Moisture rainout fraction over the Indian Ocean during austral summer based on $^{18}\text{O}/^{16}\text{O}$ ratios of surface seawater, rainwater at latitude range of 10°N – 60°S

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Oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$) of surface seawater and rainwater samples from the Indian Ocean region (10°N – 60°S) during austral summer collected onboard *ORV Sagar Nidhi* during 2011–2013 have been measured along with salinity, sea surface temperature and relative humidity. The rainwater is isotopically lighter (by $4.6 \pm 2.7\text{‰}$) compared to the equilibrium condensation of the vapour arising from the seawater at the ambient condition. The isotopic composition of the vapour at high altitude responsible for the rain formation at the sampling location is estimated from a global atmospheric water isotope model (IsoGSM2). The apparent deficit of $\sim 5\text{‰}$ can be explained by invoking a high degree of rainout (on average, about 70% of the overhead atmospheric moisture) during transport of the source vapour to the sampling location undergoing a Rayleigh fractionation. The required rainout fraction is higher ($\sim 80\%$) in the latitude belt 40° – 60°S compared to the equatorial belt ($\sim 60\%$). The pattern of variation in the rainout fraction with latitude is consistent with the well-known evaporation/precipitation processes in the Indian Ocean.

Keywords. Oxygen isotope ratio; Rayleigh distillation model; IsoGSM2 prediction; rainout fraction.

1. Introduction

The stable isotopic compositions of precipitations across the globe exhibit characteristic spatial variations that are used in the study of the hydrological cycle (Rozanski *et al.* 1993; Gat *et al.* 2001). Except

for a few recent studies (Nakamura *et al.* 2014), majority of them are confined to the processes in a continental or terrestrial atmosphere. Global Network of Isotopes in Precipitation (GNIP) program under IAEA/WMO (1998) has established a systematic pattern of latitudinal variations in the rain-

water isotope ratio (Rozanski *et al.* 1993). In this context, Bowen and Wilkinson (2002) reanalyzed the global database of isotopes in precipitation and after the critical review of the data proposed an accurate representation of their global and regional patterns. They also indicated that only scanty measurements of rainwater isotope ratios exist over the oceans and in particular, over the Indian Ocean (IO) region. Even these limited studies show some interesting features. The isotopic variation of *surface seawater* across latitude in the southern part of the IO, named Southern Ocean (SO), is small and follows a step function (Srivastava *et al.* 2007). In contrast, the isotopic variation of *rainwaters* in the SO is very large, sometimes even over a small latitude band (Nakamura *et al.* 2014; Rahul *et al.* 2018). For example, the rainwater isotopes vary by about 15‰ in the 60°–70°S latitude band in contrast to seawater variation of only ~1‰ (Schmidt *et al.* 1999). The rain and vapour over the ocean are connected by a series of fractionating processes. Vapours rising from the sea water are depleted in heavy isotopes due to fractionation caused by evaporation and boundary layer diffusion (Craig and Gordon 1965). This vapour subsequently cool, condense and precipitate with varying degrees of efficiency. It is seen that the isotopic composition of precipitation near the source region is high but decreases away from the source region in response to cooling of air masses leading to progressive rainout associated with equilibrium fractionation between vapour and condensate (Dansgaard 1964). These processes can be modelled by a Rayleigh distillation mechanism where the left-over vapour and concurrent rain decrease in isotopic ratio with a power law dependence on the fraction of moisture left (Criss 1999). Of course, it has been noted by earlier workers that there is a multitude of processes that control the isotopic ratio of water vapour (Araguás-Araguás *et al.* 2005) and the precipitation associated with it such that a simple one-stage Rayleigh model may not account for all of them (Aggarwal *et al.* 2005; Gat 1996). For example, the isotopes of rainwater on the way down can be modified by exchange with ambient vapour, evaporation from raindrop surfaces. Despite these interpretation difficulties, isotopes have proved to be extremely useful to delineate large scale evaporation–precipitation cycles in the hydrosphere (Craig and Gordon 1965; Aggarwal *et al.* 2005).

On a global scale, about 90% of the oceanic vapour returns to the ocean as precipitation (www3.

geosc.psu.edu/~dmb53/DaveSTELLA/Water/global%20water/global_water.htm) and the rest 10% is advected to the land. In other words, the average rainout fraction (fraction of the overhead moisture falling as rain) over the oceans should be close to 0.9. Of course, there would be large variations in the rainout fraction with latitude, longitude, seasons and different oceanic settings. Oceanic rainout is an important area of research since rains over the ocean dilute the salt content and play an important role in ocean currents (Berg *et al.* 2010; Ellis *et al.* 2009). However, our knowledge of the water cycle over the ocean is poor (Schmitt 1995). Since evaporation from the sea water and condensation from the vapour overhead (due to cooling by uplift) are both associated with large oxygen isotopic fractionation we thought that it may be worthwhile to investigate if oxygen isotope ratio in rains can be used as a tracer to quantify the variation in the rainout efficiency. Such studies are well-known in case of land precipitation (Rozanski *et al.* 1993; Krishnamurthy and Bhattacharya 1991; Gat *et al.* 2001). But due to logistical reasons, there are very few studies on isotopic analysis of precipitation samples that fall over the oceans. Some studies were done in the Pacific Ocean and North Atlantic Ocean (Uemura *et al.* 2008; Nakamura *et al.* 2014; Benetti *et al.* 2014), but only one (*op. cit.*) in the Indian Ocean. In the present work, we have attempted to fill in this gap by direct sampling of rainwaters collected in three Indian cruises (from the equatorial region to the polar region) and analyzing them for oxygen isotope ratios. Our purpose was to quantify the dominant factors (in particular, the rainout fraction) that determine the rainwater composition in the Indian Ocean region based on simultaneous analysis of rain and seawater samples along with model-based estimates of isotopic composition of atmospheric moisture. With a much larger database, we hope to establish firmly the characteristic features of the isotope ratio variations observed earlier in the Southern Ocean. We then aim to explain these features in a framework of isotope fractionation and Rayleigh distillation gain first-hand knowledge about rainout fraction as a function of latitude.

2. Methodology

A total of 34 rain samples (12, 7, and 15 in 2011, 2012, and 2013 respectively, during

Figure 1. Sampling locations and the corresponding 48-hr backward trajectories of air mass movement at sea level during the austral summers (December–February) of 2011, 2012 and 2013 in the longitudinal span of 88°E to 47°E and the latitudinal span of 10°N to 60°S in the Indian Ocean. The labels represent the sampling years and sample numbers consecutively (see table 1). The general pattern of wind movement and their speed (in m/sec) are also shown using colored arrows.

January–March) were collected onboard *ORV Sagar Nidhi* (during 5th, 6th, and 7th Indian Scientific Expedition to the SO). Event-integrated samples were collected on the ship deck. Care was taken to avoid contamination from sea spray and samples were preserved in cold storage to minimize evaporation. The sampling locations (figure 1) extended from 10°N to 60°S and 47°E to 80°E. Surface seawater samples were also collected at the same time from the same locations using a bucket (from within ~2 m depth) and analyzed for oxygen isotope ratios together with salinity and Sea Surface Temperature (SST). The salinity was measured using an Auto Salino Meter (Tsurumi Seiki

Co. Ltd., Japan) with a precision of ± 0.005 PSU (Practical Salinity Unit). SST was measured using a bucket thermometer (Theodor Friedrichs and Co, Germany; accuracy $\pm 0.2^\circ\text{C}$). Oxygen isotope ratios are expressed in the standard δ -notation:

$$\delta^{18}\text{O} = \left[\frac{R_s}{R_r} - 1 \right] \times 1000 (\text{‰}) \quad (1)$$

where R is the oxygen isotope ratio ($^{18}\text{O}/^{16}\text{O}$) and the subscripts s and r refer to sample and reference. Isotope ratios were measured by the equilibration method (Rangarajan and Ghosh 2011). A Thermo Finnigan-MAT 253 Isotope Ratio Mass Spectro

meter (obtained from Thermo-Fischer Company, Bremen, Germany) coupled with Gas Bench II was used for automated flushing, extraction and analysis of the equilibrated CO₂ gas. The isotope ratio ($\delta^{18}\text{O}$) of the samples is expressed relative to Vienna Standard Mean Ocean Water (VSMOW). Samples were analyzed together with the laboratory standard VOU_OASIS (-11.3‰ VSMOW) and a second standard WWW_LKD (-0.7‰ VSMOW) calibrated using the international standards VSMOW and GISP with analytical uncertainty of 0.1‰ .

2.1 Models

2.1.1 Rayleigh distillation model

During condensation of water vapour, the H₂¹⁸O concentrates in the liquid phase relative to H₂¹⁶O (called isotopic fractionation) resulting in depleted isotope ratio ¹⁸O/¹⁶O in the leftover vapour. Additionally, if the condensate is continuously removed from the system a progressive isotopic depletion occurs in the vapour as well as in the corresponding condensate. This progressive change, called a Rayleigh fractionation, is expressed by Dansgaard (1964):

$$R_f = R_i f^{(\alpha-1)} \quad (2)$$

where R_f and R_i are the isotope ratios of the remaining and initial vapour, α is the liquid–vapour fractionation factor (>1) and f is the fraction of remaining vapour. This formula assumes that the process is a single stage removal with a constant fractionation factor α and the leftover vapour mixes instantaneously. Obviously, in case of generation of oceanic vapour and its removal by rain there is a complex interplay of processes. But in this work we shall adopt a simple Rayleigh framework to obtain insight into the dominant factors that control the variation of rainwater and water vapour isotope ratios.

2.1.2 IsoGSM2 model

We have not measured the isotope ratio in the oceanic vapour but to estimate the rainout fraction we do need its composition. This was obtained by Isotope Global Spectral Model version 2 (IsoGSM2 hereafter) which incorporates isotopes as trace species and was developed by Yoshimura *et al.* (2008) from the Global Spectral Model (Caplan *et al.* 1997) originally conceptualized by the

National Center of Environmental Prediction (NCEP). This is based within the framework of an Atmospheric General Circulation Model, where the whole globe is divided into air columns with knowledge of the meteorological parameters. During the model run, the air masses are transported from one column to another containing the water molecules whose isotopic signatures are updated by considering all sources and sinks and fractionating processes. The simulation for 1979–2013 is obtained from NCEP/DOE Reanalysis (Kanamitsu *et al.* 2002) with the spectral nudging technique (Yoshimura and Kanamitsu 2008) which adjusts the IsoGSM2 winds such that they approximately match the flow patterns in the NCEP/DOE reanalysis. The nudging technique is based on the idea that ‘small-scale details are the results of the interplay between large-scale atmospheric flow and smaller-scale geographic features such as topography, land–sea distribution, or land use’ (Von Storch *et al.* 2000). Details of the assumptions and methodology behind such models are given in a recent review of Xi (2014). IsoGSM2 simulations are applied for obtaining estimates of vapour and rainwater isotopic compositions at two altitudes: ground level and 3000 m. Since these simulations are done over grids placed on the earth surface, we chose predictions at high horizontal resolution of $1.8^\circ \times 1.8^\circ$ containing the sampling point for purpose of calculation and comparison. The model $\delta^{18}\text{O}$ values of water vapour and rainwater (assuming sea water $\delta^{18}\text{O}$ as zero) were obtained for each sample-containing grid four times a day (0, 6, 12, and 18 hrs UT) for each sampling date, i.e., for 12 days in 2011, 7 days in 2012, and 15 days in 2013. The daily averages of these four values are used for calculations.

3. Results

We have recorded several physical parameters pertaining to the sampling locations in the three cruises during 2011, 2012 and 2013. Two types of water samples (seawater and rainwater from the same station) were collected and analyzed for $\delta^{18}\text{O}$ values after bringing them to the laboratory. The SST and salinity were measured at the time of sampling. Relative humidity values were not measured but calculated from the SST. The air temperature in the deck was also measured. These data are discussed below.

3.1 Latitudinal variation of sea water $\delta^{18}\text{O}$, salinity, and SST values

The $\delta^{18}\text{O}$, salinity, and SST values of surface seawaters along the latitudinal transect (20° – 60°S) display systematic variations (figure 2). Based on the pattern of variations in the first two quantities this oceanic region can be classified into three zones: zone of evaporation (20° – 40°S), zone of transition (40° – 41°S), and zone of precipitation (41° – 60°S) (Srivastava *et al.* 2007, 2010). The mean values of $\delta^{18}\text{O}$, salinity, and SST for the three zones (table S1) display small but readily discernible changes. In the zone of evaporation the mean $\delta^{18}\text{O}$ value is about $+0.5\text{‰}$ compared to the value of about -0.6‰ in the zone of precipitation. The salinity values generally follow the pattern of variations in the isotope ratios

dropping progressively from 35.5 to 33.5 PSU. In the zone of evaporation, SST gradually declines from $\sim 26^{\circ}$ to 18°C , meanwhile the salinity and $\delta^{18}\text{O}$ value increases from ~ 35 to 35.5 PSU and ~ 0.6 to 0.8‰ , respectively. This signifies that this zone, during the study period, is dominated by evaporation rather than precipitation (Tiwari *et al.* 2013). Overall the SST varies smoothly across the three zones dropping from a high value of 30° to 3°C (figure 2).

A large drop in $\delta^{18}\text{O}$ and salinity values between 41° and 47°S (figure 2) define the subtropical front (STF) and Agulhas Return front (ARF) (figure 1). The Agulhas current carries warm water from the tropics to higher latitudes (Sparrow *et al.* 1996) and finally joins with the IO gyre after retroflexion.

3.2 Latitudinal variation of $\delta^{18}\text{O}$ values of precipitation

The observed $\delta^{18}\text{O}$ values of the station precipitations vary over a small range ($-2 \pm 2\text{‰}$) from the equatorial zone to 40°S , but drop rapidly afterwards to about -16‰ near 70°S (table 1 and figure 3). In contrast, as discussed above, the seawater $\delta^{18}\text{O}$ values change only within 1‰ . The mean $\delta^{18}\text{O}$ values of rainwater as a function of latitude show a distinct trend (figure 3) despite a large dispersion beyond the 40°S latitudinal band. A large scatter in $\delta^{18}\text{O}$ values of rainwater implies corresponding variation in the overhead moisture composition. It seems that the variation comes from an interplay of moisture removal by rain-out processes (during transport) and the addition of fresh moisture by local evaporation (Laederaach and Sodemann 2016). Removal depletes the heavy isotopes in the leftover vapour, while evaporation adds vapour with a *normal* composition which is relatively enriched. The evaporative contribution seems to compensate for precipitation depletion quite well up to 40°S resulting in a flat trend. Beyond 40°S , the SST is significantly lower (2° – 6°C) resulting in reduced evaporation. Consequently, the precipitation effect dominates and significant isotopic depletion occurs in going from 40° to 60°S (figure 3). Thus our observation of decrease of rainwater $\delta^{18}\text{O}$ with increasing latitude suggests the progressive importance of precipitation over evaporation (poleward of 40°S). In contrast, the equatorial region is dominated by strong evaporation where the upward flux provides enough moisture to maintain a relatively

Figure 2. Variation in (a) the $\delta^{18}\text{O}$ value of the surface sea water, (b) salinity and (c) SST as function of latitude. Zones of evaporation and precipitation can be identified based on the $\delta^{18}\text{O}$ and salinity values. The pattern of variation can be explained by combined contributions from oceanic precipitation; evaporation and glacial melt water (see text).

Table 1. Measured values of $\delta^{18}\text{O}$ of rainwater and sea water collected over the Indian Ocean along with SST. The rainout fraction is calculated using a Rayleigh condensation model during transport assuming source vapour as evaporated sea water so that measured rainwater values are reproduced (see column 11). Rainout fractions are also obtained using IsoGSM2 3 km vapour (last column). Their difference is discussed in the text. The uncertainty in the rainout fractions is typically 0.04 (see text).

Sample number_date	Latitude, longitude	Rbs effective	SST ($^{\circ}\text{C}$)	$\delta^{18}\text{O}$ seawater (measured)	$\delta^{18}\text{O}(\text{v})$ α effective	$\delta^{18}\text{O}$ water (measured)	Cloud base Temp ($^{\circ}\text{C}$)	$\delta^{18}\text{O}$ vapour calculated from rain	Rainout fraction Rayleigh model	IsoGSM2 rain	$\delta^{18}\text{O}$ vapour 3 km	Rainout fraction IsoGSM2
2011												
SOE11.1.28/3/11	9.55, 87.8	0.720	29.4	0.3	1.0100	-9.6	10	-13.5	0.33	-5.72	-18.1	0.55
SOE11.3.8/3/11	-20, 57.5	0.888	25.0	0.4	1.0097	-9.3	10	-13.1	0.33	-4.70	-20.5	0.65
SOE11.4.23/1/11	-20.86, 57.5	0.905	25.0	0.4	1.0097	-9.2	10	-13.7	0.37	-3.01	-16.3	0.49
SOE11.5.23/1/11	-20.86, 57.5	0.905	25.0	0.4	1.0097	-9.2	10	-13.9	0.39	-3.01	-16.3	0.49
SOE11.6.6/3/11	-27.43, 53.52	0.866	25.0	0.5	1.0098	-9.3	10	-13.9	0.38	-3.95	-23.0	0.73
SOE11.7.6/3/11	-27.43, 53.52	0.866	25.0	0.5	1.0102	-9.6	10	-14.0	0.36	-3.95	-23.0	0.72
SOE11.8.6/3/11	-27.43, 53.52	0.866	25.0	0.5	1.0102	-9.6	10	-14.0	0.36	-3.95	-23.0	0.72
SOE11.9.5/3/11	-29.1, 52.42	0.950	23.5	0.5	1.0098	-9.2	10	-14.3	0.41	-4.32	-22.4	0.71
SOE11.10.5/3/11	-32.27, 50.58	0.985	23.5	0.4	1.0096	-9.1	2.5	-12.0	0.27	-4.32	-17.7	0.53
SOE11.11.28/2/11	-42, 47	0.624	16.2	0.5	1.0124	-11.8	2.5	-13.7	0.15	-4.26	-23.3	0.64
SOE11.12.28/2/11	-42, 47	0.587	16.2	0.5	1.0126	-12.0	2.5	-13.6	0.12	-4.26	-23.3	0.63
SOE11.13.16/2/11	-52, 57.5	0.593	5.5	-0.6	1.0126	-13.1	2.5	-20.4	0.44	NA	-31.4	0.80
2012												
SOE12.1.30/12/11	-0.97, 77.13	0.678	28.7	0.4	1.0110	-10.5	10	-11.9	0.13	NA	-22.4	0.68
SOE12.4.3/1/12	-10.92, 72.9	0.714	29.3	-0.2	1.0107	-10.8	10	-13.9	0.25	-3.08	-18.6	0.52
SOE12.5.3/1/12	-11.68, 72.55	0.721	29.1	-0.2	1.0107	-10.8	10	-11.8	0.1	-2.66	-19.8	0.57
SOE12.6.8/1/12	-25.85, 65.87	0.700	25.1	0.5	1.0112	-10.5	10	-11.0	0.04	NA	-33.2	0.89
SOE12.7.3/2/12	-37, 57.5	1.045	19.7	0.5	1.0095	-9.0	2.5	-16.9	0.57	-7.18	-20.7	0.64
SOE12.10.26/1/12	-46, 57.47	0.833	11.0	-0.5	1.0112	-11.5	2.5	-17.5	0.41	-4.28	-23.9	0.66
SOE12.12.22/1/12	-50, 57.5	0.552	8.6	-0.7	1.0125	-13.0	2.5	-20.5	0.46	-2.67	-36.3	0.87

Figure 3. Latitudinal distribution of $\delta^{18}\text{O}$ values of precipitation samples in the Indian Ocean region during austral summer for 2011, 2012 and 2013 along with data from Nakamura *et al.* (2014). The black line is obtained using a third order polynomial fit of the data.

constant vapour isotopic composition and corresponding rainwater $\delta^{18}\text{O}$ value. This is supported by the observed low slope in the $\delta^{18}\text{O}$ –salinity plot of sea water in this region (for details see S1). A global picture of evaporation minus precipitation ($E - P$) over the Indian Ocean region is consistent with this view (Pokhrel *et al.* 2012). We explore this idea in terms of a simple Rayleigh model.

3.3 Modelling of isotope ratios of vapour and derivation of rainout fraction

To explain the large observed variation in the $\delta^{18}\text{O}$ values of the station precipitations (e.g., from -0.5 to -5.5‰ over $35 \pm 5^\circ\text{S}$ belt) in view of the much smaller variation in the source seawater we invoke a large role of the rainout process which modifies the source vapour during transport and forms the final vapour which yields the rain. This is displayed as a schematic in figure 4. The way we estimate the source vapour, the final vapour and the rainout fraction is described below.

3.3.1 Source water

Wind direction. The vapour responsible for the rains at a given station is ultimately derived from evaporation of sea water in some region. We investigate the vapour source in the context of wind movement in the Indian Ocean region where it is known that westerly winds centered around 40°S , Easterly Trade winds centered around 15°S and the South equatorial counter-current flowing eastwards between the equator and 10°S flow mostly along a

latitude parallel direction with little cross-latitude movement (Goosse *et al.* 2008). For our sampling dates and stations the average directions of winds arriving at the sampling locations were further investigated. The climatological wind direction and wind speed obtained from NCEP reanalysis data given in figure 1 show zonal bands of easterlies and westerlies across the latitudes over the Southern Ocean. The highest wind speed and direction are found after 40°S latitude whereas low values are seen at the transition zone between easterlies and westerlies. Depending on the wind direction and wind speed the history of moisture reaching the station locations can differ.

Back trajectory analysis. Wind directions give a general pattern of air movement but for knowing the exact locations of moisture source of the rainwater samples we carried out the back trajectory analysis which provides information about the movement of the air mass from its source to the sampling location. The trajectories were obtained using Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) archived data set with NCEP Global Data Assimilation System (GDAS) at 0.5° resolution for the date of sampling at the universal standard time. The derived 48-hr backward trajectory at ground level for each date of sampling (figure 1) shows that the air mass movement is mostly parallel to the latitude band. This suggests that moisture responsible for rainout at a given station originates mostly from the surface seawater in a small latitude band containing that station. Longitude-wise the source region is assumed to extend all the way to the land masses on both sides. There are some trajectories in a few latitude zones where some cross-latitude movement is noted but in general, they are limited in number. Indeed, the back trajectories for high altitude levels (~ 3000 m) where the major part of the rain forms deviate only occasionally from a latitude parallel direction (figure S2). The back trajectories calculated by Uemura *et al.* (2008) for the longitude band 40° to 100°E also bear this out. In addition, the wind speed being particularly high ($7\text{--}12\text{ ms}^{-1}$) between 40° and 50°S (Anilkumar *et al.* 2005), it is reasonable to assume that the vapour emanating from the seawater in a small latitude band is well mixed and the surface water isotopic composition as measured for a given station can itself be used to estimate the isotopic composition of the source vapour for this band. It is also justified by the fact that longitudinal variation

Figure 4. Schematic of a model showing effect of moisture removal by rainout following a Rayleigh distillation process where an effective rainout fraction is calculated (see text). The initial vapour composition of -12.2‰ is modified to a steady state value of -19.4‰ due to a rainout fraction of 46% (data for SO13_20 from table 1) when we use rain water value to calculate the vapour at 3 km. The vapour value is -32.4‰ as per IsoGSM2 simulation and yields rainout fraction of 83%. Two models result in two different estimates of rainout fraction (see text for details).

of $\delta^{18}\text{O}$ values is small due to the mixing of water by strong ocean currents (Schmidt *et al.* 1999). Indeed, on a global scale, LeGrande and Schmidt (2006) have shown that the $\delta^{18}\text{O}$ change is only on the order of 1‰ , whichever way we move (see also table 1). However, even though the initial source vapour near the sea has nearly the same composition, it moves over a long distance on average before reaching a given station and suffers rainout over the route. This leads to isotopic depletion in the final vapour which generates the precipitation at a given station (see figure 4).

3.3.2 Fractionation factor information of the vapour from source water

The fractionation factor α associated with *source vapour* formation from the sea water is a combination of equilibrium and kinetic fractionation factors given by Merlivat and Jouzel (1979), Benetti *et al.* (2014),

$$\alpha = \alpha_{eq} \times [\alpha_k + Rh_s(1 - \alpha_k)] \quad (3)$$

where α_{eq} , α_k , and Rh_s are the equilibrium fractionation factor, kinetic fractionation factor and normalized relative humidity. The relative humidity values are normalized to sea surface condition ($Rh_s = rh \times e_{atmos}/e_{sst}$, where e_{atmos} and e_{sst} are saturation vapour pressures corresponding to the atmospheric temperature and sea surface temperature). α_{eq} for the transition from the liquid (l) to vapour (v) or α_{l-v} at a temperature T (in degree Kelvin) is given by Horita and Wesolowski (1994), valid for the temperature range 0° to 374.1°C with an uncertainty of $\pm 0.11\text{‰}(1\sigma)$:

$$\begin{aligned} 10^3 \alpha_{l-v}(^{18}\text{O}) \\ = -7.685 + 6.7123(10^3/T) - 1.6664(10^6/T^2) \\ + 0.35041(10^9/T^3). \end{aligned} \quad (4)$$

The kinetic fractionation factor α_k depends on the sea surface roughness and thus on wind speed (Merlivat and Jouzel 1979). In this context, Benetti *et al.* (2014) carried out an important study in the Atlantic Ocean at $26^\circ\text{N}, 35^\circ\text{W}$ where the wind speed was generally higher than 7 m/s and suggested a value of 1.0035 for α_k . They also suggested a value of 1.0060 for speeds less than 7 m/s. We consulted the reanalysis data from NCEP and determined the wind speeds for each station in the three sampling years and following Benetti *et al.* adopted the values for α_k . The initial vapour δ_v is then given by the equation:

$$\delta_v = (1000 + \delta_w)/\alpha - 1000 \quad (5)$$

where δ_w is the isotopic composition of the measured seawater sample from the given station as mentioned before.

3.3.3 Composition of the rain-forming vapour over the station

The *initial source vapour* isotopic composition (as discussed above) refers to the water vapour *adjacent* to the sea surface. This vapour is then uplifted and transported to the station after undergoing episodes of rainout (one or several) on the way to form the *steady-state* vapour which produces the rain. To calculate the fraction of moisture that rained out before reaching the station (through a Rayleigh framework) we need to know the composition of the rain-forming vapour at that station

(figure 4). This estimate would give us a simplified effective fraction representing how much amount of the overhead moisture is removed as rain relative to the total amount of moisture over the trajectory.

The vapour composition can be estimated in two ways: (1) using the station precipitation as input, one can calculate the vapour composition near the cloud base height over the station and (2) using the prediction from the IsoGSM2 as described before. These two methods and their corresponding output results are discussed in the two following sub-sections.

(1) Vapour compositions calculated from the station precipitations and corresponding rainout fractions. Since $\delta^{18}\text{O}$ values of the station precipitation (at various latitudes) are known we can use equation (5) to estimate the $\delta^{18}\text{O}$ value of the station vapour provided α is known. We assume that the rain that falls in a station has formed in equilibrium after convective uplift of the water vapour and its cooling at the cloud base where relative humidity is close to 100%. Therefore, kinetic fractionation can be neglected and only α_{eq} need to be used which can be calculated (equation 4) using the temperature in the rain forming zone or the cloud temperature. We now assume that condensation occurs mostly at the cloud base at about 3 km altitude for low clouds (McCoy *et al.* 2014b) at a typical temperature of 10°C for the equatorial regions ($\sim 30^\circ\text{S}$). However, for latitudes south of 30°S the cloud base temperature is much lower and following Morrison *et al.* (2011) we assume it to be 2.5°C. There is uncertainty in both these values since the altitude where major condensation takes place can be highly variable (McCoy *et al.* 2014a). To take account of this uncertainty we use $\pm 5^\circ\text{C}$ around each of these values as uncertainty; the corresponding α_{eq} values are 1.01073 ± 0.00053 and 1.01153 ± 0.00053 for these two regions. The calculated vapour compositions are given in table 1. The inherent assumption in the above derivation is that there is no enrichment or alteration when the raindrops fall from a height of ~ 3 km to the ground. This assumption need not be strictly correct but provides a first-order estimate of the vapour. The fraction of vapour remaining after rain (f) is now obtained by using

$$\ln f = 1000 * [\ln(1 + \delta_v/1000) - \ln(1 + \delta_{\text{ini}}/1000)]/(\alpha_{\text{eq}} - 1)$$

where, δ_v and δ_{ini} refer to the rain forming vapours and the *source vapour* (section 3.3.2). $(1 - f)$ is the fraction that has rained, i.e., the rainout fraction and its values for various stations are given in table 1.

Uncertainty estimation for rainout fraction $(1 - f)$ and its values. The uncertainty in the value of $(1 - f)$ at a given location is obtained by quadratic addition of four uncertainties: (1) minor variations in the seawater $\delta^{18}\text{O}$ values over the back trajectory, (2) the condensation temperature, (3) the analytical uncertainty of sea water $\delta^{18}\text{O}$ value (taken to be the standard deviation of the measured values at a given latitude), and (4) uncertainty of rainwater $\delta^{18}\text{O}$ value. The uncertainty associated with seawater $\delta^{18}\text{O}$ values over the back trajectory is calculated based on the standard deviation of $\delta^{18}\text{O}$ values of measured seawater at a given latitude band. An uncertainty of 5°C is assumed for the cloud base temperature which gives rise to an uncertainty in the fractionation factor, which in turn, leads a resultant uncertainty of $\sim 4\%$ in the estimated rainout fraction. The analytical uncertainty of 0.1‰ for the $\delta^{18}\text{O}$ value is calculated based on the external standard deviation obtained by repeated analysis of the internal laboratory standard. We find that the combination of these four factors gives rise to the typical uncertainty of 0.04 in the value of $(1 - f)$ at the 1σ level.

The rainout fraction $(1 - f)$ expressed as a percentage, varies over a large range (8–62%) for the latitude range 10°N to 60°S (figure 5) based on

Figure 5. The rainout fraction as a function of latitude using two methods of estimating rain forming vapour. On average, the rainout fractions in the zone of precipitation and zone of evaporation are $\sim 40\%$ and $\sim 25\%$ respectively in the Rayleigh model (filled circles) and are $\sim 80\%$ and 60% based on the IsoGSM2 model (hollow circles). The dotted lines (2nd order polynomial fits) are given to guide the eye.

the simplified Rayleigh model with mean and Std. dev. values: $31 \pm 16\%$. The required value is as high as 60% for the year 2013 in the latitude band of 55° to 60°S . It is seen that the latitudinal pattern of $(1 - f)$ reflects, to a large degree, the rainwater composition variation as expected because it is derived based on the rainwater values (figure 3). There is large day-to-day variation in a given latitude belt but on average $\sim 40\%$ rainout fraction fits the rain data in the zone of precipitation, while $\sim 30\%$ rainout fraction fits the data in the zone of evaporation. Since there is no equivalent study of rainout fraction (defined here as a percentage of overhead moisture resulting in precipitation over the entire track of the moisture movement) we cannot check the veracity of our results in a straightforward way. However, the global satellite system of CloudSat (<http://cloudsat.atmos.colostate.edu>) measures the presence of clouds and precipitation associated with them during the sweep of the satellites over the globe. It is of interest to compare our conclusions with the precipitation frequency data obtained by the CloudSat study over the SO region (Ellis *et al.* 2009). These data show that in the mid-latitude belt of 40° to 60°S the precipitation fraction (defined as fraction of the clouds that lead to precipitation) increases to about 0.2 from a low value of 0.1 in the belt 0° to 30°S . This measure can be taken as a proxy for the Rayleigh rainout fraction obtained here but numerically they do not represent the same concept. The rainout fraction as defined here is a cumulative measure and moreover, clouds are not always present even though the moistures are. However, the magnitude of relative increase from the equatorial zone to high latitude is similar. Why the higher latitudes have higher rainout fraction? A possible reason is suggested by the water vapour map of the Indian Ocean region. The tropics are both very humid and very cloudy, but in many months, the SO is among the cloudiest places on the planet, even though the amount of water vapour is relatively low. This pattern occurs because cloud formation depends on both water vapour and air temperature. The colder the air, the more readily any water vapour in the air will condense to generate the clouds (earthobservatory.nasa.gov/GlobalMaps). Since rains form from the clouds it is expected that rainout would be larger in the SO. Moreover, if the moisture content is lower the fraction removed as rain would be larger as $(1 - f)$ is defined as the ratio of rain amount/moisture content.

(2) Vapour composition calculated from the IsoGSM2 model and corresponding rainout fraction. As mentioned, estimates of the rain forming vapour composition can also be obtained from the IsoGSM2 at various heights. This model also provides the composition of the rain and vapour at the ground level. For the rainout fraction, we consider the vapour at an altitude of ~ 3 km where the rain is assumed to form.

Table 1 lists the rainout fraction for the IsoGSM2 vapour corresponding to the station locations. The striking feature of the result is that the rainout fractions encompass a large range of values from 17 to 94%. The very high value is a consequence of the low $\delta^{18}\text{O}$ values of the vapour at 3 km. The vapour $\delta^{18}\text{O}$ values are in the range of -12.9 to -41.3‰ much lower compared to the range of -11.0 to -23.4‰ in the Rayleigh model estimate. The IsoGSM2 values are lower on average by $9.4 \pm 6.2\text{‰}$. We also see that even at the ground level the IsoGSM2 vapour values are depleted relative to the calculated moisture composition just above the sea surface by $2.7 \pm 1.2\text{‰}$ (table 1). The average rainout fraction in the IsoGSM2 estimate is $67 \pm 19\%$. Latitudinal variation of the rainout fraction is shown in figure 5 for both cases displaying the consistent difference between the two estimates. We do not know which of these two estimates are closer to the classical picture where on average to be accepted except to note that the IsoGSM2 estimates are about 90% of the ocean vapour drains into the ocean itself as rain (http://www.meted.ucar.edu/tropical/textbook_2nd_edition/). Both the estimates however show that the rainout fraction increases with latitude beyond 40°S towards the pole. As we discussed before, this pattern agrees with one that is intuitively expected based on evaporation minus precipitation ($E - P$) decrease as we move from 40° to 60°S (*op. cit.*).

A possible explanation for the difference between the two estimates is that IsoGSM2 is a global model with several simplifying assumptions whereas the vapour values obtained from measured isotope data pertain to individual events influenced by variable local parameters like seawater isotopic composition, condensation temperature, raindrop evaporation, moisture source approximation and moisture recycling. For example, Worden *et al.* (2007) concluded ‘measurements of the isotopic composition of water vapour near tropical clouds suggest that rainfall evaporation contributes significantly to lower troposphere humidity, with

Figure 6. Measured rain composition plotted against IsoGSM2 prediction at the same station and same time. On average, IsoGSM2 values are depleted relative to the measured values by about $0.6 \pm 1.7\text{‰}$. Possible reasons for the difference are explained in the text.

typically 20% and up to 50% of rainfall evaporating near convective clouds'. Therefore, the estimated values derived from the two approaches may represent different processes. Further, in the above comparison, we assumed that the 3 km vapour values obtained from IsoGSM2 serve as the dominant source of rainwater. That may be too simplistic since rain formation mechanism could be quite complex (Aggarwal *et al.* 2016) and the local ground level rainwater may not be simply related to the local 3 km height water vapour. It is also noted that our analysis is based on individual rain samples collected on board whenever rain events occurred and explaining their individual δ -values in terms of a common simplifying model has its limitations.

3.4 Comparison of the observed and IsoGSM2 rain values

The IsoGSM2 is also used to obtain estimates of the rain composition at the station locations. These estimates of rainwater composition and the observed values differ from each other in most of the cases (see table 1) and the difference (IsoGSM2 minus observed) can be positive as well as negative (mean $\pm 1\sigma$ (Std.Dev): $-0.6 \pm 1.7\text{‰}$) varying from -3.7 to $+2.8\text{‰}$ (figure 6). Considering the way IsoGSM2 rain values are defined this is not surprising. They represent mean value over 24 hrs and correspond to a large area (about $200 \times 200 \text{ km}^2$) whereas the main samples were taken from the ship deck when the ship moved only over a small distance (about a few km). A

Figure 7. Cross-plot of $\delta^{18}\text{O}$ (measured) versus Rainout fraction based on IsoGSM2 3 km vapor showing anti-correlation between the two. The correlation coefficient (r^2) is about 0.5 indicating a dominant role of the rainout fraction in the $\delta^{18}\text{O}$ value of the rains.

cross-plot (figure 7) of observed rainwater $\delta^{18}\text{O}$ values vs. IsoGSM2 rainout fraction, as calculated above, shows a strong anti-correlation. The overall r^2 value is about 0.5 suggesting that the rainout fraction is indeed an important factor which explains about 50% of the observed variation through Rayleigh mechanism.

In summary, we propose here a simple model to explain the large variation in rainwater composition as we move from the equatorial region to the polar region. Moisture removal by rainout following a Rayleigh fractionation process leads to large depletion in the vapour responsible for the rains at the sampling station. An *effective rainout fraction* is calculated assuming that moisture loss by rain and moisture addition by evaporation from sea can be lumped together. As a numerical example, the initial vapour composition of -12.1‰ is modified to a steady state value of -19.4‰ (or to -32.4‰ using IsoGSM2 values) due to this effective rainout (e.g., see data for SO13.20 from table 1). No other physical factor can lead to such large depletion.

Two rainout estimates are obtained based on assumed vapour composition at the rain forming zone presumably at about 3 km height: one based on the measured $\delta^{18}\text{O}$ values of the rainwater and a second based on IsoGSM2 and these two estimates are quite different and their mean values are $31 \pm 16\%$ and $67 \pm 19\%$ (IsoGSM2) respectively. We believe that the latter estimates are more acceptable as they are closer to the well-known values in Classical Hydrology based on moisture budget (*op.cit.*). The latitudinal variation of the rainout fraction is quite significant being related to the variable relative strengths of evaporation and precipitation processes as a function of latitude.

4. Conclusion

The $\delta^{18}\text{O}$ values of surface seawater and rainwater along with salinity and SST were measured on samples collected onboard from the equatorial regions to Southern part of the Indian Ocean (to about 60°S). A characteristic pattern of latitudinal variation in the sea water δ -values is seen which arises due to the complex interplay between ocean currents, freshwater input via precipitation and glacial melt, evaporation, and wind induced changes. The changes are small but significant as they represent variation in a large reservoir. The $\delta^{18}\text{O}$ values of rainwaters as a function of latitude do not vary much ($-2 \pm 2\text{‰}$) from the equator to about 35°S . But then a sharp decrease with latitude occurs going as low as -16‰ at $\sim 70^\circ\text{S}$. In contrast, the seawater values over this latitude range change only by a small amount and cannot explain the much larger rainwater variations. After exhausting other possible causes we use a simple Rayleigh model to examine the role of rainout as a possible factor. We assume the local seawater as input moisture source. But this changes to a steady state oceanic moisture at a higher level which differs from the input due to balance between precipitation and evaporation. This latter moisture is depleted in isotopes and gives rise to the isotopically lighter rains. We propose a model based on Rayleigh fractionation framework where the change in $\delta^{18}\text{O}$ value of rainwater is ascribed to variation in rainout amount which changes the source moisture isotopic composition during transport by a Rayleigh fractionation mechanism. To explain the large compositional variation we require large variations in the required rainout fraction ($1 - f$), from a low value of $\sim 10\%$ at low latitudes to as high as 60% in the belt of 50° to 60°S . Indeed, the grand average over all the samples collected over three years is $31 \pm 16\%$. The required rainout fraction is still larger $67 \pm 18\%$ if we adopt the values of rain forming vapour composition from the IsoGSM2 prediction at 3 km altitude. This large rainout fraction is consistent with the classical oceanic rainout estimates based on moisture budget. The calculated water vapour and rainwater isotopic compositions at the sampling locations agree broadly (within a few per mil) with the values obtained using the IsoGSM2 applied to the sampling times and locations. This shows that the adopted simple model, despite its limitations of assuming a Rayleigh fractionation framework, is reasonable for predicting the southern ocean isotope hydrological parameters.

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