APPLICATIONS OF COSMIC RAY PRODUCED ISOTOPE SILICON-32 TO HYDROLOGY WITH SPECIAL REFERENCE TO DATING OF GROUNDWATERS

by
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एकेन वर्णेन रसेन चाम्भश्च्युतं नभस्तो वसुधाविशेषात् ।
नानारसत्वं बहुवर्णतां च गतं परीक्ष्यं क्षितितुल्यमेव ॥

> 'Water that falls from the heaven has uniform taste and colour but acquires different properties when in contact with soils. This, like other diverse earth phenomena deserves an examination.
>
> BRIHATSAMHITA by VARAHMIHIRA
> (Dakargaladhya, verse 2).

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SYNOPSIS

The primary object of the present investigation is to evaluate the applicability of cosmic ray produced silicon-32 (half life $\approx$ 500 yrs) as a tracer (radioactive) for the study of the characteristics of surface and sub-surface waters, with special reference to determination of the "ages" of groundwaters. A large number of measurements of the concentration of ^{32}Si were carried out towards this goal, using the newly developed experimental techniques, in wet precipitations, melt-waters, rivers, lakes and sub-surface waters.

To date, two radiometric techniques are used for tracing underground flow of water and for estimating the "age" of groundwaters. These methods are based on the isotopes, tritium (half-life = 12.3 yrs.) and carbon-14 (half-life = 5730 yrs.). The usefulness of ^{3}H for groundwater studies is limited to a time span of about 50-100 yrs. before present. In the case of ^{14}C, because of the fact that the groundwater system is "open" to exchange of ^{14}C atoms with stable carbon atoms in solid phases, reliable estimates of groundwater ages below 1500 years are usually not possible.

When this programme was undertaken, no suitable method was available for studying groundwaters of ages in the time bracket 100-2000 years. Experiments were, therefore, undertaken to study the usefulness of radioactive ^{32}Si for determining the ages of groundwaters in a time bracket, not covered by either ^3H or ^{14}C method. The production of ^{32}Si on the earth occurs as a result of nuclear interactions of cosmic ray particles with atmospheric argon. The ^{32}Si produced in the atmosphere is transported to the surface of the earth via rains and added to underground aquifers by downward movement of surface waters. The production rate of ^{32}Si in atmosphere is estimated to be 3×10^{-4} atoms/cm^2.sec. Due to this low production rate, the concentration of ^{32}Si in surface and subsurface waters is very small, of the order of 0.01 - 0.5 dpm/ton (1 ton = 10^3 litres) of water. Such low concentrations necessitate the collection and processing of large volumes of water, in the range of 5-30 tons, to obtain definite signals of ^{32}Si.

The concentrations of stable silica (SiO_2) in surface and subsurface waters range from 5-50 ppm. Such large concentrations of stable silica in these water samples coupled with the low production of ^{32}Si in the atmosphere makes the specific activity of ^{32}Si ($^{32}Si/SiO_2$) in natural waters very low. ^{32}Si decays by β^- emission to ^{32}P, a radioactive nuclide of 14.3 days half-life. ^{32}Si activity is, therefore, easily measurable by assaying the activity of its daughter nuclide ^{32}P.

During the course of this work, experimental techniques were developed towards :

(i) Collection and extraction of silica at the sampling site from 5-30 tons of water samples. Extraction of silica (100-400 g), by scavenging with ferric hydroxide, could be carried out with an extraction efficiency of about 95%.

(ii) Separation of ^{32}P activities from large quantities of SiO_2 extracted from water samples. The ^{32}P separation was carried out by an efficient and rapid technique involving the distillation of silica as SiF_4. The recovery of phosphorus was better than 90%. Samples of 300 gof silica could be processed in 8-10 hrs.

(iii) Assay of ^{32}P activity milked from extracted "silica" using low-background high efficiency beta counters.

With the combination of these techniques of rapid chemistry and sensitive counting, it became possible to estimate absolute ^{32}Si activities as low as 0.05 dpm (corresponding to one count per hour of ^{32}P) within an uncertainty of ±20%. The present detection limit is 3-4 times better than that was possible with the techniques previously employed.

Using the above mentioned experimental methods extensive studies of ^{32}Si concentration were carried out in natural waters collected from various geological environments, especially in the arid and semi-arid regions of India. The application of ^{32}Si as a hydrological tracer involves (a) measurement of its concentration in rainwaters and the rate of its deposition and (b) the changes in its concentration in groundwaters due to causes other than radioactive decay. Experiments were planned and conducted to obtain estimates of these parameters. The salient features of the results are summarised below:

(a) ^{32}Si concentrations in rain waters :

The measured concentrations of ^{32}Si in rainwaters from the Indian subcontinent (10°-32°N), during the year 1961-1971, range between 0.1 - 1.2 dpm/ton; the average value is 0.3 ± 0.2 dpm/ton. The ^{32}Si concentrations in rainwaters show a marked latitudinal dependence as would be expected from atmospheric production. Combining the measured ^{32}Si activities for Indian stations with the published values for (55°-70°N), the mean global fallout of ^{32}Si is estimated to be 2.5×10^{-5} dpm/cm^2.yr., which corresponds to a global average production rate of 3×10^{-4} atoms/cm^2.sec. The concentration of ^{32}Si in 1963-64 precipitation was about a factor of two higher compared to those in the preceding and succeeding years indicating that there was some production of ^{32}Si due to the testing of nuclear weapons.

(b) Geochemical behaviour of ^{32}Si in hydrological systems :

Field experiments using ^{32}Si activity present in rainwaters and laboratory experiments with artificially produced ^{31}Si (half-life = 2.6 hrs) were conducted to evaluate the extent of exchange of ^{32}Si with silicon present in soil, during its passage from surface to underground aquifers.

The results of these experiments suggest that the loss of silicon isotopes depends primarily on the nature of the soils and minerals. It was observed that the loss (for a time span of about two hours for ^{31}Si and two months for ^{32}Si) was negligible in some cases; e.g. sand, quartz and red soil. Thus for quantitative study of losses of ^{32}Si in groundwaters due to chemical exchange mechanisms it is necessary to consider the nature of soils in corresponding groundwater environments.

(c) ^{32}Si concentrations in surface and subsurface waters :

^{32}Si concentrations were measured in twentyone surface and thirtysix subsurface samples. Majority of the subsurface samples originate from the alluvial tracts of arid and semi-arid regions of Rajasthan and Gujarat.

About 70% of the groundwater samples showed unambiguous signals of ^{32}P corresponding to $\geq$0.015 dpm ^{32}Si/ton. This observation clearly indicates that the ages of these water masses are less than ~ 2000 yrs, calculated using the ^{32}Si concentrations of 0.3 dpm/ton in rainwater. This information by itself is significant because for waters older than about 100 yrs. but younger than 2000 yrs., the information based on ^{14}C (the only suitable long lived radiotracer) is ambiguous.

The ages for the subsurface water masses were calculated on the basis of the assumptions that, there is no loss of ^{32}Si in the groundwaters by processes other than radioactive decay or that there is a 50% loss of ^{32}Si by exchange/adsorption on minerals present in the environment. The ages calculated on the latter assumption differ from those by the former in absolute value by one half life of ^{32}Si. Inspite of the uncertainties involved in calculations, the model ages computed using ^{32}Si are compared with those obtained from ^{14}C measurements.

For waters older than 2500 years, where clear reproducible signals of ^{32}P were observed, the agreement in estimated ages based on ^{14}C and ^{32}Si methods is not satisfactory. In general, the ages based on ^{32}Si

are lower. This discrepancy could perhaps be due to loss of ^{14}C by exchange resulting in apparent "older" ages.

The most significant result which emerges from this study is that the ^{32}Si method can be used to establish whether waters are younger than ~ 2000 years. However, due to lack of understanding of the ^{32}Si exchange processes, absence of ^{32}Si in groundwaters does not imply that the waters are older than 2000 years. Obviously, detailed investigation of ^{32}Si in various geological systems is warranted for a proper understanding of the ^{32}Si geochemistry in groundwaters.

Statement required under ordinance 0.770.

I hereby state that the work described in this thesis has not been submitted to this or any other University for Ph.D. or any other degree.

Statement required under ordinance 0.771.

a) Statement regarding the discovery and important new facts.

Extensive measurements of ^{32}Si concentrations in natural waters (rain, surface and subsurface waters) have been carried out using quick and improved radiochemical and assaying techniques. These measurements have led to the following new facts.

The usefulness of ^{32}Si as a tracer for "dating groundwaters" has been demonstrated. Several samples of groundwaters from arid and semi-arid regions of Rajasthan and Gujarat, where the water tables are rapidly depleting have been dated, using this method. The estimated velocities of groundwater movement based on their ^{32}Si ages are not in disagreement with those deduced using conventional techniques.

The mean global fallout of cosmic ray produced ^{32}Si has been estimated to be 2.5×10^{-5} dpm/cm^{2}y, which corresponds to mean global production rate of

3×10^{-4} atoms $^{32}Si/cm^2$ sec., in modest agreement with the calculated value of 1.6×10^{-4} atoms $^{32}Si/cm^2$ sec.

b) Statement regarding contributions of the author.

One of the major task of the present work was the collection of large volumes of water samples (5-30 tons) for ^{32}Si measurements at several locations in India. Majority of the samples were collected and processed by the author: technical assistance was provided by Drs. S. Aegerter, D. P. Kharkar, B. L. K. Somayajulu, B. S. Sukhija, R. Rajagopalan and Shri B. S. Amin in the case of some of the groundwater and rain-water samples.

The extraction and purification of silica and the radiochemical separation of ^{32}P was done by author with occasional help from Dr. D. P. Kharkar, Prof. B. L. K. Somayajulu, and Shri B. S. Amin. New experimental techniques and modifications were developed by the author towards this.

The low background 2π beta counters for the assay of ^{32}P activities were assembled and used by the author for the present work. The 4π counting used in the present work was developed by Profs. B. L. K. Somayajulu, and D. Lal.

The water samples for ^3H and ^{14}C measurements were collected by the author and the measurement of the activities was carried out in collaboration with Dr.B.S.Sukhija, Dr.D.P.Agrawal and Miss Sheela Kusumgar when the tritium and radiocarbon laboratory was housed at T.I.F.R.,Bombay.

The planning of new radiochemical procedures, improvements in techniques and selection of sampling regions was done in consultation and collaboration with my guide Prof.D.Lal.

The interpretation of the experimental results have been carried out by the author in collaboration and under the guidance of Prof.D.Lal.

In all these phases of work the author carried out a significant share of the work.

A list of publications of the author together with a copy of each of the papers supporting the thesis are attached at the end of the thesis.

V.N.Nijampurkar

I certify that the above
statements are correct.

D.Lal
(Guiding Teacher)

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CHAPTER-I

INTRODUCTION

The ever increasing consumption of fresh water supplies has brought into focus the need for exploration of groundwater resources. The recent discovery of possible long term climatic changes which may bring extensive drought conditions to vastly populated areas (WENDLAND and BRYSON, 1974) greatly amplifies the urgency for developing new techniques of groundwater exploration. The Indian subcontinent depends mainly on rainfall for its water requirement. The shortage of water can become acute producing severe drought conditions especially during summer months in the year of poor monsoon. The groundwater resources in India have not been fully exploited and attempts are underway to explore the full potential of subsurface waters. At this juncture, it was thought apt to study, using radioactive tracers, the hydrogeological properties of the surface and subsurface waters of the Indian subcontinent. In this chapter, I describe in brief the development of man's knowledge on the groundwater resources and subsurface water characteristics.

Groundwater resources were exploited as early as 3000 B.C. In the ancient books of Hindu Philosophy, Rigveda, Yajurveda and Atharvaveda, mention is made of wells, canals and other groundwater reservoirs. Similar citations have also been made in Old Testaments.

Subsurface hydrology attained scientific status after the European Renaissance through the work of Leonardo da Vinci and Bernard Palissy. During the 18th century, a geological basis was provided for understanding the occurrence and movement of groundwaters. The interrelationship between surface water and groundwater was better understood during the dawn of the 19th century.

The first attempt to tap water by drilling a well was done in 1872 in U.S.A. and since then large number of artesian and subartesian wells have been constructed in U.S.A. and France (KAZAMANN, 1972). Though the first tube-well in India was drilled as early as 1895, a scientific assessment of the groundwater potential of the country was not undertaken until a few years ago. Wells were constructed on the basis of the recommendations of the water diviners and this practice continues even today in some parts of the country. Though the construction of tube-wells in Uttar Pradesh was started in 1930, this programme was expanded considerably only around 1936. The Geological Survey of India undertook a systematic study of mapping groundwater reservoirs in the country soon after the Independence. In addition to GSI, such studies are also being carried out by other organisations such as Central Ground Water Board, Exploratory Tubewell Organisation, and United Nations Development Project (Report of Irrigation Commission, 1972).

The increasing demands for water due to the growth in population and industries continue to accelerate the innovation of new technologies to tap more and more groundwater resources. These explorations are being carried out in all climatic regions but more so in arid and semi-arid areas where there is a scarcity **of** water. These developments require detailed knowledge of the abundance, origin, velocity, and recharge rate of groundwater as well as the porosity, permeability of the aquifer through which it flows.

The conventional tracers used for studying the properties of groundwater are dyes, chemical and biological tracers and surfactants (TODD, 1959 ; KNUTSSON, 1968 ; GASPAR and ONCESCU, 1972). The usefulness of these tracers is limited because of their interaction with the geological formation they traverse and the problems associated with their detection at low concentration levels. Hence a better understanding of the hydrological properties of the groundwater systems had to wait till the radioactive tracers were made use of. The radioactive time clocks have found applications in all facets of Hydrology. (For review see IAEA 1962, 1964, 1967, 1970, 1974; VOGEL, 1970; GASPAR and ONCESCU, 1972; BARC Rep. 1974, BAHADUR, 1974).

At present a number of isotope techniques exist for studying the various short and long term hydrological processess. Properties like the rate of recharge and the "age" of water masses can now be precisely determined using radioisotopes as tracers. The usefulness of a given isotope to study a particular problem is governed by its half-life, chemical behaviour in the hydrological system, and the ease with which it can be measured. A list of radioactive isotopes which are commonly used in hydrology is given in Table-I.1.

The water entering an aquifer carries with it radioactive atoms either as components of water molecules or as dissolved matter. If there is no further source or sink for these radioactive atoms in the aquifer, the radioactivity of the water (and of the dissolved matter) decreases with time according to the well known exponential law of radioactive decay. The age of water mass is estimated from the ratio of the concentration of the particular isotope in the aquifer to that in source water. The ages are calculated assuming that the aquifer behaves as a "closed" system and also that the concentration of ^{32}Si in the source water at the time of its entry into the aquifer is the same as that of the present day rains.

Further it is necessary to invoke simplified groundwater models which take into consideration the aquifer characteristics, the rate of recharge, the internal mixing of the water body within the aquifer and the relation between the recharge and the discharge rates to estimate

TABLE-I.1

LIST OF RADIOISOTOPES USED IN HYDROLOGICAL STUDIES*

Radio-nuclide.	Half-life.	Source	Principal mode of decay.	Applications.	References.
$^{24}Na_{11}$	15.02 h	Cosmic Ray interactions.	β^-, γ	Short term processes in limnology.	IAEA(1964)
$^{82}Br_{35}$	35.40 h	Reactors.	β^-, γ	Short term processes for surface water studies.	Rao *et al.*,(1968) IAEA (1968) Iya *et al.*,(1971)
$^{222}Rn_{86}$	3.82 d	Lithosphere from Radium decay.	α	Sand movement and bed load material studies.	IAEA (1968)
$^{131}I_{53}$	8.04 d	Nuclear detonations.	β^-, γ	Short term processes in surface waters.	Bahadur (1973) IAEA (1968).
$^{32}P_{15}$	14.3 d	Cosmic ray interactions. Nuclear detonations.	β^-	Velocity and direction of groundwater flow.	Hazzaa (1970)

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Radio-nuclide.	Half-life.	Source.	Principal mode of decay.	Applications.	References.
${}^{51}\mathrm{Cr}_{24}$	27.71 d	Reactors.	γ	Bed load transport of sand.	IAEA (1968) Bahadur (1973)
${}^{22}\mathrm{Na}_{11}$	2.60 y	Cosmic ray interactions; Nuclear detonations.	β^{+}, γ	Lake Hydrology.	IAEA (1964).
${}^{55}\mathrm{Fe}_{26}$	2.70 y	Nuclear detonations.	X-ray	Dating lake sediments.	Krishnaswami et al.,(1971).
${}^{85}\mathrm{Kr}_{36}$	10.73 y	Nuclear detonations.	β^{-}, γ	Dating groundwaters.	IAEA (1970).
${}^{3}\mathrm{H}_{1}$	12.33 y	Cosmic ray interactions; Nuclear detonations.	β^{-}	Dating groundwaters. Hydrological characteristics and recharging rate studies.	Begemann(1957), Eriksson(1961) Nir (1964) Sukhija(1972)
${}^{210}\mathrm{Pb}_{82}$	22.03 y	Introduced due to Radon decay.	β^{-}	Lake geochronology.	Krishnaswami et al., (1971).

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Radio-nuclide.	Half-life.	Source.	Principal mode of decay.	Applications.	References.
$^{137}Cs_{55}$	30.1 y	Nuclear detonations.	β^-, γ	Soil moisture studies.	IAEA (1968)
$^{39}Ar_{18}$	269 y	Cosmic ray interactions.	β^-	Dating groundwaters.	Loosli and Wiest (1973) Oeshger *et al.*, (1974).
$^{32}Si_{14}$	280 y	Cosmic ray interactions. Nuclear detonations.	β^-	Dating groundwaters.	Nijampurkar *et al.*, (1966) Lal *et al.*, (1970).
$^{226}Ra_{88}$	1600 y	^{238}U decay	α	Limnological and Hydrological studies.	IAEA (1968).
$^{14}C_{6}$	5730 y	Cosmic ray interactions. Nuclear detonations.	β^-	Dating groundwaters.	Munnich(1957) Vogel (1963) Lal *et al.*, (1970).

* Nuclear properties have been compiled from LEDERER *et al.*, (1967) and Chart of nuclides, General Electric Company, April, 1972.

the ages. NIR (1964) proposed two models, the 'Piston Model' and the 'Steady State Model' with a view to estimate the velocities of groundwater movement using tritium as a tracer. Similar models were later used by LAL et al.,(1970) for estimation of groundwater ages using ^{32}Si and ^{14}C. The various assumptions for these models and their implications are discussed in detail in chapter-IV.

I have considered three naturally produced isotopes ^{3}H, ^{32}Si and ^{14}C for hydrological studies in this thesis. All these isotopes ^{3}H ($t_{\frac{1}{2}} = 12.3$ y, $E_{max} = 18$ keV), ^{32}Si ($t_{\frac{1}{2}} = 500$ y, $E_{max} = 0.21$ MeV) and ^{14}C ($t_{\frac{1}{2}} = 5730$ y, $E_{max} = 156$ keV) are produced in the upper atmosphere by the cosmic ray interaction with different nuclei. Tritium, an isotope of hydrogen, is an ideal tracer for studying the groundwater characteristics since it follows the motion of water molecules in the aquifer system. The first application of ^{3}H for dating of groundwaters was made by BEGEMANN and LIBBY (1957). Since then considerable amount of work using ^{3}H for hydrological studies have been reported (ERIKSSON, 1958,1961 ; NIR, 1964 ; MUNNICH et al.,1967; SUKHIJA,1972 ; DATTA et al., 1973). The age of groundwater is estimated from the ratio of the measured specific activity $^{3}H/H$) in subsurface water to that in the source water, in the present case,rainwater (SUKHIJA,1972).This method is applicable only for samples younger than about 100 years due to the short half-life of ^{3}H.

The second isotope used in the present investigation is ^{14}C. Carbon-14, a beta emitter, is produced in the atmosphere by the interaction of cosmic ray neutrons with nitrogen nuclei; $^{14}N\,(n,p)^{14}C$ and gets oxidised to $^{14}CO_2$. Thus the atmospheric CO_2 and biogenic material are tagged with cosmic ray produced ^{14}C. The rain water that enters the soil has a very small amount of atmospheric CO_2 dissolved in it since the partial pressure of CO_2 in the atmosphere is very low. But the partial pressure of CO_2 arising from the decay of organic matter and root respiration in the upper few metres of soil is comparatively high and fairly large amounts of CO_2 of biogenic origin can be dissolved in infiltrating water.

The method of radiocarbon dating of groundwater was developed (MUNNICH, 1957) and applied in detail for waters of ages between 1000-30,000 years (LELAND and RUBIN, 1961 ; HANSHAW et al., 1965; LAL et al., 1970). Similar to the tritium technique the ages of groundwaters are estimated by comparison of $^{14}C/^{12}C$ ratio in the source and that measured in groundwater samples. In the ^{14}C method there is a possibility of additional loss of ^{14}C from the water due to chemical exchange (VOGEL,1970). Thus in the ^{14}C method of dating groundwaters, the assumption that the decrease in ^{14}C activity in the aquifer is only due to radioactive decay may not be valid in many cases and the system may be "open" for

^{14}C atoms. In fresh groundwaters, (those in which bomb ^{3}H was observed) ^{14}C levels are found to be (85 ± 5%) of the modern biogenic level (VOGEL, 1970). Because of this, there is an uncertainty in the "zero age" specific activity of ^{14}C, which amounts to an error of about 1000 years on the estimated age (MUNNICH and ROETHER, 1963 ; VOGEL and EHHALT, 1963 ; MUNNICH et al., 1967). Hence for samples younger than 2000 years the estimated ages by ^{14}C method may be unreliable. ^{14}C method is useful for dating waters which are older than about 2000 years. Recently water samples as old as 40,000 years have been dated by this method (LELAND et al., 1961; HANSHAW et al., 1965 ; GUPTA and NIJAMPURKAR, 1974).

Nuclear weapons testing has introduced into earth's atmosphere considerable amounts of ^{3}H and ^{14}C which could introduce uncertainties in the estimation of groundwater ages. ^{32}Si is also produced due to testing of nuclear weapons but its contribution is not significant for dating older water masses. Although the artificial injection of these isotopes has disturbed the equillibrium, one takes advantage of the resulting "spikes" to study water movements (SUKHIJA, 1972 ; GUPTA and NIJAMPURKAR, 1974).

When the present investigation started there was no suitable radioactive method for estimating the ages of groundwaters in the time bracket of 100-2000 years.

To surmount this difficult LAL (1964) suggested the use of two cosmic ray produced isotopes ^{32}Si (half-life = 500 years) and ^{39}Ar (half-life = 270 years). The usefulness of both these isotopes in various reservoirs of earth sciences, oceanography and glaciology have already been explored (LAL, 1962, 1969; LAL et al., 1974 ; SOMAYAJULU et al., 1973; CLAUSEN, 1973 ;LOOSLI, 1973 ; OESCHGER, 1974).

Although ^{39}Ar is a "conservative" tracer due to its suitable nuclear and chemical properties, its application to hydrological problems is still in its infancy (LOOSLI, 1973), mainly because of technological problems involved in its collection from large volumes of groundwaters and its assay. As a competing candidate, the potentiality of ^{32}Si as a tracer nuclide for estimating the ages and other hydrological properties of subsurface waters have been evaluated in this thesis.

Silicon-32, a beta emitter, (E_{max} = 0.21 MeV) is produced in the atmosphere by the interaction of cosmic ray particles with argon. ^{32}Si thus produced gets oxidised to SiO_2 and is transported to the earth's surface probably as monomeric silicic acid, H_4SiO_4, by rain (KRAUSKOFF, 1959; KHARKAR et al., 1966). The $H_4{}^{32}SiO_4$ enters the groundwater by downward movement of rain and surface waters.

The single great advantage of using ^{32}Si in hydrology, lies in the fact that it has an appropriate half-life of the order of 500 y which is ideal for dating water masses which are old enough to be completely devoid of any tritium but, are young enough not to be datable with precision by ^{14}C measurements. The presence of ^{32}Si in groundwaters by itself is an important information since it implies that the waters are not older than about 1500-2000 years, a span of time which is of importance in deciding the usefulness of a given groundwater reservoir.

However, at the outset, one is presented with a few problems in using ^{32}Si for dating water masses. These are :

(i) the half-life of ^{32}Si is not yet accurately known. The reported values range between 140-700 y (SCHINK, 1968) LINDNER (1953) estimated the half-life of ^{32}Si to be 710 y assuming that the cross section for the reactions $^{37}\mathrm{Cl}\,(p,\alpha 2pn)\,^{31}\mathrm{Si}$ and $^{37}\mathrm{Cl}\,(p,\alpha 2p)\,^{32}\mathrm{Si}$ are same. However, later experiments by RUDSTAM *et al.*, (1952) showed that the ratio was 0.2 for similar reactions in iron which would estimate the half-life of ^{32}Si to be 140 y GEITHOFF (1962) and JANTSCH (1967) estimated the half-life of ^{32}Si to be 650 y and 280 y respectively based on the assumption that the reactions $^{26}\mathrm{Mg}\,(t,p)\,^{28}\mathrm{Mg}$ and $^{30}\mathrm{Si}(t,p)\,^{32}\mathrm{Si}$ have the same cross section. Recently independent estimate of half-life of ^{32}Si was made to be 330 y by CLAUSEN (1974) by measuring ^{32}Si activities in dated firn cores.

Due to these uncertainties in the reported values of the half-life of ^{32}Si, two working values 500 and 300 y have been adopted in this thesis.

(ii) the concentration of ^{32}Si is low in geophysical reservoirs because its atmospheric production is low, 1.7×10^{-4} atoms/cm^2.sec. (LAL and PETERS, 1962). Because of this low production rate the ^{32}Si concentrations in natural waters are also expected to be small, $<$ 0.5 dpm/ton. The concentration of stable silica (SiO_2) in surface and sub-surface waters range from 5-50 ppm. Such large concentrations of stable silica in these water samples coupled with the low production rate of ^{32}Si in atmosphere makes the specific activity of ^{32}Si ($^{32}Si/SiO_2$) in natural waters very low, 0-50 dpm/kg SiO_2 (except in rain water) thereby making direct measurement of ^{32}Si difficult. Hence, the measurement of ^{32}Si has to depend on the assay of its radioactive daughter product. ^{32}Si decays to ^{32}P, a beta emitter (half-life = 14.3 days), which can be counted using low background beta counters.

(iii) the geochemical behaviour of silicon is not properly understood and it is difficult to check on the loss if any, of ^{32}Si activity other than by radioactive decay in surface and subsurface waters. This is important since the application of ^{32}Si in hydrology is based on the measurements of its absolute concentration (dpm/ton of water) in groundwaters unlike the other two naturally produced cosmic ray isotopes ^{3}H and ^{14}C , whose application involves comparing changes in the specific activities (^{3}H/H, ^{14}C/^{12}C ratios) in different geophysical reservoirs.

Several procedures and techniques were developed and modified during the course of this work to overcome some of the above problems. These include :

(i) the collection and processing of large quantities of waters (5-30 tons) at the site, in specially fabricated PVC portable (swimming pool type) tanks.

(ii) the separation of ^{32}P from large amounts of silica (100-400 g) by distilling it as SiF_4, a new distillation set up was designed and successfully used.

(iii) the assay of beta activity of ^{32}P by low background 2π and 4π sensitive flow type beta counters.

(iv) the study of geochemical behaviour of ^{32}Si present in natural waters.

With the help of these techniques and experiments, fairly extensive measurements of ^{32}Si concentrations in wet precipitations, melt-waters, streams, rivers, lakes and subsurface waters were carried out in various geological environments, particularly in arid and semi-arid regions of Indian subcontinent.

The experimental methods of analysis, results of the measurements of ^{32}Si concentrations in natural waters, and the implications of these measurements are discussed separately in the following chapters. The implications of these measurements for understanding the fallout pattern of ^{32}Si, its hydrogeochemistry and its usefulness as a hydrological tracer are discussed in chapter-IV. The estimated "ages" are intercompared with those obtained using ^{3}H and ^{14}C.

CHAPTER-II

SAMPLING LOCATIONS, EXPERIMENTAL PROCEDURES AND TECHNIQUES

The sampling procedures and experimental techniques employed for the measurement of ^{32}Si concentrations in water masses are discussed in this chapter. The estimation of the "ages" of subsurface waters by ^{32}Si method requires a knowledge of the ^{32}Si concentrations in rains, surface waters which feed deep seated aquifers and in groundwaters. In addition to ^{32}Si, ^{14}C and ^{3}H were also measured in many samples with a view to intercompare the "ages". The methods employed for the measurement of the isotopes, ^{14}C and ^{3}H are also presented here.

The concentration of ^{32}Si in natural waters is low, of the order of 0.1 dpm/ton, because of its low production rate in the atmosphere. Such low concentrations necessitate the collection and processing of large volume of water, in the range of 5-30 tons to obtain clear signals of ^{32}Si. The direct measurement of ^{32}Si from natural waters is difficult because of its extremely low specific activity, $^{32}Si/SiO_2$ $\sim$ 0.01 dpm/g coupled with the low energy of ^{32}Si betas (E_{max} = 0.21 MeV). Hence, ^{32}Si is measured by milking its short lived radioactive daughter ^{32}P (half-life=14.3 days). Quick and quantitative techniques were developed towards the separation and assay of ^{32}P from large quantities of SiO_2, (100-300 gms) during the course of this investigation. These are discussed in detail in the following sections.

II.1. Criteria for the selection of regions and locations for ^{32}Si measurements.

The sampling locations were selected depending on the type of water sample to be analysed. For fallout measurements, the stations were chosen in such a way that they would give a wide latitudinal coverage. Surface water samples were collected from a few major rivers and lakes of India. Each river was sampled at two locations, one near the source and the other near the mouth. These samplings were undertaken mainly with a view to understand the interaction of ^{32}Si with various geological formations and also to study its geochemical behaviour in surface waters. Similar studies were carried out in the Kashmir Valley, where melt waters were sampled. A large number of subsurface water samples were selected from Rajasthan and Gujarat to study the recharge rates of groundwater. This information is badly needed in these regions because there is a scarcity of fresh water supplies in summer months following a rapid fall of the water table.

The details of the various sampling locations are given below.

II.1.a Stations for fallout studies :

To understand the fallout pattern of ^{32}Si and its average concentration in rainwaters, six stations were set up in India at different latitudes (10°-32°N). Geographical locations and rainfall data for these stations are given in Table-II.1 and Fig.II.1. From Bombay and Khandala, where the rainfall is high, 3-4 samples were collected per year. Only one sample per year could be collected at Pathankot, Ludhiyana, Gwalior and Kodaikanal. The samples were collected at Bombay and Khandala during the years 1961-71 to study the annual fluctuations in the fallout of ^{32}Si. At all other locations analyses were carried out for 2-3 years during 1961-71. In addition to ^{32}Si, the concentrations of a suite of cosmic ray produced and artificially injected radioisotopes, ^{7}Be, ^{35}S, ^{22}Na, ^{32}P were also monitored in these waters during 1962-71. (BHANDARI, 1965 ; LAL *et al*., 1974).

II.1.b Sampling locations for surface water studies :

The measurement of ^{32}Si in surface waters was undertaken to study the variations incurred during their traverse on different geological terrains as well as the possible depletion brought about by biological scavenging of silica. The concentrations of ^{32}Si were measured in Himalayan streams and lakes which are the feed waters to River Jhelum. The

TABLE-II.1

SAMPLING STATIONS FOR FALLOUT STUDIES

Station	Code	Latitude (N)	Longitude (E)	Average annual* rainfall(cm).
Kodaikanal	KO	10° 14'	77° 28'	110
Khandala	KH	18° 47'	73° 25'	450
Bombay	BM	18° 54'	72° 49'	210
Gwalior	GW	26° 14'	78° 15'	87
Ludhiyana	LDH	30° 56'	75° 52'	70
Pathankot	PTK	32° 14'	75° 38'	90

* Average for the years 1958-1973.

Fig.II.1 Map showing stations selected for sampling rain water.

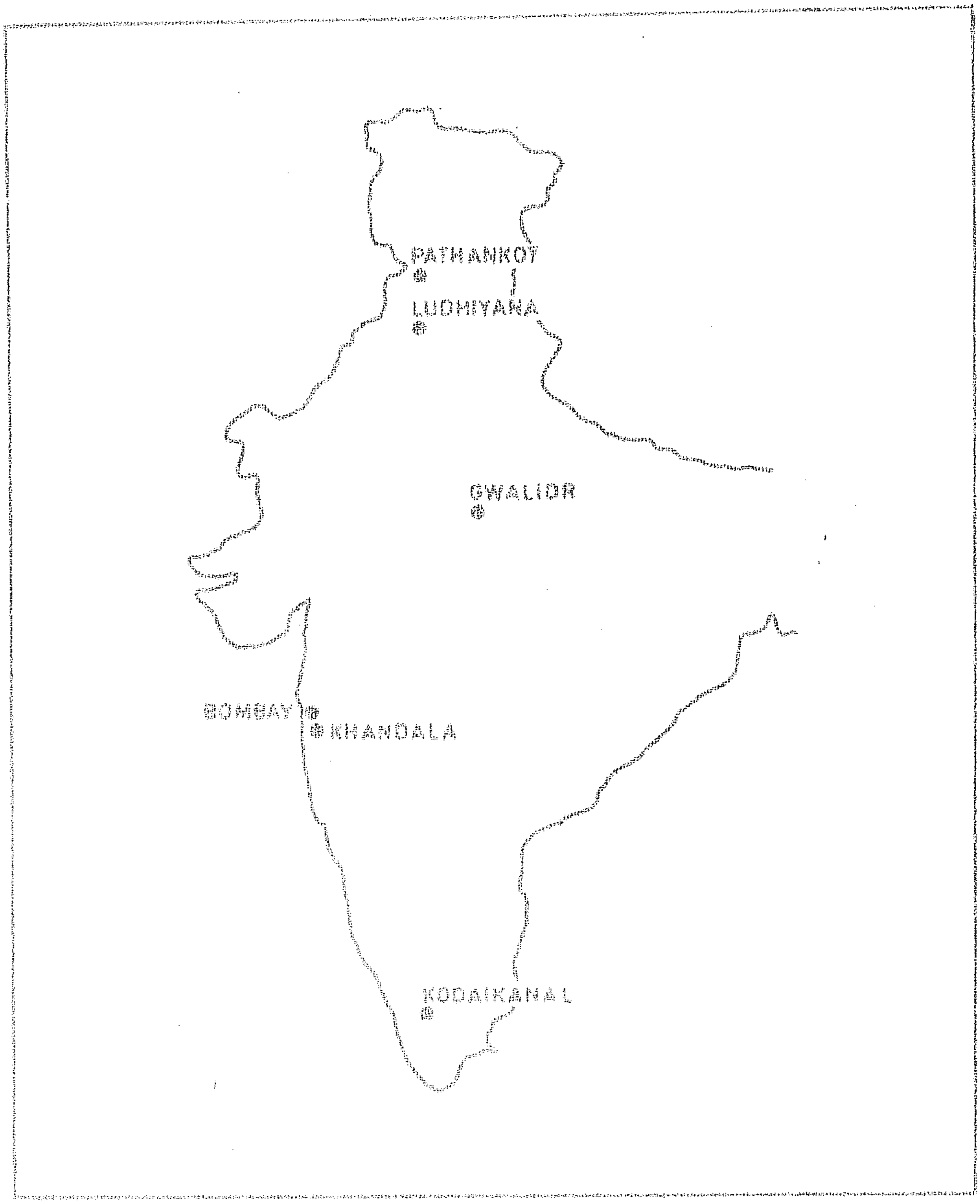


FIG. II.1

location selected for this study was the Kashmir Valley (Fig.II.2). This area was an ideal sampling site since (i) all the hydrological reservoirs, snow, streams, rivers and lakes, were easily accessible for sampling and (ii) suitable experimental facilities were available in this region from the High Altitude Research Laboratory situated about 2.6 km above mean sea level at Gulmarg. It was convenient to collect water samples from high altitudes (1.4 - 4.0 km) by camping at Gulmarg. About a dozen representative samples of meltwater, streams, brooks, lake and river were analysed for their ^{32}Si concentrations. Details of sampling locations are given in Table-II.2, Fig.II.2.

The surface waters traversing north and south of Jhelum river flow on altogether different geological formations. The Pir panjal range covering Kashmir Valley is predominantly of volcanic origin. The terraces that are less than 1000 m above the present level of the valley are fossil-lake shores accumulated during the Pleistocene. They consist mainly of limestone debris, lava and volcanic tuff. The range to the north of the valley of Kashmir is mainly dolomite (KRISHNAN, 1968).

The sample collection in the Kashmir valley was done in two expeditions, first in 1967 by Dr.S.Aegerter (who collected about 30% of the samples) and later in 1972

TABLE-II.2

* SURFACE SAMPLES COLLECTED FROM KASHMIR VALLEY FOR ^{32}Si MEASUREMENTS

Code.	Date of collection.	Altitude* (km)	Details of the sample and its location.
KAS- 3	14-8-67	4.0	Melt water; slopes of Aparvath range.
KAS- 2	13-7-67	3.7	Stream: 1.5 km down hill from KAS-3.
KAS- 6	28-6-72	3.7	Stream: 1.5 km down hill from KAS-3. Collected near Kilenmerg resthouse.
KAS- 4	17-8-67	3.0	Stream: 3 km down hill from KAS-2 in Pine forest.
KAS-11	22-7-72	2.7	Stream: 1.5 to 2.5 km below the glacial mountains and craggy peaks; collected at Sonamerg.
KAS- 1	12-8-67	2.7	Stream: representative mixture of mountain springs feeding Wular lake and Jhelum river.
KAS-13	31-7-72	2.4	Brook water: 0.4 km below KAS-1, collected near Babarishi Temple.
KAS-10	19-7-72	2.2	Stream: 1.4 km down hill of Chandanwari; collected near Pahalgan Club.
KAS- 9	12-7-72	2.1	Nala: Sample of Ferozpore Nala at Tangmarg.
KAS- 8	06-7-72	1.4	Lake: Wular lake water near Watlab.
KAS- 7	04-7-72	1.4	Lake: Wular lake water near Ningli.
KAS- 5	19-8-67	1.4	River: Jhelum water down stream of Wular lake.

* Above mean sea level.

Fig.II.2 Sampling locations for surface waters from Kashmir Valley.

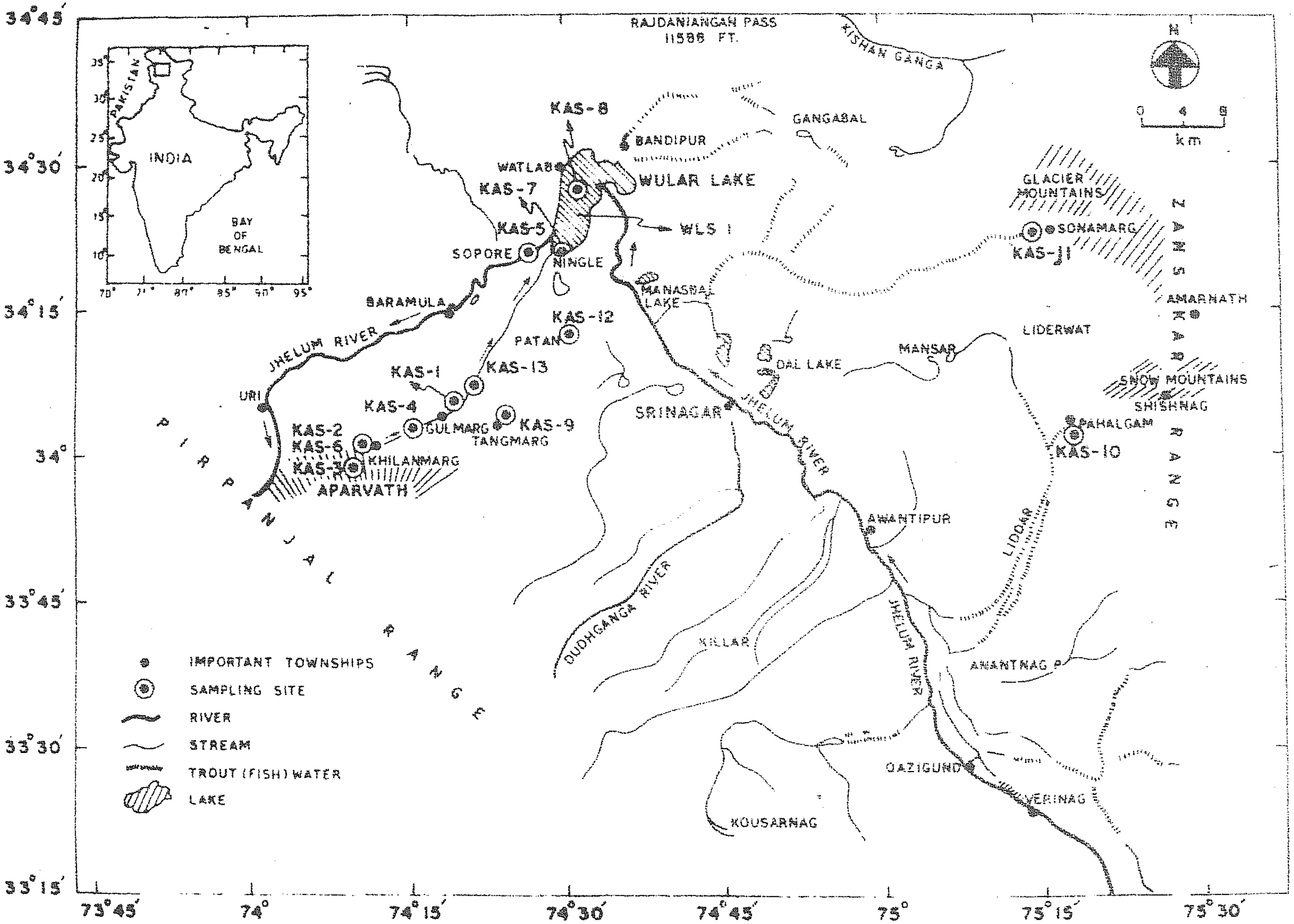

34°45'
34°30'
34°15'
34°
33°45'
33°30'
33°15'
73°45'
74°
74°15'
74°30'
74°45'
75°
75°15'
75°30'
RAJDANIANGAN PASS
11588 FT.
KISHAN GANGA
N
0
4
8
km
PAKISTAN
INDIA
BAY OF BENGAL
KAS-8
BANDIPUR
GANGABAL
WATLAB
WULAR LAKE
KAS-7
KAS-5
WLS 1
SOPORE
NINGLE
GLACIER MOUNTAINS
SONAMARG
KAS-11
ZANSKAR RANGE
AMARNATH
BARAMULA
MANASBAL LAKE
KAS-12
PATAN
LIDERWAT
MANSAR
DAL LAKE
JHELUM RIVER
KAS-1
KAS-13
SNOW MOUNTAINS
SHISHNAG
URI
KAS-4
KAS-2
KAS-6
KAS-3
GULMARG
TANGMARG
KAS-9
SRINAGAR
PAHALGAM
KAS-10
KHILANMARG
APARVATH
PIR PANJAL RANGE
AWANTIPUR
LIDDAR
DUDHGANGA RIVER
KILLAR
IMPORTANT TOWNSHIPS
SAMPLING SITE
RIVER
STREAM
TROUT (FISH) WATER
LAKE
ANANTNAG
QAZIGUND
VERINAG
KOUSARNAG

FIG.II.2

by the author. The latter expedition was planned, based on the results of the first expedition.

In addition to samples from Kashmir Valley, surface water samples from Ganges and Godavari rivers and Tansa lake were also analysed. The sampling of the rivers was done at different locations along their course to study the variation of ^{32}Si concentration during their flow through various geological formations. The periodic sampling of Tansa lake waters were carried out to study the precipitation loss (Biological or Inorganic) of ^{32}Si from the water column. The details of the samples are given in Table-II.3 and locations are given in Fig.II.3.

II.1.c Sampling locations for subsurface water studies from different geological environments.

II.1.c.(i) Shallow well samples tapping unconfined aquifers.

A few shallow subsurface well samples (open and dug wells) of depths less than about 40 m from unconfined aquifers of different geological environments were collected and analysed for their ^{32}Si concentrations. The samples were collected to study the geochemical behaviour of ^{32}Si during its vertical percolation from surface waters. Sampling locations and other relevant details of these samples are given in Table-II.4.

TABLE-II.3

RELEVANT DETAILS OF LAKE AND RIVER WATER SAMPLES

Code.	Location (State)	Latitude. (N)	Longitude. (E)	Type of Sample.	Date of collection.
MH-3	Tansa (Maharashtra)	19° 35'	73° 15'	Tap Water.	5-4-63
MH-4		"	"	Lake	31-5-63
MH-5		"	"	Tap Water	14-6-63
MH-6		"	"	Lake	15-5-68
MH-7		"	"	Lake	18-4-72
UP-5	**Hardwar** (Uttar Pradesh)	29° 57'	78° 12'	River(Ganges)	1-3-64
UP-6	Allahabad (Uttar Pradesh)	25° 27'	81° 44'	River(Ganges)	12-3-64
MH-8	Nasik (Maharashtra)	19° 59'	73° 38'	River(Godavari)	26-5-64
AP-1	Rajahmundry (Andhra Pradesh)	16° 58'	81° 50'	River(Godavari)	20-1-64

Fig.II.3 Map showing sampling locations for surface waters. Geological terrains through which the principal rivers flow are also shown.

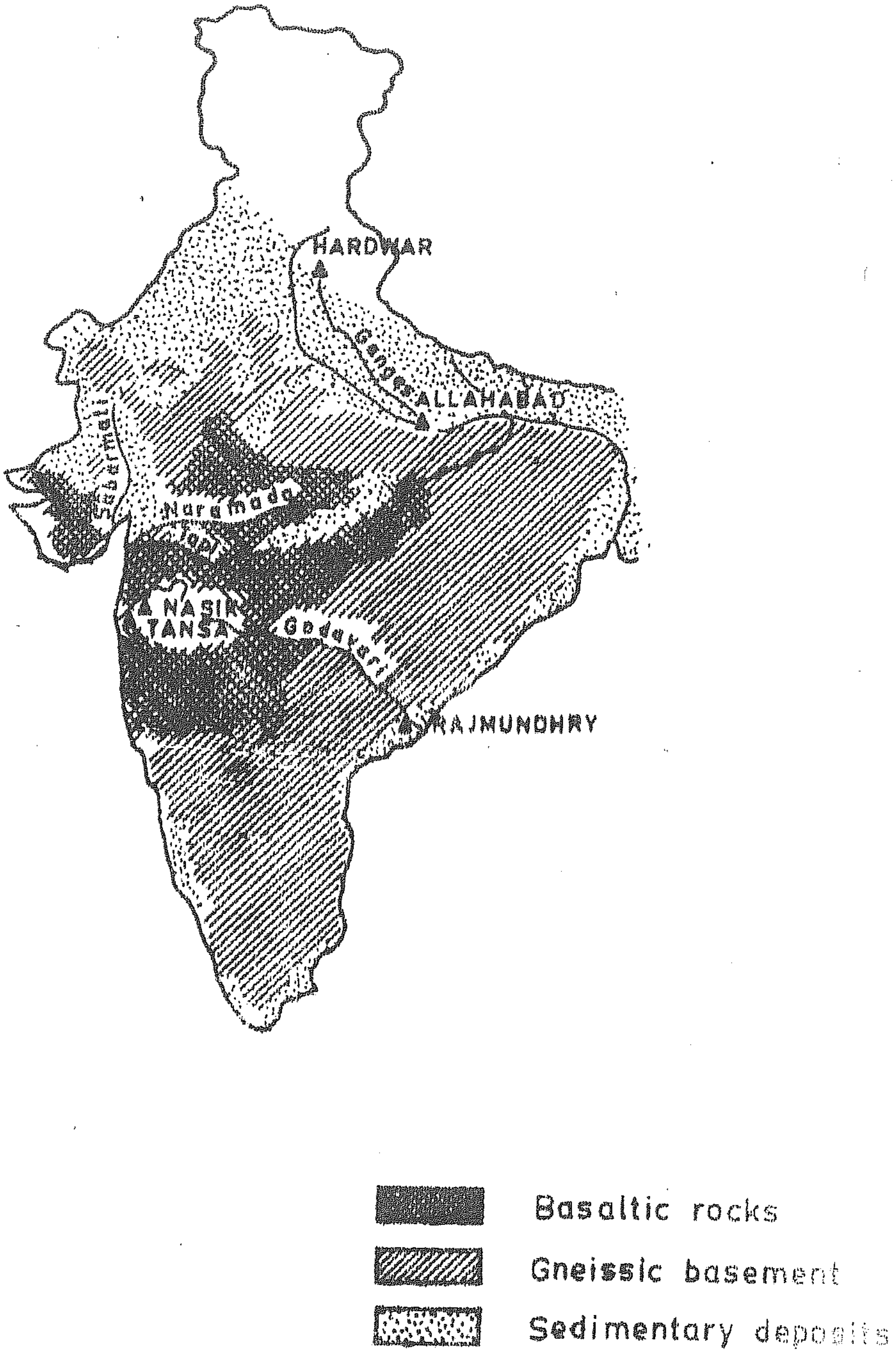

HARDWAR
Ganges
ALLAHABAD
Sabarmati
Naramada
Tapi
NASIK
TANSA
Godavari
RAJMUNDHRY
Basaltic rocks
Gneissic basement
Sedimentary deposits

FIG.II.3

TABLE-II.4

SAMPLES COLLECTED FROM UNCONFINED AQUIFERS

Code.	Location(State) Latitude. (N) Longitude. (E)	Well Type.	Date of collection.	Sampling depth(m).
KAS-12	Patan(Kashmir) 34° 10', 70° 30'	Dug-well	25-7-72	11-15
P - 2	Ropar(Punjab) 30° 58', 76° 32'	Open-well	28-3-66	23-30
RJ -12	Niraun(Rajasthan) 26° 48', 71° 28'	Dug -well	25-2-70	38-43
GJ - 1	Deesa(Gujarat) 24° 12', 72° 12'	Dug -well	17-6-68	15
GJ - 2	Cheriwad(Gujarat) 23° 50', 73° 01'	Tube-well	8-6-68	33
GJ - 3	Vijapur(Gujarat) 23° 27', 72° 48'	Tube-well	2-12-63	40
GJ - 4	Balad(Gujarat) 23° 48', 72° 45'	Tube-well	11-6-63	65
MH - 1	Mulund(Maharashtra) 19° 10', 72° 51'	Tube-well	19-5-68	33
MH - 2	Ville Parle (Maharashtra) 19° 07', 72° 51'	Open-well	21-11-63	15

II.1.c.(ii) Samples from the confined aquifers of Rajasthan.

Ground water samples from the arid deserts of Western Rajasthan were collected. The mean annual rainfall over this area is less than 30 cms and drops to about 15 cms in the western part. During exceptional drought years the rainfall is less than 5 cms. Hence, in this region, one has to depend on the deep underground reservoirs for water. The aquifer characteristics of this area were studied in detail because of the large dependence on meagre ground water resources for water supply.

Western Rajasthan is characterised by large areas covered with wind blown sand. The granitic and metamorphic rocks below the sandstones contain small quantities of water along prominent joints. Much of the groundwater is probably retained in the blown sands and alluvium (ACHUTHA RAO, 1971). The water table in this region lies around 30 m and over large areas it occurs below 65 m.

The relevant details of the sampling sites selected are given in Table-II.5 and Fig.II.3. The depths of the tubewells selected for ^{32}Si and ^{14}C analysis range between 73-288 m (Table-II.5). It is known from geological data (ACHUTHA RAO, 1968) and the water contour maps that the groundwater flow in the sample area is expected to be towards N.E. and S.W. of the line joining Devikot and Niraun(Fig.II.3).

TABLE - II.5

TUBEWELL WATER SAMPLES COLLECTED FROM CONFINED AQUIFERS OF RAJASTHAN

Code.	Site.	Location		Depth.	Date of collection.
		Latitude. (N)	Longitude. (E)	(m)	
RJ- 1	Bikaner	28° 01'	73° 18'	100	19-12-65
RJ- 2	Palna	27° 49'	73° 15'	168	29-12-65
RJ- 3	Lathi	27° 03'	71° 31'	190	14-11-64
RJ- 4	Dabla	26° 51'	71° 05'	220	11-11-64
RJ- 5	Chandan	26° 59'	71° 18'	288	10- 2-70
RJ- 6	Bhairwa	26° 55'	71° 17'	73-127	20- 2-70
RJ- 7	Bhairwa	"	"	135-165	22- 2-70
RJ- 8	Bhairwa	"	"	198-220	18- 2-70
RJ- 9	Devikot	26° 42'	71° 10'	132	24-2- 70
RJ-10	Ajasar	27° 15'	71° 43'	167	02- 3-70
RJ-11	Chandan	26° 59'	71° 18'	33	14- 2-70
RJ-13	Palna	27° 49'	73° 15'	120	25-12-65

Fig. II.4 Hydrological Map of arid region of Western Rajasthan showing sampling locations for subsurface waters for ^{32}Si and ^{14}C measurements. The proposed Rajasthan Canal is also shown.

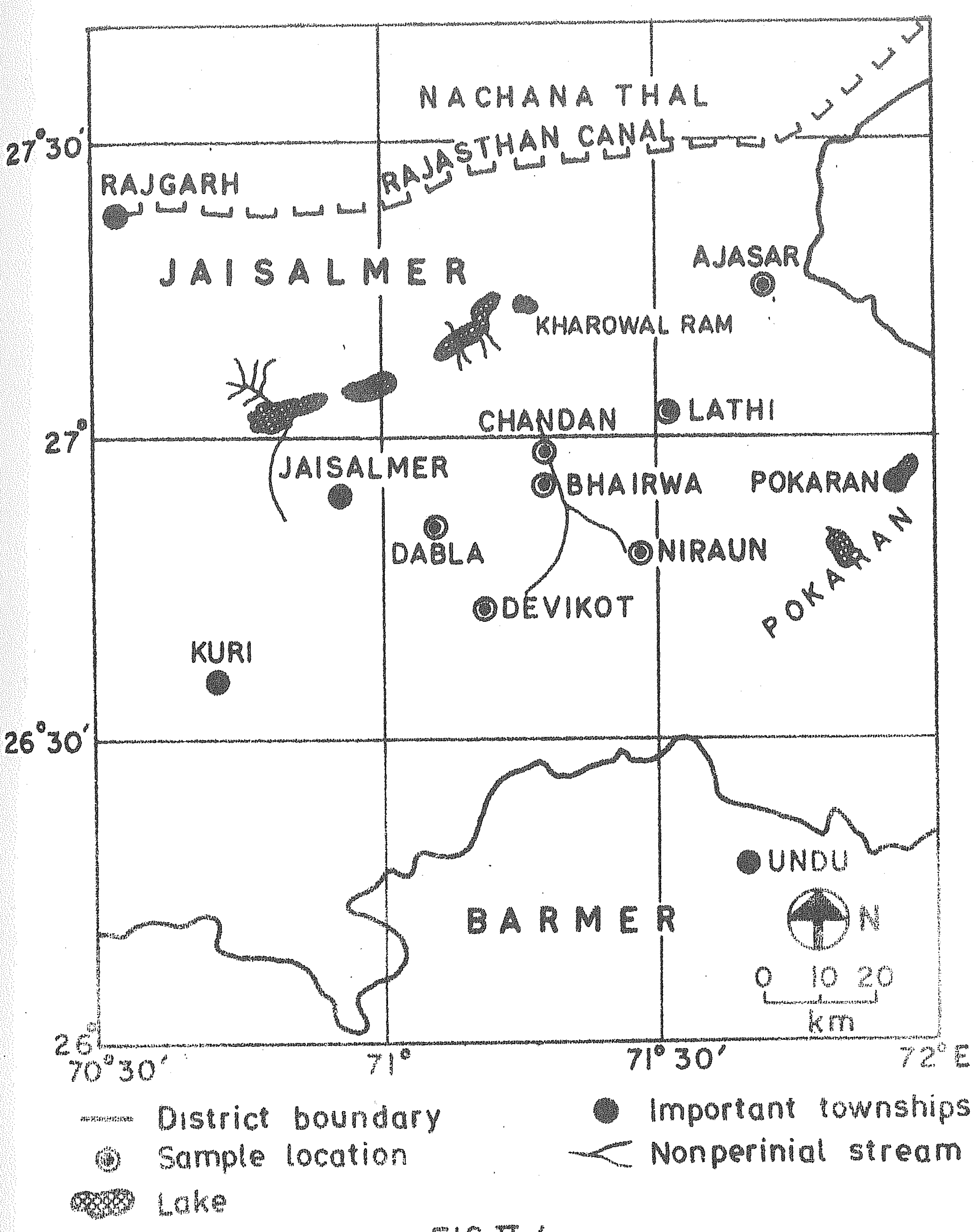

NACHANA THAL
RAJASTHAN CANAL
27°30′
RAJGARH
JAISALMER
AJASAR
KHAROWAL RAM
LATHI
CHANDAN
27°
JAISALMER
BHAIRWA
POKARAN
DABLA
NIRAUN
POKARAN
DEVIKOT
KURI
26°30′
UNDU
BARMER
N
0 10 20
km
26°
70°30′
71°
71°30′
72° E
District boundary
Sample location
Lake
Important townships
Nonperinial stream

FIG. II.4

In case of Bhairwa and Ajasar (Table-II.5) water samples from individual aquifers were collected (since these wells were in development stage) which give significant information regarding the "age" of water in individual aquifer, the continuity of the aquifers and possible vertical leakage of water from one aquifer to another.

II.1.c.(iii) Samples from confined and unconfined aquifers of semi-arid region of Gujarat.

As in the case of the arid regions of Rajasthan, the scarcity of potable water in the semi-arid regions of Gujarat State was the main criterion for studying this region. In particular, Mehsana district was selected for sampling because of rapid depletion of water level from year to year.

The mean annual rainfall over the area is about 70 cm and varies from 20 cm in north-west part to about 150 cm in south eastern part. The rainfall varies considerably from place to place and it increses from north to south. Nearly 25% of the surface area in this region is covered by alluvial tracts. The major rivers flowing through the alluvial tracts are Banas, Sabarmati, Mahi, Narmada and Tapi (Fig.II.3 and Fig.II.5). Most of the samples collected for the present investigation are along Sabarmati. This river flows through the middle of alluvial tracts and discharges in the Gulf of Cambay (Fig.II.3,5).

It is known that the occurrence of groundwater is most common in alluvial deposits. Within alluvium groundwater occurs in unconfined aquifers in the upper strata and under artesian pressure in the lower confined aquifers. Unconfined aquifers are composed of sand, silt and generally lie within 50 metres below the surface. The confined aquifers occur at two distinct depths, between 50-100 metres and 300-700 metres. The deeper aquifers contain coarse sand in northeast and fine medium sand in southwest.

In most of the regions, characterised by unconfined aquifers, the water table varies from 5-10 metres. The water tables as well as the piezometric levels indicate slope from N.E. to S.W.(along the grid line G_1, G_2, Fig.II.4) around which most of the samples have been collected. From the study of water tables and piezometric levels in this region it was suggested by SHAH (1969) that upper unconfined aquifers and lower confined aquifers may be interconnected. The sand aquifers form about 12% of the total strata. Most of the rivers, including Sabarmati, are effluent and hence precipitation plays a major role in recharge.

The upper unconfined aquifers are recharged by vertical infiltration followed by percolation. Since the confined aquifers are irregular and possibly connected to upper unconfined aquifers, the latter may contribute to recharge of the confined aquifers. Confined aquifers as shown by water contour maps have recharge area in the foot hills in the northeast.

The characteristics of groundwater collected along its hydraulic gradient (line G_1,G_2, Fig.II.5) are compared with those obtained recently by conventional methods (SHAH and PATEL, 1974). The relevant details of the sampling locations are given in Table.II.6.

II.1.c.(iv) Samples tapping confined aquifers of Neyveli Lignite Fields:

The high piezometric surface in the lignite fields of Neyveli (lying in an interfluvial zone between Gadilan river and Manimukta river, South Arcot district of Tamil Nadu), is a danger to the open shaft mining of lignite. Pumping has to be maintained round the clock to keep the water level well below the main lignite seams in the mine area (BARATAN and SUBRAMANYAM, 1969). The aim of sampling this region was to study the rate of groundwater movement from the surrounding regions to lignite mining area. With this view samples were collected adjacent to both the recharge area and the mines. The relevant details of the sampling locations are given in Table-II.7 (Fig.II.6).

Fig.II.5 Hydrological map of semi-arid region of Gujarat selected for groundwater studies. The hydraulic gradient line G_1 G_2 shows the direction of groundwater movement along which most of the samples are collected.

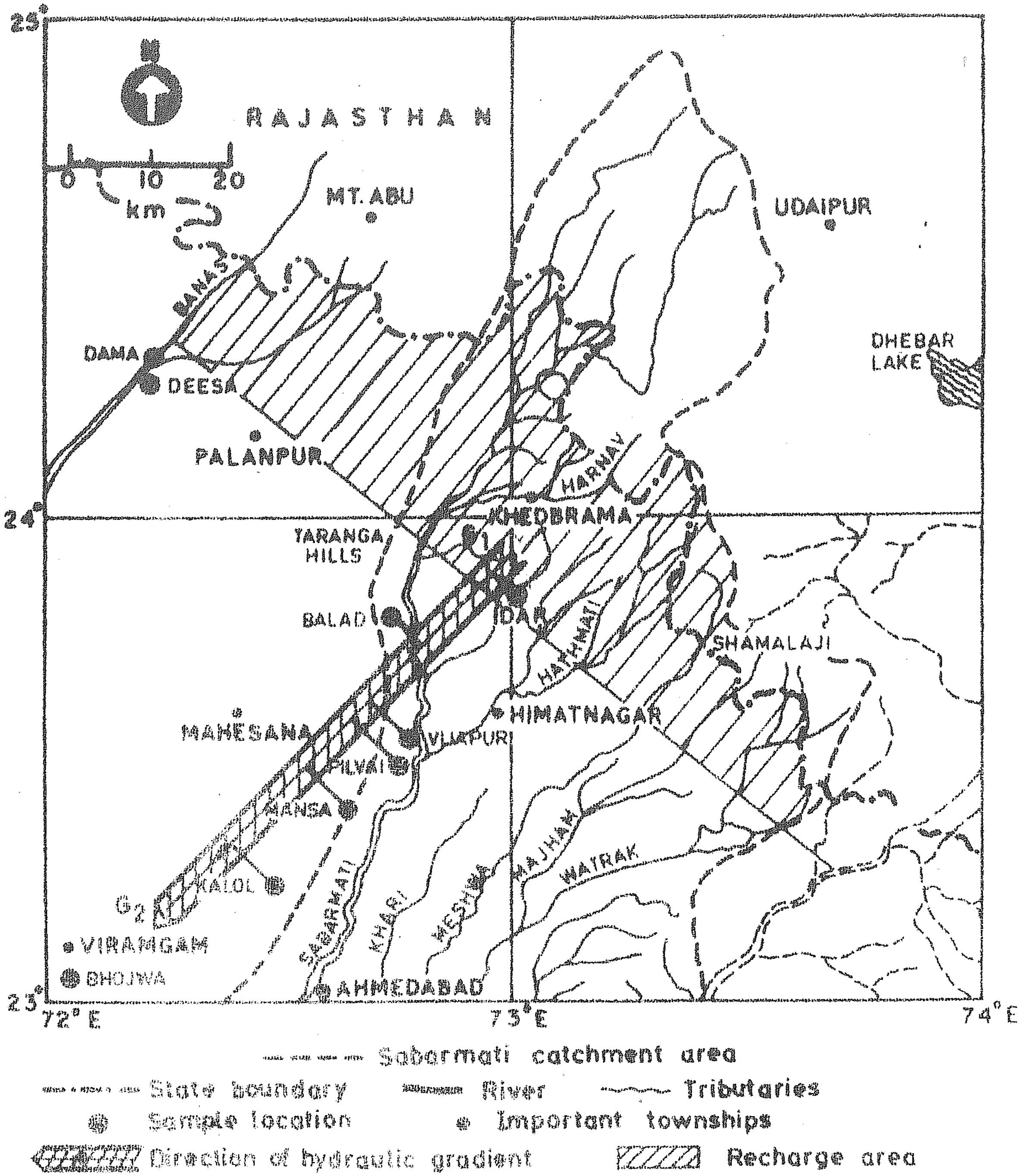

25°
24°
23°
72° E
73° E
74° E
N
0
10
20
km
RAJASTHAN
MT. ABU
UDAIPUR
DHEBAR LAKE
BANAS
DAMA
DEESA
PALANPUR
HARNAV
KHEDBRAMA
TARANGA HILLS
BALAD
IDAR
HATHMATI
SHAMALAJI
HIMATNAGAR
MAHESANA
VIJAPUR
PILVAI
MANSA
KALOL
G2
VIRAMGAM
BHOJWA
SABARMATI
KHARI
MESHWA
MAJHAM
WATRAK
AHMEDABAD
Sabarmati catchment area
State boundary
River
Tributaries
Sample location
Important townships
Direction of hydraulic gradient
Recharge area

FIG.II.5

TABLE-II.6

SUBSURFACE WATER SAMPLES COLLECTED FROM CONFINED AQUIFERS OF THE SEMI-ARID REGION OF GUJARAT

Code.	Site.	Location Latitude. (N)	 Longitude. (E)	Sample Depth (m)	Date of collection.
GJ- 5	Vijapur	23° 33'	72° 45'	116	7-1-66
GJ- 6	Dama	24° 11'	72° 23'	123	13-6-68
GJ- 7	Mansa	23° 21'	72° 45'	130	29-5-68
GJ- 8	Pilvai	23° 25'	72° 47'	133	27-5-68
GJ- 9	Pilvai	23° 25'	72° 47'	140	6-12-63
GJ-10	Kalol	23° 09'	72° 33'	185	23-5-68
GJ-11	Bhojwa	23° 04'	72° 03'	266	2-6-68

II.1.C(v) Miscellaneous samples from other geological environments:

In addition to detailed sampling of groundwaters from the above three regions in India, several samples from various geological formations were collected and details of these samples are given in Table-II.7 (See Fig.II.6).

II.2. Procedures for sample collection:

The sample collection methods for ^{32}Si measurements are similar for all samples. The volume of water collected ranged between 5-30 tons depending on the nature of the sample; 5-10 tons in case of rainwater and 20-30 tons in case of groundwater.

Generally, water samples were collected in portable swimming-pool type plastic tanks of 5-8 tons capacity. These tanks were supported either by stable framework of canduit pipes or fitted in a cement tank. In some cases, the plastic tanks were substituted with a large number of 220 litre capacity drums with plastic liners.

Prior to the sample collection the tanks were cleaned with 1:1 hydrochloric acid followed by distilled water. Since the rainwater samples were collected over

Fig. II.6 Map showing sampling locations for subsurface waters. Samples collected from arid and semi-arid regions of Western Rajasthan and Gujarat are shown separately in Fig. II.4 & Fig. II.5.

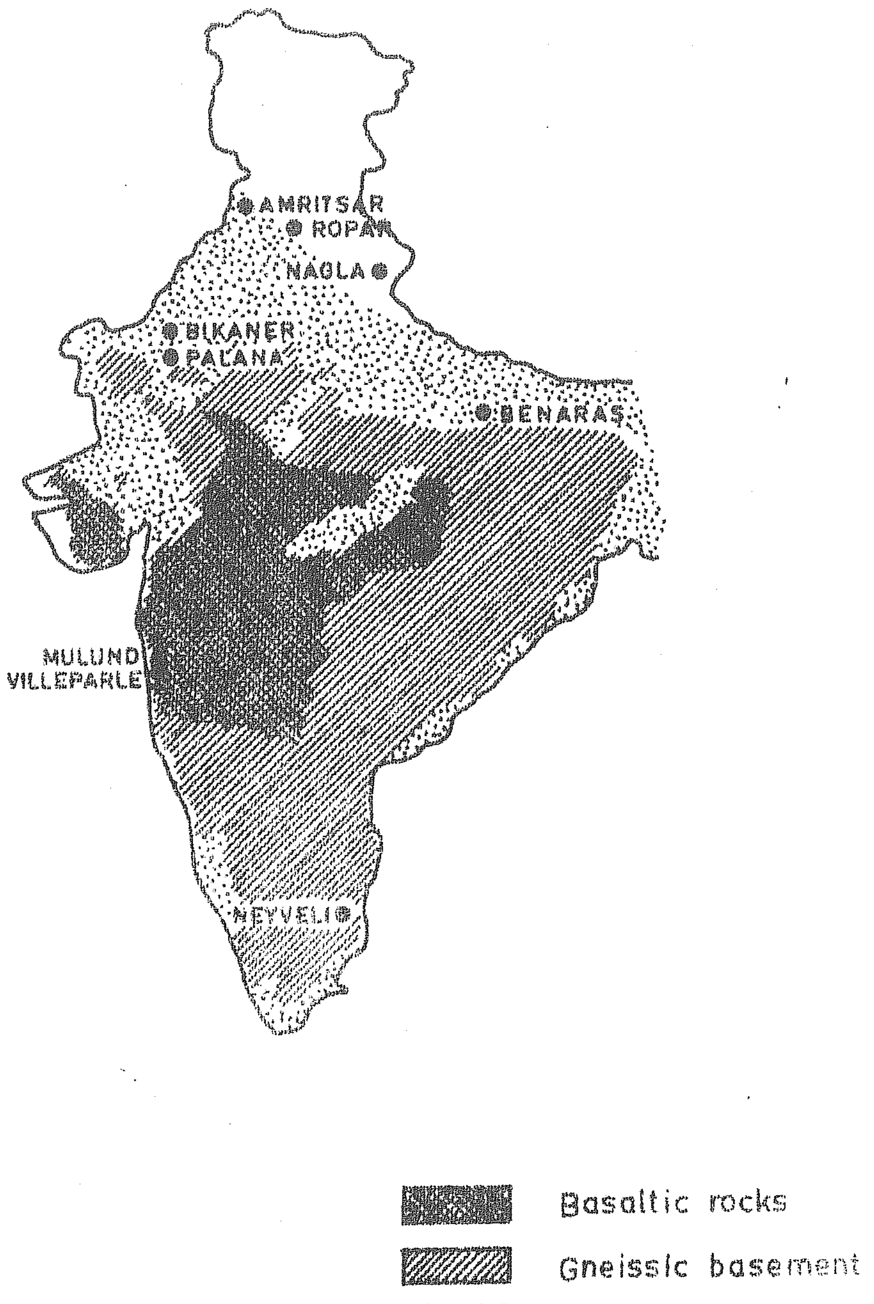

AMRITSAR
ROPAR
NAGLA
BIKANER
PALANA
BENARAS
MULUND
VILLEPARLE
NEYVELI
Basaltic rocks
Gneissic basement
Sedimentary deposits

FIG. II.6

TABLE-II.7

SUBSURFACE WATERS FROM DIFFERENT GEOLOGICAL FORMATIONS OF INDIA

Code*	Site	Depth (m)	Date of collection.
P-1	Amritsar	90	16-3-66
UP-1	Shankarpura	60	1-6-68
UP-2	Banaras	100	21-10-64
UP-3	Inchwal	225	10-6-68
UP-4	Nagla	300	3-6-68
TN-1	Neyveli-Post	131	13-6-68
TN-2	Neyveli-Yard	141	16-6-68
TN-3	Neyveli Bl-26	193	20-6-68

* P, UP and TN refer to Punjab, Uttar Pradesh and Tamil Nadu States respectively.

long period (2-10 weeks), there is a possibility of loss of water by evaporation. To estimate this correction, the rainfall at the sites were measured using rain gauge for the same period. The correction ranged between 5-40%.

Surface and subsurface water samples were collected either manually or using pumps directly into the plastic tanks spread at a convenient place near the sampling location.

II.3. Extraction and purification of silica.

Before the extraction of silica from the water samples an aliquot of about one litre of water was collected in clean plastic bottle and taken to laboratory for an accurate estimation of the stable silicon concentration. The measurement was done by spectrophotometric method(STRICKLAND and PARSONS, 1960). In addition, an approximate estimate of 'Si' content in the water samples was made at site by visual comparison of molybdenum blue colours with standards. Based on this estimate, additional silicon carrier was added if necessary. Generally, carriers equivalent to about 10 g SiO_2/ton were added to samples if their inherent concentration of silica was less than 5 ppm. Silicon carrier had to be added in rainwater samples since the stable 'Si' concentration was small, 0.2-1.2 ppm SiO_2 (Table-II.8). No carrier was added to most of the surface and subsurface waters where stable 'Si' concentrations were high, 5-50 ppm SiO_2. After the addition of carrier, the water sample was well stirred and allowed to equilibrate for 1-2 hrs. A second aliquot of the water sample was collected to check the total silica concentration (i.e. inherent + added carrier) of water. The efficiency of silica extraction was based on this measured total silica concentration in the water. The pH of the sample was brought down to about 3 by the addition of hydrochloric acid. Then ferric chloride equivalent to about 130 g Fe/ton was added to the water. The pH of the solution was raised to about 7 by adding liquor ammonia and the slurry was vigorously stirred. The precipitate of $Fe(OH)_3$ was allowed to settle for about an hour and excess of ammonia was added to raise the pH to about 10. The mixture was stirred well and allowed to settle a second time. A sample of supernatant water was collected for determination of stable silica. This value was used for the estimation of scavenging efficiencies. It was observed that by this two step addition of ammonia and vigorous mixing at intervals the precipitation efficiency could be raised to more than 80% (Table-II.9). The supernatant water was siphoned and $Fe(OH)_3$ slurry was transferred to perforated drums fitted with a filter cloth.

TABLE - II.8

SILICA CONCENTRATION IN RAIN WATERS

Station.	No. of samples.	SiO_2 concentration* (ppm)	
		Mean	Range
Kodaikanal	4	0.75	0.35 - 1.20
Khandala	12	0.32	0.10 - 0.70
Bombay	10	0.47	0.12 - 1.00
Gwalior	2	0.38	0.23 - 0.51
Ludhiyana	1	0.33	0.33
Pathankot	2	0.55	0.40 - 0.70

* Determined by spectrophotometric method (Section II.3)

TABLE -II.9

PRECIPITATION EFFICIENCY OF SILICA FROM NATURAL WATER SAMPLES

Location.	Nature of sample.	Silica concentration in water (ppm)		Efficiency for extraction of silica(%)
		Before precipitation.	After precipitation.	
Bombay	Rain	9.1	0.33	96
Ludhiyana	Rain	29.4	0.42	98
Khandala	Rain	9.1	1.30	85
Kilenmerg	Snow	9.4	0.36	97
Godavari	River	15.8	3.10	81
Tangmerg	Stream	4.1	0.07	98
Tansa	Lake	23.5	4.50	81
Wular	Lake	10.2	0.40	97
Deesa	Dugwell	36.0	8.00	78
Mansa	Tubewell	24.5	6.40	75
Chandan	Tubewell	17.0	3.50	80

This filtration was time consuming and took about 3 days to filter $Fe(OH)_3$ slurry obtained from 5-10 tons of water. Later by using filter bags made of felt cloth the filtration time was reduced to half a day to filter the $Fe(OH)_3$ recovered from about 20-30 tons of water. The $Fe(OH)_3$ was dried either on heaters or under the hot sun (especially in Rajasthan and some parts of Gujarat) and shipped to the laboratory for further processing.

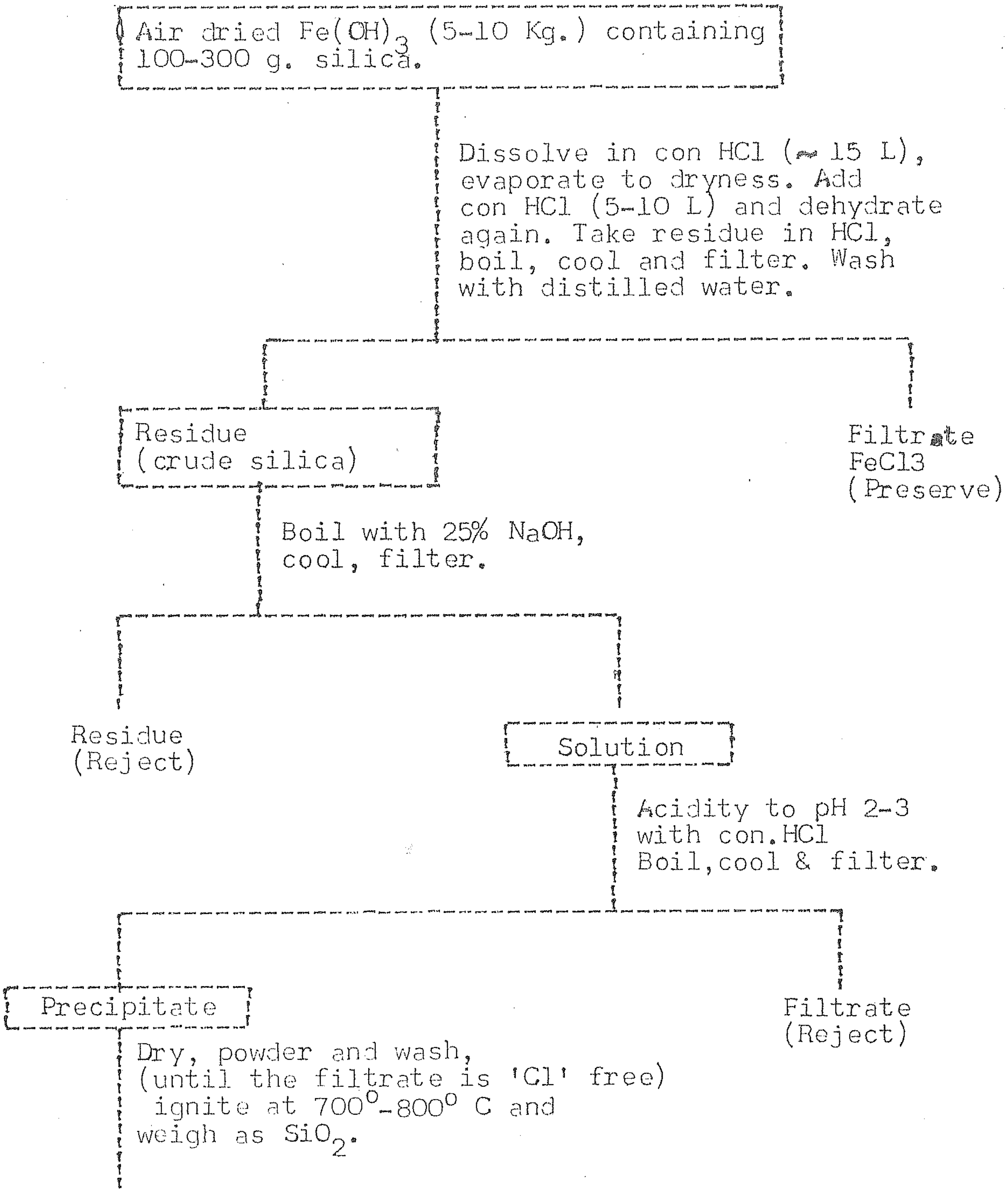
The extraction of silica from the $Fe(OH)_3$ matrix and its purification is shown schematically in Fig. II.7. The pure silica obtained was weighed and preserved in clean bottles for about 7-10 weeks for the growth of ^{32}P activity from ^{32}Si.

II.4. Extraction and radiochemical purification of ^{32}P.

II.4.a Precipitation method.

The procedures for extraction and radiochemical purification of ^{32}P from silica samples are given in detail (KHARKAR *et al.*, 1966 ; SOMAYAJULU, 1969). This method is ideal for samples of silica $\leq$ 100 gms and takes about 36 hours to complete extraction and purification of ^{32}P. In this work the silica recovered from surface and subsurface waters were in the range of 100-300 gms. Though a few surface and subsurface samples were milked by this method, for large silica samples ($>$ 100 gms) this method is laborious,

Fig. II.7 Flow chart showing extraction and purification of Silica from $Fe(OH)_3$.



Dissolve in con HCl (~ 15 L), evaporate to dryness. Add con HCl (5-10 L) and dehydrate again. Take residue in HCl, boil, cool and filter. Wash with distilled water.

Boil with 25% NaOH, cool, filter.

Acidity to pH 2-3 with con. HCl Boil, cool & filter.

Dry, powder and wash, (until the filtrate is 'Cl' free) ignite at 700°-800° C and weigh as SiO_2.

FIG. II.7

time consuming and inefficient. Hence, for separating ^{32}P from large quantities of silica the distillation of silica as SiF_4 was adopted. The technique similar to that discussed by MULLINS and LEDDICOTTE (1962) for small samples ($\lessdot$ 0.1 gm SiO_2) and was adopted in present studies with suitable modification to accommodate 300 g silica. This method is briefly discussed below.

II.4.b Distillation method.

In this method silica is distilled in the form of SiF_4 and phosphorus (^{32}P) is left behind in the distillation flask. The distillation set up is shown schematically in Fig. II.8. The distillation is carried out at 110°C. The silica sample is placed in a two litre silver (99.999% pure) flask. The capacity of the flask is sufficient for distilling silica samples of about 300 gms. Stable 'P' carrier in the form of NaH_2PO_4 (equivalent to 40-60 mg of $Mg_2P_2O_7$) was added along with HF. The quantity of HF added was in slight excess ($\sim$10%) of the stochiometric requirement to convert Si to SiF_4. The silver flask is then heated electrically using flask heaters. The temperature rose slowly to 110°C and remained constant during the conversion of Si to SiF_4. When all the 'Si' was distilled the temperature increased sharply. The distillation was stopped at this stage. The reactions

Fig. II.8 Schematic of 'Si' distillation apparatus for separation of ^{32}P from ^{32}Si. The trapped silica in the absorbers was recovered by adding excess NaOH.

A : Electrical heater
B : Long-neck silver distillation flask
C : Water condenser
E_1, E_2 : Thermometres
F_1, F_2 : Water absorbers.
F_3 : Alkali absorber
F_4 : Air trap.

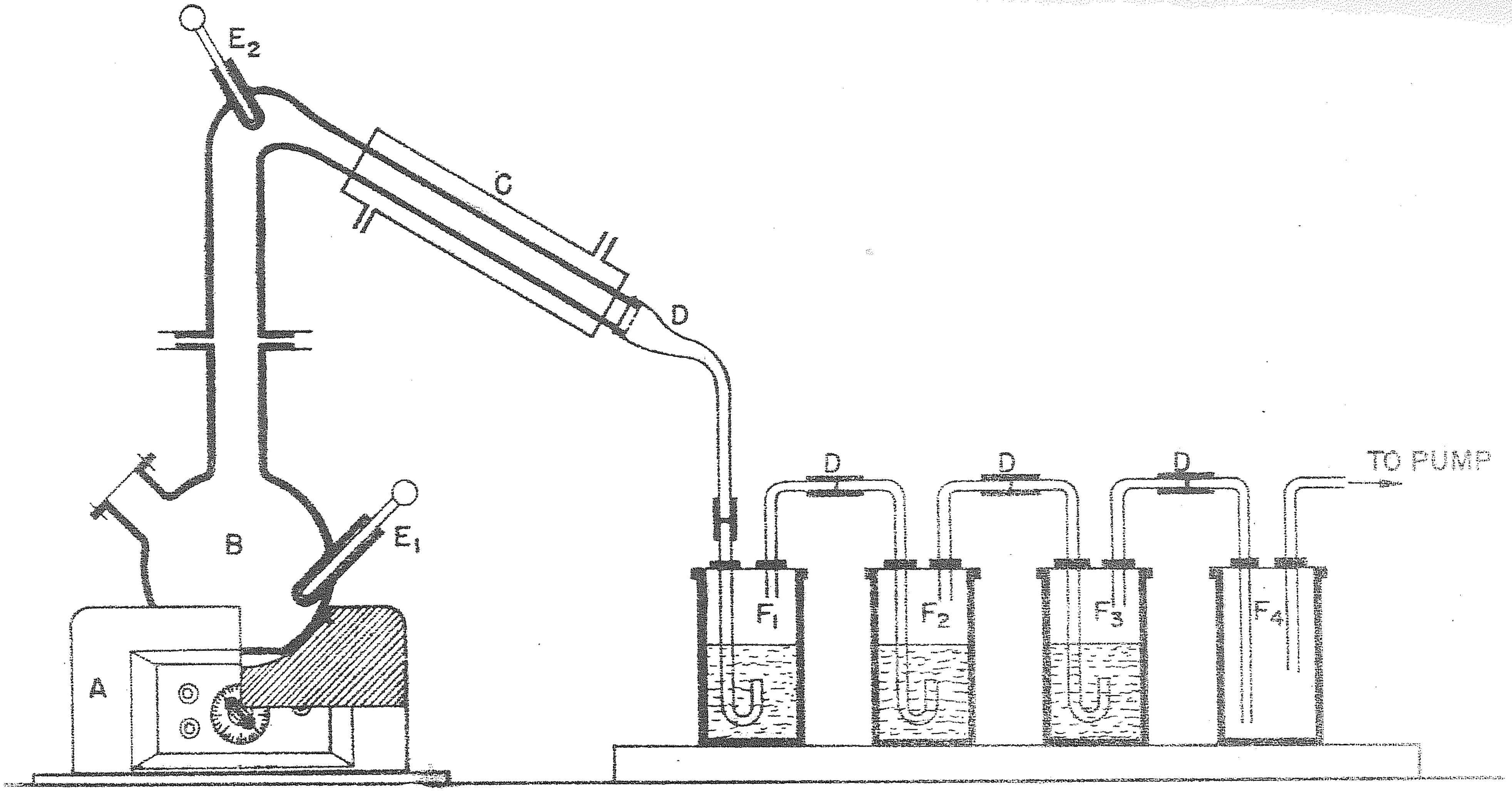


FIG.II.8

taking place in the distillation flask can be represented by the following equations:

$$SiO_2 + 4\ HF = SiF_4 + 2H_2O \quad \ldots\ldots \quad (2.1)$$

$$SiO_2 + 6\ HF = H_2SiF_6 + 2H_2O \quad \ldots\ldots \quad (2.2)$$

The distilled SiF_4 vapours were absorbed in a series of absorbers (Fig.II.6) for subsequent milkings. The first two absorbers (F_1 & F_2) contained distilled water (7 litres) where the SiF_4 gets hydrolysed to fluosilicic acid as represented by the equations:

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6 \quad \ldots. \quad (2.3)$$

$$SiF_4 + 2H_2O = 4HF + SiO_2 \quad \ldots. \quad (2.4)$$

The third absorber (F_3) contained 4M NaOH solution to remove traces of SiF_4 which might escape the water absorbers.

$$SiF_4 + 6NaOH = 4NaF + Na_2SiO_3 + 3H_2O \quad .. \quad (2.5)$$

The fourth absorber (F_4) is a trap to prevent any liquid from rushing into the pump. On an average, it takes about 8-10 hrs to distill about 300 gms of silica.

The residue in the silver flask (mainly the added phosphorus carrier) was dissolved in 1M hydrochloric acid. From the acid solution ^{32}P was radiochemically purified by the procedure previously published (KHARKAR et al., 1966; SOMAYAJULU, 1969). The chemical yield of ^{32}P by this method ranged between 60-95% compared to 50-90% obtained using the precipitation method (Fig. II.9).

Initially attempts were made to recover the silica by complexing flouride ions in the absorbers using H_3BO_3 or ammonia. Through these methods were simple the efficiency of silica recovery was only 60%. Hence, NaOH method was used to precipitate silica from fluosilicic acid solution through this was a time consuming procedure. This method gives better yields of about 80%.

$$H_2SiF_6 + 2NaOH = Na_2SiF_6 + 2H_2O \qquad \ldots. (2.6)$$

$$H_2SiF_6 + 6NaOH = 6NaF + SiO_2 + 4H_2O \qquad \ldots. (2.7)$$

The advantages of the distillation technique over the precipitation method for ^{32}P separation are :

(i) The separation of ^{32}P from large quantities of silica, about 300 g, can be carried out easily.

(ii) The time required for milking of ^{32}P is 1.2 days compared to 3-4 days by precipitation method. This increases the ^{32}P signal by about 10-15% at the time of first counting.

(iii) The chemical recovery of ^{32}P is high.

Fig.II.9 Frequency distribution of measured chemical efficiencies using the (a) precipitation method and the (b) distillation method.

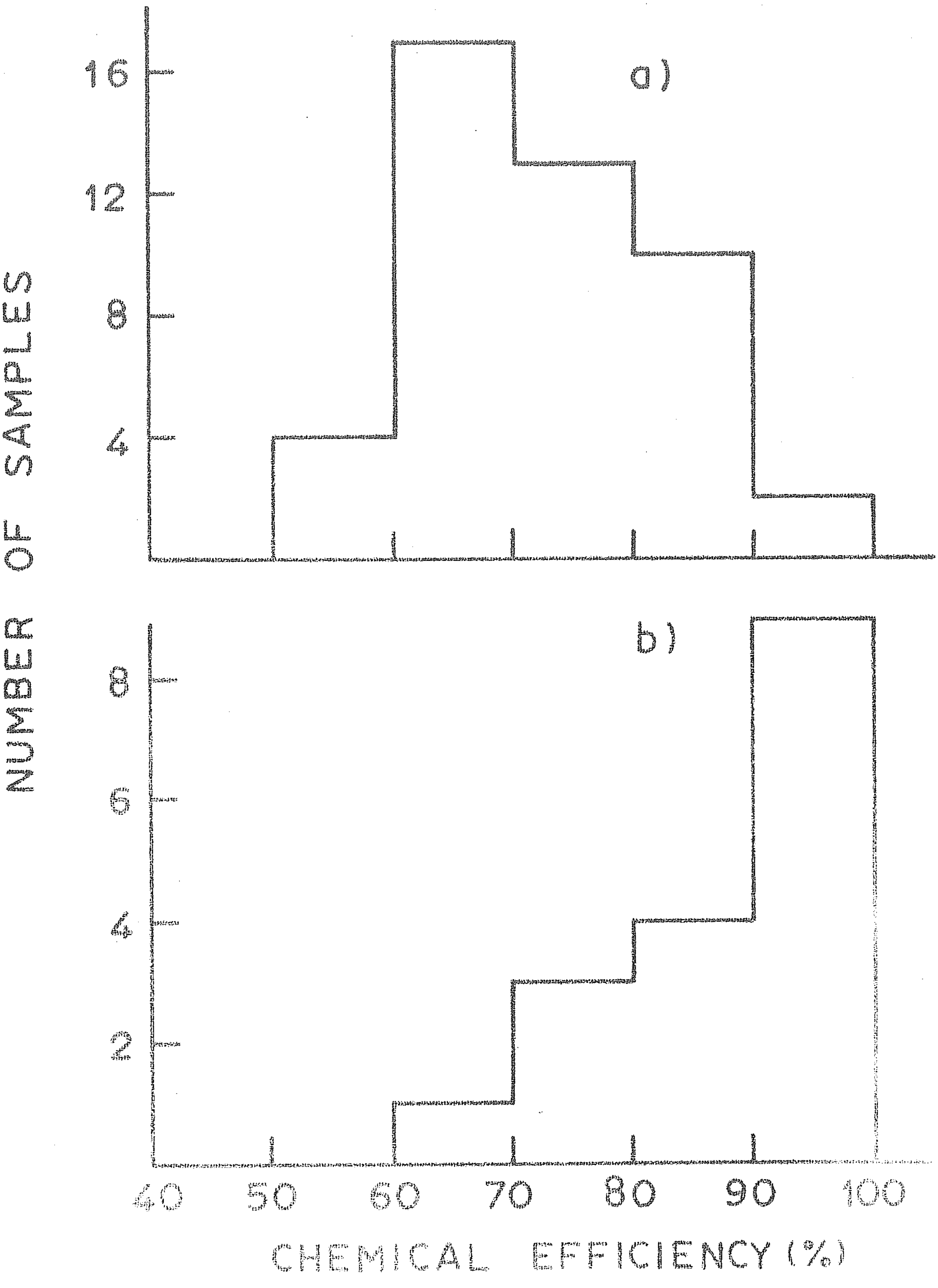

NUMBER OF SAMPLES
a)
16
12
8
4
b)
8
6
4
2
40
50
60
70
80
90
100
CHEMICAL EFFICIENCY (%)

FIG.II.9

The radiochemically purified ^{32}P was deposited on suitable holders (in the form of $Mg_2P_2O_7$). The samples were covered with a thin mylar film of 0.9 mg/cm^2 thickness. The activity of ^{32}P was assayed as described below.

II.5. Counting techniques for assaying ^{32}P activity.

During the initial phases of the work, the $Mg_2P_2O_7$ samples were deposited on copper holders (2.5 x 0.5 cm) and their activities were assayed using 2π low background gas flow geiger counters. The counting gas used was Q gas (98.7% Helium + 1.3% isobutane). The background of the counters were stable over long periods of time. During the years 1966-1970 the backgrounds were 2.3 and 2.2. Typical background data for the period 1966-1967 and 1971-72 are given in Fig.II.10(a) and Fig.II.10(b). However, towards the end of the work, 1972-73 the counter backgrounds reduced by about 30% probably due to the decay of long lived contamination present in the materials used for counter construction. The efficiency of the counters were estimated by counting natural KCl standards under the same conditions as that of the samples. The mean efficiency for the period 1966-73 for a weightless source of ^{40}K was estimated to be 33.7 ± 1.2 and 34.6 ± 1.5 respectively. The errors given represent one standard deviation in the efficiency. Frequent checks on the efficiency was made at regular intervals.

Fig.II.10(a) Background data for two 2π beta counters for the period 1966-1967.

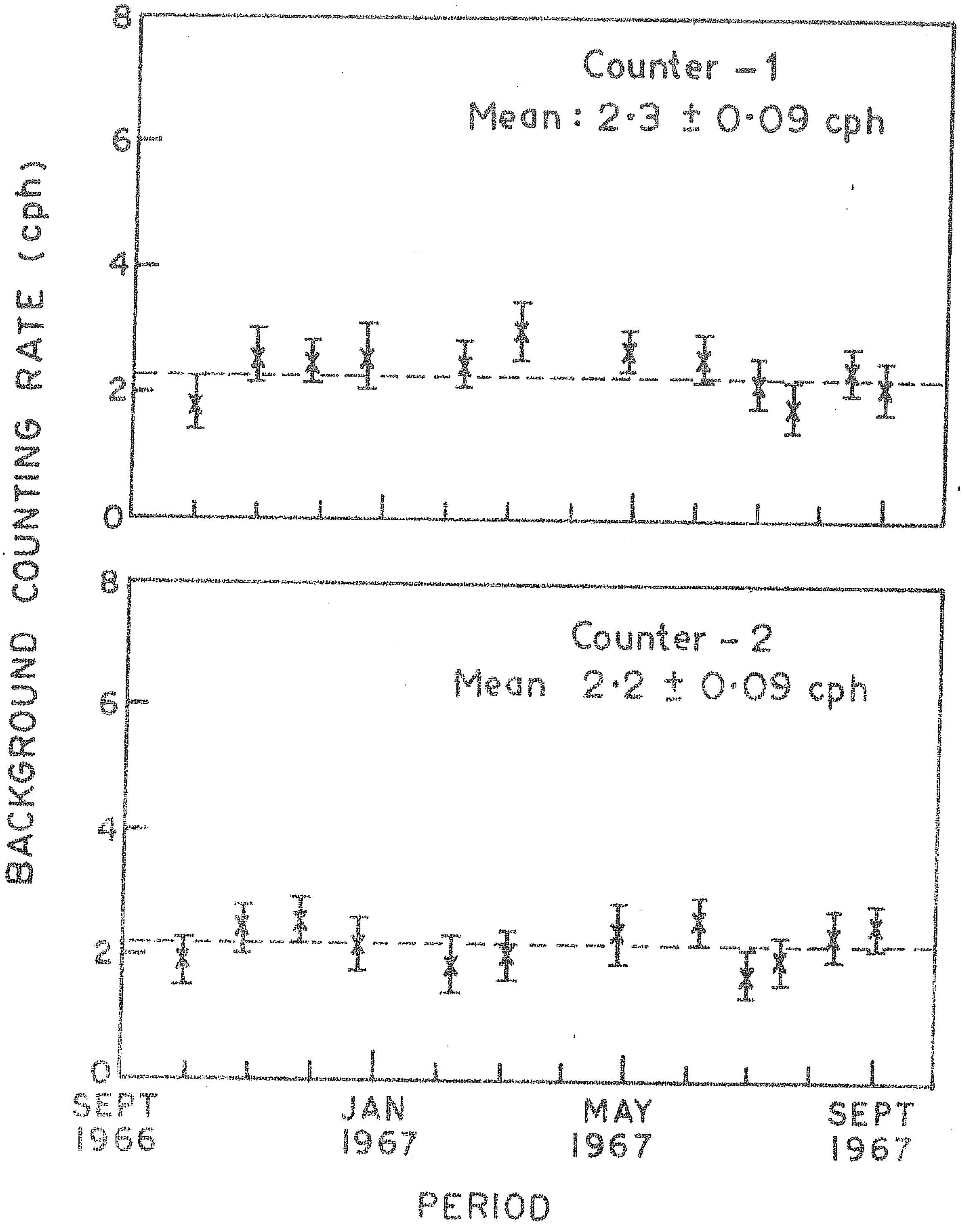

BACKGROUND COUNTING RATE (cph)
Counter -1
Mean : 2·3 ± 0·09 cph
Counter - 2
Mean 2·2 ± 0·09 cph
0
2
4
6
8
0
2
4
6
8
SEPT 1966
JAN 1967
MAY 1967
SEPT 1967
PERIOD

FIG. II.10 (a)

Fig.II.10(b) Background data for two 2π beta counters for the period 1971-1972.

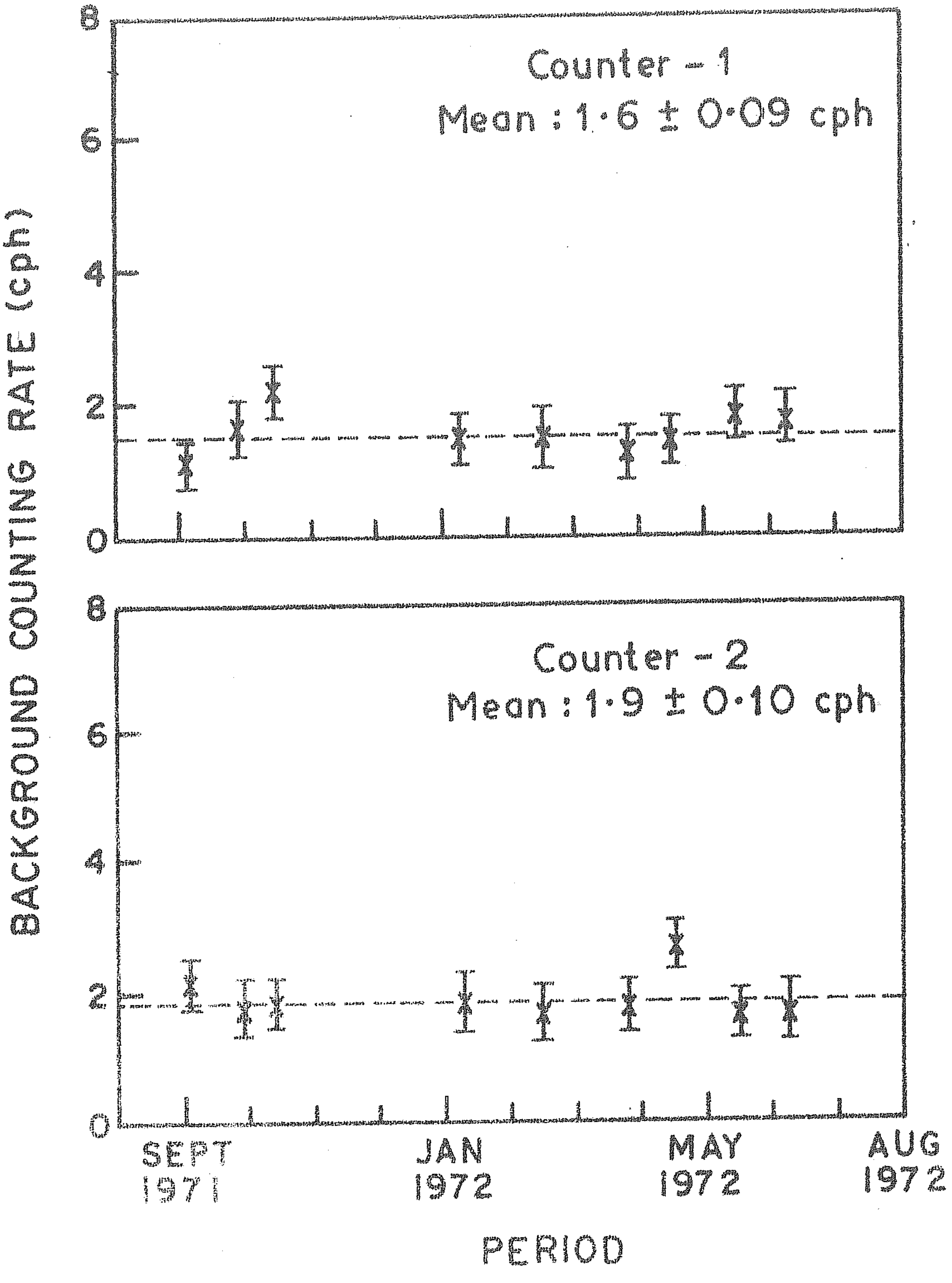

Counter - 1
Mean : 1·6 ± 0·09 cph
Counter - 2
Mean : 1·9 ± 0·10 cph
BACKGROUND COUNTING RATE (cph)
0
2
4
6
8
SEPT 1971
JAN 1972
MAY 1972
AUG 1972
PERIOD

FIG. II.10 (b)

TABLE - II.10

CHARACTERISTICS OF THE 2π AND 4π BETA COUNTING SYSTEMS.

Characteristics.	2π system		4π system		
	1	2	1	2	3
Operating Voltages*					
Beta - 1	1005	1035	975	975	1080
Beta - 2	-	-	975	975	1050
Background (counts per hour)	1.6+	1.9+	3.9	4.5	3.9
Counting efficiency(%) for ^{40}K betas.	35	38	67	72	71
Figure of merits(S^2/B)++	750	755	1150	1150	1300
Active area of counter(cm^2)	1.64	1.64	3.3	3.3	3.3

* For each counter the plateau is atleast 100 volts wide and the operating voltage is 30 volts above the starting voltage for all counters.

\+ Mean background for the year 1971-72.

++ S = counting efficiency of the counter.
B + Background.

The samples were counted at regular intervals over a period of about 2 months and the decay of ^{32}P was followed. During the later part of this work ^{32}P from many subsurface water samples were counted on a twin 2π beta system resembling a 4π system. For details of counter construction and associated electronics reference is made to SOMAYAJULU (1969) and NIJAMPURKAR and SOMAYAJULU (1974). The characteristics of 2π and 4π beta counting system used are given in Table-II.10.

II.6. Sampling procedures and experimental techniques for the measurement of ^{14}C and ^{3}H activities.

II.6.a. Collection of water samples.

For ^{14}C measurements, the samples were collected by absorbing HCO_3^- ions present in water using ion exchange resins. This method is similar to that reported by CROSSBY (1968). Since the proportional counters used for measuring the ^{14}C activity had a large volume (3 litres) about 3 g equivalent of carbon was necessary to obtain clear signals of ^{14}C. Since the HCO_3^- concentrations were generally high (300-700 ppm, Table-III.) in the samples only about 50-200 l of water was necessary to strip the HCO_3^- ions. The water was passed through perspex columns (diameter 6 cm) connected in series containing the resins IR-45(OH^- form) and IRA-400 (OH^- form). The total volume of resins used was about 800 cc. The first column removes the strong anions sulphate and chloride, whereas the second column efficiently retains bicarbonate from water. The HCO_3^- concentrations of the water were measured at site using conventional methods to approximately estimate the volume of water to be passed through the resin to give about 3 g equivalent of carbon.

The water was passed through columns at a rate of about 150-200 cc/min. After the passage of water the resins were packed and shifted to the laboratory for purification and assay of ^{14}C.

In case of tritium, the water samples were collected in clean one litre air-tight plastic bottles directly from the source water and carried to the laboratory for further processing.

II.6.b. Extraction of CO_2 and synthesis of methane.

The CO_2 from the resins were liberated in the laboratory by treating them with about 2 N'analar' grade hydrochloric acid. The CO_2 stripping was done in the glass system employed for ^{14}C work (ANAND and LAL, 1964). This CO_2 was further purified and converted into methane by earlier published method (ANAND and LAL, 1964). The purified methane was counted using Oeschger type proportional counter.

II.6.c. Methane synthesis from H_2O for assay of tritium.

The tritiated water was converted to methane directly or after enrichment depending upon the concentration levels of tritium present in the water. Hydrogen was liberated from about 5-10 cc of water using zinc dust as reducing agent and ruthenium as catalyst. The Hydrogen thus liberated was converted into methane by treating it with pure CO_2. The purified methane was counted using proportional counters.

II.6.d. Counting techniques for ^{14}C and ^{3}H activities.

The synthesised methane from water samples was filled in OESCHGER type proportional counters and the activities of ^{14}C and ^{3}H were assayed. The samples were counted for about a day. For the details of counting system and electronics reference is made to ANAND and LAL, 1964; LAL and ATHAVALE,1966.

Synthesis of methane and assay of the ^{14}C activity in the sample was carried out by Miss Sheela Kusumgar of the Radiocarbon Laboratory (when it was housed at TIFR, Bombay) and tritium measurements for few samples were carried out by Dr.B.S.Sukhija in Tritium Laboratory(when it was housed at TIFR, Bombay.).

The results of these measurements are given in Chapter III and implications are discussed in subsequent chapters.

CHAPTER-III

RESULTS OF MEASUREMENTS

The ^{32}Si concentration (dpm/ton) in natural waters are very small. Even for samples as large as 10-20 tons, the net ^{32}P activities measured give only 5-15 counts per hour at best (except rainwater). In subsurface samples it is as low as 2-5 counts per hour. Although the low background counting techniques allow one to measure activities in this range, it is difficult to carry out measurements with the precision attainable for ^{14}C.

The results of the measurements of the concentrations of Silicon-32, Carbon-14 and Tritium in rain, stream, river, lake and subsurface waters are presented in this chapter. The details of sampling locations have been described earlier in chapter-II.

III.1. Method of calculation of absolute concentration (dpm/ton) of Silicon-32.

The ^{32}Si concentrations were calculated from the measured ^{32}P counting rates using the relation :

$$\text{dpm } ^{32}\text{Si/ton} = \frac{C_o}{f_{ch} \times f_s \times f_g \times f_c \times V} \quad \ldots (3.1)$$

Where C_o = net ^{32}P activity (cpm). The value of C_o is estimated from the decay plots (see Section III.1.a) and ranged between 0.5 - 90 cph.

f_{ch} = The factor for chemical efficiency. The value of this factor ranged between 0.7-0.95.

f_s = The fraction of beta particles transmitted after self absorption. The value of f_s was calculated using standard relations and ranged between 0.85-0.95 depending on the source thickness.

f_g = The growth factor of ^{32}P from ^{32}Si given by the relation $^{32}P/^{32}Si = (1-e^{-\lambda t})$ Where λ is the decay constant of ^{32}P (0.0485 d^{-1}) and t is the time allowed for growth of ^{32}P. In general the time between repeat milkings was about 2-3 months corresponding to a growth factor of 0.94-0.98.

f_c = The factor for counting efficiency.

V = The effective volume of water (ton) processed 'V' is the ratio of the weight (gm) of SiO_2 milked to the SiO_2 concentration (gm/ton) in the water samples. The value of V ranged between 2-20 tons, depending upon the nature of the sample.

The absorption of ^{32}P in the mylar and counter window is calculated to be $\nless$ 2% and hence neglected in the present calculations.

III.1.a. Estimation of C_o

The gross counting rate, C_t of the sample ($Mg_2P_2O_7$ deposit) at any time 't' is given by (KHARKAR et al., 1966; SOMAYAJULU, 1970).

$$C_t = C_o e^{-\lambda t} + B + X \qquad \ldots (3.2)$$

Where C_o is the ^{32}P counting rate at the time of its separation from parent ^{32}Si, B is the background of the counter and X is the activity contributed to the sample by nuclides other than ^{32}P, i.e. the residual activity. If X is constant for 4-5 half-lives of ^{32}P i.e. if the contaminating activity has a half-life much longer compared to ^{32}P then equation (3.2) represents a straight line with values $(C_o + B + X)$ and $(B + X)$ respectively for $t = o$ ($e^{-\lambda t} = 1$) and $t \rightarrow \infty$ ($e^{-\lambda t} = o$). Thus the difference in the two values gives the value of C_o. In Figures III.1,2 & 3 the plot of gross counting rate are plotted as a function of $e^{-\lambda t}$ for the various types of water samples and least square lines are drawn through the points.

To check whether the value (B + X) is constant, the samples were counted a few times, 2-3 months after the separation of ^{32}P from ^{32}Si when ~ 95% of ^{32}P would have decayed. The results of these measurements (Table.III.1) show that the values of (B + X) indeed remained constant and are very close to the deduced values from least square line(also given in Table.III.1). The counting rate of the long lived contamination estimated from the least square lines are presented in Fig.III.4 for the various types of water samples. As evident from Fig.III.4, the high values of X are associated with rain and surface waters, which have higher values of residual activity than subsurface waters probably due to the presence of relatively short lived isotopes in them a part of which could have been carried through the chemistry. In subsurface waters the contamination levels are low in the range of 0-1.5 cph with a mean value of 0.4 cph. The long lived contamination reported for oceanic ^{32}Si work, range from 1-4 cph (SCHINK, 1962 ; SOMAYAJULU, 1969). The reason for high contamination levels is not clear but could be due to some long lived isotopes scavanged along with silica from sea water, or due to the contamination in the reagents used for processing silica samples. From the deduced values of C_o (Fig.III.1,2 &3), the ^{32}Si activity of water masses were calculated using relation (3.1).

Fig. III.1 Variation of gross ^{32}P activities milked from rainwaters as a function of $e^{-\lambda t}$.

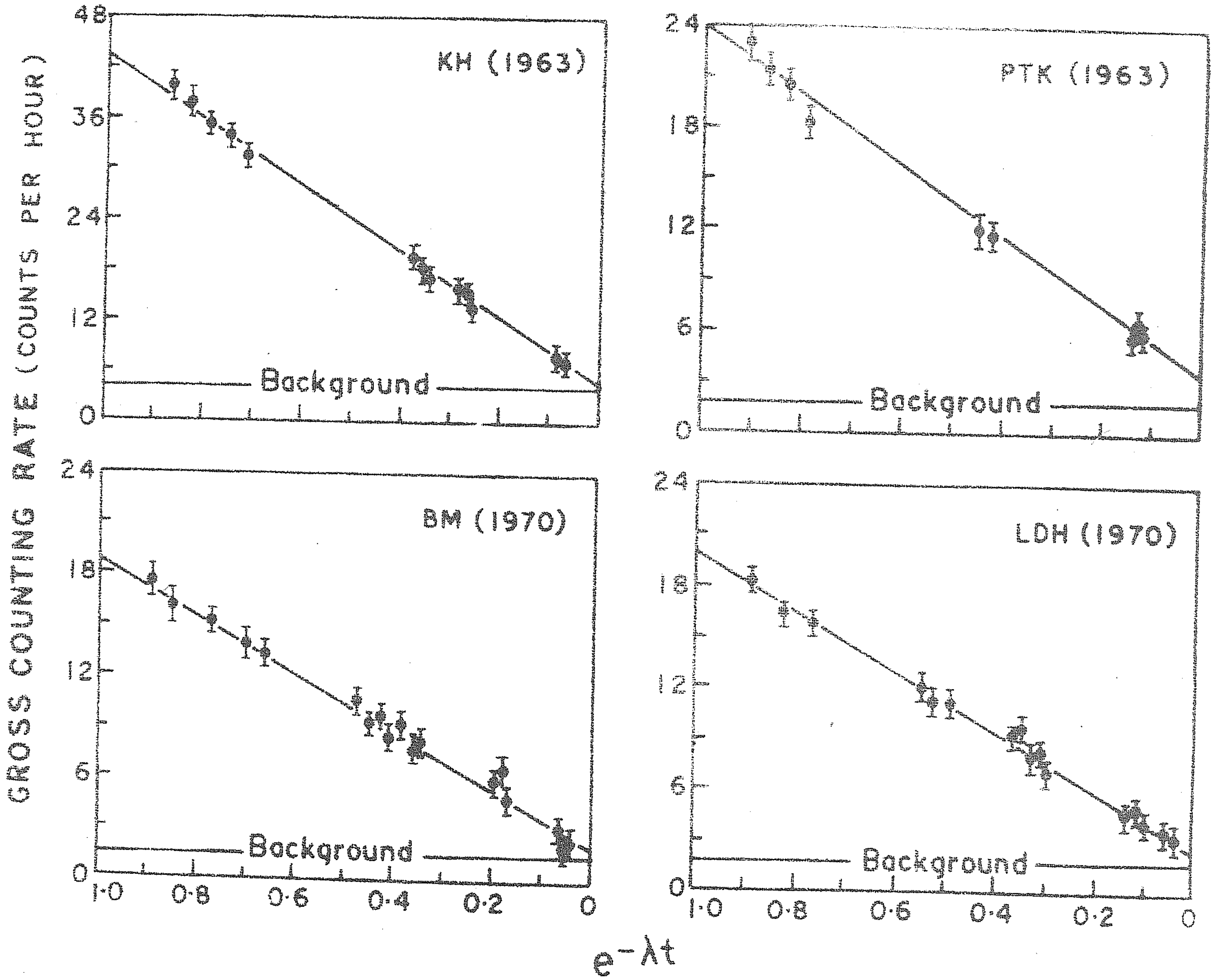

GROSS COUNTING RATE (COUNTS PER HOUR)
KH (1963)
PTK (1963)
BM (1970)
LDH (1970)
Background
48
36
24
12
18
6
0
1·0
0·8
0·6
0·4
0·2
0
$e^{-\lambda t}$

FIG.III.1

Fig. III.2 Variation of gross ^{32}P activities milked from surface waters as a function of $e^{-\lambda t}$

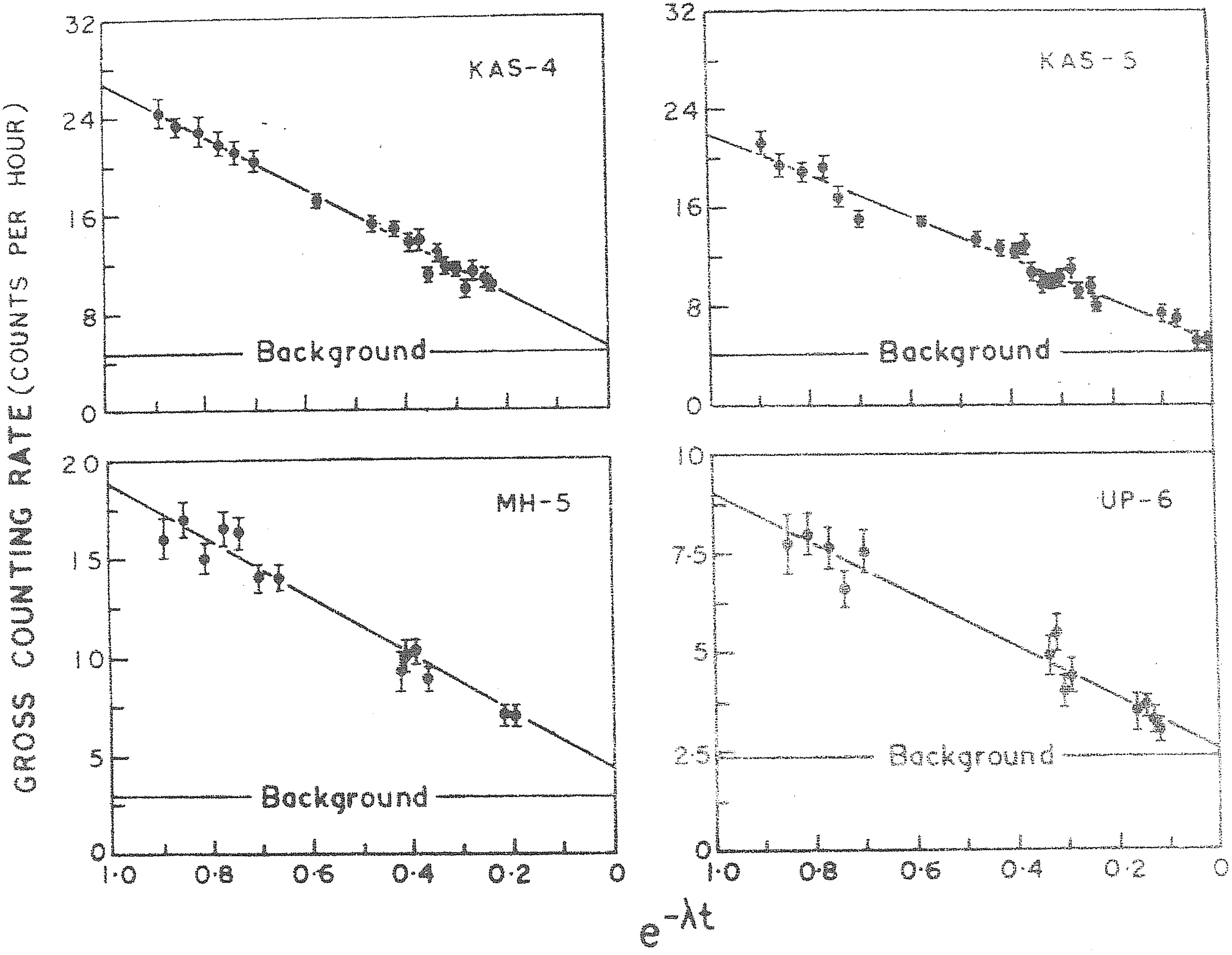

GROSS COUNTING RATE (COUNTS PER HOUR)
KAS-4
KAS-5
MH-5
UP-6
Background
32
24
16
8
0
20
15
10
5
7·5
2·5
1·0
0·8
0·6
0·4
0·2
$e^{-\lambda t}$

FIG. III.2

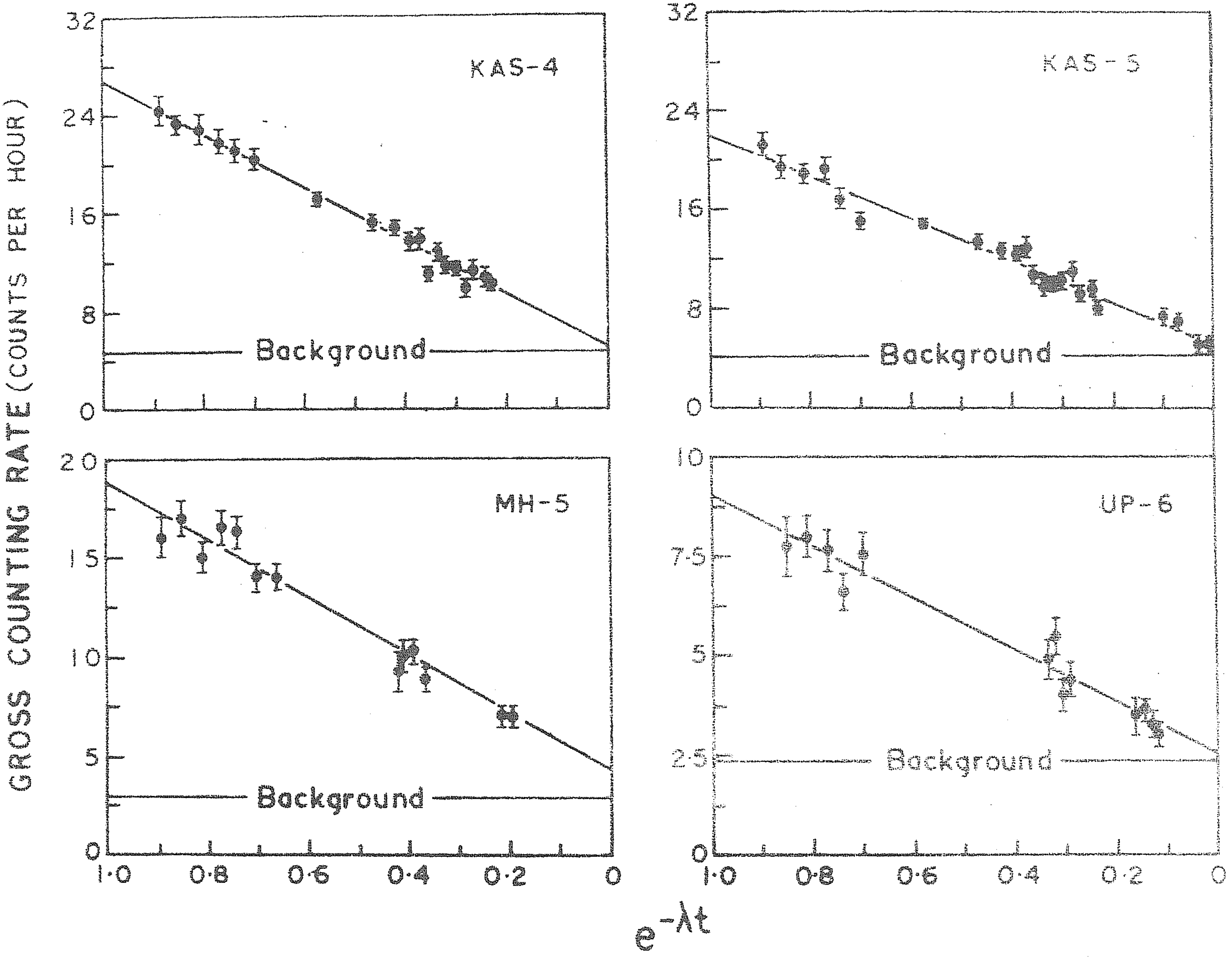

GROSS COUNTING RATE (COUNTS PER HOUR)
KAS-4
KAS-5
MH-5
UP-6
Background
32
24
16
8
0
20
15
10
5
7·5
2·5
1·0
0·8
0·6
0·4
0·2
$e^{-\lambda t}$

FIG. III.2

Fig.III.3 Measured gross counting rate for groundwater samples as a function of $e^{-\lambda t}$.

a) Bhairwa T.W. (2nd Aquifer)

b) Pilkai T.W.

c) Niraun Dug well

d) Bhairwa TW (1st Aquifer)

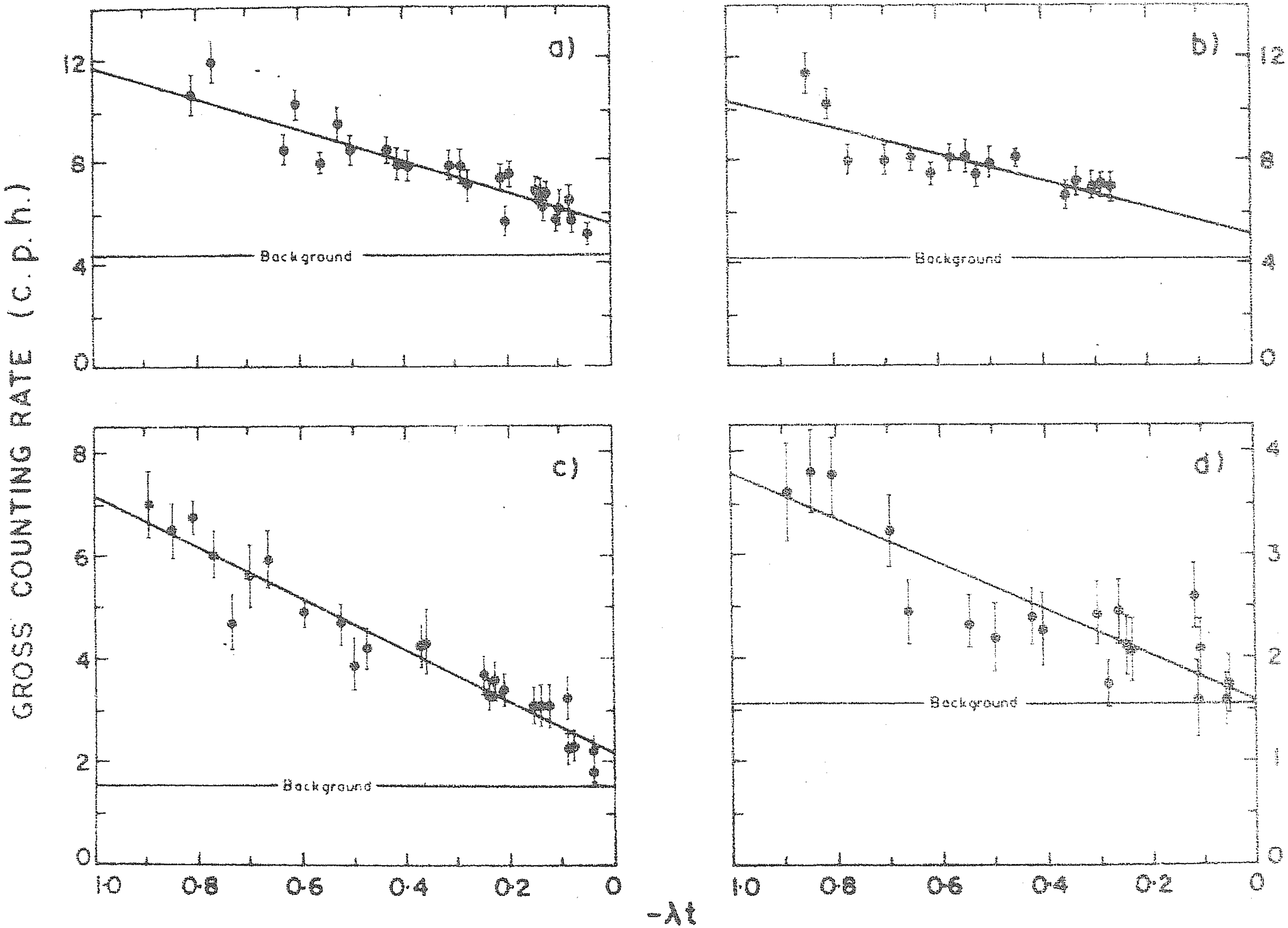

GROSS COUNTING RATE (c. p. h.)
a)
b)
c)
d)
Background
12
8
4
0
6
2
3
1
1·0
0·8
0·6
0·4
0·2
0
$e^{-\lambda t}$

FIG. III.3

TABLE-III.1

ACTIVITY OF LONG-LIVED CONTAMINATION IN GROUNDWATERS AS COUNTED FOR 2-4 MONTHS

Sample Code.	Date of ^{32}P separation.	Details of last counting of sample		(B + X) Value (cph)	
		Date	Gross cph.	Average of last countings.	From least square line.
UP - 5	26-10-64	9-2-65	3.75 ± 0.4		
		10-2-65	3.26 ± 0.4	3.7	3.8
		11-2-65	3.90 ± 0.4		
MH - 8	28-10-64	15-2-65	3.97 ± 0.4		
		16-2-65	4.22 ± 0.4	4.0	3.7
		17-2-65	3.90 ± 0.4		
MH - 1	17- 7-69	16-9-69	2.70 ± 0.3	2.7	2.7
KAS- 2	2- 7-69	1-9-69	2.75 ± 0.3	2.6	2.5
		3-9-69	2.50 ± 0.3		
GJ - 1	10- 9-69	9-11-69	2.20 ± 0.3		
		10-11-69	2.70 ± 0.3	2.6	2.5
		15-11-69	2.86 ± 0.2		
		19-11-69	2.86 ± 0.3		
GJ - 2	21- 7-69	4-10-69	1.19 ± 0.2	2.0	1.8
		5-10-69	2.02 ± 0.2		
GJ - 6	23- 9-69	3-12-69	1.60 ± 0.2	1.6	1.4
		4-12-69	1.65 ± 0.2		
RJ - 9	30-10-72	10- 1-73	1.85 ± 0.4	2.1	2.1
		11- 1-73	2.25 ± 0.4		
RJ -11	15-12-72	16- 2-73	1.95 ± 0.4	2.0	1.9

III.1.b Estimation of errors.

In majority of rain and surface water samples where the ^{32}P signals are large ($\geqslant$5 cph) the errors quoted are one standard deviation due to counting statistics.

These values have been estimated from the net sample counting rates for the first 1-3 days. The estimated statistical errors for the samples range between 10%-20% of the activities.

For low active samples, the errors are estimated from (i) the net ^{32}P signals and (ii) the scatter in the gross counting rate (cph) versus $e^{-\lambda t}$ plot. The errors quoted in Tables.III.3,4 & 6 to 11 are the larger of the two. Because of this, in some cases eventhough the estimated C_o values are higher the errors are also large.

III.2. Reliability and Reproducibility of the ^{32}Si measurements.

Before calculating the absolute concentration of ^{32}Si in the water samples and study its implications, it is necessary to establish that the signals measured are indeed due to ^{32}P. Several direct and indirect methods to ascertain the radiochemical purity of the ^{32}P activity adopted in this work are described below.

Fig. III.4 Frequency distribution of long lived residual activities present in natural waters. Arrows indicate the mean values.

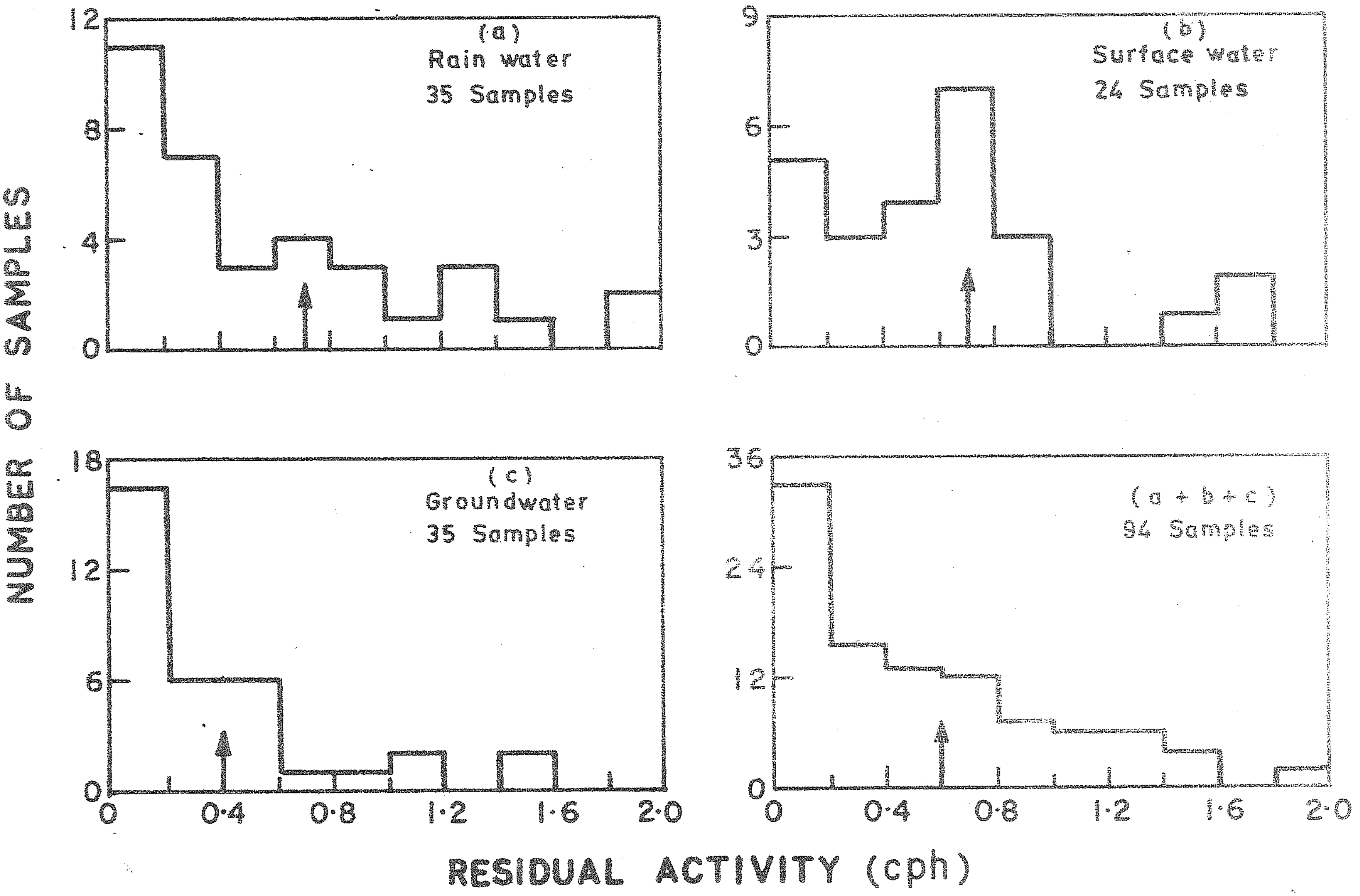

(a)
Rain water
35 Samples
(b)
Surface water
24 Samples
(c)
Groundwater
35 Samples
(a + b + c)
94 Samples
NUMBER OF SAMPLES
RESIDUAL ACTIVITY (cph)
0
4
8
12
3
6
9
6
12
18
24
36
0·4
0·8
1·2
1·6
2·0

FIG. III.4

III.2.a. Half-life measurements of ^{32}P

The reliable method to ensure the purity of any radioisotope is either to measure its half-life or its particle energy. In the present case the low levels of activity coupled with the short half-life of ^{32}P made it difficult to measure the half thickness of its beta radiation within a reasonable accuracy. However, the half-life measurements for a few "active" samples (having counting rates $\gg 5$ counts per hour) have been carried out.

Fig.III.5 shows the variation of the net counting rate of the $Mg_2P_2O_7$ sample with time. The net counting rates were calculated using the relation :

$$C_{net} = C_{gross} - (B + X) \qquad \ldots \qquad (3.3)$$

The value of (B + X) was taken as the counting rate observed after 2-3 months of ^{32}P separation from ^{32}Si. In many cases an average value of 0.6 counts per hour was used for the value of X , (Fig.III.4).

The half-life of the radionuclide as deduced from Fig.III.5 ranges between 14 to 15 days for various samples. This represents very well the half-life of ^{32}P (14.3 d) within experimental uncertainties.

III.2.b. Analyses of Blank samples.

After having ascertained that the activity being measured is ^{32}P, it now remains to ensure that the ^{32}P activity observed is from the ^{32}Si in samples and not from reagents used in the analysis. To assess the contribution of ^{32}P from the various chemicals used in its radiochemical separation and purification from silica samples and whether any significant contribution was present due to ^{32}P activity produced at sea level by cosmic rays interacting with Cl nuclei in the hydrochloric acid (RAMA and HONDA, 1961), a large number of reagent blank measurements were carried out. The blank analysis involved mostly the measurement of ^{32}P contamination in ~ 10 litres of HCl (which was always stored in the basement to reduce contributions from cosmic rays). By a least square analysis similar to that carried out for the various samples, a net counting rate of 0.2 ± 0.5 cph. was deduced due to ^{32}P activity. Taking a net signal of 1.0 cph as the upper limit from this experiment and considering the amount of hydrochloric acid used in the processing of ground-water silica, it was estimated that the contribution due to cosmic ray interactions in HCl amounts to less than 0.02 dpm ^{32}Si/kg SiO_2. This corresponds to a possible signal of 10^{-3}-10^{-4} dpm per 10^3 litres of water which is equivalent to values of 5-50 ppm for natural stable silica concentrations in

Fig. III.5. Variation of net beta activity of $Mg_2P_2O_7$ samples with time. The samples are extracted from rain, surface and subsurface waters. The deduced half-life of radionuclide in these samples ranges between 14-15 days which cover the half-life of ^{32}P (14.3 d) very well.

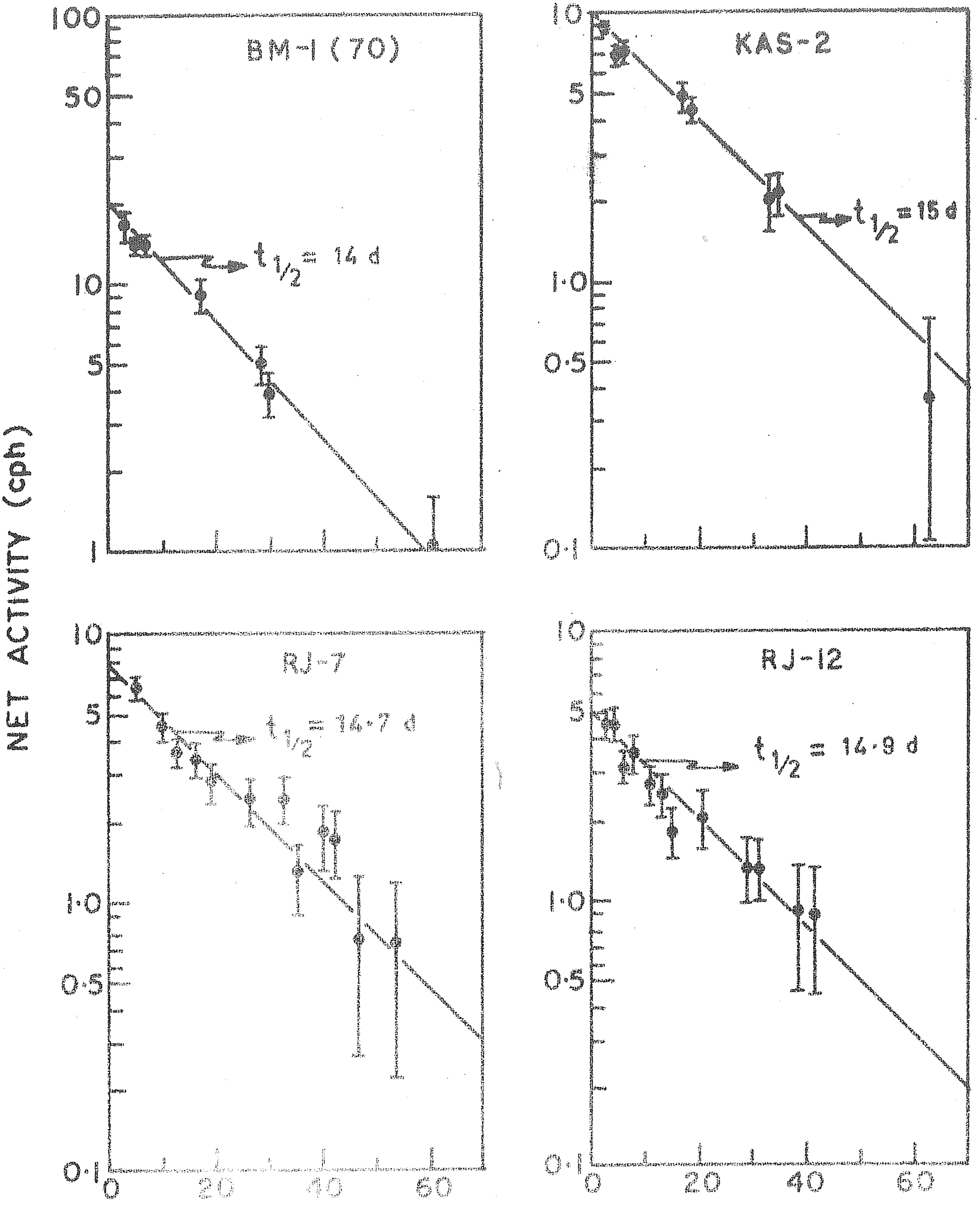

NET ACTIVITY (cph)
BM-1 (70)
$t_{1/2}$ = 14 d
100
50
10
5
1
KAS-2
$t_{1/2}$ = 15 d
10
5
1·0
0·5
0·1
RJ-7
$t_{1/2}$ = 16·7 d
10
5
1·0
0·5
0·1
RJ-12
$t_{1/2}$ = 14·9 d
10
5
1·0
0·5
0·1
0
20
40
60
0
20
40
60
t (days)

FIG.III.5

groundwater. Therefore in the present work it seems safe to consider the results ≥ 0.005 dpm/ton of water as reliable.

Similarly the contamination levels of ^{32}P in reagent HF, analar grade SiO_2 was measured by milking ^{32}P activities in them. As a further check, some samples were remilked immediately after first milking (within 48 hours). The results of these measurements are presented in Table-III.2.b. In many of these samples since the signals were very low (< 0.5 cph) it was not possible to observe its radioactive decay with time. Hence the numbers presented in Table-III.2.a are the upper limits and in many cases represent the difference between the first counting rate (counted within 48 hours of ^{32}P separation) and the background.

The data presented in Table-III.2.a, 2.b, indicate that the contribution of ^{32}P by reagents is small, 0.2 ± 0.5 cph. As a further proof of this it must be mentioned here that few groundwater samples (RJ-2; UP-4), marine siliceous sponge (T.F.73) (LAL <u>et al.</u>,1970) and old glacier samples(supplied by Dr.S.Aegerter of University of BERN, SWITZERLAND) showed net ^{32}P signals of < 0.2 cph implying that the blank contributions are indeed small.

III.2.c. Reproducibility of ^{32}P measurements.

To check on the reproducibility of the results, many of the silica samples were remilked, the results of which are presented in Table-III.3. The data presented in Table-III.3 show that inspite of the small signals of ^{32}P encountered, the results of repeat milkings are in satisfactory agreement, except in the case of Ist milking of Neyveli PTW sample which shows unusually high value over subsequent milkings. This can most probably be attributed to laboratory contamination.

III.3. Silicon-32 concentrations in wet precipitations, surface and subsurface waters.

III.3.a. Wet Precipitations.

Silicon-32 measurements in rainwater have been carried out at different stations in India (Table-II.1) during 1961-71. Similar measurements for snow and precipitations have been reported earlier (DANSGAARD *etal*., 1966; KHARKAR *et al*., 1966 ; LAL *et al*., 1970). These measurements were undertaken to estimate the global ^{32}Si fallout as well as to check the contribution of nuclear weapons, if any, to the inventory of ^{32}Si (DANSGAARD *et al*., 1966).

TABLE - III.2.a

^{32}P ACTIVITY IN REAGENTS AND BLANK SAMPLES.

Sample code Date of milking.	Nature of sample.	Net ^{32}P activity (cph).
B1-1 26-1-70	HCl (10 litres)	0.2
B1-2** 20-7-73	HF (2 litres)	$<$ 0.5
B1-3** 27-10-72	Pure Silica (100 g)	$<$ 0.2

** In samples B1-2 and B1-3 decay was not followed as the initial activity was very small and measured activity for first 2 days has been corrected for background.

TABLE - II.2.b

^{32}P ACTIVITY IN SAMPLES REMILKED WITHIN 48 HRS OF FIRST MILKING

Sample Code Date of milking.	Nature of sample	Net ^{32}P activity* (cph)
GJ-5 21-1-68	Silica from tubewell water at Vijapur.	$<$ 0.7
UP-5* 24-1-73	Silica from river water at Hardwar.	2.8

* The measured signals in samples GJ-5 and UP-5 can be attributed to ^{32}P growth from ^{32}Si during 48 hours.

TABLE - III.3

RESULTS OF REPEAT MILKINGS OF SILICA SAMPLES

Code	Sample		Wt. of Silica milked (g)	Equivalent volume of water (tons)	Net ^{32}P activity* (cph)	dpm ^{32}Si/ton
BM-63	Bombay rain	(i)	65	3.8	18.8	0.310 ± 0.030
		(ii)	56	3.5	18.4	0.350 ± 0.030
UP- 5	Hardwar RW	(i)	70	8.4	13.9	0.140 ± 0.010
		(ii)	68	8.2	14.2	0.133 ± 0.010
RJ-12	Niraun DW	(i)	262	8.1	5.0	0.033 ± 0.005
		(ii)	193	6.1	7.0^{++}	0.036 ± 0.005
TN- 3	Neyveli TW	(i)	242	2.3	3.0	0.075 ± 0.020
		(ii)	213	2.3	2.2	0.070 ± 0.020
UP- 1	Shankarpura TW	(i)	197	6.2	1.3	0.017 ± 0.008
		(ii)	175	5.5	2.3^{++}	0.014 ± 0.006
RJ- 6	Bhairwa TW (Ist aquifer)	(i)	180	11.5	2.2	0.010 ± 0.005
		(ii)	150	9.6	1.8	0.014 ± 0.006
RJ- 9	Devikot TW	(i)	165	9.8	2.1	0.015 ± 0.005
		(ii)	135	6.1	2.2	0.020 ± 0.005
RJ- 7	Bhairwa TW (2nd aquifer)	(i)	240	14.1	6.2^{++}	0.012 ± 0.003
		(ii)	145	8.5	4.9^{++}	0.018 ± 0.004

TABLE-III.3.

con..2..

Code	Sample		Wt.of Silica milked (g)	Equivalent volume of water (tons)	Net ^{32}P activity* (cph)	dpm ^{32}Si/ton
GJ- 9	Pilvai TW	(i)	141	4.4	1.3	0.017 ± 0.008
		(ii)	132	3.9	5.1++	0.030 ± 0.004
MH- 1	Mulund TW	(i)	225	6.6	10.3	0.090 ± 0.010
		(ii)	70	1.9	1.7	0.060 ± 0.030
TN- 1	Neyveli PTW +	(i)	270	12	118	0.860 ± 0.020
		(ii)	84	3.81	4.6	0.080 ± 0.010
		(iii)	76	3.62	2.9	0.058 ± 0.010
		(iv)	146	6.95	4.7	0.060 ± 0.010

* The value at the time of ^{32}P separation is estimated from least square line drawn on decay plots.

+ The repeat milkings were done on aliquots of silica.

++Samples counted by 4 Π geometry.

In Table-III.4, the results of the concentration of ^{32}Si in rainwater collected from different latitudes of India are presented. Table-III.5 gives available data in literature for the ^{32}Si concentrations for latitudes 30°-65°N (DANSGAARD *et al.*,1965).

III.3.b. Surface waters.

Results of the ^{32}Si concentration of surface water samples collected from the Kashmir Valley are presented in Table-III.6. The results for lake Tansa and the two rivers Godavari and Ganges are given in Table-III.7. The measurements in Tansa lake were made over a period of five years to understand the long term variations of ^{32}Si concentrations. The ^{32}Si activity in surface waters range between 0.08-0.33 dpm/ton, Table-III.6 & 7.

III.3.c. Subsurface waters.

For the sake of convenience, the results of the concentrations of ^{32}Si in the subsurface waters are presented in two Tables (i) waters from unconfined aquifers and (ii) samples tapped from confined aquifers. The results of the subsurface water samples from unconfined and confined aquifers are presented in Table-III.8,9,10 & 11 and Fig.III.6 shows the range of the measured concentrations. As is evident, the ^{32}Si concentrations in groundwater varies from 0.001 to 0.11 dpm/ton.

T A B L E - III.4

^{32}Si CONCENTRATION IN WET PRECIPITATIONS*

Station.	Period of collection	Rainfall (cm) during period of collection.	Rainfall (cm) during Total year	Volume processed (tons)	Net ^{32}P activity observed (cph)	^{32}Si concentration (dpm/ton)
Pathankot	26- 8-1961 5- 3-1962	60	125	1.5	3.0 ± 0.8	0.27 ± 0.07
"	29- 6-1963 28- 9-1963	80	95	1.5	20.7 ± 3.0	0.70 ± 0.10
"	1- 2-1968 12-12-1968	71	71	0.7	5.0 ± 0.8	0.47 ± 0.08
Ludhiyana	31- 7-1970 18-10-1970	44	71	3.6	17.5 ± 0.9	0.38 ± 0.04
Gwalior	7- 7-1963 6-10-1963	95	105	8.7	49.6 ± 2.0	0.29 ± 0.02
"	6- 6-1968 15-12-1968	80	80	0.8	3.5 ± 0.9	0.28 ± 0.07

TABLE-III.4.

con..2..

Station	Period of collection.	Rainfall (cm) during		Volume processed (tons)	Net ^{32}P activity observed (cph)	^{32}Si concentration (dpm/ton)
		period of collection.	Total year			
Bombay	17- 6-1963 6- 7-1963	55	255	2.9	10.7 ± 0.9	0.34 ± 0.03
"	12- 7-1963 6- 8-1963	50	255	2.8	33.5 ± 1.6	0.94 ± 0.05
"	9- 8-1963 20- 8-1963	45	255	1.5	3.0 ± 0.5	0.17 ± 0.03
"	June-July 1964	55	250	2.1	18.6 ± 1.7	0.85 ± 0.08
"	20- 7-1966 12- 9-1966	65	150	3.9	18.8 ± 0.4	0.31 ± 0.04
"	3- 6-1967 26- 6-1967	43	241	3.9	11.8 ± 1.1	0.20 ± 0.02
"	27- 6-1967 19- 7-1967	66	241	5.2	16.3 ± 1.3	0.20 ± 0.02
"	20- 7-1967 2- 8-1967	66	241	4.2	8.1 ± 0.7	0.15 ± 0.02
"	3- 8-1967 9-10-1967	52	241	4.3	8.5 ± 0.7	0.16 ± 0.02

T A B L E -III.4.

con..3..

Station	Period of collection.	Rainfall (cm) during period of collection.	Rainfall (cm) during Total year	Volume processed (tons)	Net ^{32}P activity observed (cph)	^{32}Si concentration (dpm/ton)
Bombay	25- 5-1968 16- 6-1968	75	75	5.5	17.9 ± 1.8	0.36 ± 0.04
"	25- 5-1970 16- 6-1970	54	263	5.8	19.0 ± 0.9	0.19 ± 0.02
"	17- 6-1970 16- 7-1970	51	263	5.5	12.8 ± 0.7	0.18 ± 0.02
"	16- 7-1970 2- 8-1970	50	263	6.6	16.9 ± 1.0	0.15 ± 0.02
Khandala	25- 9-1961 12-12-1961	70	500	5.5	5.0 ± 0.7	0.10 ± 0.01
"	21- 5-1963 12- 7-1963	125	510	4.2	90.0 ± 5.0	1.15 ± 0.06
"	17- 7-1963 7- 8-1963	115	"	2.0	13.3 ± 0.9	0.48 ± 0.04
"	11- 8-1963 18- 8-1963	80	"	4.5	37.9 ± 1.9	0.70 ± 0.04

T A B L E - III.4.

con..4..

Station	Period of collection.	Rainfall (cm) during		Volume processed (tons)	Net ^{32}P activity observed (cph)	^{32}Si concentration (dpm/ton)
		period of collection.	Total year			
Khandala	19- 8-1963 10- 9-1963	75	510	4.2	41.0 ± 2.1	0.60 ± 0.03
"	1- 6-1967 4- 7-1967	78	271	4.6	12.3 ± 0.8	0.23 ± 0.02
"	5- 7-1967 27- 7-1967	51	"	2.4	8.5 ± 0.7	0.29 ± 0.02
"	31- 7-1967 23- 8-1967	88	"	6.2	20.5 ± 0.8	0.23 ± 0.09
"	26- 8-1967 1- 9-1967	55	"	2.6	6.0 ± 0.6	0.20 ± 0.02
"	30- 5-1970 25- 6-1970	100	491	3.8	11.3 ± 1.0	0.19 ± 0.02
"	26- 6-1970 9- 7-1970	65	"	6.4	14.5 ± 1.1	0.23 ± 0.02
"	10- 7-1970 30- 7-1970	80	"	5.4	17.9 ± 0.9	0.21 ± 0.02

T A B L E -III.4

con. 5..

Station.	Period of collection.	Rainfall (cm) during period of collection.	Rainfall (cm) during Total year.	Volume processed (tons)	Net ^{32}P activity observed (cph)	^{32}Si concentration (dpm/ton).
Khandala	31- 7-1970 16- 8-1970	75	491	7.5	18.5 ± 0.9	0.21 ± 0.02
"	17- 8-1970 29- 8-1970	65	"	7.7	19.8 ± 0.9	0.18 ± 0.02
"	30- 8-1970 26- 9-1970	90	"	4.9	17.0 ± 0.9	0.18 ± 0.02
Kodaikanal	14- 1-1961 31-12-1961	140	170	1.0	2.2 ± 0.7	0.20 ± 0.06
"	25- 6-1963 1-11-1963	110	195	3.7	14.7 ± 1.0	0.28 ± 0.02
"	10- 6-1968 22-11-1968	82	82	2.6	9.4 ± 0.7	0.21 ± 0.02

Part of the data presented in this table is published earlier (LAL *et al.*, 1966, 1970).

* For relevant details of stations, see Table.II.1.

TABLE-III.5

** REPORTED CONCENTRATIONS OF ^{32}Si IN PRECIPITATIONS.

Station (Lat., Long.)	Period of collection.	^{32}Si concentration (dpm/ton)	Mean
REYKJAVIK (Iceland) 64°N, 21°58'W.	November December 1965	0.61	1.3
	March April 1966	0.81	
	May June 1966	1.46	
LEIRVASSBU + (Norway) 61.33°N, 8°15'E	1961	0.23 + 20%	-
STOREBREEN ++ (Norway)	1961-1962	0.19 ± 20%	-
GLOSTRUP (Denmark) 55.41°N, 12.25°E.	15- 4-1963 and 17- 4-1963	4.3	4.3
	9- 9-1964 5-11-1964	0.85	0.71
	6-11-1964 16-12-1964	0.63	
	17-12-1964 17- 1-1965	0.64	
	16- 3-1965 17- 5-1965	0.69	1.5
	18- 5-1965 23- 6-1965	2.70	
	24- 6-1965 3- 9-1965	1.07	
	March-April, 1966 May-June 1966	1.23 1.36 1.47	1.35
DENMARK 65°N, 30°W	September 1964 September 1965	0.95	-

\+ Represents snow sample. ++ Represents melt water sample.

* The values are correcred for bomb activity.

** The data is due to DANSGAARD, et al., (1966) & DANSGAARD, (1968).

TABLE -III.6

^{32}Si CONCENTRATIONS OF STREAMS, LAKE AND RIVER FROM KASHMIR

Code+	Inherent SiO_2 concentration (ppm)	Effective volume of water processed. (tons)	Net ^{32}P* activity (cph)	Concentration of ^{32}Si (dpm/ton)
KAS - 3	5.5	2.7	11.2	0.33 ± 0.03
KAS - 2	4.1	3.3	9.6	0.23 ± 0.02
KAS - 6	3.7	3.4	19.1	0.29 ± 0.02
KAS - 4	4.0	3.1	21.8++	0.25 ± 0.02
KAS -11	1.4	3.2	8.0	0.19 ± 0.03
KAS - 1	4.0	5.2	20.5	0.31 ± 0.03
KAS -13	5.4	4.0	19.0	0.24 ± 0.02
KAS -10	1.2	4.4	12.6	0.25 ± 0.03
KAS - 9	4.1	4.1	15.4	0.33 ± 0.03
KAS - 8	3.1	2.5	5.6	0.15 ± 0.03
KAS - 7	3.4	3.6	12.7	0.27 ± 0.03
KAS - 5	6.1	3.0	16.8++	0.15 ± 0.02

+ For relevant details of samples see Table II.2.

* Represents the counting rate at the time of ^{32}P separation, as deduced from the least square line.

++ Counted by 4 π geometry.

TABLE -III.7

SILICON-32 CONCENTRATIONS IN LAKES AND RIVER WATER SAMPLES

Code	Location	Inherent SiO_2 concentration (ppm)	Effective volume (tons)	Net ^{32}P* activity (cph)	Concentration of ^{32}Si (dpm/ton)
MH-3	Tansa Lake	21.0	2.5	3.1	0.21 ± 0.02
MH-4	Tansa Lake	20.8	4.8	5.9	0.21 ± 0.02
MH-5	Tansa Lake	21.6	8.0	14.5	0.20 ± 0.02
MH-6	Tansa Lake	21.0	7.6	15.3	0.14 ± 0.01
MH-7	Tansa Lake	20.8	2.6	4.8	0.12 ± 0.02
UP-5	Ganges at Hardwar.	9.1	8.3	13.9	0.14 ± 0.01
UP-6	Ganges at Allahabad.	11.2	6.5	6.5	0.08 ± 0.01
MH-8	Godavari at Nasik.	21.0	7.8	9.0	0.11 ± 0.01
AP-1	Godavari at Rajamundry.	15.8	8.2	8.6	0.08 ± 0.01

---

* Represents the counting rate at the time of ^{32}P separation, as deduced from the least square line.

TABLE - III.8

SILICON-32 CONCENTRATIONS IN SUBSURFACE WATER SAMPLES FROM UNCONFINED AQUIFERS

Code	Location	Inherent SiO_2 concentration (ppm)	Effective volume of water (tons)	Net ^{32}P* activity (cph)	Concentration of ^{32}Si (dpm/ton).
KAS-12	Patan	26.0	4.1	2.3	0.092 ± 0.020
P - 2	Ropar	22.0	9.0	6.5	0.070 ± 0.020
RJ -12	Niraun	32.5	8.1	5.1++	0.033 ± 0.010
GJ - 1	Deesa	36.2	15.4	4.0	0.028 ± 0.003
GJ - 2	Choriwad	30.6	15.3	2.7	0.012 ± 0.002
GJ - 3	Vijapur	28.2	4.7	2.6	0.040 ± 0.010
GJ - 4	Balad	28.0	3.5	4.4	0.110 ± 0.010
MH - 1	Mulund	34.4	6.6	10.3	0.090 ± 0.009
MH - 2	Ville Parle	22.4	7.8	3.7	0.040 ± 0.015

---

* Represents the counting rate at the time of ^{32}P separation, as deduced from the least square line.

++ Counted by 4π geometry.

TABLE - III.9

SILICON-32 CONCENTRATIONS OF CONFINED AQUIFERS OF RAJASTHAN

Code	Location	Inherent SiO_2 concentration (ppm)	Effective volume of water (tons)	Net ^{32}P* activity (cph)	Concentration of ^{32}Si (dpm/ton)
RJ- 1	Bikaner	21.4	7.5	3.1	0.038 ± 0.010
RJ- 2	Palana	19.3	4.6	0.1	< 0.020
RJ- 3	Lathi	13.3	4.3	1.6	0.030 ± 0.010
RJ- 4	Dabla	12.7	4.6	2.1	0.030 ± 0.010
RJ- 5	Chandan	16.1	23.4	1.8	0.005 ± 0.002
RJ- 6	Bhairwa (Ist aquifer)	15.7	11.5	2.2	0.010 ± 0.005
RJ- 7	Bhairwa (2nd aquifer)	16.0	14.1	6.2++	0.012 ± 0.003
RJ- 8	Bhairwa (3rd aquifer)	17.0	8.2	1.6++	0.004 ± 0.002
RJ- 9	Devikot	17.0	9.8	2.1	0.015 ± 0.004
RJ-10	Ajasar	17.0	4.0	1.5++	0.012 ± 0.004
RJ-11	Chandan	17.0	11.2	1.6	0.010 ± 0.003
RJ-13	Palana	19.3	8.3	3.1	0.030 ± 0.010

* Represents the counting rate at the time of ^{32}P separation as deduced from the least square line.

++ Counted by 4π geometry.

TABLE - III.10

^{32}Si CONCENTRATIONS IN WATER SAMPLES FROM CONFINED AQUIFERS OF GUJARAT

Code	Location	Inherent SiO_2 concentration (ppm)	Effective volume of water (tons)	Net ^{32}P* activity (cph)	Concentration of ^{32}Si (dpm/ton)
GJ- 5	Vijapur	35.0	6.7	4.0	0.038 ± 0.005
GJ- 6	Dama	22.5	16.6	3.2	0.018 ± 0.002
GJ- 7	Mansa	24.5	11.4	2.5	0.016 ± 0.002
GJ- 8	Pilvai	26.2	10.3	0.9	0.008 ± 0.002
GJ- 9	Pilvai	32.2	4.4	1.3	0.017 ± 0.008
GJ-10	Kalol	28.8	15.4	5.0	0.028 ± 0.006
GJ-11	Bhojwa	15.6	21.0	2.6	0.009 ± 0.002

* Represents the counting rate at the time of ^{32}P separation as deduced from the least square line.

A mention must be made to the result of Amritsar Tubewell (Table-III.10) where the Ist milking gave high value of 0.3 dpm/ton. The 2nd milking however gave a value of 0.02 ± 0.002. In case of Neyveli PTW (TN-1) repeated milkings gave consistent results whereas in case of Amritsar (P-1) repeated milkings were not done. Most probably the spurious results in both the Ist milkings could be due to laboratory contamination.

III.4 Specific activity of ^{14}C ($^{14}C/^{12}C$) in subsurface waters.

The measured Carbon-14 activities in subsurface waters are given in Table-III.12. The net ^{14}C counting rate varied between 1.8 - 16.3 cpm compared to the background of 1.5 cpm. The bicarbonate and free CO_2 concentrations of these samples are also presented in the same Table.

III.5. Specific activity of ^{3}H ($^{3}H/H$) in subsurface waters.

The specific activities of ^{3}H in eighteen groundwater samples were measured. Of these only two showed measurable concentrations ($\geqslant 5$ TU). These are GJ-1 (30 ± 5 TU) and MH-1 (100 ± 5 TU).

T A B L E – III.11

SILICON-32 CONCENTRATIONS IN CONFINED AQUIFERS OF DIFFERENT GEOLOGICAL FORMATIONS OF INDIA.

Code	Location	Inherent SiO_2 concentration (ppm)	Effective volume of water. (tons)	Net ^{32}P* activity (cph)	Silicon-32 concentration (dpm/ton).
P -1	Amritsar	29.6	6.0	22.5 1.9	0.310 ± 0.020 0.020 ± 0.005
UP -1	Shankarpura	32.0	6.2	1.3	0.016 ± 0.010
UP -2	Benaras	29.2	2.8	$\leq$0.5	$\leq$0.015
UP -3	Inchwal	26.8	9.3	2.6	0.023 ± 0.006
UP -4	Nagla	23.4	10.0	$\leq$0.2	$\leq$0.001
TN -1	Neyveli Post	21.0	3.8	4.6	0.084 ± 0.010
TN -2	Neyveli Yard	68.0	3.0	4.0	0.110 ± 0.010
TN -3	Neyveli Bl 26	98.0	2.3	3.0	0.075 ± 0.010

---

* Represents the counting rate at the time of ^{32}P separation as deduced from the least square line.

Fig. III.6 A histogram showing ^{32}Si concentration (dpm/ton) versus number of samples for groundwater samples collected from unconfined and confined aquifers .

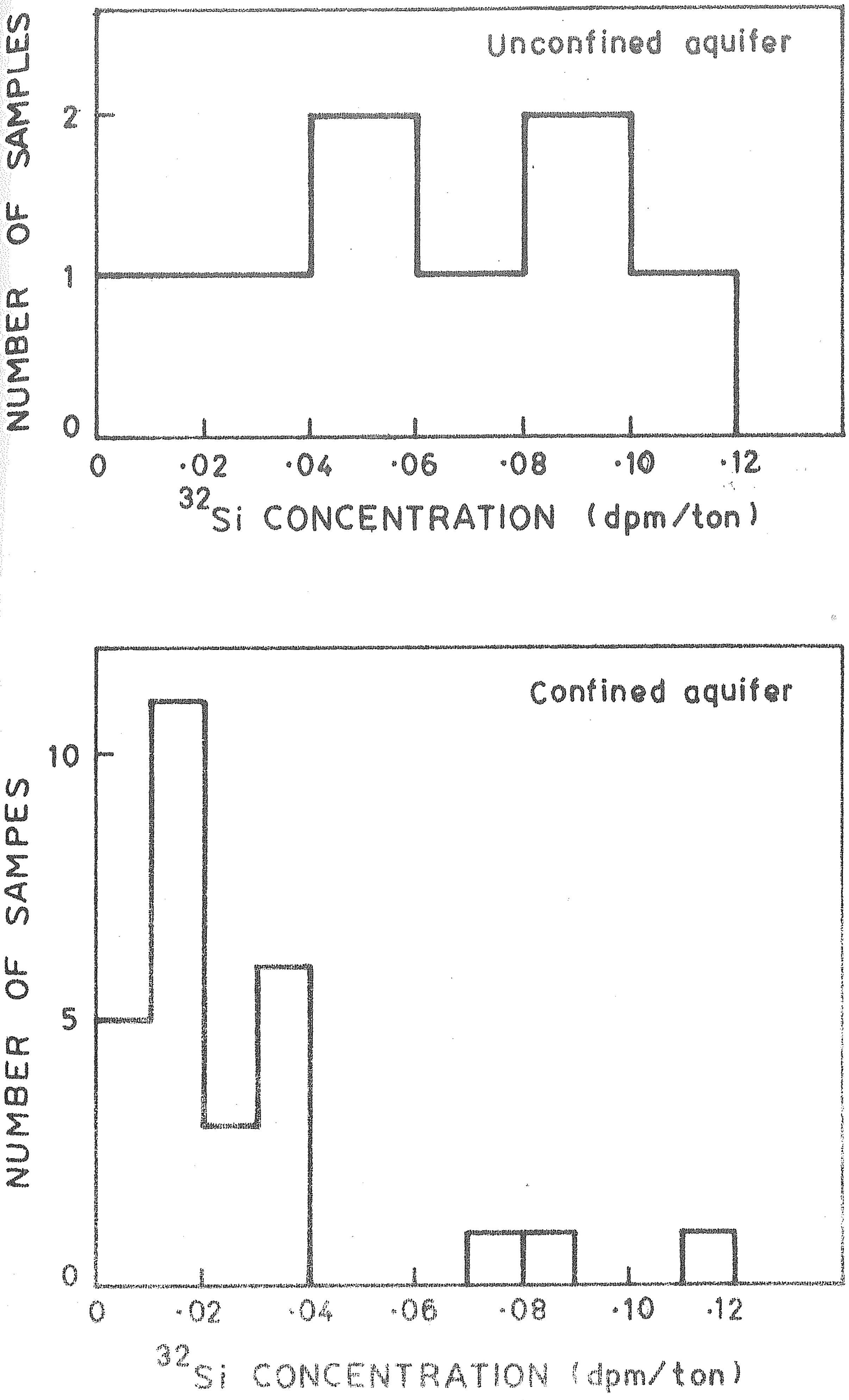

Unconfined aquifer
NUMBER OF SAMPLES
0
1
2
0
·02
·04
·06
·08
·10
·12
32Si CONCENTRATION (dpm/ton)
Confined aquifer
NUMBER OF SAMPES
0
5
10
0
·02
·04
·06
·08
·10
·12
32Si CONCENTRATION (dpm/ton)

FIG. III.6

TABLE-III.12

CARBON-14 ACTIVITY IN SUBSURFACE WATERS

Code	Site	Free CO_2 (ppm)	HCO_3 (ppm)	Net ^{14}C activity (cpm)
RJ- 2	Palana	9.0	350	6.6
RJ- 5	Chandan	7.5	294	6.2
RJ- 6	Bhairwa (Ist aquifer)	NM	242	6.1
RJ- 7	Bhairwa (2nd aquifer)	NM	226	6.2
RJ- 8	Bhairwa (3rd aquifer)	2.5	231	5.4
RJ- 9	Devikot	6.0	229	12.7
RJ-10	Ajasar (Ist aquifer)	NM	NM	4.0
RJ-10	Ajasar (2nd aquifer)	NM	NM	3.8
RJ-10	Ajasar (3rd aquifer)	NM	NM	1.7
RJ-12	Niraun	NM	NM	4.3
RJ-13	Palana	5.0	350	5.9
GJ- 1	Deesa	7.5	357	16.3
GJ- 4	Balad	NM	NM	7.5
GJ- 5	Vijapur	9.0	336	8.2
GJ- 6	Dama	6.7	326	11.3
GJ- 7	Mansa	12.5	487	9.6
GJ- 8	Pilvai	14.8	650	8.3
GJ-10	Kalol	19.8	595	7.3
MH- 1	Mulund	89.0	344	12.3
P - 1	Amritsar	6.0	403	7.8
P - 2	Ropar	10.0	400	10.5
UP- 1	Shankarpura	NM	275	10.0
UP- 4	Nagla	NM	104	8.8
TN- 1	Neyveli Post	95.0	120	10.2

NM = Not Measured.

TABLE-III.12

CARBON-14 ACTIVITY IN SUBSURFACE WATERS

Code	Site	Free CO_2 (ppm)	HCO_3 (ppm)	Net ^{14}C activity (cpm)
RJ- 2	Palana	9.0	350	6.6
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RJ- 8	Bhairwa (3rd aquifer)	2.5	231	5.4
RJ- 9	Devikot	6.0	229	12.7
RJ-10	Ajasar (Ist aquifer)	NM	NM	4.0
RJ-10	Ajasar (2nd aquifer)	NM	NM	3.8
RJ-10	Ajasar (3rd aquifer)	NM	NM	1.7
RJ-12	Niraun	NM	NM	4.3
RJ-13	Palana	5.0	350	5.9
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GJ- 4	Balad	NM	NM	7.5
GJ- 5	Vijapur	9.0	336	8.2
GJ- 6	Dama	6.7	326	11.3
GJ- 7	Mansa	12.5	487	9.6
GJ- 8	Pilvai	14.8	650	8.3
GJ-10	Kalol	19.8	595	7.3
MH- 1	Mulund	89.0	344	12.3
P - 1	Amritsar	6.0	403	7.8
P - 2	Ropar	10.0	400	10.5
UP- 1	Shankarpura	NM	275	10.0
UP- 4	Nagla	NM	104	8.8
TN- 1	Neyveli Post	95.0	120	10.2

NM = Not Measured.

The results of the comparison of ^{14}C and ^{32}Si ages and the implications of ^{32}Si concentrations for evaluating atmospheric production rate are discussed in Chapter-IV.

CHAPTER-IV

DISCUSSION

Fairly extensive measurements of ^{32}Si in wet precipitations, rivers, melt waters and subsurface water have been carried out with a view (i) to determine experimentally, its fallout pattern on the earth's surface, (ii) to obtain estimates of its atmospheric production rate, (iii) to study its geochemical behaviour during its traverse through various geological formations and (iv) to evaluate its applicability as a chronometer for estimating the 'ages' of groundwaters younger than about 2000 years. In this Chapter the approaches to obtain meaningful information on these aspects are discussed. The sampling methods, their analyses and the measured ^{32}Si concentrations in the various reservoirs were described in the previous Chapters.

IV.1. The global fallout of ^{32}Si.

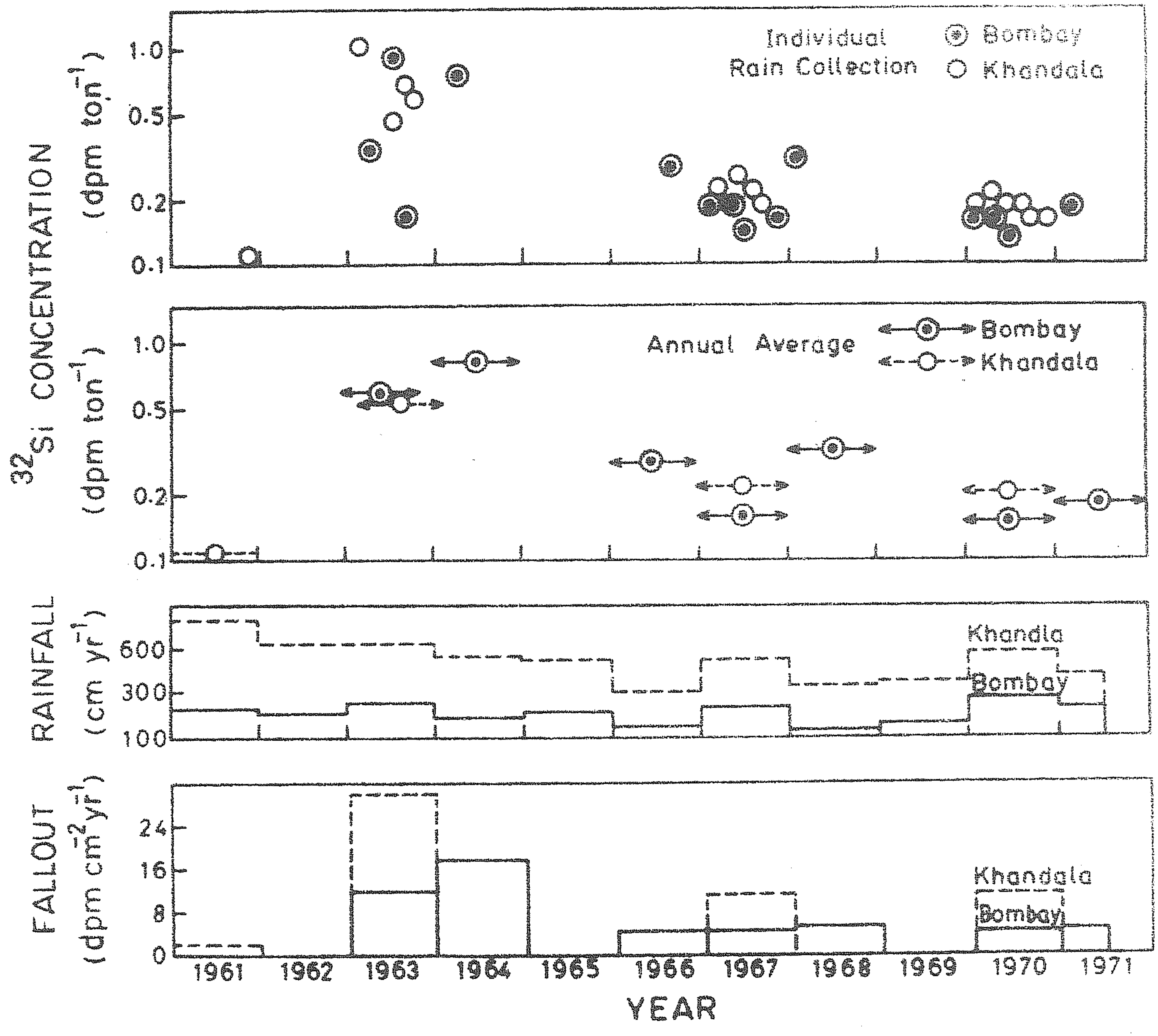
The weighted mean of ^{32}Si concentrations in rain water for the years 1961-1971 are given in Table-IV.1 and Figs.IV.1 & IV.2. The ^{32}Si concentrations in individual rain water collections are presented in Table-III.4. Extensive measurements were carried out only at Bombay and Khandala.

TABLE -IV.1

MEAN ANNUAL ^{32}Si CONCENTRATIONS IN RAINWATER

Station.	Year	Weighted average ^{32}Si concentration (dpm/ton)
PATHANKOT	1961-62	0.27 ± 0.07
	1963	0.70 ± 0.07
	1968	0.47 ± 0.08
LUDHIYANA	1970	0.38 ± 0.04
GWALIOR	1963	0.29 ± 0.02
	1968	0.28 ± 0.07
BOMBAY	1963	0.60 ± 0.10
	1964	0.85 ± 0.08
	1966	0.31 ± 0.04
	1967	0.21 ± 0.04
	1968	0.36 ± 0.04
	1970	0.20 ± 0.06
	1971	0.20 ± 0.06
KHANDALA	1961	0.10 ± 0.02
	1963	0.59 ± 0.04
	1967	0.24 ± 0.03
	1970	0.22 ± 0.06
KODAIKANAL	1961	0.20 ± 0.06
	1963	0.28 ± 0.02
	1968	0.21 ± 0.04

Fig. IV.1. Seasonal variation and mean ^{32}Si concentrations (dpm/ton) in rain water at Bombay and Khandala for the period 1961-71. The estimated annual fallout (dpm cm^{-2}yr^{-1}) and rainfall are also shown.



Individual Rain Collection
Bombay
Khandala
Annual Average
Bombay
Khandala
^{32}Si CONCENTRATION
(dpm ton^{-1})
(dpm ton^{-1})
1.0
0.5
0.2
0.1
RAINFALL
(cm yr^{-1})
600
300
100
Khandla
Bombay
FALLOUT
(dpm cm^{-2}yr^{-1})
24
16
8
0
Khandala
Bombay
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
YEAR

FIG. IV.1

Fig. IV.2. Mean-annual concentrations of ^{32}Si (dpm/ton) and its fallout (dpm $cm^{-2}yr^{-1}$) for the stations Pathankot, Gwalior and Kodaikanal.

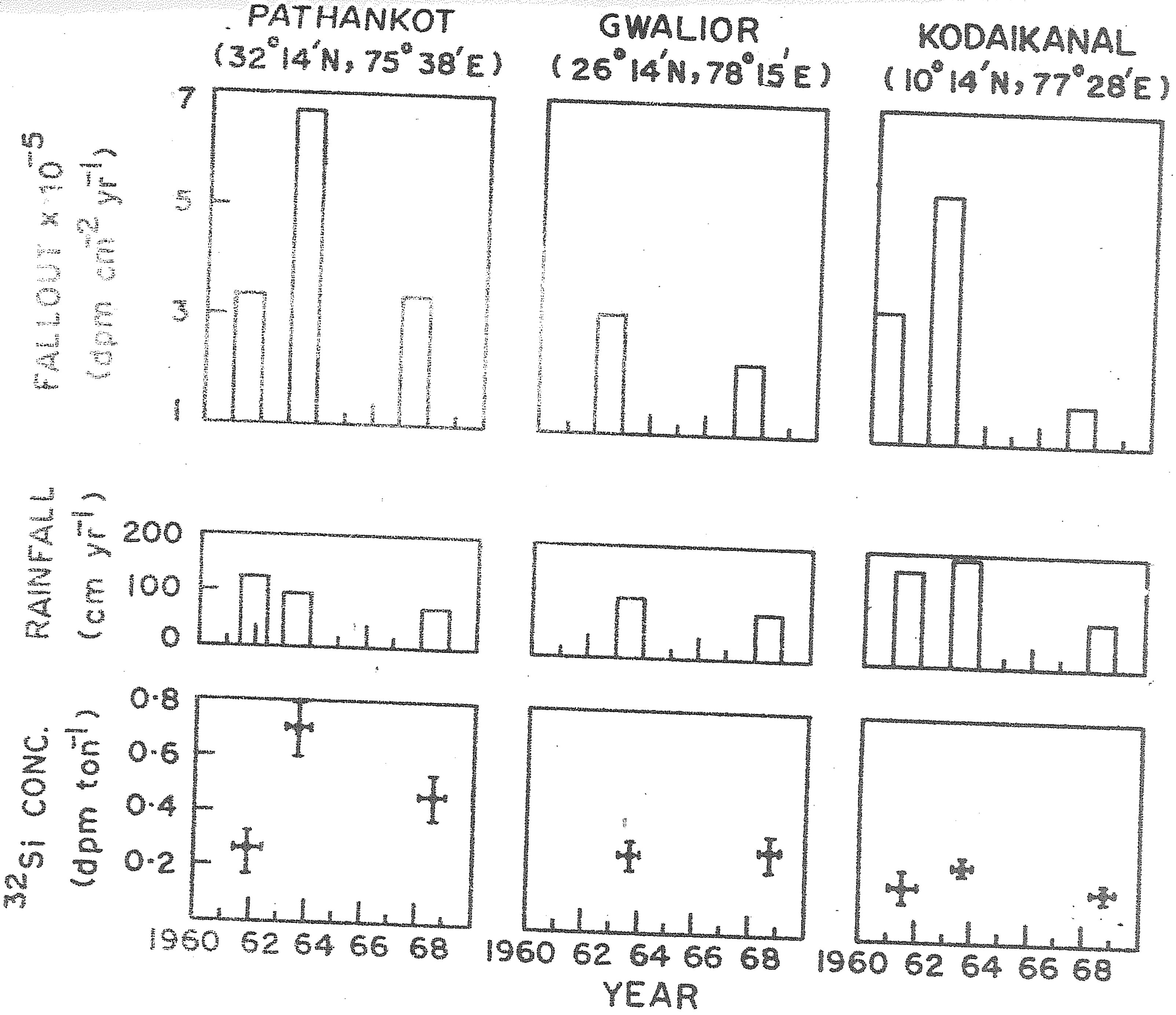

PATHANKOT
(32°14′N, 75°38′E)
GWALIOR
(26°14′N, 78°15′E)
KODAIKANAL
(10°14′N, 77°28′E)
FALLOUT x 10^{-5}
(dpm cm^{-2} yr^{-1})
7
5
3
1
RAINFALL
(cm yr^{-1})
200
100
0
^{32}Si CONC.
(dpm ton^{-1})
0·8
0·6
0·4
0·2
1960 62 64 66 68
1960 62 64 66 68
1960 62 64 66 68
YEAR

FIG IV 2

The measured ^{32}Si concentrations in rainwaters can be used to study the characteristics of its global fallout pattern. Several variable parameters can be eliminated if we compare in individual rain samples the concentration ratios of an isotope pair rather than the concentrations of an individual isotope. For this purpose, we will compare the ^{32}Si results with those of ^{7}Be (half-life, 53 days), a short lived cosmic ray produced isotope. The cosmic ray production of ^{32}Si and ^{7}Be in the troposphere is essentially latitude independent, and in both the cases, the average global amount produced in the stratosphere is twice that produced in the troposphere (LAL and PETERS, 1962). It is known that the fallout of ^{7}Be derives mainly from its production in the troposphere because of its short half-life (LAL and PETERS, 1962). The half-life of ^{32}Si is long compared to the mixing time between the stratosphere and troposphere and hence its global deposition must equal its global production rate. Therefore ^{32}Si/^{7}Be represents stratospheric and tropospheric contributions rather well (LAL et al., 1974). This activity ratio remained at (4-8) x 10^{-6} over 1961-70 except for the years 1963 and 1964 when it was (15 and 25) x 10^{-6} respectively. The enhancement of ^{32}Si was presumably due to its injection in the stratosphere following large scale nuclear weapons' testing during 1961-1962.

The amount of ^{32}Si produced in the stratosphere would be distributed at different latitudes following the pattern of large scale air circulation. The recent results based on the global dispersion of bomb-produced ^{14}C, ^{3}H and ^{90}Sr (LAL and RAMA, 1966) have shown that most of the stratosphere-troposphere air exchange occurs in the latitudinal belt 30-90°, during the summer months of March-August. The mean time of mixing of air in this region with that in the tropics, 0-30°, is about two months . A considerable influx of stratospheric ^{32}Si is thus expected to occur in the tropics during summer.

Most of our measurements are confined to June-August, the period of South West monsoon. No data exist for winter months and hence with the present results it is difficult to make an appraisal of the seasonal variations of ^{32}Si fallout in the Indian subcontinent. However, the fallout at Khandala and Bombay show considerable fluctuations with low values occuring after August or September (Fig.IV.1). DANSGAARD et al.,(1965) found similar variations in rains collected at Glostrup, Denmark (Table.III.5). The results of DANSGAARD et al., (1966) and that of the present work show that the magnitude of the variation in the concentration of ^{32}Si can be upto a factor of 5,(Table.III.4),which is larger than that for ^{7}Be(± 50%) BHANDARI,1965 . This difference between ^{32}Si and ^{7}Be is expected since for ^{7}Be , the stratospheric contributions are small even during periods of peak stratosphere-troposphere exchange. Thus it can be inferred from ^{32}Si results that stratospheric-tropospheric exchange occurs during summer and also this exchange is very important for all latitudes. The contribution from stratosphere will decrease progressively as one goes from polar to equatorial latitude.

The annual deposition of cosmic ray produced ^{32}Si in various latitude bands has been calculated based on its mean concentration in post 1967 rain water samples(Table.IV.2, Fig.IV.3); the results prior to 1967 have not been used for these calculations since the measured ^{32}Si concentrations in them include contribution from nuclear weapons' testings (Section.IV). These calculations are based on the assumption that the measured ^{32}Si activity levels at various stations are representative of the belt. The estimated annual deposition (dpm/cm^{2}yr) for the 10° bands are given in Table.IV.2.

The mean deposition of ^{32}Si in the 10-32° latitude belt is estimated to be 2.5 x 10^{-5} dpm/cm^{2}y (Table.IV.2) which is expected to be higher than the actual annual deposition in the tropical belt since during the sampling period undertaken Indian stations (June-September), appreciable influx of radioisotopes occurs by mixing with the tropospheric air

TABLE - IV. 2

ANNUAL DEPOSITION OF COSMIC RAY PRODUCED ^{32}Si AT TROPICAL LATITUDES

Station (Lat. , Long.)	Annual rainfall in the belt (cm)	Mean ^{32}Si concentration in rain water* (dpm/litre)		Mean deposition** in 10° latitudinal belt (dpm/cm^{2}y).
		At site of collection.	For the 10° latitudinal belt.	
Pathankot (32°N , 76°E)	71	4.7×10^{-4}	4.3×10^{-4}	3.1×10^{-5}
Ludhiyana (31°N , 76°E)		3.8×10^{-4}		
Gwalior (26°N , 78°E)	64	2.8×10^{-4}	2.8×10^{-4}	1.8×10^{-5}
Bombay (19°N , 75°E)	86	2.4×10^{-4}	2.4×10^{-4}	2.0×10^{-5}
Khandala (18°N , 74°E)		2.3×10^{-4}		
Kodaikanal (10°N , 77°E)	154	2.1×10^{-4}	2.1×10^{-4}	3.1×10^{-5}

* Represents the average of samples collected after 1967.

** Calculated by multiplying the mean ^{32}Si concentrations in the latitudinal belt by annual rainfall in corresponding zones (Moeller, 1951).

at higher latitudes. From the observed seasonal fluctuations at Bombay and Khandala, we estimate that the mean annual deposition would be lower by about 20% if the precipitation was distributed uniformly throughout the year.

Thus we take for deposition of ^{32}Si in the 0-30° tropical cell a value of 2×10^{-5} dpm/cm^{2}y. It is found that for the cosmic ray source function, approximately 40 and 60 percent of ^{32}Si activities will be deposited in the 0-30° and 30-90° cells respectively. Hence, the global fallout of ^{32}Si is expected to be about 25% higher than that observed in 0-30° cell. The expected mean concentration of ^{32}Si in this belt is about 0.5 dpm/ton using an average rainfall of 60 cm (MOELLER, 1951). This is in agreement with reported results of DANSGAARD (1965). Fig.IV.3 shows the ^{32}Si concentrations at various stations in the latitudinal belt 10°N-70°N for the post bomb era i.e. after 1967.

The global mean fallout of ^{32}Si is estimated to be 2.5×10^{-5} dpm/cm^{2}y based on the measured value of 2×10^{-5} dpm/cm^{2}y for its fallout in the 0-30° tropical cell and the calculated value of 3×10^{-5} dpm/cm^{2}y for the 30-90° cell (the surface areas are identical in the two cells).

Fig.IV.3. Mean concentration of cosmic ray produced ^{32}Si in snow and wet precipitations at various stations in the latitudinal band of 0-70°N for the years 1961-71. The results of 1963 and 1964 have not been indicated since they contain significant amounts of artificial ^{32}Si due to its injection in the stratosphere by bombs. The station averages appear to show an increasing trend with latitude.

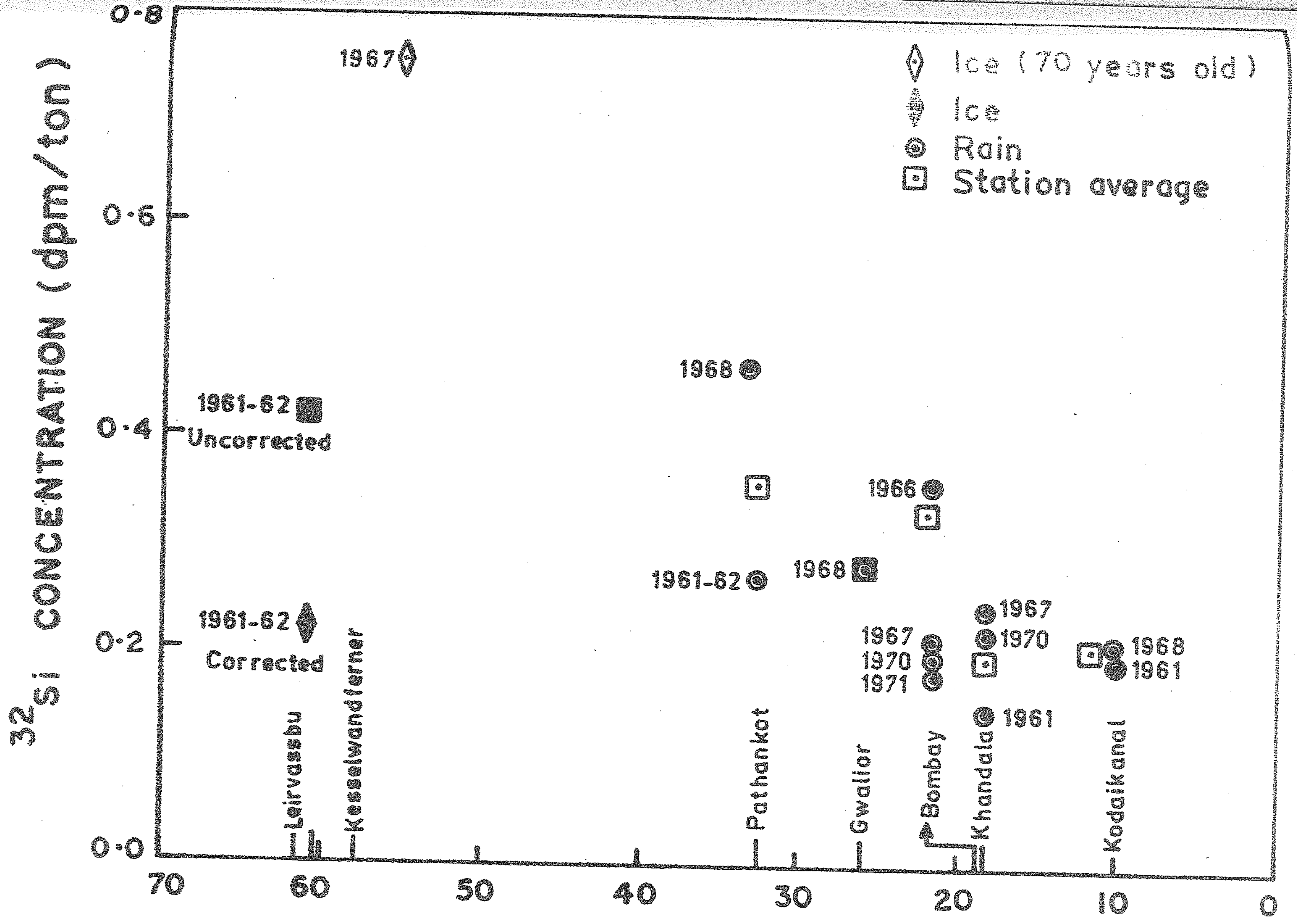

Ice (70 years old)
Ice
Rain
Station average
^{32}Si CONCENTRATION (dpm/ton)
0·8
0·6
0·4
0·2
0·0
1967
1961-62
Uncorrected
1961-62
Corrected
1968
1966
1968
1961-62
1967
1970
1967
1970
1971
1968
1961
1961
Leirvassbu
Kesselwandferner
Pathankot
Gwalior
Bombay
Khandala
Kodaikanal
70
60
50
40
30
20
10
0
LATITUDE (°N)

FIG. IV.3

The fallout of 2.5 x 10^{-5} dpm/cm^2y corresponds to a mean global production rate of 3 x 10^{-4} atoms $^{32}Si/cm^2$ sec. (calculated using 500 y for the half-life of ^{32}Si). The estimate is higher than the calculated value of LAL and PETERS (1962), 1.6 x 10^{-4} atoms/cm^2 sec. by a factor of about two. This discrepancy could be due to uncertainties either in the cross sections used for calculating the ^{32}Si production rate or in the half-life of ^{32}Si. If it is due to half-life, to obtain agreement with the measured production rate, the half-life has to be closer to 300 y, similar to the values recently reported, 280 y (JANTSCH, 1967 ; CLAUSEN *et al.*, 1973).

IV.2. ^{32}Si production by nuclear weapon testings.

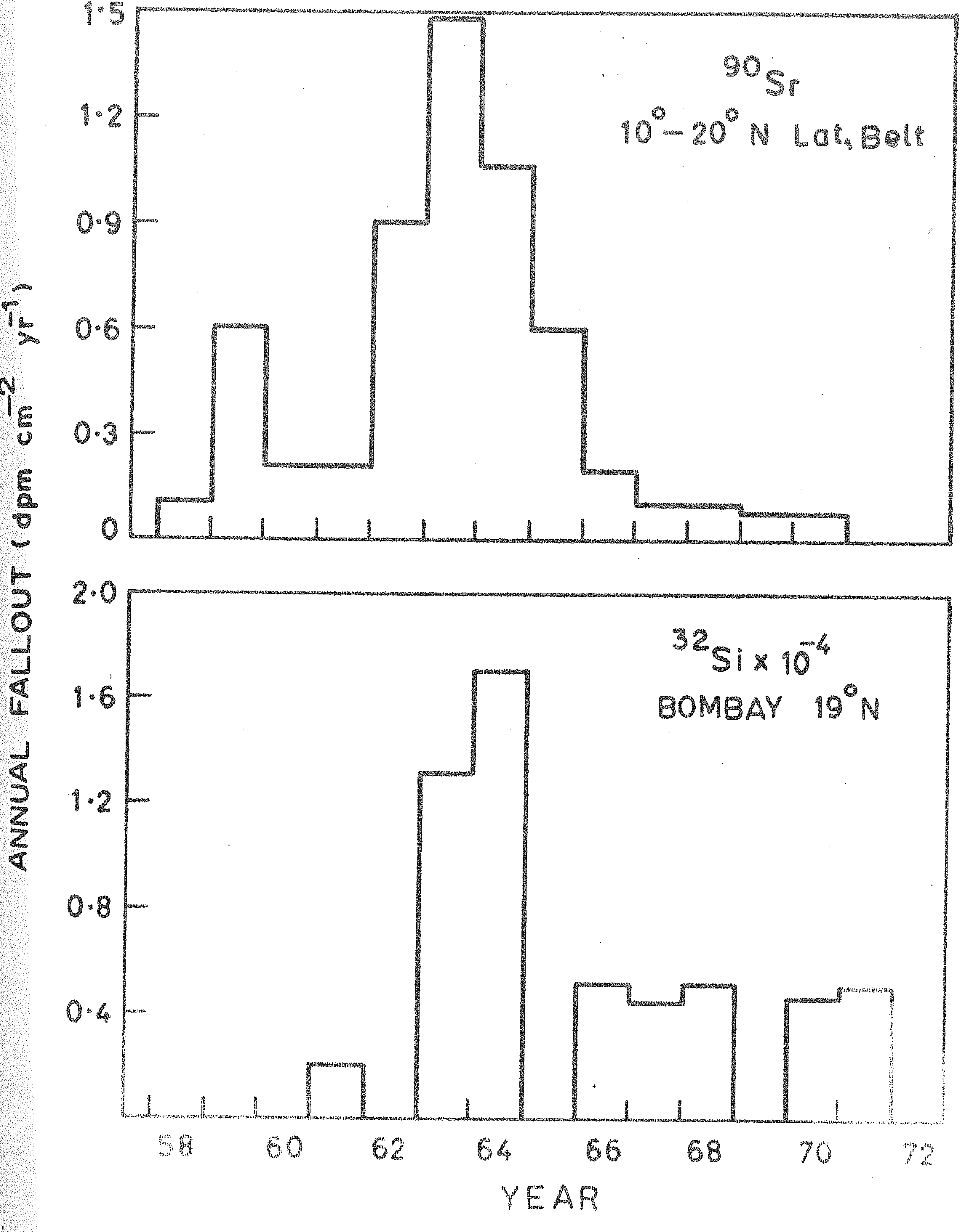
The weighted mean ^{32}Si concentrations in rain water for various years during 1961-1970 (Table.IV.1.,Fig.IV.1,2) show that at Bombay, Khandala and Pathankot the ^{32}Si activity levels and its average annual deposition rates in 1963 and 1964 was higher by a factor of two to three compared to those in preceding and succeeding years. The results for Kodaikanal,and Gwalior however do not show such variations. Since Kodaikanal is a near equatorial station, this may be expected considering the stratosphere-troposphere injection and mixing patterns within the troposphere. However, we cannot offer a logical explanation for the lack of observation of higher ^{32}Si concentrations during 1963 at Gwalior.

The observed peak in the ^{32}Si concentrations in 1963-64 is probably due to its injection by nuclear weapons' testing as found in case of many other isotopes. Similar results were reported by DANSGAARD et al., (1966), who observed a linear relationship between ^{32}Si and ^{90}Sr concentrations in the mid latitude atmosphere, Fig. IV.4 shows the fallout of ^{32}Si during 1958-71 as compared with that of ^{90}Sr (VOLCHOK and KLEINMAN, 1971). The ^{32}Si deposition since 1966 has remained essentially constant suggesting that most of the artificially injected ^{32}Si has been washed out. A removal time of less than four years for the bomb produced ^{32}Si from the atmosphere is indicated by this observation .

The production mechanism of ^{32}Si in nuclear weapons' testing is still not well understood. It can be produced by double neutron capture on ^{30}Si (3 percent abundance); it cannot result from the neutron capture reactions (n,γ), (n,p), or (n,α) since the target nuclides involved are short lived and do not exist in nature (KHARKAR et al., 1966). Its production from sulphur or heavier target nuclides is unlikely since these spallation reactions involve high energy projectiles which do not exist in sufficient influx in a nuclear blast.

Though the results of the present investigation and those of DANSGAARD (1966) show evidence for production of ^{32}Si by bombs, its artificial injection is only a small

Fig. IV.4. Fallout (dpm $cm^{-2}yr^{-1}$) of ^{32}Si at Bombay and ^{90}Sr in 10-20°N latitudinal belt for the years 1958-71. The peak in the ^{32}Si fallout during 1963-64, similar to that of ^{90}Sr suggests that ^{32}Si is introduced into earth's atmosphere by nuclear weapons' testing. The ^{32}Si fallout after 1966 is constant at 0.5×10^{-4} (dpm $cm^{-2}yr^{-1}$) indicating that the bomb contribution is washed out in less than four years.



ANNUAL FALLOUT (dpm cm^{-2} yr^{-1})
1·5
1·2
0·9
0·6
0·3
0
^{90}Sr
10°– 20° N Lat. Belt
2·0
1·6
1·2
0·8
0·4
^{32}Si x 10^{-4}
BOMBAY 19°N
58
60
62
64
66
68
70
72
YEAR

FIG. IV.4

perturbation in its fallout and is negligible to invalidate its application in ^{32}Si hydrology.

IV.3. ^{32}Si in surface waters.

The ^{32}Si activity levels of surface waters were measured mainly with a view to study its interaction with the various soils and rocks during its passage from one reservoir to another . For this purpose, two sets of samples were collected, the Kashmir Valley samples and the major river and lake samples. For the sake of convenience the results of these measurements are discussed separately.

IV.3.1. Surface water samples of Kashmir Valley.

The results of ^{32}Si measurements in the Kashmir Valley samples are presented in Table.III.6. (Chapter-III) and is shown schematically in Fig.IV.5. The data in Table.III.6 and Fig.IV.5 lead to the following observations.

(i) The ^{32}Si concentration for the melt water samples, KAS-3, 0.33 dpm/ton (collected near the annual snow field) is the same as the mean rainwater concentration, 0.3 dpm/ton.

(ii) The ^{32}Si concentration in melt water stream samples (KAS-1,2,4,6,9,10,12 & 13) originating from APARVATH hills and that in KAS-7 collected near Ningli (See Fig.II.2)

Fig.IV.5. A schematic diagram of ^{32}Si concentration in the samples from Kashmir Valley. The average concentration in melt water samples centre around 0.28 dpm/ton. The decrease in the ^{32}Si concentration 0.15 dpm/ton in the Wular lake and Jhelum river flowing from the lake is evident.

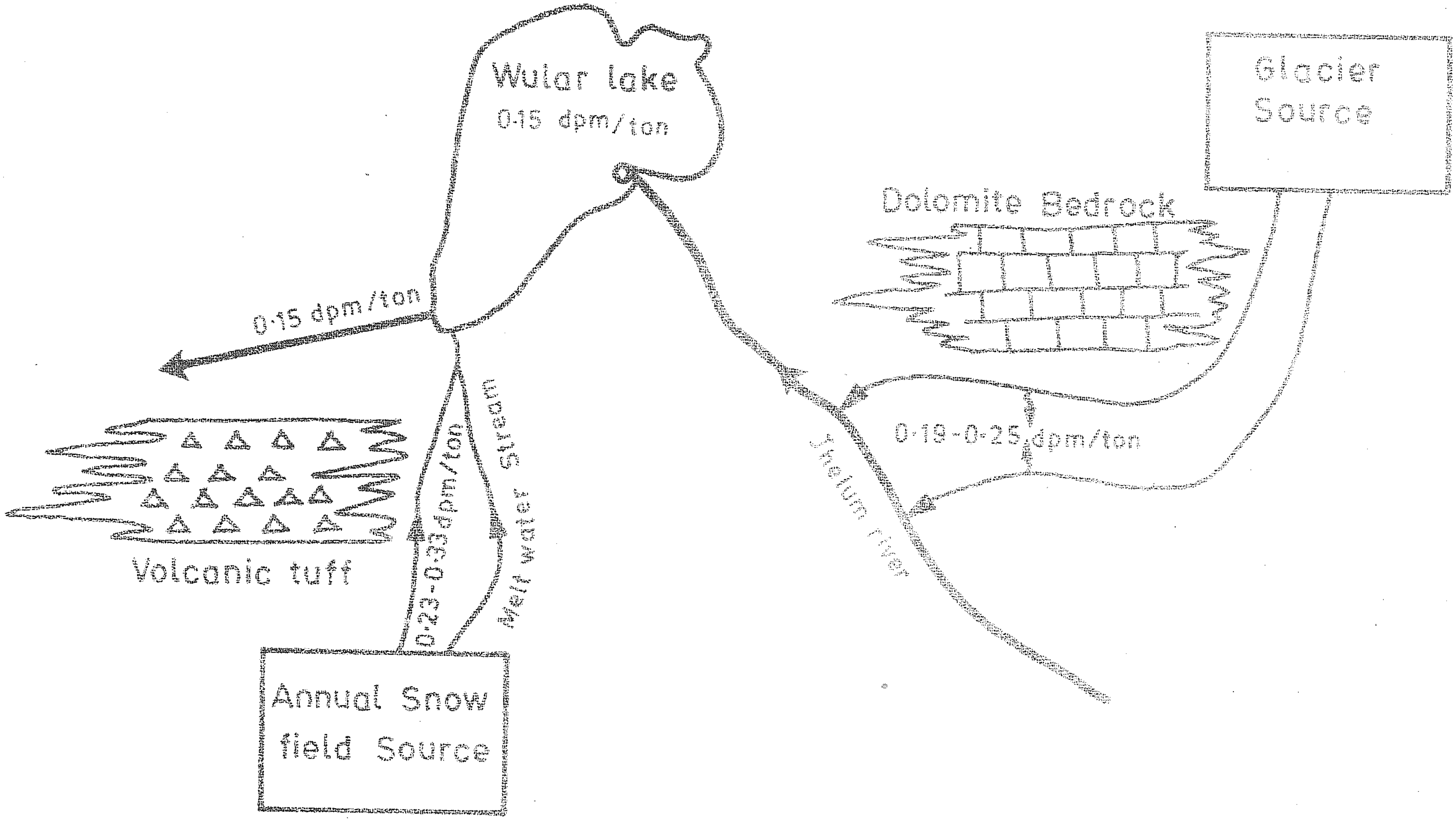

Wular lake
0·15 dpm/ton
Glacier Source
Dolomite Bedrock
0·19-0·25 dpm/ton
Jhelum river
0·15 dpm/ton
Volcanic tuff
0·23-0·33 dpm/ton
Melt water Stream
Annual Snow field Source

FIG. IV.5

the region of melt water input into Wular lake range between 0.23-0.33 dpm/ton with a mean of 0.28 dpm/ton. Two samples KAS-2 and KAS-6 collected at the same location 5 years apart gave consistent results, 0.23 ± 0.05 and 0.29 ± 0.02 dpm/ton respectively. The ^{32}Si activity levels do not show any systematic trend along the path of the stream. The small variations observed in its concentrations is probably due to the experimental uncertainties.

(iii) The ^{32}Si concentration in one sample of Wular lake KAS-8 and the Jhelum river water sample flowing out of Wular lake is about a factor of two lower than the melt water.

Based on these observations, the following conclusions about the geochemical behaviour of ^{32}Si can be drawn :

(i) The ^{32}Si concentration in fast flowing streams is essentially constant and is similar to that of annual snow field samples. This suggests that there is no measurable loss of ^{32}Si in melt-water-streams during their flow.

(ii) The ^{32}Si concentration in the Wular lake water sample is 0.15 dpm/ton compared to the melt water values ranging from 0.19 to 0.33 dpm/ton. This decrease could be due to removal of Si and ^{32}Si to sediments by inorganic and/or biogenic precipitation from the lake water. Further studies on the relative contributions of different melt waters to the lake together with ^{32}Si concentrations will be very useful in understanding this problem.

Stable silica measurements together with seasonal diatom productivity studies were carried out in lakes adjacent and inter-connected with the Wular lake (RAZDAN,1974). During summer months i.e.,May-October the diatom productivity was higher and the stable 'Si' concentration were lower by a factor of 4-5 compared to the values measured for the rest of the year (1.2-5.0 ppm SiO_2) suggesting the removal of 'Si' by diatoms. Hence, ^{32}Si like Si also gets depleted from surface waters of Wular lake resulting in the reduction of the absolute concentration of ^{32}Si.

IV.3.2. ^{32}Si concentrations in major river and lake water samples.

The results of these measurements are given in Table.III.7. The ^{32}Si concentrations of rivers measured near their origins, Ganges at Hardwar and Godawari at Nasik are 0.14 and 0.11 dpm/ton respectively. These values are similar to that in Wular lake and Jhelum river, but are lower by about a factor of 2-3 compared to melt-water samples. However, the ^{32}Si activity levels in samples of these rivers collected about a thousand kilometers downstream are lower by a factor of 1.5 compared to the value at their origin. The ^{32}Si concentration in Tansa lake samples range between 0.12-0.2 dpm/ton for the years 1963-72, the activity levels are 30-40% lower compared to that in rain waters for the corresponding years. These results suggest that there is a measurable loss of ^{32}Si in lakes and rivers either by its absorption or exchange with silicates present in these reservoirs or its biogenic removal through diatoms. Laboratory experiments were carried out with a view to assess the regulatory effect of silicates in governing the concentration of ^{32}Si in natural waters. These experiments are discussed in brief below.

IV.4. Interaction of silicon isotopes with soils and minerals.

IV.4.1. Experiments using natural silicon-32.

These experiments consisted of shaking lateretic red soil with rain water. Rain water samples of about 3-5 tons were split into two or three aliquots, one aliquot was processed directly for ^{32}Si measurement and was used as reference sample. To a second aliquot red soil was added at a level of 20 kg/ton of rainwater and was left for a period of about two months with periodic stirring. The release of silica by soil was monitored occasionally to ascertain the attainment of equilibrium. The supernatant water was separated and its ^{32}Si activity was measured. With a view to increase the time of contact of the water with soil, experiments were repeated using the third aliquot of rain water which was passed through a column (diameter = 20 cm, height = 125 cms, flow rate = 30 ml/min.) containing 50 kg of red soil. The results of these experiments are given in Table-IV.3. The results in Table-IV.3 suggest that there is no measurable loss of ^{32}Si from rain water when it is shaken with red soil.

TABLE-IV.3

INTERACTION OF NATURAL ^{32}Si WITH RED SOIL

Sample	Details of aliquots processed.	Volume processed (ton)	Inherent SiO_2 concentration (ppm)	Net ^{32}P* activity (cph)	^{32}Si concentration (dpm/ton)
Rain water (1964)	Direct (1964)	2.10	0.5	18.6	0.85 ± 0.09
	After shaking with 80 Kg. red soil.	0.95	8.0	7.8	0.80 ± 0.08
Rain water (1971)	Direct	4.00	0.3	17.8	0.22 ± 0.02
	After passing through column containing (50 Kg) red soil.	2.50	6.0	9.5	0.20 ± 0.02
	After shaking with 50 kg. red soil.	3.20	4.0	8.9	0.19 ± 0.02

* The value at the time of ^{32}P separation is estimated from least square line drawn on decay plots.

IV.4.2. Experiments using Silicon-31.

It is clear at the outset that with an isotope like ^{31}Si having a short half-life ($t_{\frac{1}{2}}$ = 2.6 h), one cannot quantitatively study the loss in soil-water system and extrapolate to groundwater systems in nature. The very fact that one observes ^{32}Si activity in groundwaters, implies that the loss due to exchange processes is small. However, in order to study the behaviour of ^{31}Si with soils/minerals, it was considered apt to do a few experiments in the laboratory using ^{31}Si.

Artificially produced ^{31}Si in the form of silicic acid was passed through various soils and minerals (~10g) packed in perspex columns at different pH, flow rates and silica concentrations. The ^{31}Si beta activity before and after its interaction with soil/mineral was assayed by a liquid scintillation beta counter at BARC, Bombay.

The results of these experiments are given in Table IV.4. Systems involving fine sand, quartz, are ideal since the loss of ^{31}Si activity is negligible (<5%). However, the losses range from 10-85% for soils and minerals like Kaolinite and Montmorillonite. It is observed that the loss of ^{31}Si decreases by washing the columns with increasing volumes

TABLE - IV.4

INTERACTION OF ^{31}Si ACTIVITY WITH SOILS AND MINDERALS.

Nature of Sample.	+ Clay % (<2 µ)	+ Silt % (2-20 µ)	+ Coarse fraction (>20 µ)	++ C.E.C. m.eg./100 g.	Loss of ^{31}Si activity %
Coarse Sand	0	0	100	0	0
Quartz Powder	0	0	100	0	0
Fine Sand	1.1	1.4	97.5	0	5
Zeolite	-	-	-	-	12
Red Soil	42	2.0	55	9	45-50
Kaolinite	100	0	0	5	35
Black Soil	18.6	45.4	28.2	8	85
Montmorillonite	100	0	0	32	85

\+ Clay, silt and coarse fraction analyses were done with different size-fractious.

++ C.E.C. is the Cation Exchange Capacity.

of active solution. Unfortunately the exchange experiments could not be carried out for more than four hours in view of its very short half-life. Though it is very difficult to extrapolate these results to natural systems involving ^{32}Si exchange over periods longer than the half-life of ^{32}Si (500 y), the important observation one can make is that the losses taking place due to adsorption, if any, of ^{32}Si activity (like that of ^{31}Si on soil/mineral) will be subsequently released into the water.

Since the groundwater systems are old compared to half-life of ^{32}Si the fact that ^{32}Si activity is observed in groundwaters suggests that the exchange mechanism may not be very important.

From above discussions it appears that the removal of ^{32}Si by chemical exchange between the dissolved silicon and minderals of the water bearing rocks is unimportant, unlike ^{14}C where depletion of ^{14}C/^{12}C ratio can occur by exchange process (VOGEL,1970). However, as the rocks and soil-types may change considerably along the migratory routes of water, significant losses of ^{32}Si may occur. The magnitude of losses can possibly be ascertained by measuring the concentrations of dissolved silicon at different regions.

Presently available results do not offer a simple explanation as why the Ganges and Godavari river waters near the points of their origin, Hardwar and Nasik respectively, are depleted by a factor of about 2-3 in their ^{32}Si concentrations compared to the melt-waters. Probably biogenic processes play a dominant role in regulating the ^{32}Si concentrations in these reservoirs.

IV.5. Silicon-32 in groundwaters.

IV.5.1. Samples collected from unconfined aquifers.

The ^{32}Si concentrations in the samples from unconfined aquifers range between 0.01-0.11 dpm/ton (Table.III.8). ^{14}C and ^{3}H measurements were carried out on some of these samples. (Tables.III.12, IV.5 & IV.6). The results of ^{14}C and ^{3}H analyses show that most of these samples contain artificially injected activities of these isotopes. This suggests that the aquifers are recharged quickly which is consistent with the expectation since they lie in the unconfined zone. If these aquifers are recharged quickly, the ^{32}Si concentrations in them should be similar to that in surface waters, 0.1-0.15 dpm/ton. However, the measured values are lower. A closer examinations of the results in Table.III.8 show that the lowest concentration are for open well samples, 0.01-0.09 dpm/ton (mean 0.045 dpm/ton). In the three tubewell samples GJ-3, GJ-4 and MH-1, the ^{32}Si concentrations are 0.04, 0.09 and 0.11 dpm/ton respectively. The concentrations in GJ-4 and MH-1 are similar to what is expected from the river and lake water data.

The observed low concentrations of ^{32}Si in the open well samples is intriguing. It is likely that the low concentration is due to biogenic removal processes in these wells. Such an hypothesis is based on the results of red soil, rain water experiments (Section.IV.4.1) coupled with the possibility that high biogenic productivity can occur in open wells.

IV.5.2. Samples collected from confined aquifers.

The sampling and measurement of ^{32}Si in confined aquifers were carried out mainly with a view to study its applicability as a radiotracer for dating. Towards this purpose twenty seven samples were collected from confined aquifers (depth 60 m) of Gujarat, Rajasthan and Neyveli.

The results of these measurements are given in Tables. III.3, 9, 10 & 11. The measurements made were reproducible and good signals of ^{32}P (2-6 cph) observed in most of the samples.

The dating of a water mass at different points and depths of an aquifer allows one to estimate some of its characteristics, viz. flow velocity, rate of recharge, water volume. The ages of the groundwaters can be calculated using the relation

$$A = A_o e^{-\lambda T_a} \qquad \ldots \qquad (4.1)$$

where A and A_o are the concentrations of the radioisotope in the groundwater and source water respectively, λ is the decay constant of the isotope and T_a is its "radiotracer age" which represents the time elapsed since meteoric water enters into the surface soil. In case of ^3H and ^{14}C their specific activities, $^3H/H$ and $^{14}C/^{12}C$ are used unlike the case of ^{32}Si where the absolute concentration (dpm/ton) is employed for the age calculations. The ages are estimated assuming that the aquifers behave as a closed system i.e. there is no loss of the isotope under consideration other than by the radioactive decay. Thus for estimating the ages, the values of the various parameters A, A_o, and λ (e.g. 4.1) have to be known.

The problem of groundwater chronology and its usefulness in assessing recharge rates are well known (VOGEL, 1967) ; RAMA, 1968). The relationship between the aquifer parameters and the radiotracer concentrations is ambiguous because of the variability existing in the spatial rates of recharge, confinement and stratification of water. Additionally in tube-well samples, water pumped out often represents a mixture of water derived from different strata. Inspite of these problems some general features of the aquifer can be deduced from the estimated radiotracer ages using simplified models which take into consideration the variability in the rate of recharge, internal mixing with the aquifer etc.

The rate of recharge which is the quantity of interest is related to the volume of water in the reservoir by

$$T = V/R \qquad .... \qquad (4.2)$$

where T is the mean residence time of water molecules in an aquifer, V is volume of the aquifer and R its recharge rate. Thus to estimate the mean residence time T, it is necessary to have an idea of R, and the state of internal mixing within the aquifer.

NIR (1964), proposed two models for groundwater aquifers (i) the 'piston model' where one assumes that the system is a closed parcel and bounded by planes parallel to flow lines of constant and equal velocity. Additional assumption of fast vertical mixing allows one to treat the system as one dimensional, where the concentration of the tracer in planes perpendicular to flow lines will be constant, (Case:I, Fig.IV.6) and (ii) the 'steady state model' where we assume that the recharged water is quickly mixed throughout the whole water body, and the volume of recharge is small compared to the volume of aquifer. The recharge and discharge rates R and D are equal i.e. the volume of aquifer is constant. Similar models were used for calculating ^{32}Si and ^{14}C ages (LAL et al., 1970). A simplified schematic of these models are given in Fig.IV.6.

At steady state we have -

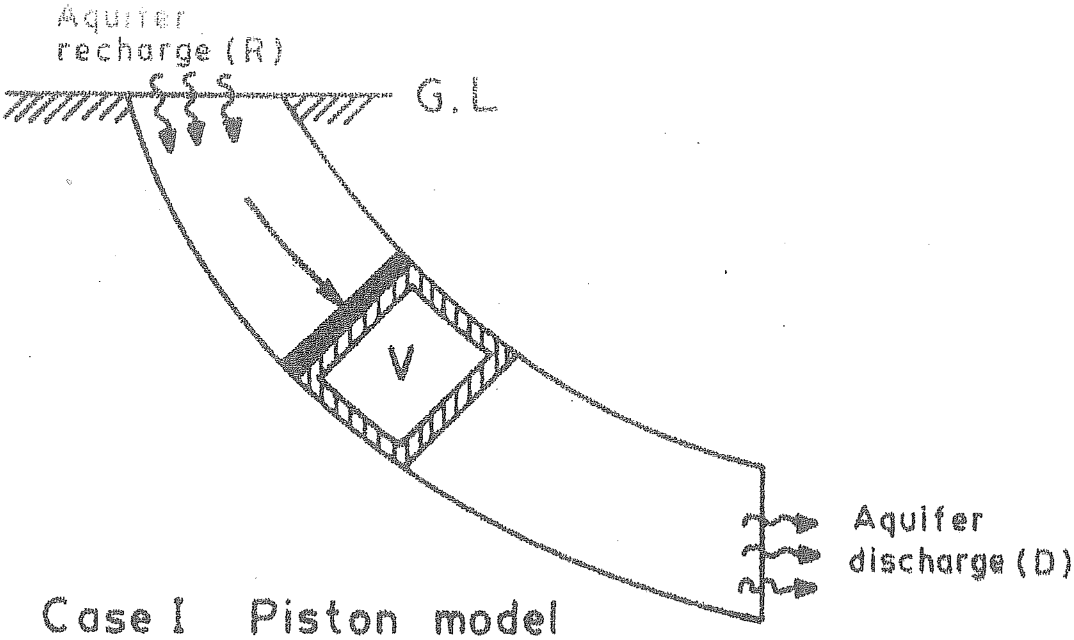
$$RA_o = RA + VA\lambda \qquad \ldots \qquad (4.3)$$

where A_o and A are the concentration of the isotope in the feed waters and the well mixed aquifer respectively. The relation between the residence time T and radiotracer age T_a is given by :

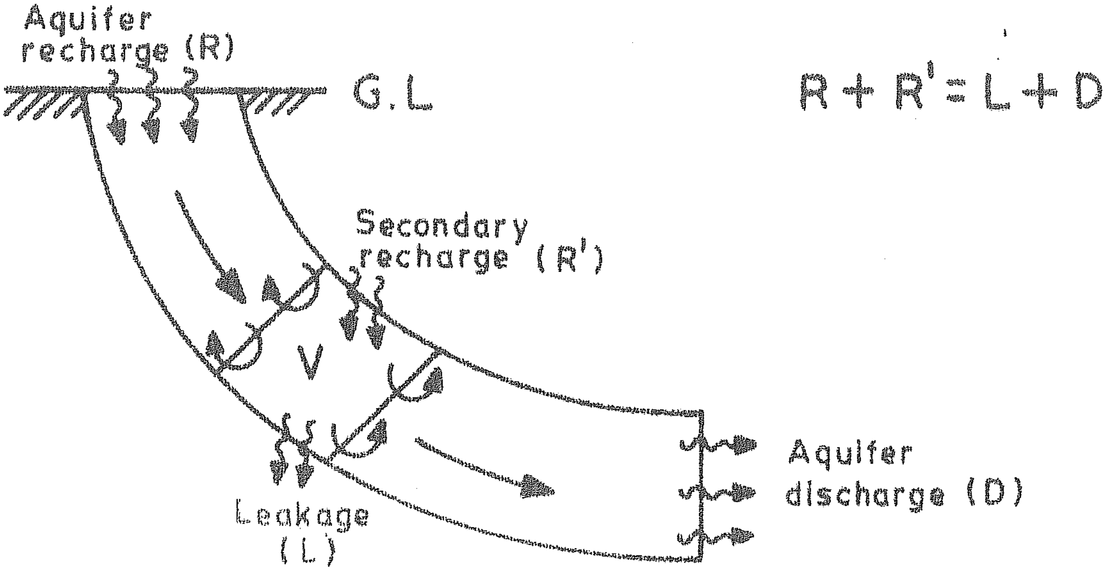
$$T_a = \frac{1}{\lambda} \ln (1+\lambda T) \qquad \ldots \qquad (4.4)$$

which can be obtained from equations (4.1), (4.2) and (4.3). T_a vsT is plotted in the Fig.IV.7 (CRAIG, 1963 ; LAL, 1967).

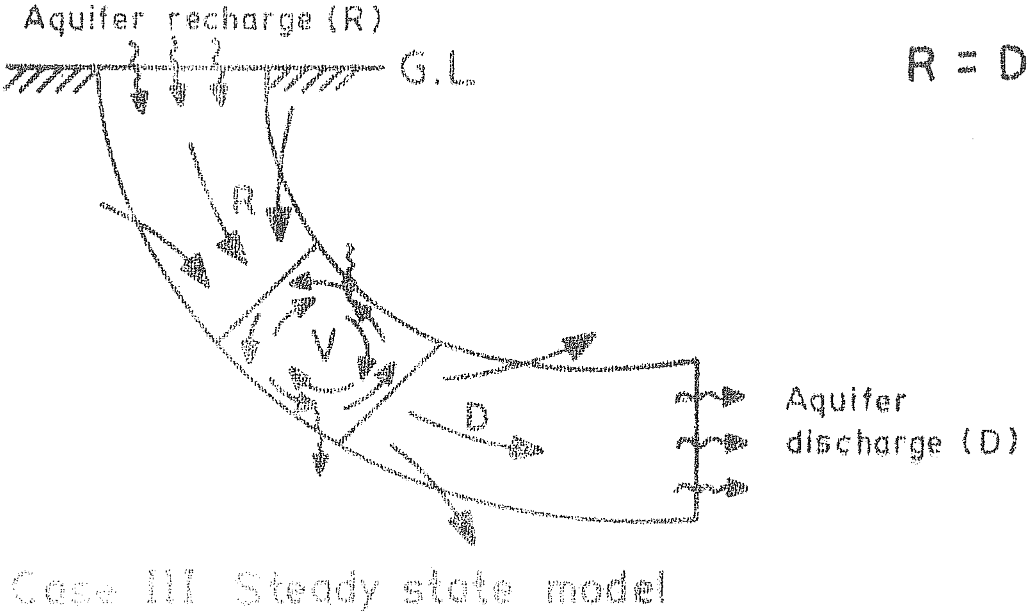
Fig. IV.6 A schematic of groundwater models used for calculation of their ages. The interrelation between recharge rates and the volume of the aquifer are given.



Case I Piston model

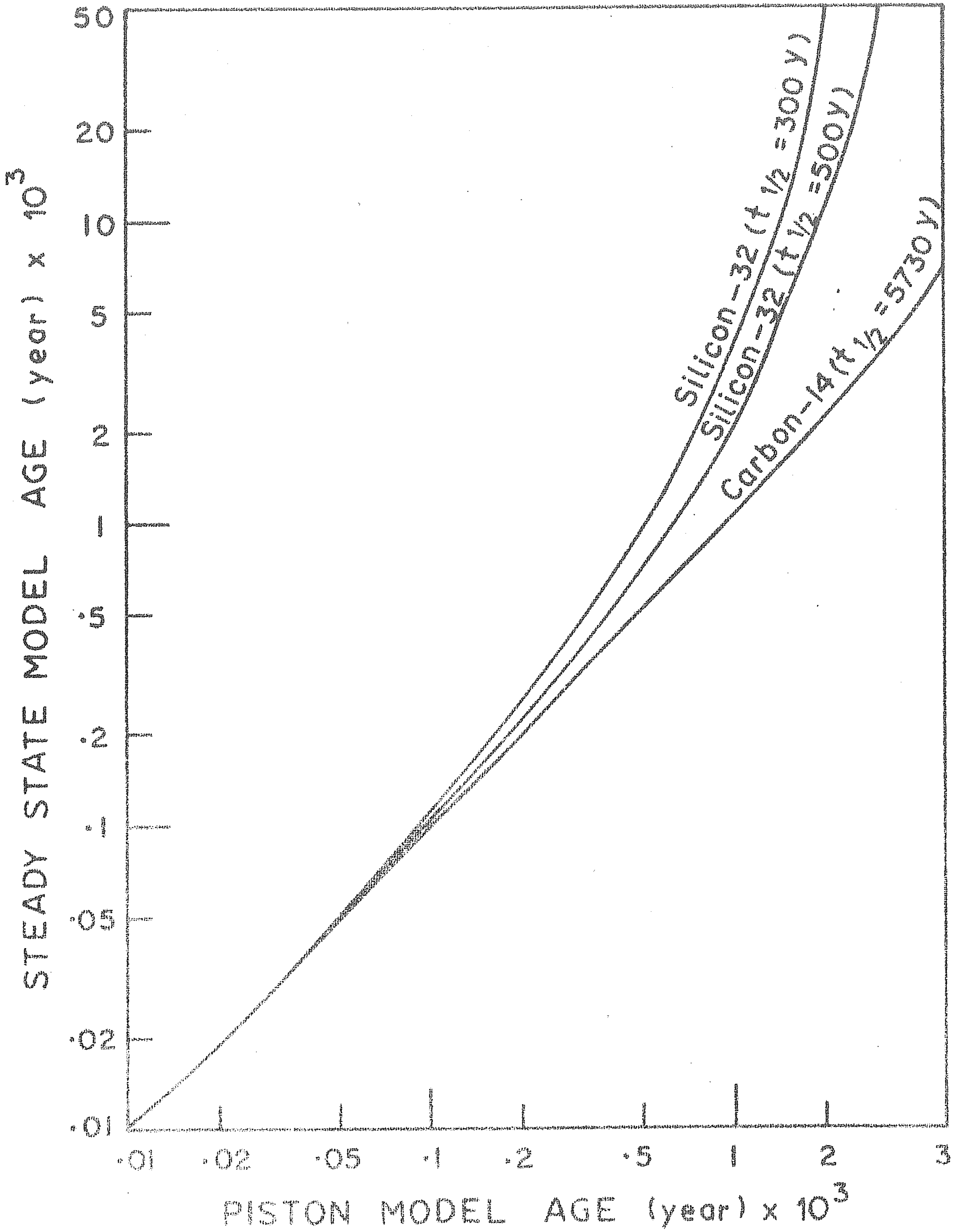


Case II Intermidiate model



Case III Steady state model

Fig. IV.7 Relation between "Piston" model age (T_a) and "Steady State" model age (T) calculated using equation (4.4). It is evident that good agreement between the T_a and T are obtained, for ages less than about a mean life of the isotope.



STEADY STATE MODEL AGE (year) x 10^3
50
20
10
5
2
1
·5
·2
·1
·05
·02
·01
PISTON MODEL AGE (year) x 10^3
·01
·02
·05
·1
·2
·5
1
2
3
Sillicon-32 (t 1/2 =300 y)
Sillicon-32 (t 1/2 =500y)
Carbon-14 (t 1/2 =5730 y)

FIG. IV. 7

The relation predicts that the residence time or the "steady state" model age T should be progressively larger than the radio-tracer age (i.e. "piston" model age) T_a. The difference becomes particularly important when $T_a >> \frac{1}{\lambda}$. For $T_a << \frac{1}{\lambda}$ the difference between T_a and T is not significant.

It is apparent from relation (4.4) that the estimated value of T is dependent on the half-life of the isotopes. Thus if a concurrent age is obtained using two isotopes of different half-lives, it implies that the deduced radiotracer age is closer to the residence time T of the aquifer. With this view the ages are estimated using both ^{14}C and ^{32}Si isotopes whose half-lives differ by more than an order of magnitude. However, if this is not so, it would be expected that a given water body will look younger on the basis of a short lived radioisotope and that the "true age" would be even greater than that obtained on the basis of the longer-lived isotope.

IV.6. Initial concentration of ^{32}Si in the source water (INSIRT).

The water feeding underground aquifers are surface waters and hence the ^{32}Si concentrations in feed waters can be assumed to be the same as that in river and lakes. The concentrations in these surface reservoirs are about a factor of two lower compared to that in wet precipitation, probably because of biological removal processes. Hence, in regions where the recharge occurs directly, the feed values are expected to be the same as that in rain water.

Fig. IV.8 presents the range of the measured ^{32}Si concentrations in rain and surface water. The data in Fig. IV.8(a) show that most of the rain water samples have concentrations in the range of 0.2–0.3 dpm/ton. The high values (0.5 dpm/ton) are during 1963-64 when considerable amount of ^{32}Si have been artificially injected into earths atmosphere by nuclear weapon testings (DANSGAARD, 1966 ; Section. IV.2, present work). Table. IV.2 gives the average ^{32}Si concentration in wet precipitation for the post-bomb era (after 1967). From the data in Table. IV.2 the mean ^{32}Si concentration in rain water for 0-30°N belt is calculated to be 0.3 dpm/ton. The ^{32}Si activity levels in major rivers and lakes of India (excluding the melt water samples of Kashmir) range between 0.08–0.21 dpm/ton (Table. III.7) with a mean of 0.15 dpm/ton. The ages of groundwaters have been estimated using both 0.3 and 0.15 dpm/ton for the initial concentration (dpm/ton) of ^{32}Si in source waters, hereafter known as INSIRT. The calculated ages of groundwaters differ by one half-life of ^{32}Si because of this uncertainty of factor of two in its feed value.

Fig. IV.8 Frequency distribution of ^{32}Si concentration in rain and surface waters. The shaded area represents the concentrations in the melt water samples of Kashmir. Majority of the rainwater samples have concentrations in the range 0.2-0.3 dpm/ton. The higher values (>0.5 dpm/ton) are for the samples collected during 1963-64 after the nuclear weapons' testing. The mean concentration in the melt water stream is 0.28 dpm/ton, similar to rain water. The low ^{32}Si concentrations of 0.1-0.2 dpm/ton for surface water samples is probably due to its removal by biogenic processes.

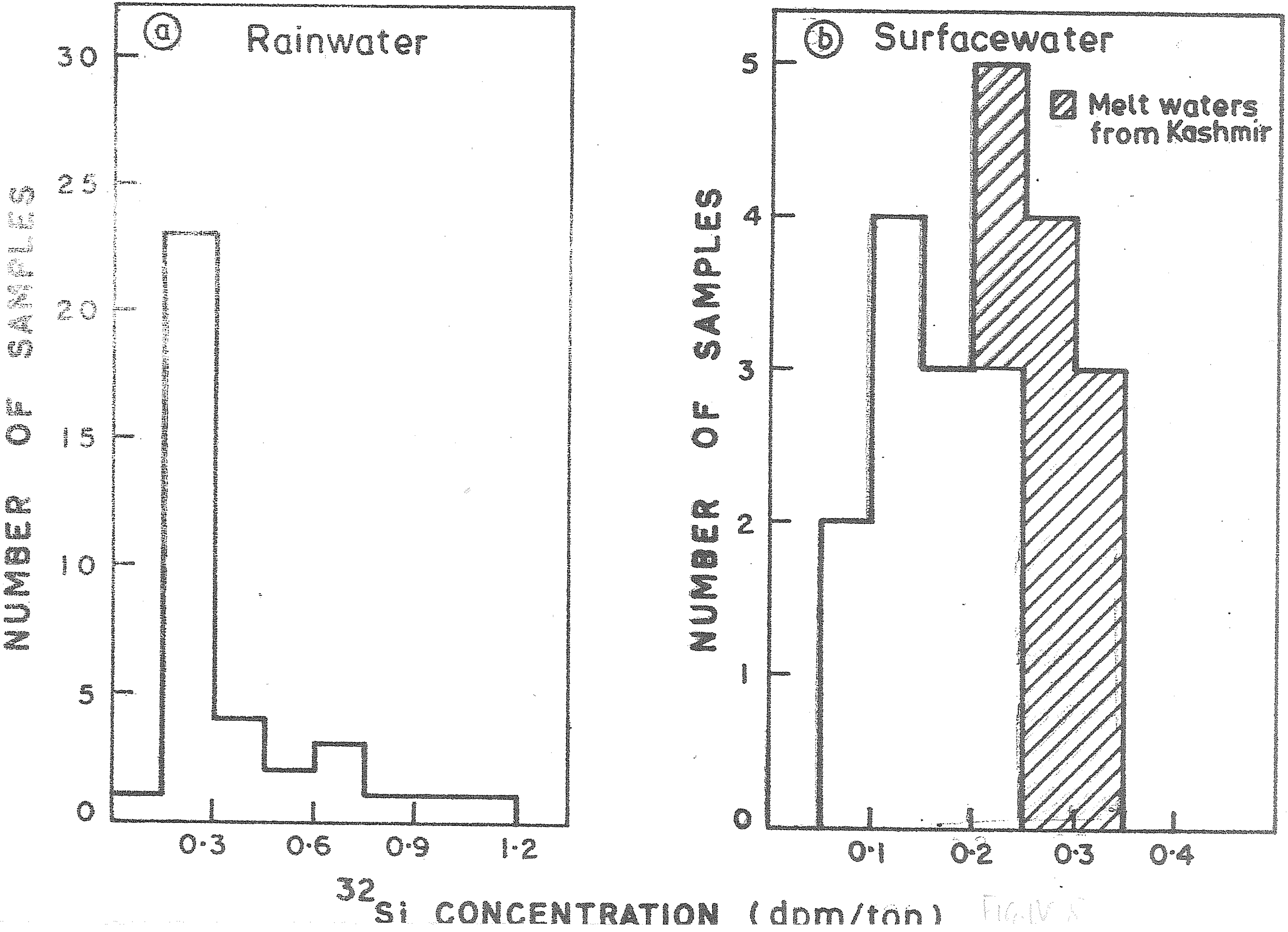

NUMBER OF SAMPLES
30
25
20
15
10
5
0
ⓐ Rainwater
0·3
0·6
0·9
1·2
NUMBER OF SAMPLES
5
4
3
2
1
0
ⓑ Surfacewater
▨ Melt waters from Kashmir
0·1
0·2
0·3
0·4
^{32}Si CONCENTRATION (dpm/ton)

FIG.IV.5

IV.7. Initial concentration of ^{14}C in the source water.

In the ^{14}C method, the specific activity ($^{14}C/^{12}C$) of the feed waters should be same as PIPN (Pre Industrial Pre Nuclear) wood value if the system is closed for ^{14}C atoms. However, the dissolved CO_2 in water may be partially consumed during the dissolution of carbonate minerals present in the rock formation.

$$CaCO_3 + {}^{14}CO_2 + H_2O = (H^{14}CO_3^- + HCO_3^-) + Ca^{++} \quad .. (4.5)$$

Thus, the bicarbonate ions produced by the dissolution process derives half of its carbon from biogenic CO_2 containing ^{14}C and the other half from the mineral carbonate which normally does not contain ^{14}C because of their old age. Thus the specific activity of ^{14}C of bicarbonate ion is reduced to 50% of that of biogenic CO_2. The observed ^{14}C activities in young waters based on ^{3}H data centre around 85% of that of biogenic CO_2 (VOGEL, 1970). Because of this loss of ^{14}C by exchange processes the ages of groundwaters have been calculated using two values for the $^{14}C/^{12}C$ specific activity in the source water (i) PIPN value and (ii) 0.85 x PIPN (VOGEL,1970). The calculated ages differ by 1300 years using two feed values.

IV.8. Half-lives of ^{32}Si and ^{14}C used for calculation of groundwater ages.

The reported half-life of ^{32}Si ranges between 140-700 years (SCHINK, 1968). The recent measurements indicate a value of about 300 y for its half-life (For discussion See Chapter.I). Two working values of 500 and 300 years have been used to calculate the ages of groundwaters in the present work. For ^{14}C a value of 5730 has been used.

IV.9. Comparison of the ^{32}Si and ^{14}C ages of groundwater.

The ^{32}Si and ^{14}C ages of groundwaters have been calculated by considering the "piston" and "steady state" models using relations (4.1) and (4.4) respectively. The different values of the half-life of ^{32}Si, INSIRT values for ^{32}Si and initial concentrations for ^{14}C in source water are given below:

Isotope	Half-life (y)	A_0
Silicon-32	500 ; 300	0.3 ; 0.15 (dpm/ton)
Carbon-14	5730	PIPN, 0.85 x PIPN

The estimated ages are given in Tables. IV.5 & IV.6 and Fig. IV.9, 10, 11, 12, 13 & 14.

T A B L E - IV.5

CALCULATED ^{32}Si AND ^{14}C "PISTON MODEL" AGES OF GROUNDWATER SAMPLES

Code	Site	Silicon-32 Age*				Carbon-14 Age**	
		(a)	(b)	(c)	(d)	(i)	(ii)
	RAJASTHAN						
RJ- 2	Palana	2100	1600	1300	1000	5000	3700
RJ- 5	Chandan	3000	2500	1900	1600	4700	3400
RJ- 6	Bhairwa	2500	2000	1500	1200	7100	5800
RJ- 7	Bhairwa	2300	1800	1400	1100	7000	5700
RJ- 8	Bhairwa	3100	2600	1900	1600	8100	6800
RJ- 9	Devikot	2200	1700	1300	1000	^{14}C excess@	^{14}C excess@
RJ-10	a) Ajasar	2400	1900	1400	1100	8400	7100
RJ-10	b) Ajasar						
RJ-10	c) Ajasar						
RJ-12	Niraun	1600	1100	1000	700	1300	^{14}C excess@
RJ-13	Palana	1600	1100	1000	500	5000	3700

T A B L E -IV.5

con..2..

Code	Site	Silicon-32 Age*				Carbon-14 Age**	
		(a)	(b)	(c)	(d)	(i)	(ii)
GUJARAT							
GJ- 1	Deesa	1700	1200	1000	700	^{14}C excess$^{@}$	^{14}C excess$^{@}$
GJ- 4	Balad	700	200	400	100	2800	1400
GJ- 5	Vijapur	1500	1000	900	600	2300	1000
GJ- 6	Dama	2100	1600	1300	900	1800	500
GJ- 7	Mansa	2000	1500	1200	900	1300	-
GJ- 8	Pilvai	2500	2000	1600	1300	2600	1200
GJ-10	Kalol	1700	1200	1000	700	3600	2300
UTTAR PRADESH							
UP- 1	Shankarpura	2100	1600	1300	900	2400	1100
UP- 4	Nagla	3800	2500	2400	2100	3400	2100
PUNJAB							
P - 1	Amritsar	2000	1500	1200	900	2700	1400
P - 2	Ropar	1000	500	600	300	300	^{14}C excess$^{@}$

T A B L E -IV.5

con..3..

Code	Site	Silicon-32 Age*				Carbon-12 Age**	
		(a)	(b)	(c)	(d)	(i)	(ii)
TAMIL NADU							
TN- 1	Neyveli	900	400	600	250	500	^{14}C excess@
MAHARASHTRA							
MH- 1	Mulund	900	400	500	200	^{14}C excess@	^{14}C excess@

* The ages are calculated using the following values for ^{32}Si half-life (yrs) and feed values (dpm/ton) (INSIRT) : (a) 500, 0.3 ; (b) 500, 0.15 ; (c) 300, 0.3 ; (d) 300, 0.15.

** The ages are calculated using the following values for initial ^{14}C concentration ($^{14}C/^{12}C$) : (i) PIPN and (ii) 0.85 x PIPN.

@ In these cases, the groundwaters are observed to have excess ^{14}C activities above natural level and hence these groundwater samples are recent, i.e. post-bomb (later than 1954).

T A B L E - IV.6

CALCULATED ^{32}Si AND ^{14}C "STEADY STATE" MODEL AGES OF GROUND-WATER SAMPLES

Code	Site	Silicon- 32 Age*				Carbon-14 Age**	
		(a)	(b)	(c)	(d)	(i)	(ii)
	RAJASTHAN						
RJ- 2	Palana	13,000	6,000	7,700	3,600	6,900	5,520
RJ- 5	Chandan	51,000	23,000	30,000	15,000	6,300	4,970
RJ- 6	Bhairwa	21,000	10,000	13,000	6,000	11,000	9,790
RJ- 7	Bhairwa	17,000	8,000	11,000	5,000	11,000	9,670
RJ- 8	Bhairwa	51,000	26,000	30,000	15,000	14,000	11,370
RJ- 9	Devikot	14,000	6,700	8,000	4,000	^{14}C excess@	^{14}C excess@
RJ-10	a) Ajasar					14,000	13,000
RJ-10	b) Ajasar	17,000	8,700	11,000	5,000	16,000	15,000
RJ-10	c) Ajasar					61,000	60,000
RJ-12		6,000	2,600	3,500	1,600	1,400	80
RJ-13	Palana	6,000	2,600	3,700	1,600	6,800	5,500

TABLE -IV.6

con..2..

Code	Site	Silicon-32 Age*				Carbon-14 Age**	
		(a)	(b)	(c)	(d)	(i)	(ii)
GUJARAT							
GJ- 1	Deesa	7,000	3,100	4,200	190	^{14}C excess@	^{14}C excess@
GJ- 4	Balad	1,300	250	750	150	3,300	1,900
RJ- 5	Vijapur	5,000	2,100	3,000	1,200	3,100	1,800
GJ- 6	Dama	13,000	6,100	7,700	3,600	2,000	690
GJ- 7	Mansa	12,000	5,300	7,200	3,200	1,400	80
GJ- 8	Pilvai	29,000	14,000	17,000	8,200	3,000	1,700
GJ-10	Kalol	1,000	700	7,000	3,200	4,400	3,100
UTTAR PRADESH							
UP- 1	Shankarpura	13,000	6,000	7,700	3,600	3,100	1,800
UP- 4	Nagla	1,80,000	90,000	114,000	54,000	4,300	2,900
PUNJAB							
P - 1	Amritsar	10,000	4,700	6,000	2,800	3,200	1,900
P - 2	Ropar	2, 00	900	1,600	320	330	0

TABLE - IV.6

con..3..

Code	Site	Silicon-32 Age*				Carbon-14 Age**	
		(a)	(b)	(c)	(d)	(i)	(ii)
TAMIL NADU							
TN- 1	Neyveli	2,500	570	1,500	340	560	0
MAHARASHTRA							
MH- 1	Mulund	2,400	500	1,400	290	^{14}C excess@	^{14}C excess@

---

* The ages are calculated using the following values for ^{32}Si half-life (yrs) and feed values (dpm/ton) (INSIRT) : (a) 500, 0.3 : (b) 500, 0.15 ; (c) 300, 0.3 ; (d) 300, 0.15.

** The ages are calculated using the following values for initial ^{14}C concentration ($^{14}C/^{12}C$) : (i) PIPN and (ii) 0.85 x PIPN.

@ In these cases, the groundwaters are observed to have excess ^{14}C activities above natural level and hence these groundwater samples are recent, i.e. post-bomb (later than 1954).

Fig.IV.9 Plot of ^{32}Si vs ^{14}C ages deduced using the "piston" model approach. The values adopted for ^{32}Si half-life, its feed value (INSIRT) and initial specific activity of ^{14}C (i.e. $^{14}C/^{12}C$) are also given. Samples RJ-9, GJ-1 and MH-1 show excess Carbon-14 activity and as such they are recent(later than 1954). Sample GJ-4 shows a very young ^{32}Si age which is not unexpected considering its proximity to the recharge area. Some samples like GJ-6,7,8 ; RJ-12; TN-1; P-2; UP-4 show a close agreement between ^{32}Si and ^{14}C ages.

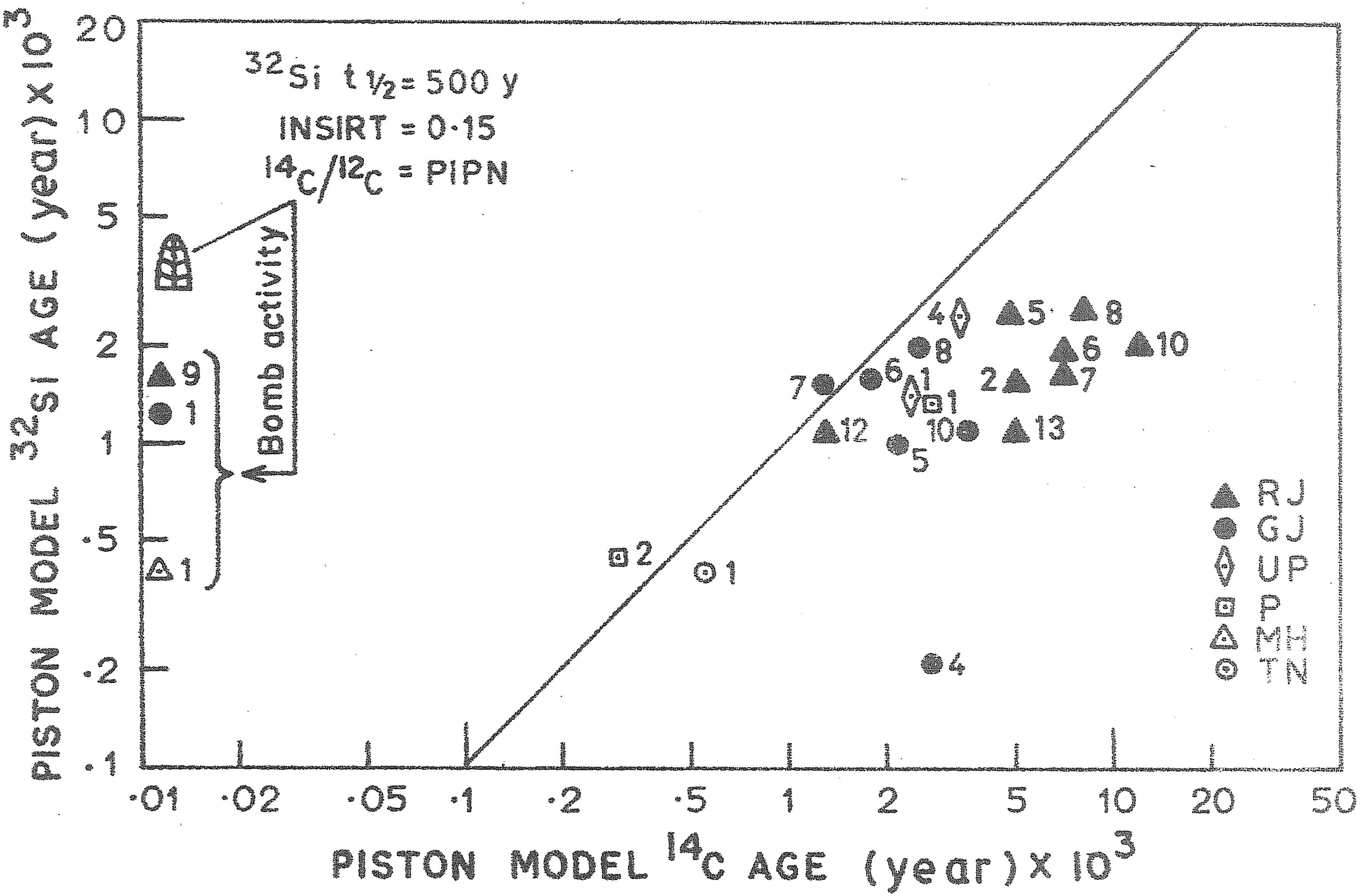

PISTON MODEL ^{32}Si AGE (year) X 10^3
PISTON MODEL ^{14}C AGE (year) X 10^3
20
10
5
2
1
·5
·2
·1
·01
·02
·05
·1
·2
·5
1
2
5
10
20
50
^{32}Si t$_{1/2}$ = 500 y
INSIRT = 0·15
^{14}C/^{12}C = PIPN
Bomb activity
9
1
1
4
5
8
8
6
10
7
6
1
2
7
1
12
10
13
5
2
1
4
▲ RJ
● GJ
◊ UP
⊡ P
△ MH
⊙ TN

FIG. IV.9

Fig.IV.10 Plot of ^{32}Si vs ^{14}C ages obtained by using the "steady state" model. The values adopted for ^{32}Si half-life, its feed value (INSIRT) and initial specific activity of ^{14}C considered are also shown. Samples RJ-9; GJ-1 and MH-1 show excess ^{14}C activity. The deduced ages are in satisfactory agreement for the samples RJ-2,6,7,8,12 ; MH-1 and P-2(Average ^{14}C age of three aquifers of sample RJ-10 is plotted against average ^{32}Si age of these aquifers since unlike ^{14}C, ^{32}Si ages of individual aquifers of these samples were not measured).

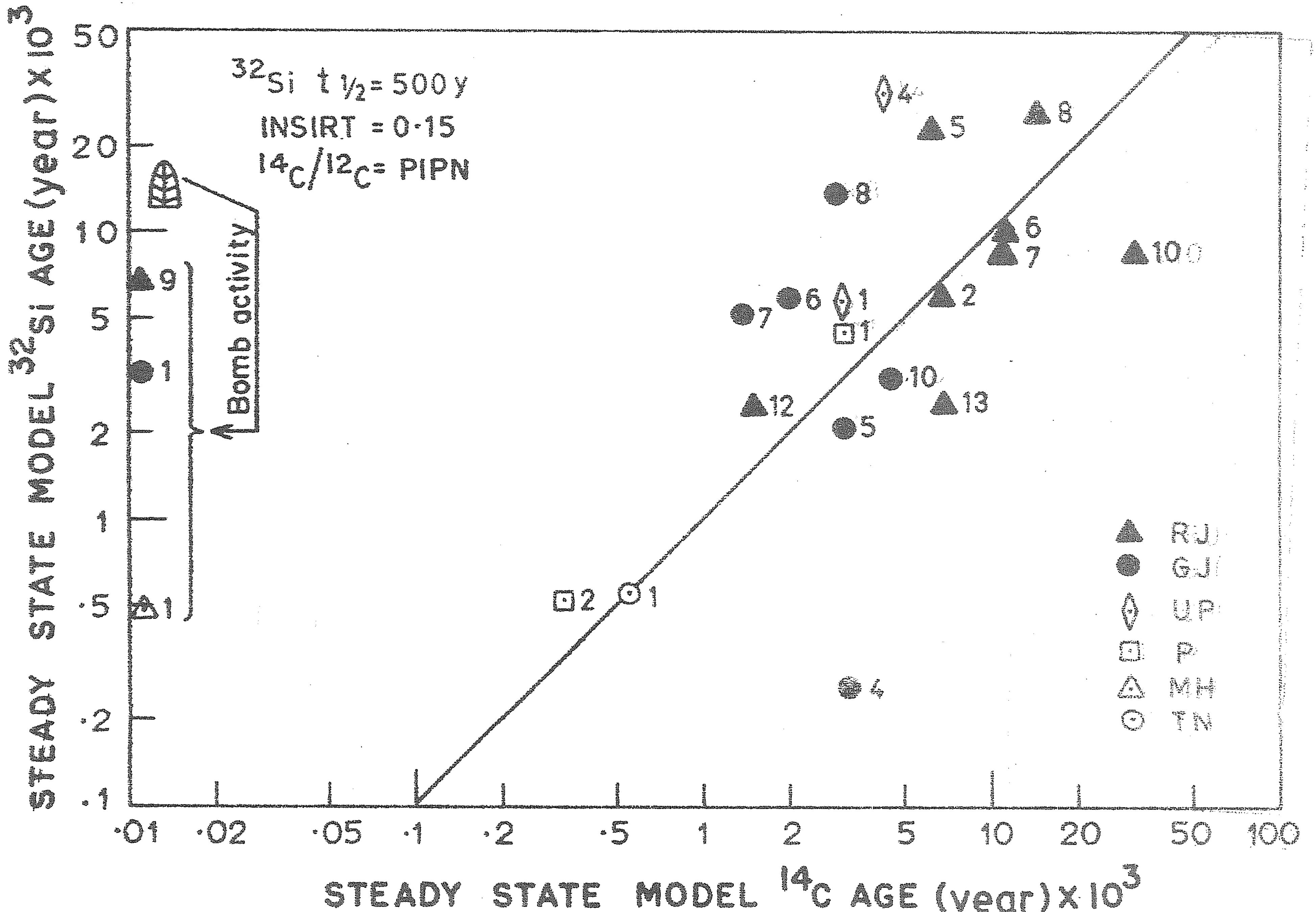

^{32}Si t ½ = 500 y
INSIRT = 0·15
$^{14}C/^{12}C$ = PIPN
Bomb activity
STEADY STATE MODEL ^{32}Si AGE (year) x 10^3
50
20
10
5
2
1
·5
·2
·1
·01
·02
·05
·1
·2
·5
1
2
5
10
20
50
100
STEADY STATE MODEL ^{14}C AGE (year) x 10^3
RJ
GJ
UP
P
MH
TN
9
1
1
4
5
8
8
6
7
10
6
1
1
7
2
10
12
13
5
2
1
4

FIG. IV.10

Fig.IV.11 ^{32}Si and ^{14}C ages obtained by consideration of "piston" model for ^{32}Si half-life = 500 yrs and for different values of parameters of INSIRT and $^{14}C/^{12}C$ initial activity.

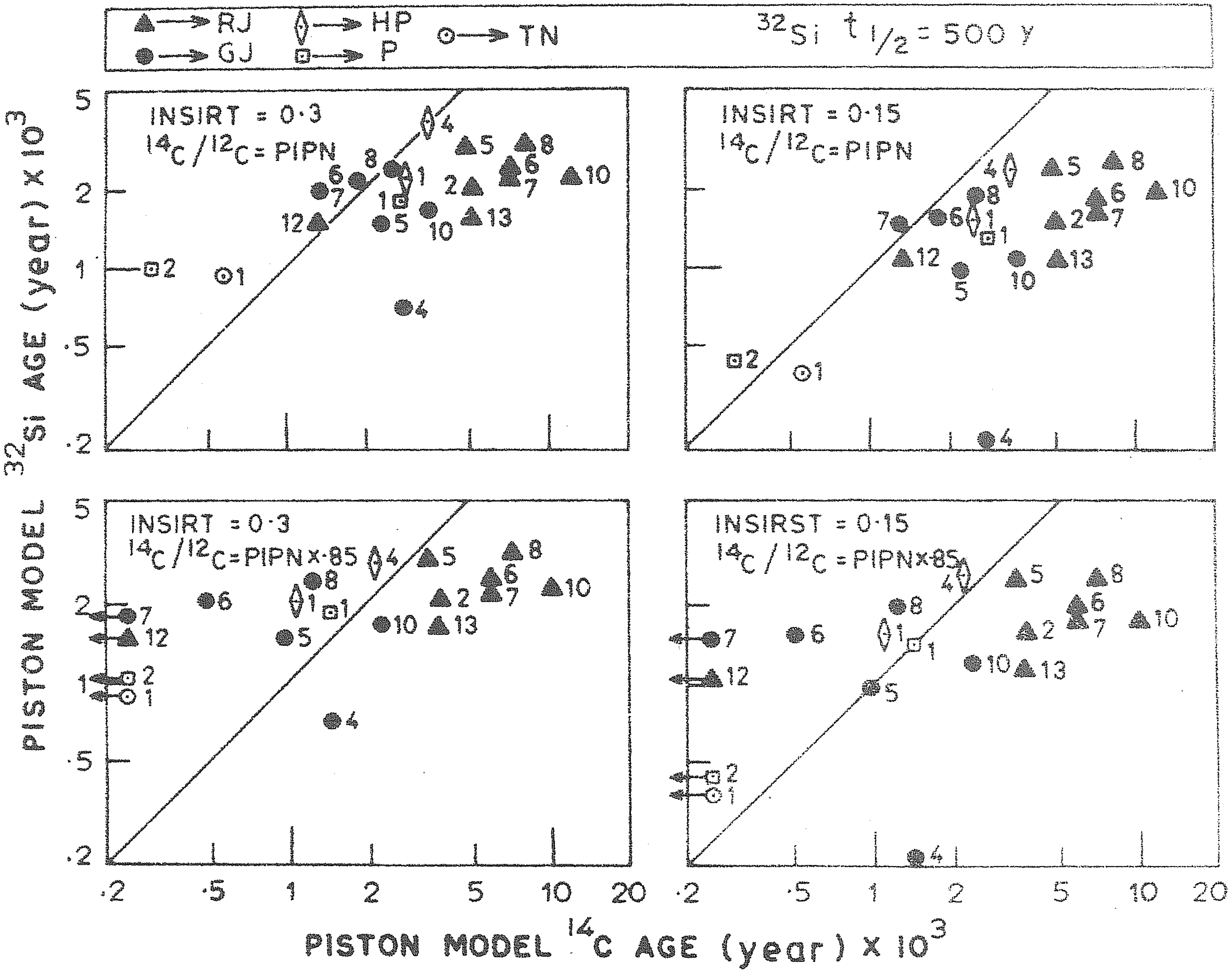
▲ → RJ
● → GJ
◊ → HP
⊡ → P
⊙ → TN
^{32}Si $t_{1/2}$ = 500 Y
INSIRT = 0·3
^{14}C/^{12}C = PIPN
INSIRT = 0·15
^{14}C/^{12}C = PIPN
INSIRT = 0·3
^{14}C/^{12}C = PIPN x·85
INSIRST = 0·15
^{14}C/^{12}C = PIPN x·85
PISTON MODEL ^{32}Si AGE (year) x 10^3
PISTON MODEL ^{14}C AGE (year) x 10^3
·2
·5
1
2
5
10
20

FIG.IV.11

Fig.IV.12 ^{32}Si and ^{14}C ages obtained by consideration of "piston" model for ^{32}Si half-life = 300 yrs and for different values of parameters of INSIRT and ^{14}C/^{12}C initial activity.

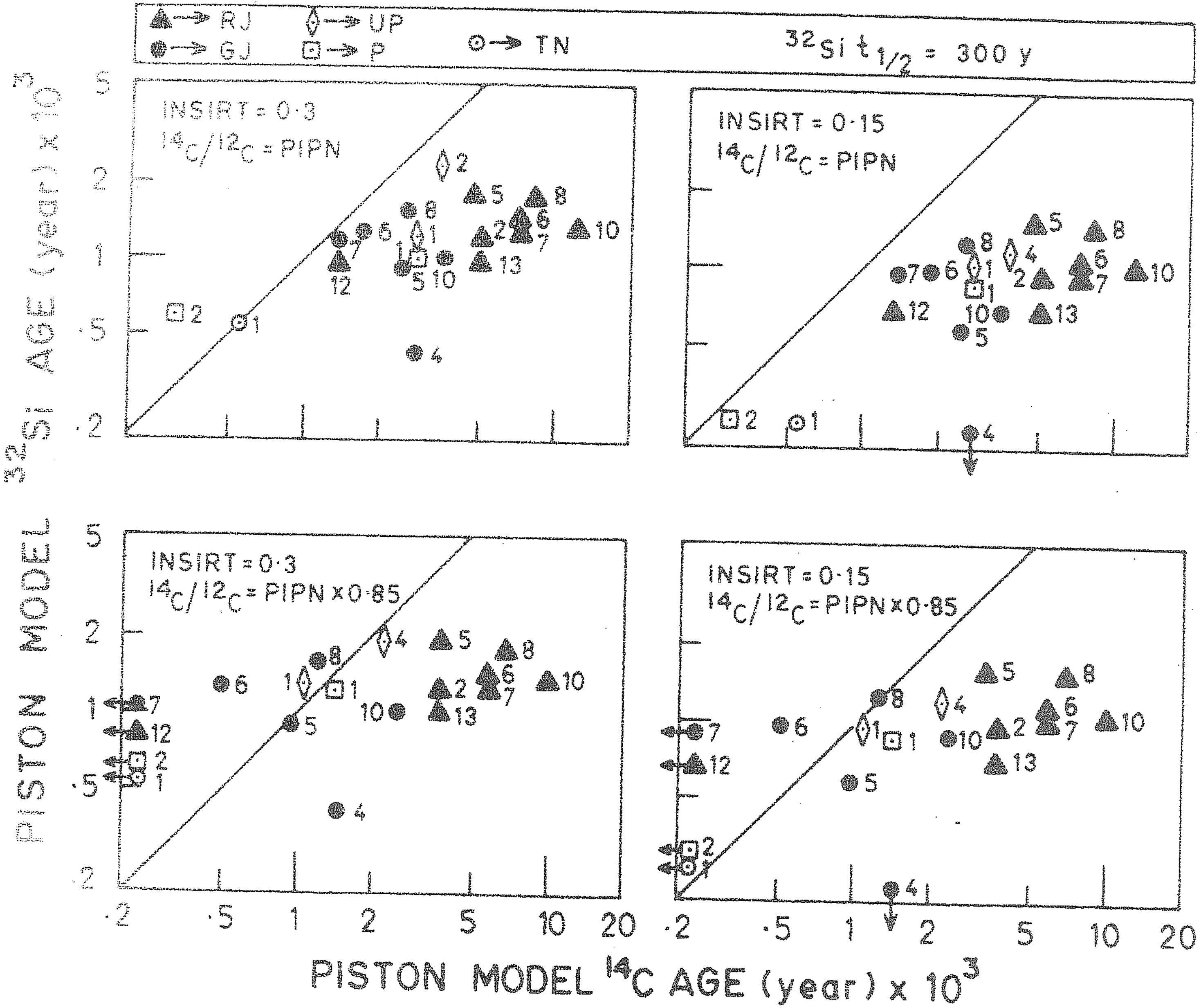

▲→ RJ
●→ GJ
◊→ UP
⊡→ P
⊙→ TN
$^{32}Si\ t_{1/2} = 300\ y$
INSIRT = 0·3
$^{14}C/^{12}C$ = PIPN
INSIRT = 0·15
$^{14}C/^{12}C$ = PIPN
INSIRT = 0·3
$^{14}C/^{12}C$ = PIPN x 0·85
INSIRT = 0·15
$^{14}C/^{12}C$ = PIPN x 0·85
PISTON MODEL ^{32}Si AGE (year) x 10^3
PISTON MODEL ^{14}C AGE (year) x 10^3
·2
·5
1
2
5
10
20

FIG. IV.12

Fig. IV.13 ^{32}Si and ^{14}C ages obtained by consideration of "steady state" model for ^{32}Si half-life = 500 yrs and for different values of parameters in INSIRT and $^{14}C/^{12}C$ initial activity.

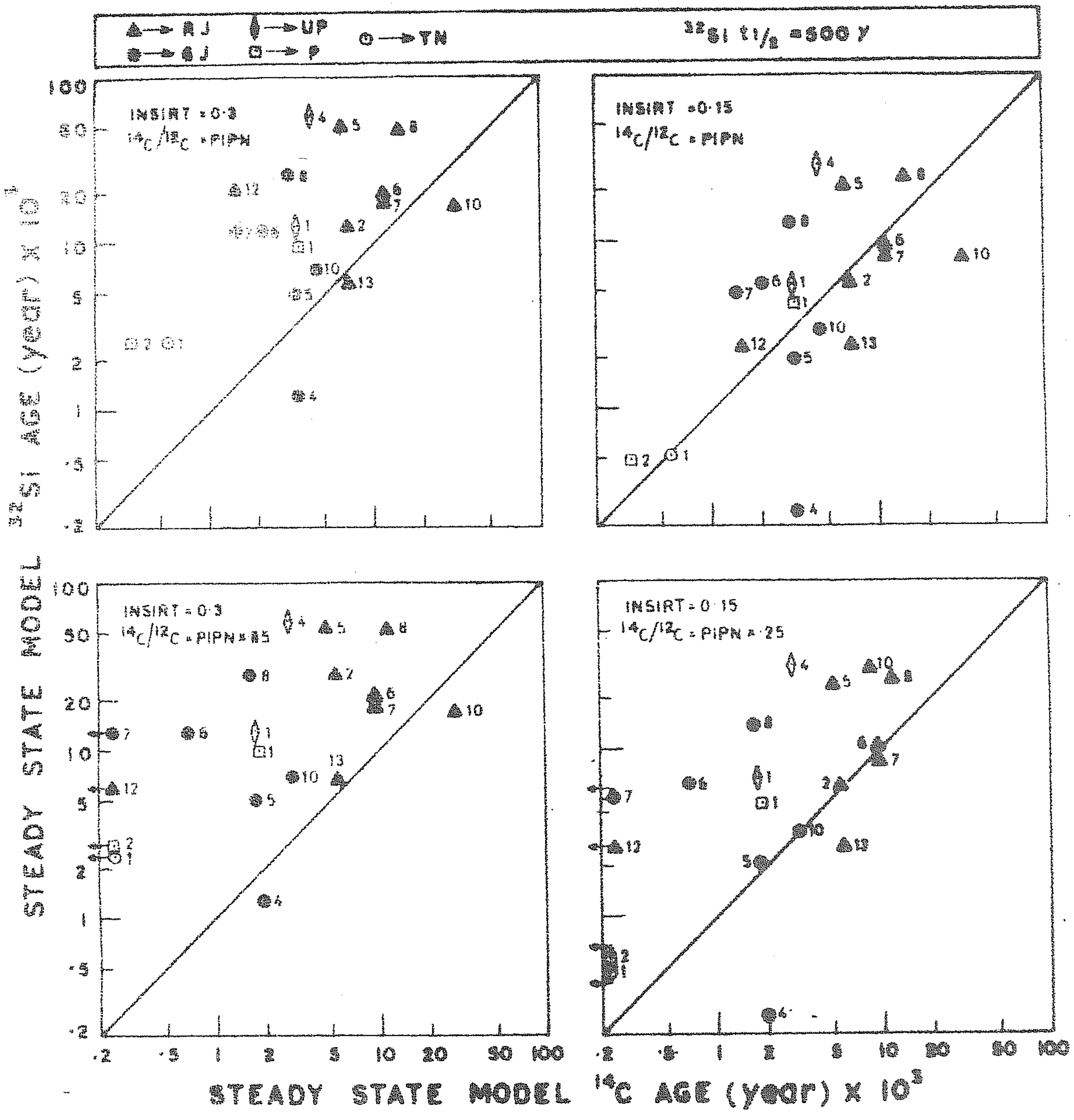

▲→ RJ
●→ GJ
⧫→ UP
□→ P
⊙→ TN
³²Si t½ = 500 y
INSIRT = 0·3
¹⁴C/¹²C = PIPN
INSIRT = 0·15
¹⁴C/¹²C = PIPN
INSIRT = 0·3
¹⁴C/¹²C = PIPN × ·85
INSIRT = 0·15
¹⁴C/¹²C = PIPN × ·25
STEADY STATE MODEL ³²Si AGE (year) × 10¹
STEADY STATE MODEL ¹⁴C AGE (year) × 10³
·2
·5
1
2
5
10
20
50
100

FIG IV 13

Fig.IV.14 ^{32}Si and ^{14}C ages obtained by consideration of "steady state" model for ^{32}Si half-life = 300 yrs and for different values of parameters in INSIRT and $^{14}C/^{12}C$ initial activity.

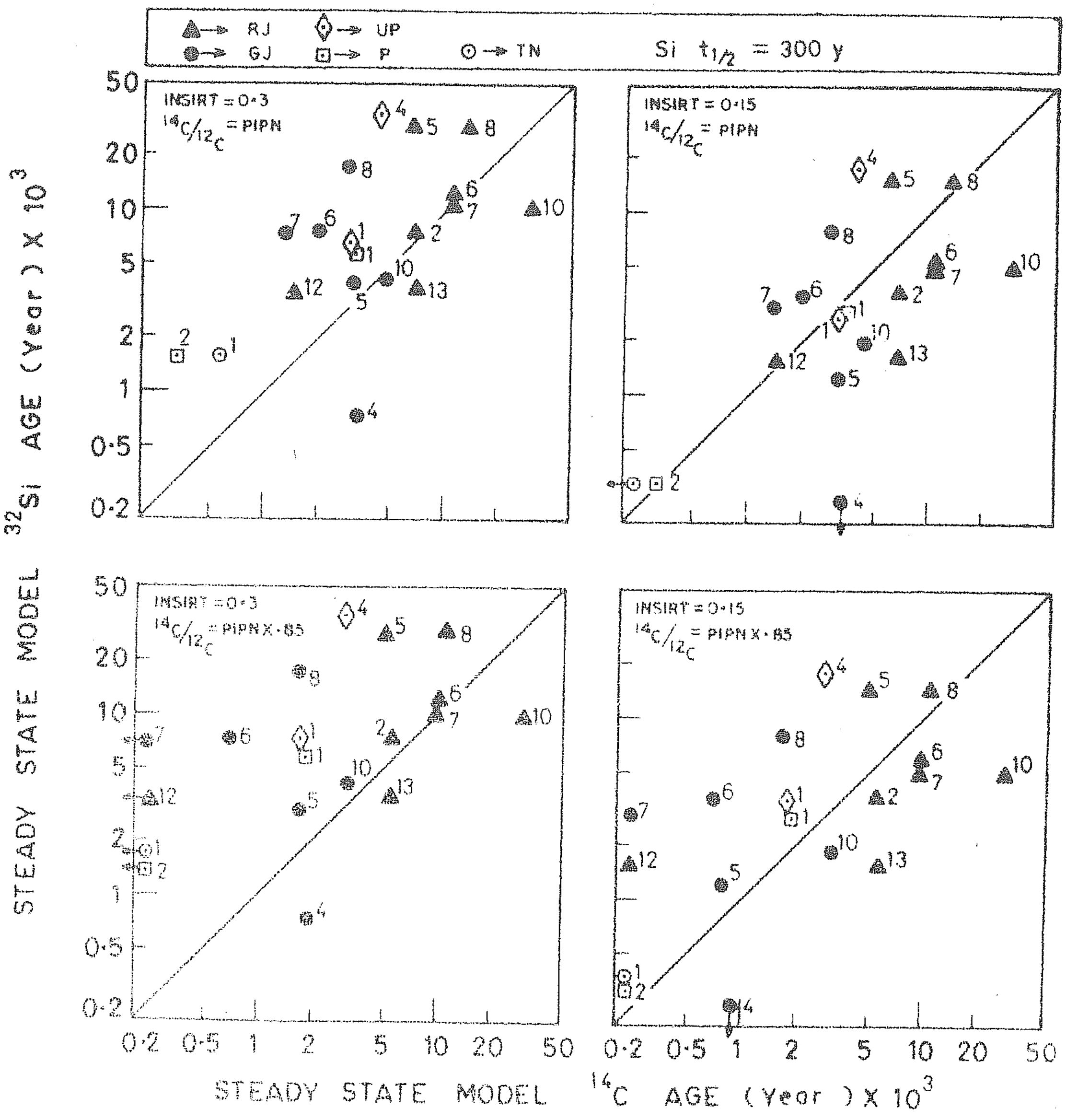

▲→ RJ
●→ GJ
◇→ UP
⊡→ P
⊙→ TN
Si $t_{1/2}$ = 300 y
INSIRT = 0·3
$^{14}C/^{12}C$ = PIPN
INSIRT = 0·15
$^{14}C/^{12}C$ = PIPN
INSIRT = 0·3
$^{14}C/^{12}C$ = PIPN X·85
INSIRT = 0·15
$^{14}C/^{12}C$ = PIPN X·85
STEADY STATE MODEL ^{32}Si AGE (Year) X 10^3
STEADY STATE MODEL ^{14}C AGE (Year) X 10^3
0·2
0·5
1
2
5
10
20
50

FIG. IV.14

From the data presented in these tables and figures, the following conclusions can be drawn.

(i) The "piston" model ^{32}Si and ^{14}C ages are in general younger than "steady state" model ages as would be expected from relation (4.4).

(ii) Satisfactory agreement exists between ^{32}Si and ^{14}C "piston" model ages for samples GJ-6,7 ; TN-1 ; P-2 ; RJ-12 and UP-4 using the following values for the variables, half-life and INSIRT. ^{32}Si : 500 y ; 0.15 and ^{14}C : 5730 y and PIPN (Fig.IV.9). The ^{14}C ages calculated by "piston" model are much higher than those of ^{32}Si ages for samples from west Rajasthan. The ^{14}C ages do not agree with that of ^{32}Si even if the highest values for half-life and INSIRT for ^{32}Si are used for age calculation.

(iii) The agreement between ^{14}C and ^{32}Si "piston" model ages calculated using a ^{32}Si half-life of 300 y and various values for INSIRT is poor (Fig.IV.12).

(iv) The ages obtained by "piston" model are lower by higher margin when ^{14}C ages are higher. This agreement would be better if the half-life of ^{32}Si were more than 500 y but this conclusion does not hold when an intercomparison is made between ^{14}C and ^{32}Si ages based on the "steady state" model.

(v) The samples MH-1; RJ-9 and GJ-1 are modern, based on ^{14}C data.

(vi) The sample GJ-4 shows younger ^{32}Si age as expected considering its distance from recharge area. The ^{14}C age of this sample gets closer to ^{32}Si age if the specific activity of ^{14}C is taken as 0.85 x PIPN.

vii) Because of the 15% reduction in the ^{14}C feed values, N x 0.85) the ages of (i) GJ-7;RJ-12;TN-1 and P-2 become very young, less than 100 yrs., and (ii) rest of the samples get closer to ^{32}Si ages.

(viii) Contrary to "piston" model case, in the "steady state" model, the ^{32}Si ages are much higher than ^{14}C ages. This is but expected as the relationship between "steady state" age (T) and "piston" age (T_a) given by,

$$T = \frac{e^{+\lambda T_a} - 1}{\lambda}$$

The values for T_a of ^{32}Si range from 3-5 whereas for ^{14}C they are always 1. The exponential increase of T with T_a explains the apparent discrepancy.

(ix) In "steady state" model ages (Figs. IV.10,13,& 14), the spread is large, the agreement is generally better with ^{32}Si half-life as 500 y but a closer agreement could be obtained by a half-life less than 500 y.

(x) The ^{32}Si and ^{14}C ages as obtained by "steady state" model show satisfactory agreement for samples GJ-5;RJ-2,6,7,8, 12; TN-1;P-1,P-2 for half-life of ^{32}Si = 500 y, INSIRT = 0.15 and $^{14}C/^{12}C$ = PIPN. A fairly good agreement is seen for another set of values of parameters $t_{\frac{1}{2}}$ (^{32}Si) = 300 y, INSIRT = 0.3 and $^{14}C/^{12}C$ = PIPN. This probably suggests that the "steady state" model describes more appropriately the Rajasthan aquifers.

(xii) All other samples fall in between the two situations discussed above. In fact, all these samples are apparently best described by an intermediate situation between the "steady state" and "piston" models (Fig. IV.6, Case. II). However, samples mentioned in (ii) and (xi) seem to follow better the "piston" and "steady state" models respectively.

From the above observations, the author feels that the values of parameters of INSIRT $\doteq$ 0.22 dpm/ton and $^{14}C/^{12}C$ = 0.92 x PIPN would give a closer agreement using a value of 350 yrs for the half-life of ^{32}Si.

Fig. IV.15 shows the frequency distribution of calculated ages obtained by "piston" model and "steady state" models for Gujarat and Rajasthan based on the values of parameters $t_{\frac{1}{2}}$ (^{32}Si) = 500 y, INSIRT = 0.15 and $^{14}C/^{12}C$ = PIPN, we note that the ages of these samples lie between 1500-8000 yrs.

Thus we see that ages for most of the confined aquifer samples obtained by either models show that these waters are older than 1000 yrs and younger than 8000 yrs.

Fig.IV.15 Frequency distribution of ^{32}Si ages calculated using the "piston" and "steady state" models for groundwater samples from Gujarat and Rajasthan. For majority of the samples ages centre around 1000-2000 yr and 2000-4000 yr for the"piston" and "steady state" models respectively.

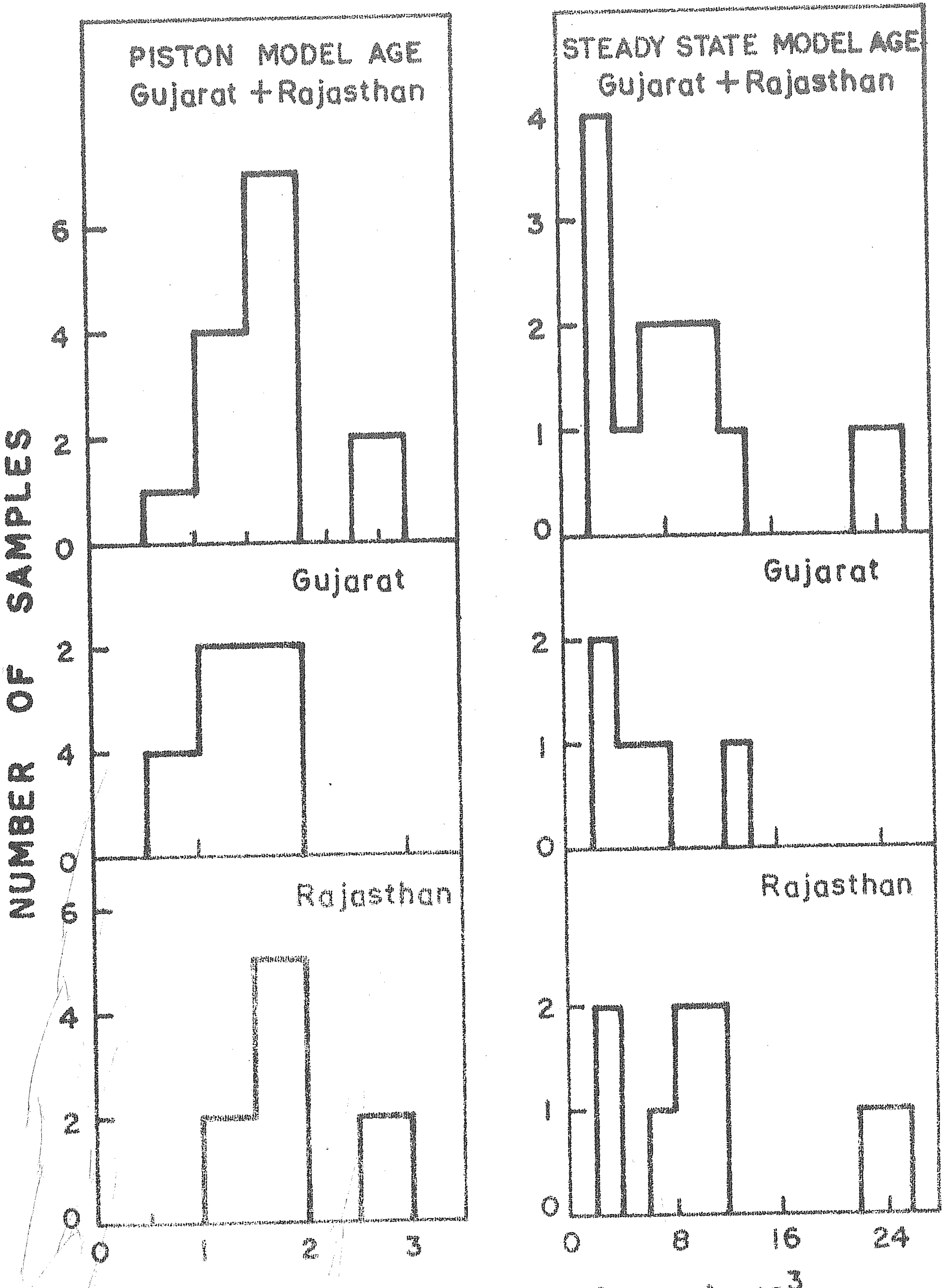

PISTON MODEL AGE
Gujarat + Rajasthan
STEADY STATE MODEL AGE
Gujarat + Rajasthan
Gujarat
Gujarat
Rajasthan
Rajasthan
NUMBER OF SAMPLES
0
2
4
6
0
1
2
3
4
0
1
2
3
0
8
16
24
SILICON-32 AGE (year) x 10^3

FIG. IV.15

IV.10. Calculation of velocity of groundwater movement in arid and semi-arid regions of Gujarat and Rajasthan.

The velocities of groundwater movement have been calculated for few regions of Gujarat and Rajasthan. Mostly (i) the sampling had been done in synoptic manner and (ii) the stable Si in all the samples remained constant despite change in the ^{32}Si concentration (dpm/ton) (Fig.IV.16) which indicates that the changes in the ^{32}Si concentrations due to processes other than radioactive decay may be insignificant.

Based on the ages obtained by "piston" model and "steady state" model in Mehsana district of Gujarat and West Rajasthan the velocities of groundwater movement have been calculated for each region.

Fig.IV.17 shows a typical strata chart (obtained from Director, Central Ground Water Board,Gujarat and Rajasthan) of various tubewells sampled and the direction of groundwater movement in Mehsana district of Gujarat.

The calculated velocities by both the models using ^{32}Si and ^{14}C ages (Fig.IV.17), range from 13-40 m/yr. The velocities calculated by "steady state" model ages of both

Fig. IV.16 Variation in the stable silica with ^{32}Si concentration (dpm/ton) for samples from Gujarat and Rajasthan. It is evident that the variation in the stable silica is insignificant.

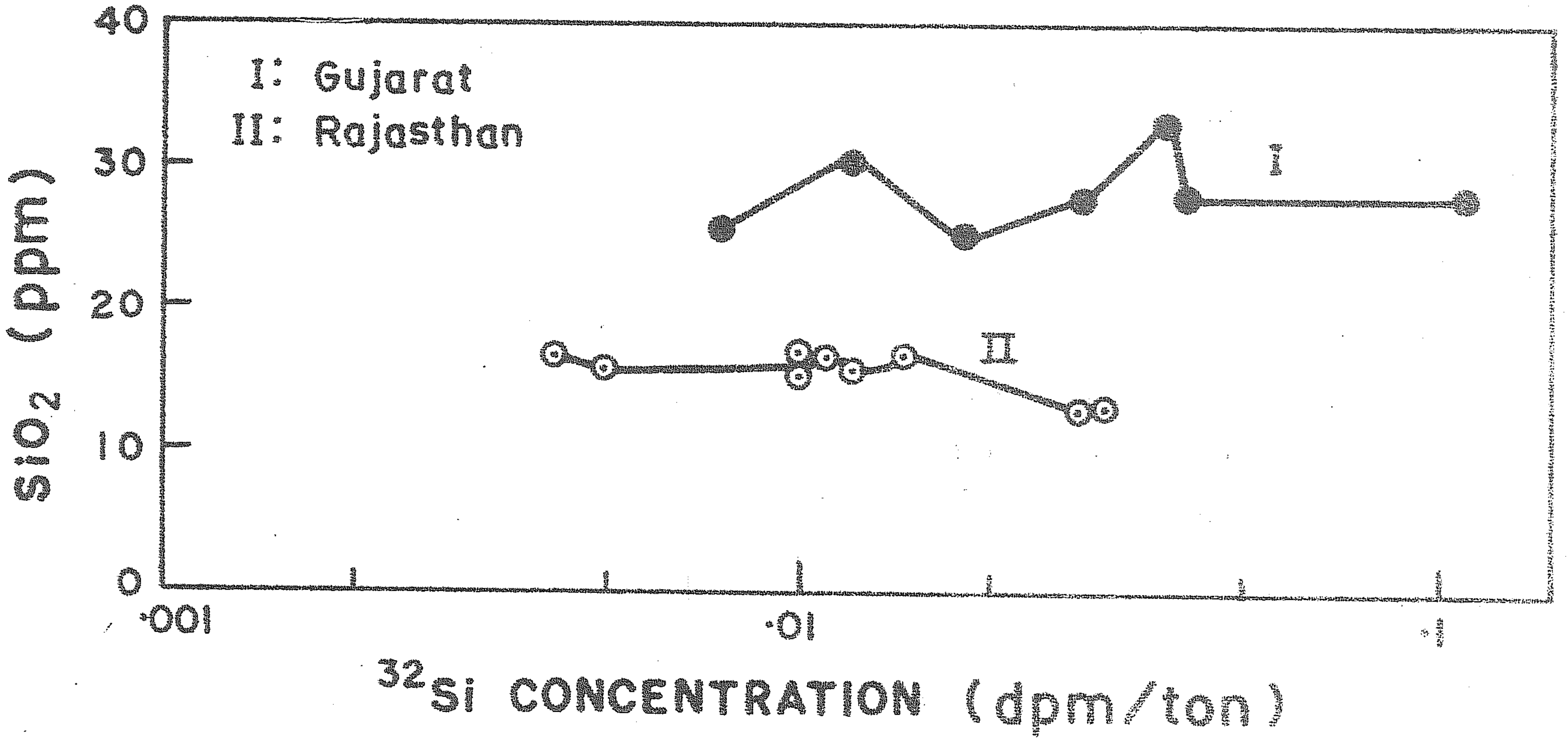

40
30
20
10
0
SiO₂ (ppm)
I: Gujarat
II: Rajasthan
I
II
·001
·01
^{32}Si CONCENTRATION (dpm/ton)

FIG. IV.16

Fig.IV.17 A cross sectional view of the Gujarat aquifer system corresponding to section G_1G_2 in Fig.II.4. The velocities of groundwater movement calculated by the "piston" and "steady state" model ages range between 10-40 m/yr. The deduced velocities using ^{32}Si and ^{14}C ages are in better agreement for the "steady state" model.

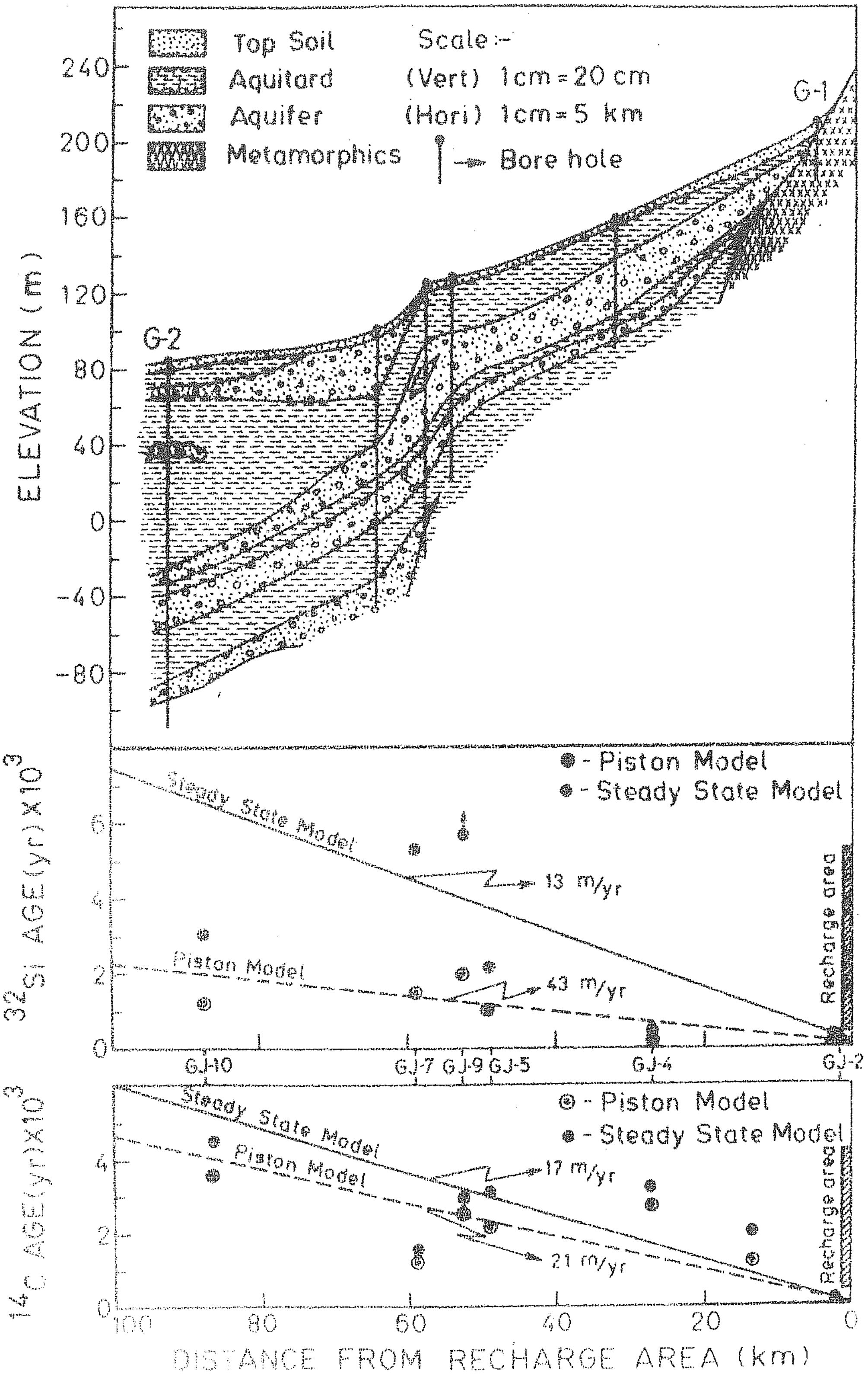

Top Soil
Aquitard
Aquifer
Metamorphics
Scale :-
(Vert) 1cm = 20 cm
(Hori) 1cm = 5 km
Bore hole
G-1
G-2
ELEVATION (m)
240
200
160
120
80
40
0
-40
-80
● - Piston Model
● - Steady State Model
Steady State Model
Piston Model
13 m/yr
43 m/yr
Recharge area
^{32}Si AGE (yr) X10^3
6
4
2
0
GJ-10
GJ-7
GJ-9
GJ-5
GJ-4
GJ-2
⊙ - Piston Model
● - Steady State Model
Steady State Model
Piston Model
17 m/yr
21 m/yr
Recharge area
^{14}C AGE (yr) X10^3
4
2
0
100
80
60
40
20
0
DISTANCE FROM RECHARGE AREA (km)

FIG IV 17

Fig.IV.18 The velocities calculated by "piston" model and "steady state" model ages of ^{32}Si and ^{14}C are shown for the western Rajasthan. The velocities obtained by ^{32}Si and ^{14}C "steady state" model ages show closer agreement.

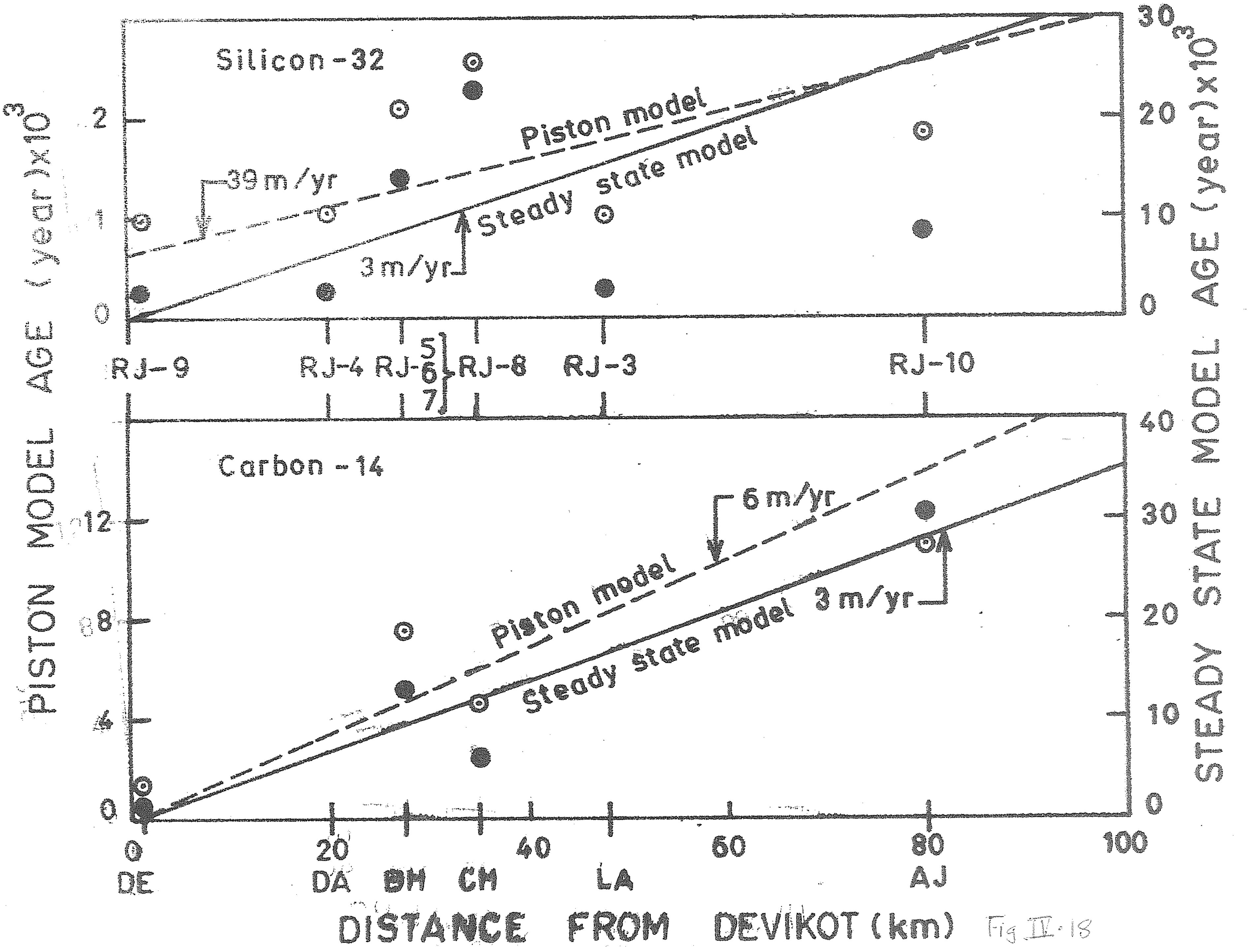

Silicon-32
Piston model
Steady state model
39 m/yr
3 m/yr
RJ-9
RJ-4
RJ-5
RJ-6
RJ-7
RJ-8
RJ-3
RJ-10
Carbon-14
6 m/yr
Piston model
Steady state model 3 m/yr
PISTON MODEL AGE (year)x10^3
0
1
2
0
4
8
12
STEADY STATE MODEL AGE (year)x10^3
0
10
20
30
0
10
20
30
40
0
20
40
60
80
100
DE
DA
BH
CH
LA
AJ
DISTANCE FROM DEVIKOT (km)

Fig IV.18

the isotopes are in good agreement and equals 15 ± 2 m/yr which agrees with the velocities obtained by conventional methods (SHAH and PATEL, 1974). The high velocities in this region are probably due to excessive pumping.

In west Rajasthan, the velocities range between 3-40 m/yr (Fig. IV.18). Similar to samples from Gujarat, better agreement for velocities are obtained from the "steady state" model ages. The deduced value of 3 m/yr is about an order of magnitude higher than the values reported by ACHUTHA RAO (1968).

From the above discussion and from Fig. IV.16 it appears to emerge out that based on the velocities obtained in these regions and the numbers available for comparison by conventional methods (SHAH and PATEL, 1974 and ACHUTHA RAO, 1968), the ages obtained by "steady state" model appear to be closer to realistic conditions in these regions.

CHAPTER - V

CONCLUSIONS

Measurements of ^{32}Si concentrations in natural waters - snow (melt), rain, stream, river, lake and groundwaters have been carried out (Fig.IV.1) using the quick and improved radiochemical procedures and counting techniques which can measure ^{32}Si (^{32}P) concentrations as low as 0.005 dpm/ton. These measurements have led to the following observations.

(i) The concentrations of ^{32}Si in rain waters at several stations in India (10-32°N) range between 0.1-1.2 dpm/ton for the years 1961-71. The higher values of concentration of ^{32}Si (>0.5 dpm/ton) observed only during 1963-64, suggest that a measurable amount of ^{32}Si is produced into the earth's atmosphere by testing of nuclear weapons. However, the amount of artificial ^{32}Si injected is small and hence any uncertainties due to this do not invalidate ^{32}Si as a tool for dating of old groundwaters.

(ii) The mean annual concentrations of cosmic ray produced ^{32}Si in wet precipitations over the Indian subcontinent range between 0.2-0.5 dpm/ton and centre around 0.3 dpm/ton.

Fig. V.1 A schematic diagram showing the production of ^{32}Si in atmosphere and its concentration in natural waters. Number of samples versus the ^{32}Si concentrations in the histograms a, b, c, & d show the variation of ^{32}Si concentrations in rain waters, surface waters and subsurface waters tapped from unconfined and confined aquifers.

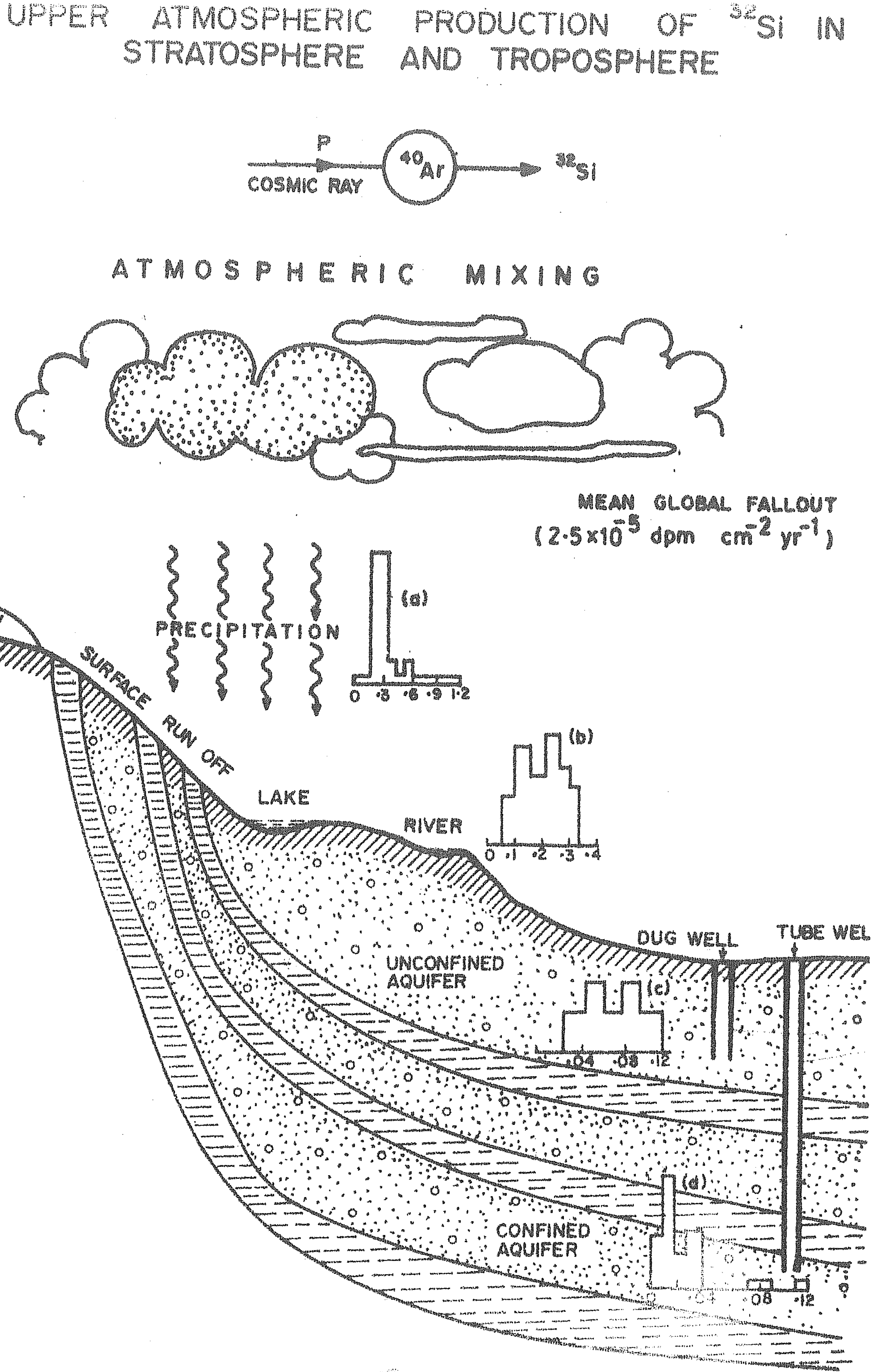

UPPER ATMOSPHERIC PRODUCTION OF ^{32}Si IN STRATOSPHERE AND TROPOSPHERE
P
COSMIC RAY
^{40}Ar
^{32}Si
ATMOSPHERIC MIXING
MEAN GLOBAL FALLOUT
(2·5×10^{-5} dpm cm^{-2} yr^{-1})
PRECIPITATION
(a)
0 ·3 ·6 ·9 1·2
SNOW
SURFACE RUN OFF
LAKE
RIVER
(b)
0 ·1 ·2 ·3 ·4
DUG WELL
TUBE WEL
UNCONFINED AQUIFER
(c)
·04 ·08 ·12
(d)
CONFINED AQUIFER
·04 ·08 ·12

FIG. V.1

(iii) From the measured ^{32}Si concentrations at various latitudes in India, its global fallout is estimated to be 2.5×10^{-5} dpm/cm^{2}y which corresponds to its mean global production rate of 3×10^{-4} atoms/cm^{2}sec. The estimated production rate is higher than the calculated value of 1.6×10^{-4} atoms/cm^{2}sec. by about a factor of two, which is probably due to the uncertainty in ^{32}Si half-life.

(iv) In surface waters (excluding melt waters of Kashmir) the concentrations of ^{32}Si are in the range : 0.1-0.2 dpm/ton a factor of 1.5-2 lower compared to that in rains. In melt water samples of Kashmir the ^{32}Si concentration is around 0.3 dpm/ton nearly same as that in rain water. However, when the melt water enters the Wular lake, the ^{32}Si concentration decreases to 0.15 dpm/ton.

(v) The depletion of ^{32}Si activity levels in surface waters, compared to that in rains, is intriguing. The removal of ^{32}Si from these reservoirs probably takes place through biological processes since the loss of ^{32}Si by adsorption on soils seems unlikely based on laboratory experiments.

(vi) Based on the ^{32}Si concentrations of groundwaters which range between 0.005 to 0.1 dpm/ton, ages have been calculated for different groundwater masses using the "piston" and "steady state" models. These ages, calculated using different values of parameters, half-life of ^{32}Si, its initial concentration and the initial concentration of ^{14}C i.e. ^{14}C/^{12}C, in source water, centre around 1000-2000 yrs and 2000-4000 yrs. respectively.

(vii) The deduced groundwater velocities in arid and semi-arid regions of Rajasthan and Gujarat range from 3-39 m/yr and 13 to 40 m/yr respectively. The results obtained for Gujarat are in satisfactory agreement with those reported by conventional methods (SHAH and PATEL, 1974) whereas in case of Rajasthan the present results are higher by an order of magnitude than reported by conventional methods (ACHUTHA RAO, 1968, 1971).

Thus the groundwaters younger than about 2000 yrs can be dated with advantage by ^{32}Si method since the uncertainty in ^{14}C dates is of the order of 1000-1500 yrs. This advantage mainly arises from the short half-life of ^{32}Si. Other uncertainties due to loss of ^{32}Si and ^{14}C from groundwater by processes other than decay are common to both methods.

An attempt has been made in this thesis to show the usefulness of ^{32}Si as a tracer for groundwater studies. However, this work has brought into light some of the problems associated with the behaviour and distribution of ^{32}Si in the natural systems. In particular, studies pertaining to the interaction of natural and artificial ^{32}Si with soils/minerals, the seasonal variation of concentration of silicon isotopes alongwith biological activity and the systematic measurement of ^{32}Si in waters younger than 25 years need to be carried out in order to make the "^{32}Si dating method" widely applicable.

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