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# Oxygen and hydrogen isotopic ratios in groundwaters and river waters from India

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Abstract. A comprehensive set of measurements of oxygen and hydrogen isotopic ratios in groundwaters as well as waters from rivers, lakes, hot springs etc. taken from a variety of locations in India has been carried out for the first time. Isotopically the most depleted samples occur in the high altitude precipitations in the Himalayas e.g. in the lakes of Bhutan and the source water of the Ganga. The shallow groundwater data display a continental effect where the heavy isotope content decreases with distance from the coast (about 4 to 6 per mil decrease in  $\delta^{18}$ O per 1000 km). The  $\delta$ D and  $\delta^{18}$ O of these fresh waters are linearly related and an analysis of this relation vis-a-vis the meteoric water line shows the unambiguous effect of enrichment due to evaporation from soils.

Keywords. Isotopic composition; groundwater; continental effect; monsoon vapour.

## 1. Introduction

Oxygen and hydrogen isotope ratios,  ${}^{18}O/{}^{16}O$  and D/H, in groundwaters and precipitations hold important clues to a variety of problems related to regional hydrogeology. These ratios have been used to determine the origin and recharge area of local groundwaters (Burgman *et al* 1979; Weyer *et al* 1979), to infer palaeoclimatic conditions (Sonntag *et al* 1979), to study the mixing of large rivers and to determine the water balance of lakes (Fritz 1981; Gat 1981) etc. These studies are normally comprehended in the context of some prior knowledge about the characteristics of isotopic behaviour in any given region based on an initial data base. From this point of view there is very little available information pertaining to the Indian subcontinent except for the isotopic composition of precipitation which has been studied for about two decades at only one station, New Delhi and for a few intermittent years in Bombay and Shillong under a IAEA/WMO programme. The present study, originally aimed at filling this major gap, has revealed some interesting features in isotope hydrology of the North and Central Indian regions.

# 2. Sampling locations

In the initial phase of this study, attention was devoted to shallow groundwaters from North India. Eighty samples of shallow groundwaters were collected from an area located within the triangular sector, Ahmedabad–Calcutta–Delhi, in a field trip in March, 1983. The names of the places along the route are given in table 1 and sample numbers are marked in figure 1. The samples were collected mostly from open dug wells (Dw) or hand pump wells (HP) whose depths were within 10 metres from the

Sample no.	Place (source)*	$\delta^{18}O(\%_{00})$	$\delta  \mathrm{D}(\mathscr{V}_{\mathrm{oo}})$
Groundwater	<u></u>		
1	Lasundra (HS)	-2.0	-12
2	Lasundra (Dw)	-2.2	- 9
3	Tuva (HS)	-1.5	- 3
4	Tuva (DW)	+01	- 2
5	Bhatwada (Dw)	-2.3	- 8
6	Dahod (Dw)	-2.9	-13
7	Sardarpur (Dw)	-1.9	-12
8	Mandu (Dw)	-1.9	-12
9	Arjun Baroda (HP)	_	- 6
10	Bhorasa (DW)	-2.2	-14
11	Ashta (Dw)	-2.0	-14
12	Bhopal (DW)	-2.4	-14
13	Bamori (HP)	-2.2	-10
14	Udaipura (Dw)	-2.6	-10
15	NH 22/26 Crossing (HP)	-2.5	- 7
16	Mankadi (HP)	-2.8	
17	Sihora (HP)	-3.3	-23
18	Murwara (HP)	-4.5	- 30
19	Vikrampur (Dw)	5.5	<b>4</b> 1
20	Nagod (Dw)	-3.6	-24
21	Agdal (DW)	-4-4	- 34
22	Dugdhua (DW)	-5.7	- 38
23	Naidi (DW)	- 5.5	-38
24	Kabsaur (HP)	-7.3	- 50
25	Chandoli (HP)	- 5.1	- 36
26	Muthani (HP)	- 5.9	-43
27	Sasaram (HP)	-5.2	35
28	Kusanh (Dw)	-5.1	-33
29	Jindapur (DW)	- 5.8	- 36
30	Barhi (HP)	- 5.4	-32
31	Demonta (DW)	-7.5	-49
32	Kadal (DW)	-4.8	- 34
33	Bagaldi (HP)	4.9	-31
34	Khadia (HP)	- 5.3	-37
35	Barsol (DW)	3.8	-18
36	Kharagpur (HP)	-2.8	-12
37	Chinsura (HP)	-5.0	-30
38	Burdwan (HP)	-4.6	-31
39	Durgapur (HP)	-4.3	-28
40	Kanchandi (DW)	-3.3	-22
41	Tundi (нр)	-7.1	46
42	Dwarpahari (HP)	-6.6	-41
43	Chakai (HP)	-6.8	-47
44	Mallipur (Dw)	- 5.6	-37
45	Avadhev (HP)	-5.6	-38
46	Raigir (HS)	-8.1	-53
47	Nalanda (HP)	-5.5	-39
48	Bitha (HP)	-7.2	-49
49	Arrah (HP)	- 5.9	-42

 Table 1. Oxygen and hydrogen isotope composition in water samples from

 North and Central India.

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Sample no.	Place (source)*	δ <sup>18</sup> O(% <sub>00</sub> )	$\delta D(\%_{00})$
50	Sinha Chawar (HP)	6.6	42
51	Mau (HP)	- <b>4</b> ·1	-26
52	Mahamadpur (HP)	-7.5	45
53	Surapur (HP)	-7.9	- 50
54	Sultanour (HP)	-7.5	44
55	Asranur (HP)	-7.6	
55	Lucknow (up)	-6.3	-41
57	Chakarnur (un)	-65	40
50	Decembur (up)		-46
50	Mahura (up)	-0.8	+0 /2
39 (0	Menwa (HP)	-0.4	42
60	Sirsaganj (HP)	- 3.9	-42
61	Shahdra (DW)	- /.0	44
62	Mathura (HP)	-6.3	46
63	Gomat ka Pyau (HP)	6.8	-42
64	Bulandsher (HP)	-7.7	48
65	Shahdra Gandhi (HP)	-7.5	-47
66	Dunda Hera (HP)	-6.5	-47
67	Oddi (BW)	-6.3	- 39
68	Sajapur (нр)	- 5.3	-41
69	Sangteda (HP)	-6.3	- 39
70	Shahpura (HP)	- 5.7	-37
71	Kesupura (HP)	-5.3	- 32
72	Ramnagar (DW)	-4.0	-27
73	Aimer (HP)	-4.4	-27
74	Rarr (HP)	- 3-3	-21
75	Jadan (HP)	_4.9	31
76	Sanderao (up)	_1.3	- 8
70	Koire Pupy (DW)	-13	- 0 - 26
70	Kojia-Fyau (Dw)		20
78	Amirgarn (Dw)	- 3.0	-19
79 80	Gota (HP)	3·0 3·1	-15
Groundwater	r (Contd.)		
RJ-1	Churu (HP)	-4.0	—
G-1	Khedbrahma (Dw)	- 3.3	
G-2	Parsa (Dw)	-4.1	
G-3	Ahmedabad (Dw)	-3.0	_
G-4	Chotila (Dw)	-2.5	
G-5	Tulsi Shyam (HS)	-1.1	
G-6	Samni, Veraval (HS)	-1.8	
G-7	Chota Udaipur (HP)	-1.5	- 5
G-8a	Nawagam (OW)	-14	
G-8h	Nawagam (BW)	- 3.0	-15
G-00	Surat (UD)	_A5	00
G 10	Sunai (nr) Saputara (laka)		0.0
G-10 MD 1	Norsinghous (122)	-1.9	
MD 2	Ivarsingnpur (HP)	- 5-0	22
MP-2		-4.3	-21
MP-3	Amarkantak (DW)	-4.9	-40
M-1	Dhule (DW)	-08	- 6
M-2a	Ambolinaka, Bombay (HP)	-0.7	
М-2b	Malad, Bombay (Tw)	+0-2	
M-3	Arabian Sea, Bombay (coast)	+0-5	
M-3	Arabian Sea, Bombay (coast)	+0-8	

Sample no.	Place (source)*	$\delta^{18}{ m O}(\%_{ m oo})$	$\delta D(\%_{00})$
M-4	Pune (DW)	-2.0	
AP-1	Hyderabad (BW)	-2.4	
AP-2a	Waltair (HP)	-1·9	
AP-2b	Waltair (HP)	-2.9	
<b>WB-</b> 1	Calcutta, Kashba (HP)	-4.4	-24
WB-2	Calcutta, Bandel (HP)	-4.1	-23
<b>A</b> -1	Jorhat (HP)	- 5.1	-32
A-2	Bokakhat (HP)	-6.1	- 32
A-3	Nowgaon (HP)	-6.0	
A-4	Gauhati (HP)	-4·8	-31
UP-1	Nainital (lake)	- 7.3	- 49
UP-2	Bhimtal (lake)		-43
UP-3	Ranibag (lake)		-43
<b>K</b> -1	Srinagar (tap)	-6.5	-38
K-2	Dal (lake)	7.5	44
K-3	Wular (lake)	- 7.5	-41
K-4	Manasbal (lake)	- 5.8	-43
K-5	Telbal (lake)	-4.9	- 39
BH-1	Phochu, Bhutan (lake)	-10.9	
BH-2	Lunana (lake)	-12.4	
BH-3	Thanza (lake)	-11·2	
BH-4	Rimzichola (lake)	9.9	
River water			
R-1	Jhelum, Kashmir (June 82)	-7.0	- 39
R-2	Koolnala, Kashmir (June 82)	-7.0	-37
R-3	Romu, Kashmir (June 82)	- 7.4	-41
R-4	Sabarmati, Ahmedabad (October 81)	-1·9	-13
R-5	Bhagirathi, Devprayag (March 82)	-9.6	-61
R-6	Ganga, Rishikesh (March 82)	-9.2	-61
<b>R-7</b>	Yamuna, Mathura (March 82)	- 7.8	- 50
R-8	Chambal, Dholpur (March 82)	-2.4	- 19
R-9	Betwa, Hamirpur (March 82)	- 3.6	- 29
R-10	Son, Ara (March 82)	-2.9	
<b>R</b> -11	Gomti, Dobni (March 82)	- 7.1	48
R-12	Ghaghara, Elginbridge (March 82)	-8.4	- 54
R-13	Gandak, Hajipur (March 82)	-8.9	-63
R-14	Damodar, Dhanbad (February 85)	<b>4</b> ·8	
<b>R-</b> 15	Brahmaputra, Goalpara (April 82)		-37
R-16	Manas, Goalpara (April 82)	6.6	-41

Table 1 (Contd.)

\*Dug well-Dw; hand pump--HP; tube well--Tw; bore well-Bw; hot spring--HS; oil well-Ow.

surface and are located, as far as possible, away from big rivers or canals of major irrigation systems. Subsequently, well samples were collected from cities like Surat, Bombay, Hyderabad (150 m bore well), Waltair, Calcutta, Gauhati, Srinagar etc. (see figure 1). In addition, several samples were taken from lakes and rivers from Kashmir,



Figure 1. Locations from which groundwater (wells, lakes and hot springs) and river water samples were collected (see table 1 for names of the places).

UP, MP, Bhutan etc. including big rivers like the Ganga and the Brahmaputra at several places. These diverse water bodies were sampled to establish the isotopic characteristics of all available sources of surface waters.

During collection water was filled to the brim in pre-cleaned dry glass or plastic bottles and sealed tight to avoid evaporation. For dug wells, care was taken to sample the bottom part of the water column by sending an air-filled bottle upside down to the bottom and then tilting it. The samples were always analysed within about a month after they were brought to the laboratory to minimise evaporation during storage. Plastic bottles are especially susceptible to this effect (Prof. Munnich, private communication).

## 3. Experimental methods

The <sup>18</sup>O/<sup>16</sup>O ratio in water samples was determined by slight modification of the standard Epstein-Mayeda technique (1953) (Krishnamurthy 1984). 2 ml of water was equilibrated with a fixed amount of cleaned tank  $CO_2$  (28.6 ml at 8.6 cm Hg) in a glass

bottle (8 ml volume) at 25°C for 48 hours. After equilibration the  $CO_2$  was purified of moisture and air in three stages and measured for oxygen isotope ratio in a vG Micromass 602 D mass spectrometer. One laboratory water standard (SAB) was measured for every set of 4 samples to (i) keep track of the reproducibility of the procedure and (ii) convert the measured ratios to final values relative to an international standard.

The D/H ratio was determined by following the procedure of Bigeleisen *et al* (1952) and Friedman and Hardcastle (1970). Briefly, about 10 mg of water, sealed in a capillary tube, was taken in a vacuum line and reduced to  $H_2$  gas by reacting with uranium at 800°C. The completion of reduction was checked by measuring the yield of  $H_2$  which was close to 100%. The gas was measured for its D/H ratio in a second vG Micromass 602D machine within 12 hours of preparation. A constant check was maintained on the whole procedure by running the water standard (SAB) for every set of (5–10) samples.

The isotopic ratios are reported as deviations from the international standard Vienna-smow (standard mean ocean water) in parts per thousand (or per mil,  $^{\circ}\!\!/_{\infty}$ ) as defined below:

$$\delta(^{18}\text{O or } \mathbf{D}) = \left[\frac{R_{\text{sample}}}{R_{\text{V-SMOW}}} - 1\right] \times 10^3 \,(^{\circ}\!/_{\text{oo}})$$

where R refers to either <sup>18</sup>O/<sup>16</sup>O atom ratio (for  $\delta^{18}$ O) or D/H atom ratio (for  $\delta$  D). The analytical reproducibility determined by repeated analysis of the laboratory standard is  $\pm 0.1^{\circ}$  for  $\delta^{18}$ O and  $\pm 1.5^{\circ}$  for  $\delta$ D.

## 4. Results and discussion

The results of the measurements of  $\delta^{18}$ O and  $\delta$ D in water samples are given in table 1. The data display a wide range in isotopic variation as expected from a large subcontinent. The  $\delta^{18}$ O values range from  $+0.8 \,^{\circ}{}_{00}$  (Arabian sea) to  $-12.4 \,^{\circ}{}_{00}$  for a high altitude lake in Bhutan (Lunana).  $\delta$ D values of these two extreme cases were not measured. But for other samples  $\delta$ D values also show a large spread, ranging from  $0 \,^{\circ}{}_{00}$  (for Surat with  $\delta^{18}$ O of  $-0.5 \,^{\circ}{}_{00}$ ) to  $-63 \,^{\circ}{}_{00}$  (Gandak at Hajipur in March, 1982 with  $\delta^{18}$ O of  $-8.9 \,^{\circ}{}_{00}$ ). Some of the notable features of the data are discussed below.

#### 4.1 Continental effect

A survey of the  $\delta$ -values in shallow groundwater (dug well and hand pump) samples with reference to figure 1 shows that as one moves away from coastal stations to interior stations the  $\delta$ -values tend to decrease. To facilitate the visualisation of this effect the  $\delta^{18}$ O values for the sample numbers (locations) 22 to 57 and A1 to A4 (eastern sector, figure 1) are plotted as a function of their distances from the nearest coast (close to the Hooghly estuary at Ganga Sagar) in figure 2. Similarly, the sample numbers (locations) 58 to 80 and a few other places in Gujarat and Rajasthan constitute the



**Figure 2.**  $\delta^{18}$ O values of the groundwater samples collected east of Lucknow (sample numbers 22 to 57 and A1 to A4 in table 1) as a function of the distance of the sampling locations from the nearest coastal point (taken as Ganga Sagar).  $\times$ —samples taken from places close to big rivers and irrigation systems; O—samples taken from higher altitudes.

western sector and their  $\delta^{18}$ O values are plotted as a function of their distances from the coast near Okha-Dwaraka in figure 3. Both these figures show that there is a gradual decrease in the heavy oxygen isotope concentration (i.e. in  $\delta^{18}$ O) with distance from the coast. Since it will be shown later that  $\delta$  D and  $\delta^{18}$ O are linearly related, the same phenomenon is also seen in the case of heavy isotope of hydrogen.



Figure 3.  $\delta^{18}$ O values of the groundwater samples, collected west of Lucknow (sample numbers 58 to 80) and some locations from Gujarat, as a function of the distance of the sampling locations from the nearest coastal point (taken as Dwarka). ×---samples unusually enriched (see text).

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The above phenomenon is readily explained by considering the groundwater at any place as being essentially derived from the local precipitation. Zimmerman *et al* (1967) showed that year by year precipitations are deposited as different layers within the soil and are gradually mixed on their way down through the soil column. As a result the isotopic composition of shallow and locally derived groundwater generally matches the long term mean composition of precipitation over the recharge area (Gat 1981). Therefore, the observed variation in the isotopic composition of groundwaters with distance can be attributed to a similar variation found in the composition of precipitation on a continent.

The progressive <sup>18</sup>O depletion in rains falling over the continent can be explained by considering the formation of precipitation as a Rayleigh process, whereby a given airmass carrying a large amount of moisture evaporated from the ocean enters a continent through the coast and undergoes successive stages of rain-out as it moves farther and farther into the continent. The process of rain-out is accompanied by isotopic fractionation where the condensate is enriched relative to the vapour. Due to preferential removal of the heavy isotope in the liquid phase the remaining vapour becomes depleted in it and consequently each stage of precipitation is lower in <sup>18</sup>O/<sup>16</sup>O or D/H than the preceding one. This phenomenon is known as the "continental effect" and has been described in detail by Rozanski *et al* (1982) in a model to explain the factors controlling the stable isotope composition of European precipitation.

In view of the above, the rationale for measuring distance from the nearest coast along the Calcutta-Lucknow direction for the eastern sector (figure 2) and along the Ahmedabad-Delhi direction for the western sector (figure 3) becomes clear. The first direction coincides with the general pattern of lower level wind movement in the Gangetic plains in North India during the south-west monsoon season (June to September) which accounts for more than eighty percent of the yearly precipitation (Rao 1976). These airmasses carry considerable amounts of moisture into the country through coastal West Bengal which is finally released as rains by convective cooling of the vapour masses at various regions as they gradually propagate along with the monsoon wind in the Nww direction.

For the Ahmedabad-Delhi sector the chief source of moisture is the Arabian sea since the low level wind in West India is nearly westerly or westsouthwesterly. The choice of an appropriate coastal point to measure the distance for the western sector cannot therefore be made unambiguously. We have taken the coast of Okha-Dwaraka as the representative point for the purpose of illustration.

The continental effect displayed in figures 2 and 3 is associated with relatively large scatter in  $\delta^{18}$ O values. Part of this scatter in figure 2 is from 6 samples (denoted by crosses) which were taken from locations in close proximity to the Ganga (sample 24) and to the Gomti and the Ghaghara. The low lying areas in this region occasionally get flooded in the monsoon season by the Ganga and its tributaries. Additionally, extensive canal irrigation is prevalent in this area and therefore, in some cases the shallow groundwaters may have a substantial contribution from river waters with more negative  $\delta^{18}$ O (e.g. Ghaghara water in March 1982, was found to have  $\delta^{18}$ O of  $-8\cdot4^{\circ}/_{00}$ ) than that of the local precipitation.

A second set of 4 deviant points (denoted by open circles) from the systematic trend in figure 2 are from locations 31, 41, 42 and 43. These places are all on the Hazaribagh Plateau at elevations ranging from 300 m to 900 m. One possibility for the more negative  $\delta^{18}$ O values of these samples is that they are derived from high altitude precipitations (Siegenthaler and Oeschger 1980). In figure 2 there are 3 samples which tend to show more positive values than the trend. These could be due to enrichment by intense evaporation in case of unused dugwells or recharge by locally evaporated water bodies in case of hand pumps.

The  $\delta^{18}$ O values of near coastal stations in the eastern sector (e.g. Calcutta, Chinsura) are between  $-4^{\circ}/_{\circ\circ}$  to  $-5^{\circ}/_{\circ\circ}$  which are more negative than those for corresponding stations in the western sector (e.g. Ahmedabad, Chotila) lying between  $-2^{\circ}/_{\infty}$  to  $-3 \gamma_{00}$ . Here again we suspect that a considerable contribution from rivers in the Gangetic West Bengal makes the resultant groundwater  $\delta$ -values more negative than their local sources. This contamination would also render the apparent continental effect derived from groundwaters in the eastern sector less steep than it actually is. The western sector being free from the riverine contribution may therefore represent the real continental effect - which is about  $6 \gamma_{oo}$  decrease per 1000 km distance from the coast (figure 3). This value is slightly higher than the value of about  $4 \, {}^{\circ}/_{\infty}$  per 1000 km obtained by Sonntag et al (1979) based on their analysis of modern European groundwaters. This difference can be attributed to two factors: (a) in the present case the coastal distance is tentatively defined along a straight line from Dwaraka to Delhi which assumes that moisture is carried only from sw to NE thereby giving a smaller estimate of the distance involved and (b) the mechanism of rain production by convective lifting in western India is very different from the frontal lifting in western Europe which can result in a difference in fractionation mechanism operative in the Rayleigh process.

# 4.2 $\delta D - \delta^{18}O$ relation

A plot of  $\delta D$  versus  $\delta^{18}O$  for all the stations where both the measurements are available is shown in figure 4. This shows that  $\delta D$  and  $\delta^{18}O$  are linearly correlated (correlation coefficient, r = 0.94) and the best fit line to the set of points is given by

$$\delta \mathbf{D} = (6.8 \pm 0.1) \,\delta^{18} \mathbf{O} + (2.2 \pm 0.4) \tag{1}$$

In contrast the weighted average  $\delta D$  and  $\delta^{18}O$  values of precipitation for worldwide network stations of IAEA is given by (Yurtsever and Gat 1981).

$$\delta \mathbf{D} = (8.2 \pm 0.1) \delta^{18} \mathbf{O} + (10.6 \pm 0.6) \tag{2}$$

The slope s and intercept d of (1) are less than those of (2) which are based on much larger range of  $\delta D$  and  $\delta^{18}O$  values ( $\delta^{18}O$  range from  $0 \circ_{00}^{\prime} - 26 \circ_{00}^{\prime}$ ) and hence more definitely determined. In regional analysis it is often seen that the  $\delta D - \delta^{18}O$  relationship in precipitation differs from the global equation. For example, the slope and intercept for tropical island stations are 6.2 and 4.0 (Yurtsever and Gat 1981) respectively. The reasons for such deviations from the precipitation line (or the global meteoric water line, defined by Craig 1961) have been extensively discussed earlier by Dansgaard (1964) and later by Gat (1981, 1983) especially in relation to groundwater hydrology. It was shown that the intercept d (similar in concept to the deuterium excess parameter defined by  $d = \delta D - 8\delta^{18}O$ ) tends to decrease as a result of evaporative processes at various stages from precipitation upto recharge of the groundwater aquifer.

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Figure 4. Plot of  $\delta D$  versus  $\delta^{18}O$  for water samples for which both the measurements were done. The data show that these two variables are linearly related (see text).

In order to assess the role of evaporation in the present case the limited amount of precipitation data available for three Indian IAEA stations (New Delhi, Bombay and Shillong) are shown in figure 5 as a  $\delta D - \delta^{18}O$  plot. It seems that the monsoonal rains are characterised by the following equation,

$$\delta \mathbf{D} = (7 \cdot 2 \pm 0 \cdot 1) \delta^{18} \mathbf{O} + (5 \cdot 1 \pm 0 \cdot 1). \tag{3}$$

As can be seen, the values of s and d are less than those of the global meteoric water line (8.2 and 10.6 respectively). This suggests that the isotopic composition of



**Figure 5.** Plot of  $\delta$  D versus  $\delta^{18}$ O for rain-water samples collected during monsoon season (June to September) from three Indian stations showing a linear relation between these two variables. The data are taken from IAEA reports.

precipitation is modified by evaporation from falling raindrops. Similarly the still lower values of s (6.8) and d (2.2) in groundwater [see (1)] are indicative of evaporation or evapotranspiration from soils during the process of recharge. This will in turn mean that the groundwater isotopic composition is expected to be somewhat different relative to local precipitation (see §4.3 below). This evaporative effect should depend on local temperature, humidity, vegetation cover and a host of other regional parameters and thereby may introduce some part of the scatter superimposed on the continental effect as discussed earlier.

# 4.3 Selection effect in Delhi

In the context of groundwater investigations data of twenty four years of  $\delta D$  and  $\delta^{18}O$ analyses (1961–1984) in total monthly precipitations in an IAEA operated station in New Delhi are available for comparison (see IAEA Technical Reports Series No. 96, 117, 129, 147 and 165). From these data yearly weighted average values are first computed and then, based on 24 yearly averages, grand weighted averages of  $\delta D$  and  $\delta^{18}O$ are computed to be  $-38 \,\%_{00}$  and  $-6.0 \,\%_{00}$  respectively. In contrast, the average groundwater  $\delta D$  and  $\delta^{18}O$  values in the region around New Delhi (within 100 km from Delhi corresponding to stations 63 to 68) are  $-44 \, \%_{00}$  and  $-6.6 \, \%_{00}$  respectively. Thus there seems to be a small depletion of  $6^{\circ}/_{\infty}$  in  $\delta D$  and  $0.6^{\circ}/_{\infty}$  in  $\delta^{18}O$  in groundwater relative to that in precipitation which presumably is feeding the underground aquifers. This difference can be explained by proposing a selection effect operating in the recharge of the groundwater by precipitation, similar to one discussed by Vogel and Van Urk (1975) to explain parallel results obtained in South Africa. The IAEA data also show that the pre-monsoon rains (May and June) in Delhi are usually enriched as compared to monsoon showers (July and August). The late monsoon precipitations in September are further depleted and usually characterised by average  $\delta^{18}$ O values as low as  $-10^{\circ}/_{\circ\circ}$ . The difference in average monthly  $\delta^{18}$ O in precipitations during May to September in Delhi is intriguing since one would expect that the moisture required for the rains in these months is derived from the same two seas, namely, the Arabian Sea and the Bay of Bengal. The enrichment in pre and early monsoon rains of May and June can be explained by an amount effect (Dansgaard 1964) whereby the heavier  $\delta$ -values are due to the lower amount of precipitation in those months. The amount effect is possibly related to evaporation from the falling raindrops (§4.2) whose influence is more pronounced in hot and relatively dry premonsoon months (less rainfall). The reason for the depletion of heavy isotopes in the September rains is not very clear. One possible cause could be the change in the lower level wind pattern in September whereby the supply of moisture from the Arabian sea is significantly reduced. The bulk of the September rains are thus derived from vapour supplied by the Bay of Bengal through easterlies and have depleted  $\delta$ -values owing to the continental effect discussed earlier. Notwithstanding the real mechanism of this effect it is likely that the early monsoon rains falling on parched grounds are more easily evaporated, leading to less recharge in these two months. This will cause selection in groundwater recharge in favour of isotopically depleted rain showers in the later part of monsoon. It is interesting to note that though the selection effect is essentially due to evaporation it does not cause an enrichment in groundwater composition but a depletion contrary to a simple expectation.

## 4.4 Arabian sea vapour

Two samples of Arabian sea water near the Bombay coast were measured and found to have  $\delta^{18}$ O values of 0.5 %/00 and 0.8 %/00 which lie within the range of values obtained by Duplessy *et al* (1981), namely, 0.5 %/00 to 0.8 %/00. Regarding the vapour composition, it was pointed out by Dansgaard (1964) that as a result of fast evaporation from the Arabian sea, monsoon vapour is not in thermodynamic equilibrium with sea water but more depleted in <sup>18</sup>O due to kinetic fractionation. Therefore, the first condensate from such vapour, being controlled essentially by equilibrium condensation, will be slightly lower in <sup>18</sup>O than the sea water. The groundwaters of Surat and Bombay (coastal stations) are expected to be derived from such condensation and will have consequently  $\delta^{18}$ O value lower than the local sea water which is indeed the case.

# 5. Conclusions

This paper reports the first extensive set of oxygen and hydrogen isotope analyses in groundwaters, river and lake waters taken from a variety of locations in India. In addition to providing an overall view of the isotopic scenario the following interesting features are noted.

(i) The groundwaters show a large continental effect both in Ahmedabad-Delhi (western) sector and Calcutta-Delhi (eastern) sector. In the former, it is about  $6 \, ^{\circ}\!/_{oo}$  decrease per 1000 km distance from the coast, while in the latter case, only a lower limit ( $4 \, ^{\circ}\!/_{oo}$  decrease per 1000 km) can be obtained due to possible river water contribution to aquifers.

(ii) The  $\delta D - \delta^{18}O$  relationship is linear and has slope and intercept lower than those of the meteoric water line indicating evaporative enrichment. A comparison with similar relations found in IAEA data for precipitation at 3 Indian stations (New Delhi, Bombay and Shillong) shows that the evaporation takes place during (a) the fall of raindrops to the ground and (b) the recharge of groundwater through surface percolation.

(iii) The monsoon vapour over the Arabian sea and the west coast is derived from seawater by fast and non-equilibrium (kinetic controlled) evaporation.

(iv) The most depleted <sup>18</sup>O values in the subcontinent are found in the high altitude lakes of Bhutan followed by the upper reaches of the Ganga water near Devprayag and Rishikesh.

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#### References

Bigeleisen J, Perlman M L and Prosser H C 1952 Anal. Chem. 24 1356

- Burgman J O S, Eriksson E, Kostov L and Moller A 1979 Isotope hydrology 1978 (Proc. Int. Symp. Neuherberg) (Vienna: IAEA) Vol. 1, p. 40
- Craig H 1961 Science 133 1702
- Dansgaard W 1964 Tellus 16 436
- Duplessy J C, Be A W H and Blanc P L 1981 Palaeogeogr. Palaeoclimatol, Palaeoecol. 33 9
- Epstein S and Mayeda T 1953 Geochim. Cosmochim. Acta 4 213
- Friedman I and Hardcastle K 1970 Geochim. Cosmochim. Acta 34 125
- Fritz P 1981 Stable isotope hydrology: deuterium and oxygen-18 in the water cycle (eds) J R Gat and R Gonfiantini (Vienna: IAEA) p. 177
- Gat J R 1981 Stable isotope hydrology: deuterium and oxygen-18 in the water cycle (eds) J R Gat and R Gonfiantini (Vienna: IAEA) p. 203
- Gat J R 1983 Palaeoclimates and palaeowaters: a collection of environmental isotope studies (Vienna: IAEA) p. 3
- Krishnamurthy R V 1984 Stable isotope studies on sedimentary deposits and groundwaters and their climatic implications Ph.D. thesis, Gujarat University p. 52
- Rao Y P 1976 South-West Monsoon, Meteorol. Monograph, No. 1, India Meteorol. Dept., p. 1
- Rozanski K, Sonntag C and Munnich K O 1982 Tellus 34 142

Siegenthaler V and Oeschger H 1980 Nature 285 314

- Sonntag C, Klitzsch E, Lohnert E P, El-Shazley E M, Munnich K O, Junghans Ch, Thorweihe U, Weistroffer K and Swailem F M 1979 Isotope hydrology 1978 (Proc. Int. Symp. Neuherberg) (Vienna: 1AEA) Vol. 2, p. 580
- Vogel J and Van Urk H 1975 J. Hydrol. 25 23
- Weyer K U, Krouse H R and Horwood W C 1979 Isotope hydrology 1978 (Proc Int. Symp. Neuherberg) (Vienna: IAEA) Vol. 1, p. 263
- Yurtsever Y and Gat J R 1981 Stable isotope hydrology: deuterium and oxygen-18 in the water cycle (eds) J R Gat and R Gonfiantini (Vienna: IAEA) p. 103
- Zimmerman U, Ehhalt D and Munnich K O 1967 Isotopes in Hydrology (Proc. Symp. Vienna) p. 567