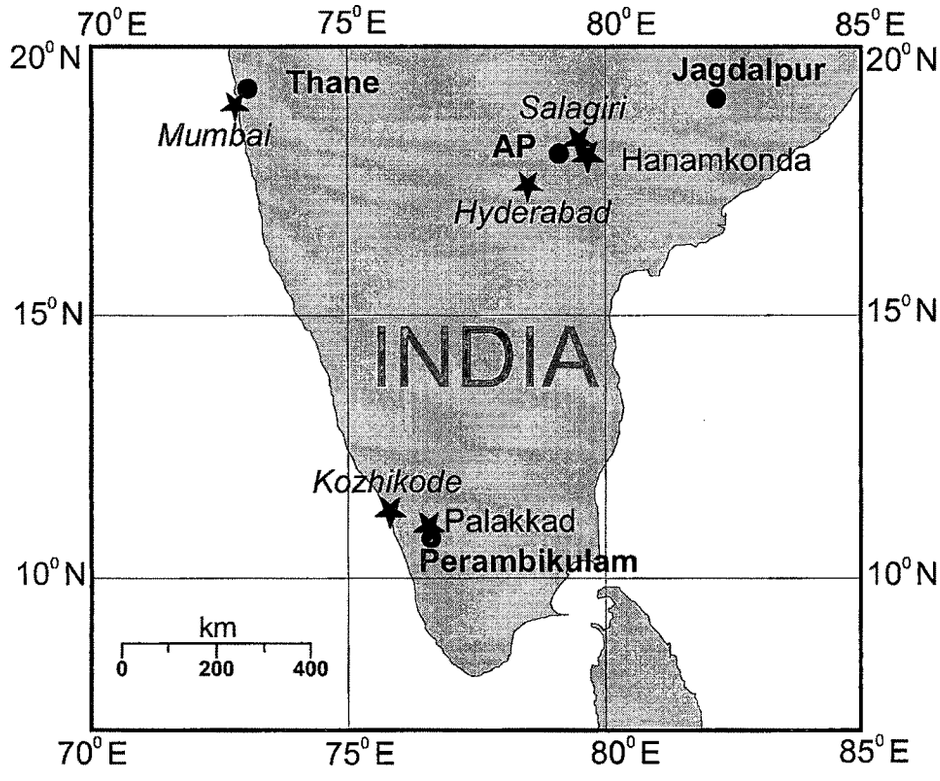


Fig.2.1. Locations of the teak tree samples (circles and bold letters) and IMD/GNIP stations (starts and letters in italics).

2.2 Climatology of sample locations

To understand how teak growing in different climatic settings responds to ambient climate, trees from different parts of the peninsular India were selected. While selecting the locations care was taken with respect to duration, pattern and amount of rainfall these locations receive. **Fig.2.1** shows locations of the trees used in the present study (locations indicated by circles and bold letters). The samples are from locations near Thane, Jagdalpur, Hanamkonda and Perambikulam. **Fig.2.1** also shows IMD weather stations (Mumbai, Jagdalpur, Hanamkonda and Palakkad- also known as Palghat) near the sample locations. **Fig.2.2** shows climatologies of IMD weather stations nearest to the respective locations. The data used in these figures is monthly mean data of climatological parameters based on observations from year 1951 to 1980. Among these locations, Palakkad receives the highest amount of

rainfall (2163 mm) and has the highest number of rainy days (~103 days). Mumbai (earlier called Bombay), although receives rainfall comparable to Palakkad, yet has only ~76 rainy days. Hanamkonda receives the lowest amount of rain and has the least number of rainy days.

Summer monsoon is the prominent source of rainfall at Mumbai, Jagdalpur and Hanamkonda. The summer rainfall is associated with formation of monsoon depressions which form in the Bay of Bengal north of 18°N latitude and their west-northwest movement along the monsoon trough (Pant and Rupa Kumar, 1997). It is also known that the north-south movement of the monsoon trough can affect rainfall over this region: north-ward shift of monsoon trough towards the foot-hills of the Himalaya results in decrease and increase in the rainfall over the peninsular India and the foot-hills of the Himalaya, respectively. Rainfall over Palakkad, on the contrary, is also dominated by winter monsoon, mainly due to the passage of cyclonic systems passing over the southern part of India during October to December. The ratios of NE to SW monsoon rainfall at these stations are ~0.04 (Mumbai), ~0.11 (Jagdalpur), ~0.17 (Hanamkonda) and ~0.27 (Palakkad).

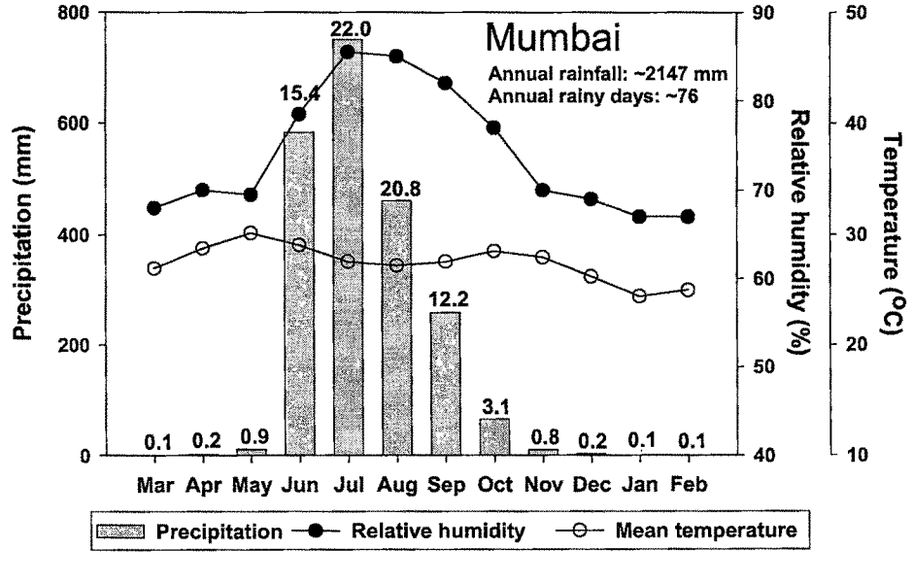


Fig.2.2a. Climatology of Mumbai. Numbers above the histogram bars indicate number of rainy days in the respective month.

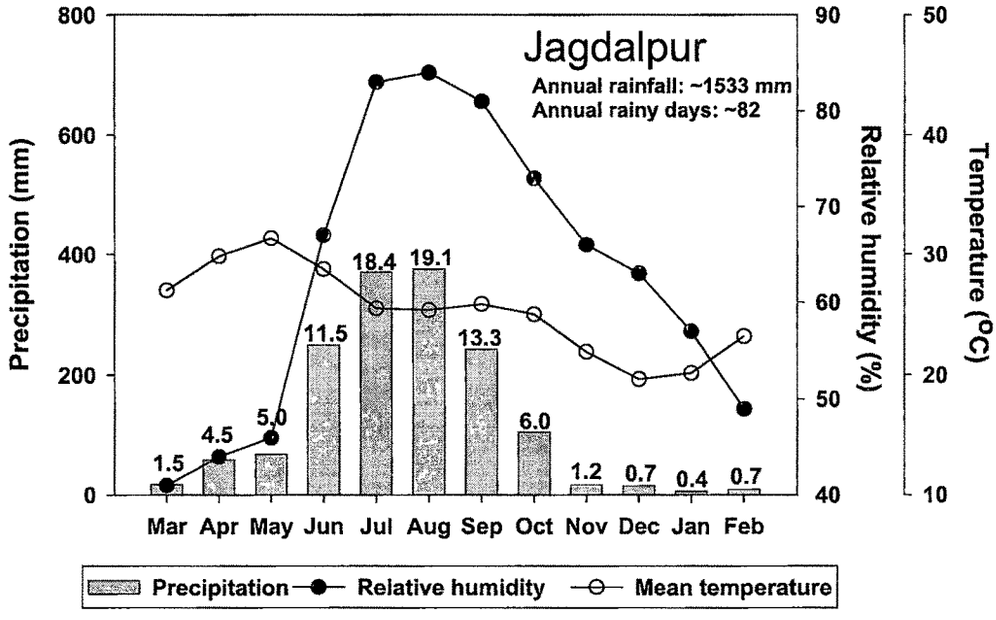


Fig.2.2b. Climatology of Jagdalpur. Numbers above the histogram bars indicate number of rainy days in the respective month.

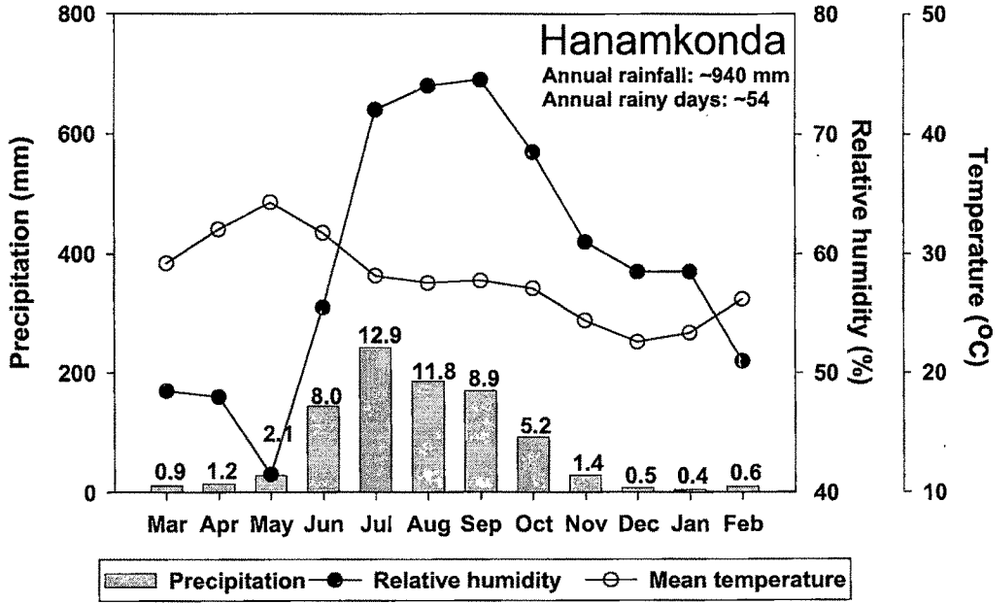


Fig.2.2c. Climatology of Hanamkonda. Numbers above the histogram bars indicate number of rainy days in the respective month.

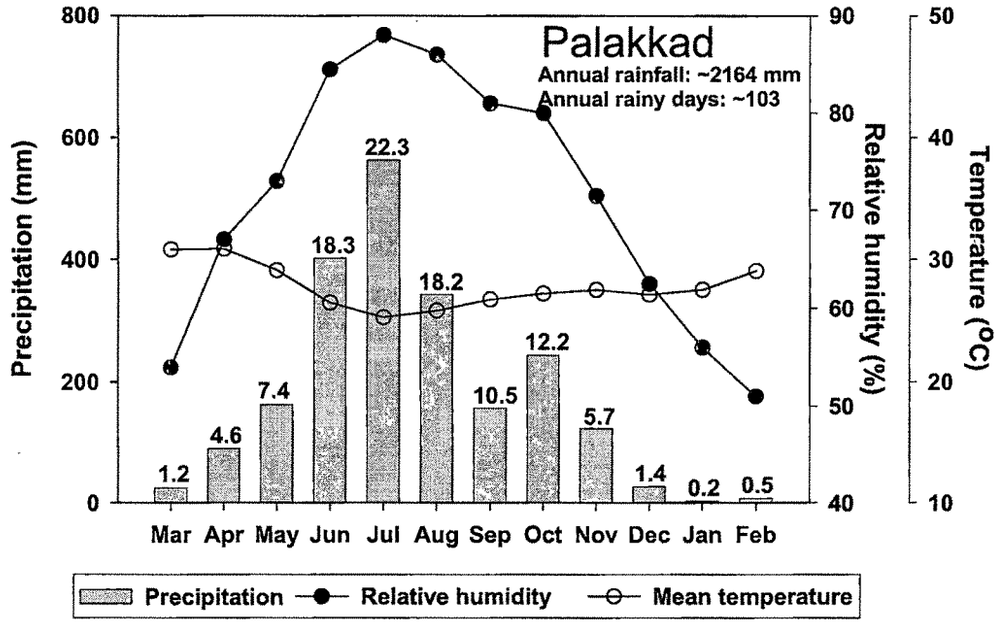


Fig.2.2d. Climatology of Palakkad. Numbers above the histogram bars indicate number of rainy days in the respective month.

2.3 Rainfall $\delta^{18}O$ record

Isotope data of rainwater is available for GNIP (Global Network of Isotopes in Precipitation) stations located nearby the sample locations (**Fig.2.1**, location indicated by 'star' marks and letters in italics). These stations are Mumbai (18.9°N, 72.82°E), Kozhikode (11.25°N, 75.78°E), Hyderabad (17.45°N, 78.47°E) and Salagiri (18.19°N, 79.44°E). Mumbai covers data from year 1961 to 1966 A.D. and from 1972 to 1976 A.D.; Hyderabad, from 1997 to 2000 A.D.; Kozhikode, from 1997 to 2004 A.D.; and Salagiri, for 1977 A.D. only. Mean weighted (by amount of precipitation) monthly oxygen isotopic composition ($\delta^{18}O$) of rainfall and monthly precipitation for the corresponding period for Mumbai, Kozhikode and Salagiri is shown in **Table 2.1**. Along with Salagiri, GNIP has also recorded monthly $\delta^{18}O$ of nearby stations viz. Bhopalpalli (18.27°N and 79.52°E), Chinpak (18.28°N and

79.44°E), Kamalpur (18.29°N and 79.54°E), Nasarampur (18.26°N and 79.47°E) and Tundla Buzurg (18.32°N and 79.47°E). All these stations show (**Fig.2.3**) a similar pattern of monthly $\delta^{18}O$ values indicating similarity in the monthly $\delta^{18}O$ of rainfall

Month	Mumbai		Salagiri		Kozhikode	
	Amount, mm	Weighted Mean $\delta^{18}O$, ‰	Amount, mm	Weighted Mean $\delta^{18}O$, ‰	Amount, mm	Weighted Mean $\delta^{18}O$, ‰
April					73	-4.3
May					335	-3.0
June	544	-1.1			687	-2.1
July	698	-1.7	286	-2.2	608	-1.8
August	395	-1.1	145	-3.6	396	-1.5
September	248	-1.8	140	-10.7	181	-3.4
October	90	-4.8	18	-7.8	311	-4.5
November	15	-5.4	51	-9.1	125	-7.3
December	19	-0.2			58	-6.2

Table 2.1. Monthly $\delta^{18}O$ of rainfall for the locations near to the sample locations.

on that scale. Yearly fluctuations in the amount weighted mean yearly $\delta^{18}O$ of rainfall for Kozhikode are shown in **Fig.2.4**. For Mumbai, such yearly fluctuations in $\delta^{18}O$ can be as high as 2 ‰. Relation between weighted (by amounts of precipitation) monthly rainfall $\delta^{18}O$ and monthly amount of rainfall for station Kozhikode is shown in **Fig.2.5**. $\delta^{18}O$ record at Kozhikode shows a large variation in the mean monthly rainfall $\delta^{18}O$ values which are not necessarily correlated with the amount of rainfall in the respective months. **Fig.2.6** shows the spread in monthly rainfall $\delta^{18}O$ values based on observations from year 1997 to 2004 A.D. In addition to GNIP stations, Yadava and Ramesh (2005) monitored rainfall isotopic composition near Jharsuguda (22°N and 84°E) for the year 1999 and Yadava et al., (2007) near Mangalore for June to October 2000 to 2002 A.D. Yadava and Ramesh (2005) found an inverse relation between amount of rainfall and its $\delta^{18}O$ i.e. amount

effect. They observed a depletion rate of -9.2 ± 1.1 ‰ and -2.2 ± 0.8 ‰ for 100 mm rain for each rain event and total monthly rain, respectively for Jharsuguda. The ^{18}O depleted nature of rainfall during NE monsoon and a positive amount effect for Mangalore was reported by Yadava et al., (2007).

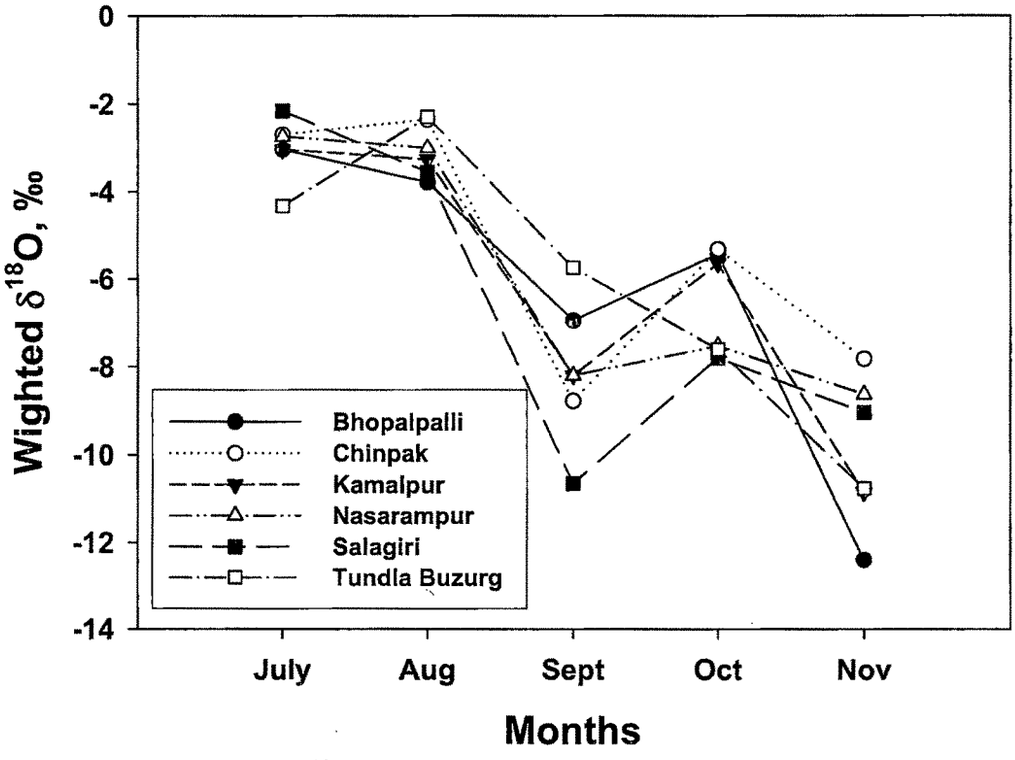


Fig.2.3. Monthly rainfall $\delta^{18}O$ values for various stations in central India for year 1977.

Based on GNIP precipitation and its $\delta^{18}O$ record and work done by Yadava and Ramesh (2005), Yadava et al., (2007) the following points can be deduced:

1. NE monsoon rainfall is depleted in ^{18}O than the SW monsoon rainfall
2. Amount effect is observed in individual rain events and monthly rainfall of particular season i.e. the SW or NE monsoon season
3. During the SW monsoon season, rain at central India (Salagiri) is more depleted in ^{18}O than at southern India (Kozhikode)

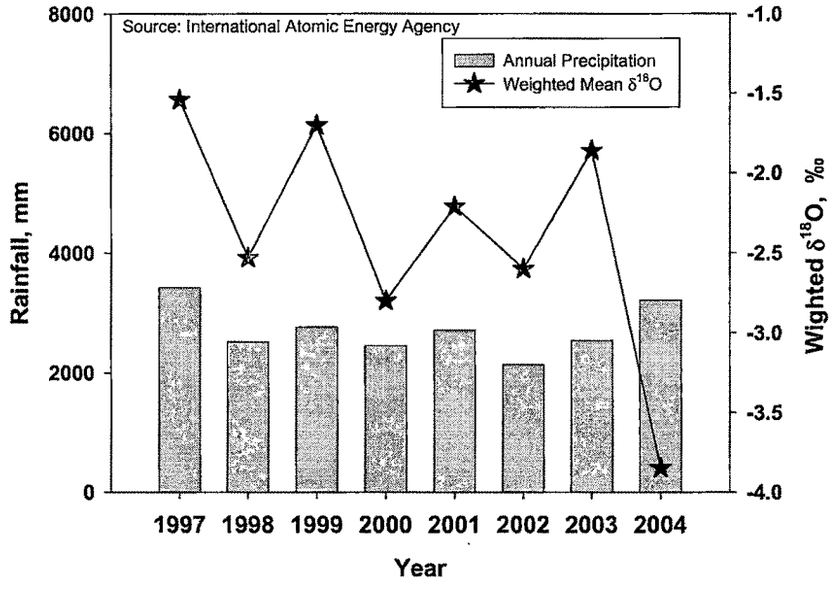


Fig.2.4. Yearly rainfall (bars) and weighted annual rainfall $\delta^{18}O$ (stars) observed at Kozhikode.

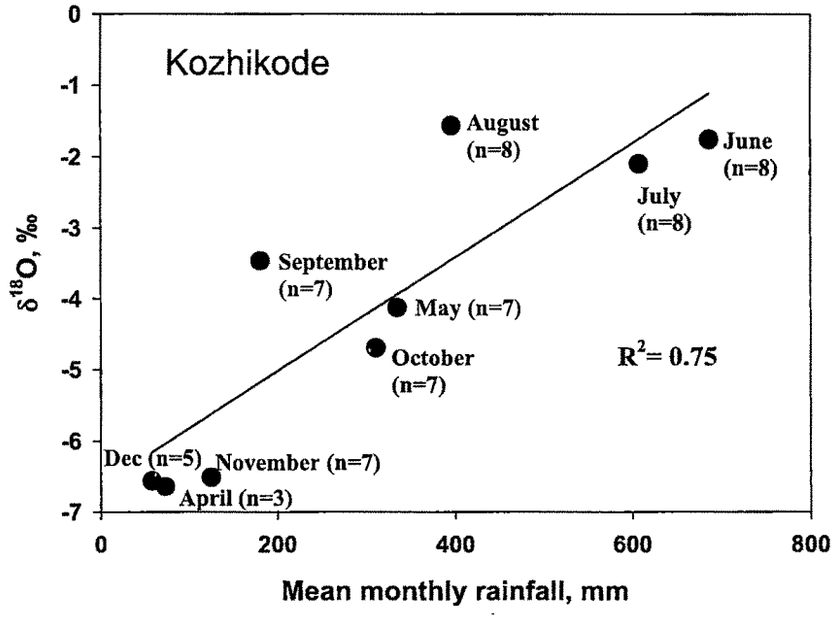


Fig.2.5. Relation between monthly rainfall and amount weighted monthly $\delta^{18}O$ observed at Kozhikode.

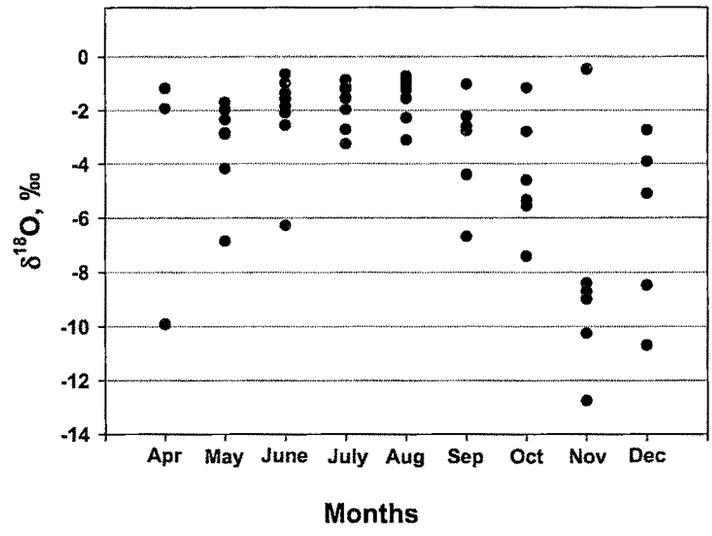


Fig.2.6. Mean monthly rainfall $\delta^{18}O$ values observed at Kozhikode based on observations from year 1997 to 2004 A.D.

2.4 Sample collection

All the samples used in the present study are tree discs collected either by the Indian Institute of Tropical Meteorology (IITM), Pune, India or the Birbal Sahani Institute of Palaeobotany (BSIP), Lucknow, India. IITM and BSIP are routinely involved in tree-ring width based dendrochronological and dendroclimatological investigations. The locations and time spans covered by the samples used in the present study are given in **Table 2**.

Sample Name	Nearest town	Latitude	Longitude	Years covered
THN	Thane	19°12' N	73°02' E	1920-1962
Jag03	Jagdalpur	19°03' N	82°03' E	1824-2003
Jag04	Jagdalpur	19°05' N	82°20' E	1866-2004
AP1	Hanamkonda	18°03' N	79°02' E	1875-1960
AP2	Hanamkonda	18°03' N	79°02' E	1729-1952
PKLM	Perambikulam	10°20'-10°26'N	76°35'-76°50'E	1743-1988

Table 2.2. Names and locations of the samples collected in the present study and time spans covered by them.

The samples from the western (Thane) and central (Jagdalpur and Hanamkonda) India were obtained from the IITM collection. The details regarding collection and dating of the sample from Thane is given by Pant and Borgaonkar (1983). They collected several tree discs from the Murbad forest, Maharashtra, India (19°14′ N, 73°24′ E). Standard procedures were employed for dating these discs and the discs showed a good cross-match with no double or missing rings. Dr. H. P. Borgaonkar collected (years 2000 and 2004 A.D.) several tree cores and discs from central India and found a good cross matching between the cores from the same tree and from different trees at the same site for some sites (Borgaonkar et al., 2007). These discs and cores are currently being studied for the development of tree ring index chronologies. In the present study, two tree discs (Jag03 and Jag04) were selected out of this collection and used for climate reconstruction. These discs were taken from wind-felled tree from Chattisgarh and the distance between them is about 25 km. Based on their year of fall, years A.D. 2003 and 2004 were assigned to the outermost rings of Jag03 and Jag04, respectively.

Two more cross dated tree discs (AP1 and AP2) were selected from the IITM collection. These trees belong to area near Hanamkonda, Andhra Pradesh and are located about 100 km south of trees selected from Chattisgarh. Tentative cross dating yielded years A.D.1960 and 1952 to the outermost rings of AP1 and AP2.

The sample from southern India was collected and dated by Dr. Amalava Bhattacharyya of BSIP. The sample was collected from area near Perambikulam (10°20′–10°26′N; 76°35′–76°50′E) during March 2000 A.D.. It is a disc cut out of a wind-felled tree. The dating of the sample was done through cross dating with the master tree ring plot for the area. The sample dates from 1743 to 1986 A.D. and the dates were checked using the computer program COFECHA (Holmes, 1983). The details regarding sample collection and the master tree ring plot is described by Bhattacharyya et al., (2007). For the purpose of the present work, it is assumed that the dates are correct to ± 1 year.

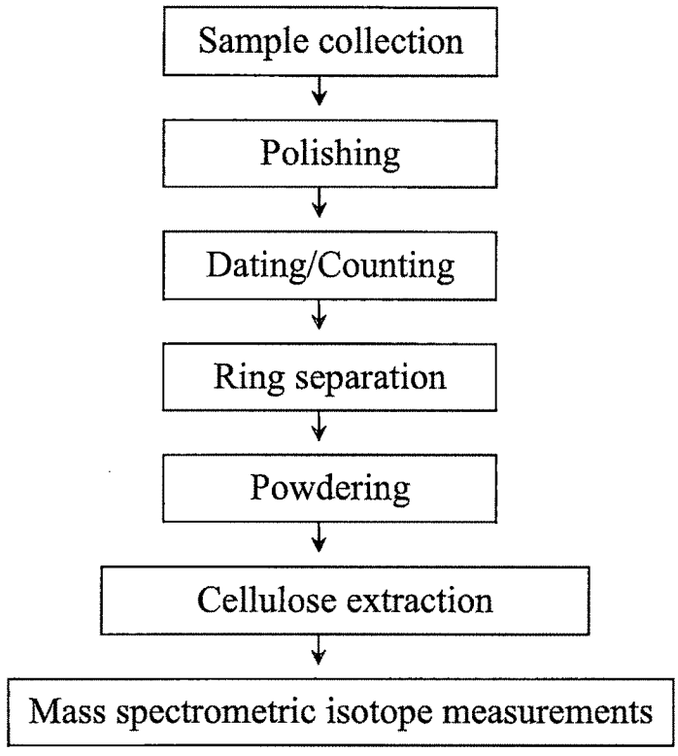


Fig.2.7. Flow chart showing the experimental procedure followed in the present study.

2.5 Ring separation and powdering

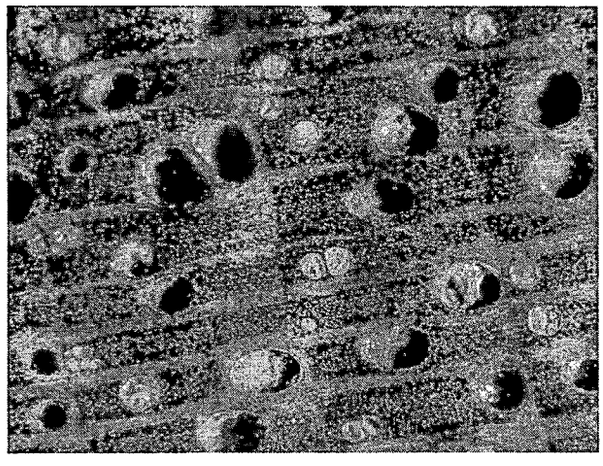


Fig.2.8. Ring porous vesicle structure observed in the teak samples.

The experimental procedure adopted in the present study is shown in **Fig.2.7**. Radial strips along the selected directions were cut from the discs mentioned above. The radial strips were manually polished thoroughly using different grades of sandpaper. Upon polishing all the samples showed clear ring-porous structure (**Fig.2.8**). The vesicle size and frequency decreased from the pith-side to the bark-side. Rings were counted under microscope and calendar years were assigned to them by counting the rings, knowing the year of felling/fall.

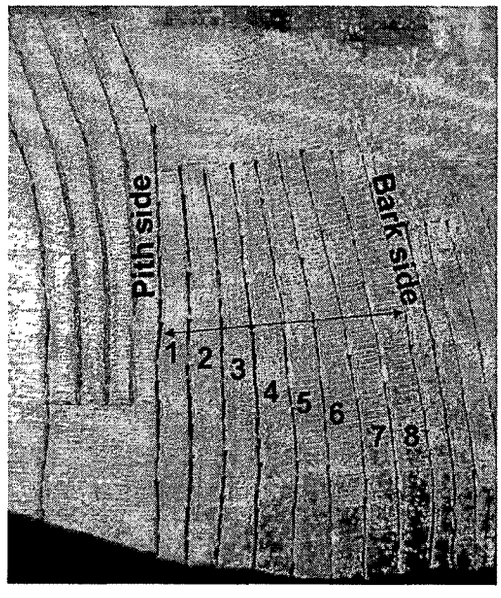


Fig.2.9. Photograph of a ring subdivided into 8 parts for studying sub-annual $\delta^{18}O$ variations.

Subsequent to the dating of samples, individual rings were separated using scalpel, chisel and hammer. The resolution with which the rings were separated depended upon width of the rings; rings with widths less than 0.6mm were combined together. Use of recently developed cellulose extraction methods, which are described later, enabled to extract cellulose from small amounts of wood material and hence facilitated a higher resolution sampling. While separating the rings, maximum care was taken to avoid contamination from the adjacent rings. Intra-ring sampling was done to understand how the isotopic composition of photosynthates varied along the radial direction within a ring. For this, about 10 rings from each sample (except the

sample from Thane) were selected randomly and further separated into four equal parts. Some of these rings which were comparatively wider were sampled with higher as well as lower resolutions. In the higher resolution sampling, the rings were subdivided into 6 or 8 or 12 or 16 parts. The widest ring from central Indian sample (Jag03) was sampled with the highest resolution: the ring was subdivided into 16 parts. **Fig.2.9** depicts a representative photograph of a ring which was subdivided into 8 parts. The separated rings/parts of the rings were powdered in a Wiley mill. The mill was cleaned thoroughly after powdering of each ring sample. The powdered material was transferred to a plastic vial with screw cap and stored for further treatment.

2.6 Extraction of α-cellulose

α-cellulose was extracted from the powdered wood material using a method suggested by Gaudinski et al., (2005) with some modifications. Gaudinski et al., (2005)'s method, called 'MBrendel' method, is a modification of the method given by Brendel et al., (2000). The steps followed in the present study are as follows

STEP 1

- Take about 50 mg of wood powder in a dry round bottom glass tube with stoppers
- Add 2ml of 80% acetic acid
- Add 0.2ml of 69% nitric acid
- Seal the tube with stoppers using Teflon tape
- Boil at 120°C for 30 minutes

STEP 2

- Allow the tubes to cool (~5-10 min)
- Transfer the solution to glass centrifuge tubes having screw caps with Teflon inliers
- Add 2.5 ml 99% ethanol

STEP 3

- Vortex
- Centrifuge for 5 minutes at 3500 rpm or higher
- Decant supernatant

STEP 4

- ADD 2 x 2.5 ml 99% ethanol in tow steps; the first 2.5 ml is added and mixed, the second addition is to make wash sown the sides of the glass tube to force samples back to solution
- Repeat step 3

STEP 5

- Add 2 x 2.5ml of distilled deionised water (DDI)
- Repeat step 3

STEP 6

- Add 2 x 2.5 ml 17% (w/v) NaOH using glass pipettes
- Stir the sample pellets with thin glass rod
- Ultrasonicate the mixture for ~5 min
- Let the mixture sit for one hour
- Repeat step 3

STEP 7

- Add 2 x 2.5 ml DDI water
- Repeat step 3

STEP 8

- Add 2.2 ml DDI water + 0.6 ml acetic acid
- Vortex
- Add 2.2 ml DDI water to wash the sides of the glass tubes and mix gently
- Repeat step 3

STEP 9

- Repeat step 3 three times

STEP 10

- Add 2 x 2.5 ml 99% ethanol
- Repeat step 3

STEP 11

- Add 2 x 2.5 m acetone
- Repeat step 3

STEP 12

- Allow the sample to dry overnight in an oven at 50°C
- Transfer the sample to 1.5 ml polypropylene centrifuge tube and keep the tube in desiccator

In the present study, some modification were introduced in the STEP 6 of Gaudinski et al., (2005)'s method. These modifications are ultrasonicating the mixture (sample and NaOH) for ~ 5min and keeping the solution for one hour instead of ~10 min as

suggested in the original method. In a day, cellulose was extracted from two batches of samples each containing 16 samples, a number determined by the capacity of the centrifuge.

Gaudinski et al., (2005) pointed out that the Brendel's method adds carbon and nitrogen to the cellulose and left a residue that contains remnant lipids and waxes. In case of oxygen, the authors reported that cellulose extracted using Brendel's method is enriched in ^{18}O relative to the other methods and proposed a method, MBrendel, involving an additional step that treats the cellulose further with 17% NaOH, followed by water rinsing and acidification.

2.7 FTIR spectroscopy of extracted α-cellulose

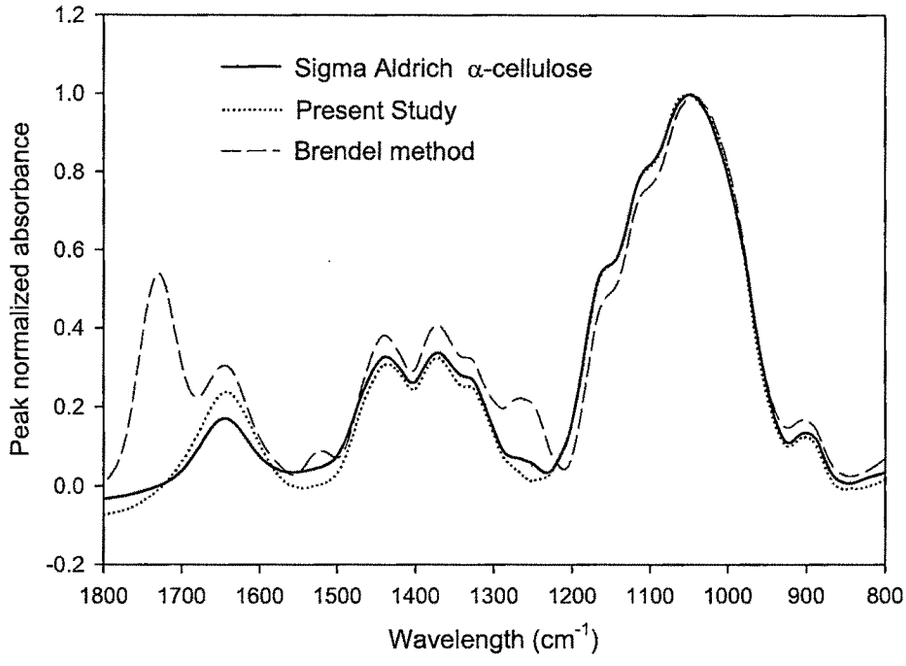


Fig.2.10. Representative FTIR spectra of α-cellulose extracted using present method, Brendel et al., (2000)'s method and commercial available α-cellulose of Sigma Aldrich.

Purity of the α–cellulose extracted in the present study was checked by Fourier transform infrared spectroscopy (FTIR) using Varian 3100 FT-IR spectrometer at Ahmedabad Textile Research Institute (ATIRA), Ahmedabad, India. All the measurements were done using KBr pellets. **Fig.2.10** shows representative spectra of α-cellulose extracted using the present method, Brendel et al., (2000)'s method and commercial available α-cellulose of Sigma Aldrich. Anchukaitis et al., (2008) reported that α-cellulose extracted using Brendel et al., (2000)'s and Gaudinski et al., (2005) methods resulted in acetylation of cellulose with its peak in FTIR spectra at 1720 cm^{-1}. It can be seen from the **Fig.2. 10** that FTIR spectra of the α-cellulose extracted in the present study does not show acetylation peak. Thus, there is no significant contribution of oxygen atoms to α-cellulose from acetic acid through cellulose acetylation.

2.8 Mass spectrometric isotope measurements and analytical precision

The isotopic measurements were done using Thermo Quest's Finnigan Delta plus continuous flow Isotope Ratio Mass Spectrometer (IRMS) available at the National Facility, University of Agricultural Sciences, Bangalore, India. The peripherals attached with the mass spectrometer were High Temperature Conversion Elemental Analyzer (TC/EA) and ConFlo III. TC/EA was operated at 1350°C to ensure complete pyrolysis of the samples. To avoid isotopic interference of CO and N_2 the pyrolyzed gases were then passed through Gas Chromatograph (GC) column (0.6m x 1/4" x 4mm, Stainless Steel). The molecular sieve used in GC was 5Å, 80-100 mesh size. ConFloIII is a device coupling TC/EA and IRMS. It works with an open-split arrangement whereby a gas flow of ~80-100 ml/min coming from TC/EA is reduced to ~0.3ml/min, a rate at which gas in introduced into the IRMS. ConFloIII contains two open split cells: one 'sample section' and the other 'reference section'. 'Sample section' and 'reference section', splits the gas coming from TC/EA and reference gas cylinder, respectively.

For isotopic measurement, about 0.85 mg of cellulose was packed in silver foil and the sample capsules were put in oven kept at 60°C for at least 10 hours before measurements. Typically, 50 samples were analyzed in a single run. These contained 44 cellulose samples and 6 standards with standards at 1st, 10th, 20th, 30th, 40th and 50th positions. The standards used were in-house calibrated starch ($\delta^{18}O$ = 26.8‰) and Australian National University (ANU) sucrose ($\delta^{18}O$ = 36.4‰). All the measurements were done with ConFloIII on 'He dilution ON' mode. During measurement of a sample, three reference gas pulses were injected in IRMS first followed by a sample gas injection and again reference gas injection. Time required for the measurement of one sample was 10 min. The reference gas injections gave internal precision less than 0.1 ‰. The external precision of the measurements were consistently less than 0.3 ‰. **Table 2.3** gives precisions of the ANU sucrose $\delta^{18}O$ values measured during individual runs and the date of respective runs. Plot of $\delta^{18}O$ measurements of all the ANU sucrose standards used during cellulose sample measurements is shown in **Fig.2.11** Oxygen isotopic composition all the samples reported in the present study are relative to VSMOW.

Date	External Precision	Date	External Precision	Date	External Precision
July 7	± 0.3	July 14	± 0.3	July 22	± 0.4
July 8	± 0.3	July 14	± 0.2	July 23	± 0.3
July 8	± 0.2	July 15	± 0.3	July 24	± 0.4
July 9	± 0.1	July 15	± 0.2	July 25	± 0.3
July 10	± 0.3	July 16	± 0.3	July 26	± 0.3
July 10	± 0.3	July 16	± 0.2	July 26	± 0.2
July 11	± 0.3	July 17	± 0.1	July 28	± 0.2
July 12	± 0.2	July 17	± 0.2	July 29	± 0.2
July 13	± 0.2	July 21	± 0.3	July 30	± 0.2

Table 2.3. Standard deviations (1 sigma) of $\delta^{18}O$ measurements of ANU sucrose samples measured during various runs in July 2008. Mean of the measurements is 36.4 ‰.

Typically the reactor was changed every 250 samples. The system was degassed overnight with TC/EA at 1350°C and GC at 300°C after changing the reactor. After checking for leak in the connections, background levels were measured. The typical background on CUP1 for peaks 28, 29 and 30 were 7mV, 4mV, and 29mV, respectively with He dilution in ConFloIII ON (48mV, 32mV, and 29mV when He dilution in ConFloIII was OFF). The backgrounds for masses 18, 28, 32 and 44 on CUP 2 were 7000mV, 500mV, 900mV and 105mV, respectively. After this, internal precision of the mass spectrometer was checked by 'ZERO ENRICHMENT or Standard ON/OFF' method in which a reference CO gas was injected repeatedly and its $\delta^{18}O$ was measured. This is followed by $\delta^{18}O$ measurements of external standards (in-house calibrated starch and ANU sucrose) for checking external precision.

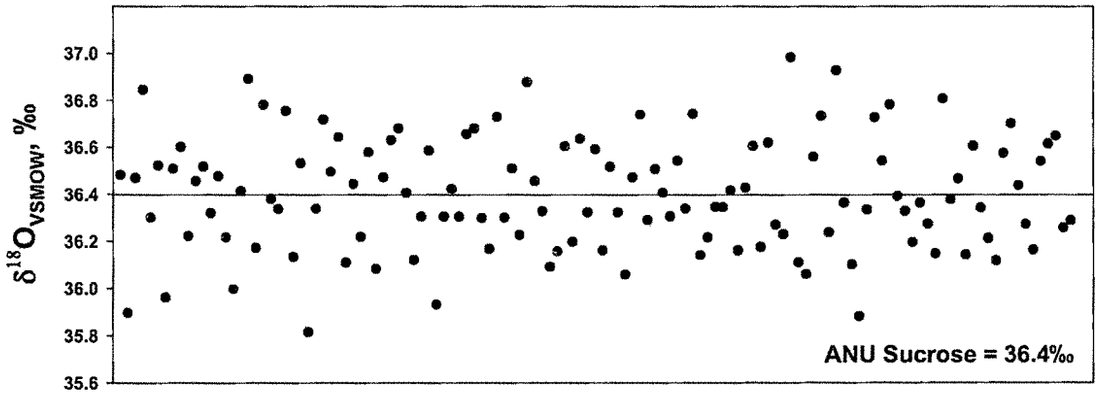


Fig.2.11. Scatter plot showing $\delta^{18}O$ values of all the ANU sucrose standards measured along with cellulose samples in the present work over a period of ~ 20 days.